DOE/ET/15346-T1

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RESEARCH AND DEVELOPMENT OF
THE OSMO-HYDRO POWERTM HEAT ENGINE

Final Report
Contract No. DE-AC05-78ET15346

25 November 1980
ITC/Solar Report No. 251180

Prepared for
U. S. Department of Energy

InterTechnology/Solar Corporation
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ABSTRACT

The Osmo-Hydro PowerTM (OHP) or Pressure-Retarded Osmosis (PRO) heat engine is a possible means for producing economical electric power from low-temperature heat sources. The engine utilizes semipermeable membranes to cause the permeation of a solvent from a dilute low-pressure solution to a concentrated high-pressure solution. The potential energy thus acquired is converted to useful energy by means of a turbogenerator. The process can be considered as one in which the free energy of mixing is converted to useful power. By appropriate application of a heat source and a heat sink, the original dilute and concentrated solutions are recovered, thus completing the heat engine cycle.

Thus far four thermal unmixing methods have been examined. These include distillation and conjugation--in the latter a homogenous solution is divided into a dilute and a concentrated solution by virtue of a temperature change. According to the analysis, both of these methods offer the possibility of generating electricity at a cost of perhaps 0.12 \$/kWh with membranes having reasonable permeation characteristics. However, both methods utilize organic chemical species, which attacked all of the large number of membranes tested.

To enable the use of existing membranes, precipitation and stratification unmixing were considered. These require an electrolyte for which the solubility increases with temperature. In stratification unmixing a saturated pond utilizing either solar or waste heat is used, and in contrast to all other unmixing methods considered, stratification has the advantage that no phase change occurs. Initial success was obtained with aqueous disodium phosphate solutions.

The results of this initial project to study osmotic power generation from waste heat indicate what research paths must be followed to continue the development of distillation and conjugation as unmixing methods. In addition precipitation and stratification have been shown to be desirable because of the possibility of readily matching a binary system with either a membrane presently available or one readily modified from an existing membrane.

The OHP heat engine in its ultimate development would have the following general characteristics: 1) It would be able to utilize low-grade heat sources, such as unconcentrated solar energy or waste heat below 100°C. Heat sources as low as 50°C can be used; 2) The engine should be able to produce electricity for 0.12 \$/kWh, or less, but the thermal efficiency will be less than 25 percent of Carnot efficiency at the same temperature limits; 3) The engine would be modular; i.e., it could be scaled up or down largely by adding or subtracting discrete permeator and heat exchanger units.

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ACKNOWLEDGMENTS

Several people contributed to the technical work on this project, and their efforts should be acknowledged. These contributors are:

Sidney Loeb (Principal Investigator), Gurmukh D. Mehta, Satish C. Jain, Barry F. Brandon (Laboratory), and Donald Close (Laboratory).

From Gulf South Research Institute the contributors were James Smith, Israel Cabasso, and Satyanarayana Gupta. Thomas Hanley, Lynn Groome, and Khan Akmal were responsible for the work done at Tulane University.

The typing and reproduction were ably handled by Mary Kahler and Barbara Bacon.

Finally, the support, interest, and patience of Harry Arnold, Oak Ridge National Laboratory, the project technical monitor for the Department of Energy, are gratefully acknowledged.

Malcolm D. Fraser
Project Manager and
Co-Principal Investigator

I. EXECUTIVE SUMMARY

A. Principles

The Osmo-Hydro PowerTM (OHP) heat engine produces useful power from the free energy of mixing during the permeation of a solvent from a dilute solution through a semipermeable membrane into a pressurized concentrated solution, a process called Pressure-Retarded Osmosis (PRO). The Mixed Solution is unmixed by application of a heat source and a heat sink, thus closing the heat engine cycle. Various means of unmixing the Mixed Solution into a dilute and a concentrated solution of solvent and solute can be used, including distillation, conjugation, precipitation, and stratification, which are discussed below.

Paramount in the development of the OHP engine is the choice of the membrane and also the permeator geometry. With regard to the latter, the hollow fiber appears to be especially appropriate since the wall thickness can be relatively thin, on the order of 25-30 microns. Thinness is important to facilitate permeate transport rate, which is an inverse function of total membrane thickness in PRO due to the diffusive nature of transport in the porous substructure of the membrane and to internal polarization induced by the presence of solute in the porous substructure. For this reason the relatively thick flat-sheet membrane (150-200 microns), used in the spiral-wound module geometry, will probably not be economically viable in PRO.

B. Salient Features of the OHP Heat Engine

The OHP heat engine will always have at least the following operational units: a) PRO permeator; b) turbogenerator; c) two pumps; d) heat source; e) heat sink; and f) a device for separating the unmixed solutions. If conjugation, precipitation, or stratification (all discussed below) are used for unmixing, a heat regenerator may be included.

The OHP heat engine is able to utilize low-grade heat sources such as waste heat below 100°C, or even heat sources as low as 50°C. This feature is associated with the fact that the heat source and heat sink are used only for separating the Mixed Solution.

Calculations indicate that with a membrane having relatively modest transport properties, the OHP engine can produce useful energy at a cost equal to or less than 0.12 \$/kWh. As another advantage the OHP engine is modular. It can be scaled up or down largely by adding or subtracting discrete permeator and heat-exchanger units.

The main disadvantage of the OHP engine is that the overall thermal efficiency will be less than 25 percent of Carnot efficiency, due to mechanical efficiency restrictions, and the necessity of maintaining an adequate driving pressure (osmotic minus hydraulic pressure) during permeation through the membrane.

C. Objectives of Project and Methodology

The general objective of this project was to investigate the utility of the OHP heat engine for producing economical electrical power from waste heat or other low-grade thermal energy sources. To achieve this general objective required research on two interrelated sections of the engine: first, the membrane permeator; and second, the thermal unmixer, in which the heat source and the heat sink are used to recover the original concentrated and dilute solutions prior to mixing again in the PRO permeator. Interrelated experiments were carried out on binary systems (solute and solvent chemical species), hollow fiber and flat-sheet membrane materials, unmixing methods, and engine operating conditions. The experimental data were placed into calculation models developed to determine energy cost and thermal efficiency. These models served to point the way to further experimentation.

Necessary physical chemical data such as osmotic pressure, liquid-vapor equilibrium data, and phase diagrams of conjugating systems were obtained for selected binary systems by experimentation. Semipermeable membranes were then acquired and tested with the most promising binaries. The tests on membranes included reverse osmosis (RO), osmosis, and Pressure-Retarded Osmosis (PRO) experiments with promising binaries, frequently after extended immersion in solutions of the binaries. The membranes were examined as flat sheets (RO and osmosis) and as hollow fiber permeators (RO, osmosis, and PRO). With the data obtained from the membrane

tests and the physical chemical data on the binaries, it was then possible to obtain more realistic estimates of energy costs and thermal efficiency.

As a final task in the project, a design for a working model was developed.

D. Summary of Work and Conclusions

The results are discussed below according to the categories of unmixing methods investigated, all of which can utilize heat sources below 100°C.

With the distillation method of unmixing, no membranes were found which could adequately resist the combination of hydraulic pressure differences and chemical reactivity of the volatile solvents considered, such as methanol. If such a membrane were available, the unit energy cost, dollars per kilowatt-hour, would be low, probably less than 0.11 \$/kWh, because very appreciable osmotic pressure differences can be developed. On the other hand the thermal efficiency is low at present because of the high latent heat of those volatile species capable of permeating existing membranes. Development of membranes comprised of nonpolar and/or non-hydrogen bonding chemical compounds should be pursued.

With the conjugation method of unmixing in which unmixing of two liquids occurs by changing the temperature of a solution until two immiscible (conjugating) solutions are formed, the osmotic pressure differences were frequently found to be lower than desired. This is because, within the temperature limits imposed by the use of waste heat, the miscible region is quite close to the highly nonideal immiscible region. Only a few conjugation binaries did have adequate osmotic pressure and phase diagram characteristics, and some of these had to be rejected because of toxicity. At present only the ethyl acetate/ethylene glycol system, which is a conjugating binary system having an upper critical solution temperature, looks promising for the conjugation method of unmixing. Providing a durable membrane with a reasonable permeation coefficient can be found, the energy cost would be 0.12 \$/kWh. However, ethyl acetate attacked all membranes tested; i.e., again the problem was that of matching a binary system to a membrane, specifically to find a membrane for the ethyl acetate/ethylene glycol binary.

Most commercially available membranes have been developed for use with aqueous electrolyte solutions. Therefore, aqueous electrolyte systems were also examined as binary systems, specifically electrolytes for which the solubility increases appreciably with temperature. Two unmixing methods were examined for use with electrolytes. The first of these is precipitation in which unmixing occurs by cooling a near-saturated solution well into the two-phase region, thus obtaining a dilute (Permeate Donor) solution and a slurry, which ultimately becomes the concentrated (Permeate Receiver) solution.

With stratification, a novel unmixing method conceived and successfully tested at ITC/Solar, no phase change occurs, giving this method of unmixing the advantage over precipitation in that there are no solids-handling problems. Furthermore, stratification has the additional advantage over all other unmixing methods considered that there is no latent heat of phase change, thus decreasing heat-transfer requirements and increasing thermal efficiency. In stratification the feed solution is unmixed in a temperature-, density-, and concentration-stratified pond. The pond is stratified by application of a heat source at the bottom and a heat sink at the top of a pond containing a saturated solution in which the solubility of the electrolyte increases appreciably with temperature.

Aqueous disodium phosphate (DSP) was examined as an electrolyte solution to be used in precipitation or stratification. DSP was selected because it has a steep solubility curve in the region of 30°-50°C. This enables the use of membranes in the soluble region, just above 50°C, i.e., within the upper operating limit permissible with existing membranes. Of the membranes tested, the ABC-PBIL (Abcor Corporation, asymmetric polybenzimidazole) flat-sheet membrane was the most promising in that it appears quite resistant to attack by the hot concentrated DSP solutions.

The stratification method of unmixing offers sufficient promise that considerable effort should be devoted to testing saturated ponds with appropriate binary systems. While stratification offers the advantage of using waste heat sources approaching 55°C, more economical operation

could be obtained with heat sources approaching 100°C in order to obtain a greater solubility (osmotic pressure) difference between the cold dilute solution and the hot concentrated solution. Thus membranes should be developed capable of operating at about 90°C.

E. The Working Model

A working model was designed, based on the stratification method of unmixing with aqueous DSP solutions. The PRO permeator for this model may utilize the ABC-PBIL membrane, described above. Since this membrane is available only as a flat sheet, the PRO permeator module would be of the spiral-wound module type. However, the schedule that would have been involved in getting the module built precluded building the working model in this project.

The working model would possess all of the operating components of the full-scale OHP heat engine except the turbogenerator, which would be replaced by a back-pressure regulator. Potential power output would be calculated from the permeation rate into the high-pressure side of the permeator.

II. INTRODUCTION

A. Principles of the Osmo-Hydro PowerTM (OHP) Heat Engine

1. Pressure-Retarded Osmosis

The OHP heat engine utilizes the osmotic region known as Pressure-Retarded Osmosis (PRO). In PRO a semipermeable membrane separates a solution having low osmotic and hydraulic pressures from another solution having high osmotic and hydraulic pressures. It is arranged that the osmotic pressure difference $\Delta\pi$ is greater than the hydraulic pressure difference Δp . Under these conditions the solvent chemical species, but not the solute species (the two species constitute a binary system), will permeate from the low- to the high-hydraulic-pressure solution*; i.e., the solvent species will become compressed. The potential energy thus acquired in PRO from the free energy of mixing is ultimately converted to useful power by means of a turbogenerator, and the original two solutions are recovered by a thermal unmixing process, thus completing the OHP cycle. Thermal unmixing can readily be accomplished with low-grade heat sources, i.e., those below 100°C.

Paramount in the development of the OHP engine is the choice of the membrane and the permeator geometry. Pressure-Retarded Osmosis requires relatively unimpeded flow of streams introduced on both sides of a membrane across which a large hydraulic pressure difference exists. An appropriate membrane geometry is the hollow fiber, a very fine tube having an outer-to-inner diameter ratio adequate for high compressive strength. Hollow fibers are now made both commercially and experimentally for reverse osmosis desalination. They are generally asymmetric; that is, they consist of a relatively thick porous substructure surmounted by a thin but dense semipermeable skin on the outside (high-pressure side) of the fiber. The porous substructure provides the necessary strength, the denseness of the skin imparts semipermeability,

*The term $(\Delta\pi - \Delta p)$ is the driving force for the permeation flux J which is permeation rate per unit area of membrane. Specifically, $J = A (\Delta\pi - \Delta p)$, where A is the permeation coefficient. The term A is characteristic of the membrane.

and its thinness ensures adequate permeate flux. The hollow fibers are mounted in a cluster of parallel fibers and are contained within a pressure shell having two inlets and two outlets, thus completing the permeator.

2. Unmixing Methods

In this project we investigated three solution unmixing methods requiring phase changes. These were: conjugation (liquid-liquid unmixing), distillation (liquid-vapor unmixing), and precipitation (liquid-solid unmixing). In a fourth solution unmixing method, stratification, no phase change occurs. These four methods are discussed in detail in the sections following. All unmixing methods were considered for use with heat sources below 100°C.

a. Conjugation

Example: Binary System with Lower Critical Solution Temperature (LCST)*. The flow diagram of an OHP heat engine using conjugation for unmixing is shown in Fig. 1. By virtue of being heated into the partially miscible region at T_h , the Separator Feed (S) is divided under high pressure into the (permeate) Donor Solution (D) and the Receiver Solution (R) as shown on the phase diagram in Fig. 2. After these two streams separate by density differences, they preheat the incoming Separator Feed (S); then, still pressurized, they are finally cooled by the heat sink to T_c in the completely miscible region, also as shown in the phase diagram. Only in this region is there an appreciable osmotic pressure difference between the two solutions.

The Donor Solution is depressurized through the hydroturbine, thus furnishing gross power from which parasitic losses to the generator and the pumps must be subtracted to supply net power. The Donor Solution and the Receiver Solution (the latter still pressurized) both enter the PRO permeator, in which permeate passes through the membrane from the low- to the high-hydraulic-pressure side, thus forming the Mixed Solution. The latter is joined by the Flushing Solution. The Flushing Solution is necessary to remove solute which entered with the Donor Solution and

*Conjugation binaries having an upper critical solution temperature can also be used.

Fig. 1. - OHP heat engine using conjugation as the unmixing technique

Fig. 2 - Phase diagram for OHP heat engine using conjugation

that which permeated from the high-pressure to the low-pressure side of the membranes. The mixture of Mixed Solution and Flushing Solution constitutes the Separator Feed, which is preheated by the regenerator and then finally heated by the heat source to T_h , thus completing the cycle.

b. Distillation

The flow diagram of an OHP heat engine using distillation for unmixing is shown in Figs. 3 and 4. The low-pressure Still Feed is divided by the still at the hot temperature T_h into Donor and Receiver Solutions. In contrast to the conjugation cycle discussed below, distillation separation is not accomplished at the high pressure p_h of the permeator because this pressure may be close to or greater than the critical pressure of the volatile species. Both the Donor and Receiver Solutions are cooled to the cold temperature T_c by the heat sink. The Receiver Solution is repressurized to p_h after which it enters the PRO permeator.

Meanwhile the Donor Solution enters the low-hydraulic-pressure side of the permeator in which permeate passes through the membrane from the low- to the high-hydraulic-pressure side, forming the Mixed Solution. This solution is depressurized through the hydroturbine, thus furnishing gross power from which parasitic losses to the generator and pumps must be subtracted to supply net power. After depressurization, the Mixed Solution is joined by the Flushing Solution to form the Still Feed, thus completing the cycle.

c. Precipitation

Precipitation unmixing requires a binary in which solute concentration increases significantly with temperature. The flow diagram of an OHP heat engine using precipitation for unmixing is shown in Fig. 5. By virtue of being cooled into the precipitation region at T_c , the Settler Feed (S) is divided under high pressure into a dilute solution and a precipitate as shown in the phase diagram of Fig. 6.

Part of the dilute solution becomes the source stream of the Donor Solution (D), and the remainder mixes with the precipitate to become a

Fig. 3 - OHP heat engine using distillation as the unmixing technique

Solutions

R = Receiver F = Flushing
M = Mixed D = Donor
S = Still Feed

Fig. 4 - Phase diagram for OHP heat engine using distillation

Fig. 5 - OHP heat engine using precipitation as the unmixing technique

Solutions

R = Receiver F = Flushing
M = Mixed D = Donor
S = Settler
Feed

Fig. 6 - Phase diagram for OHP heat engine using precipitation

slurry stream at T_c , shown at the bottom of the Settler in Fig. 5. These two streams precool the incoming Settler Feed (S). Then, still pressurized, they are finally heated by the heat source to T_h . At this temperature the precipitate completely dissolves to form the Receiver Solution (R).

The Donor Solution is depressurized through the hydroturbine as in conjugation. The remainder of the cycle is also similar to conjugation up to formation of the Settler Feed, which is precooled by the regenerator and then finally cooled by the heat source to T_c , thus completing the cycle.

d. Stratification

In stratification unmixing, as in precipitation unmixing, a binary system is required for which the solute concentration increases strongly with temperature. However, in contrast to precipitation, no solid phase is formed and indeed no phase change occurs at all (Fig. 8), thus eliminating heat-transfer requirements due to a latent heat of phase change. The separation vehicle is an unpressurized saturated self-stratifying pond, referred to in Fig. 7 simply as the "saturated pond." By the use of a binary system as above, together with the heat sink at the top and the waste heat source at the bottom,* the saturated pond feed is separated thermally into a cool low-density dilute solution on top, and a hot high-density concentrated solution on the bottom, the Receiver Solution. The free energy difference between these two solutions can be used to produce useful energy.**

Both of these solutions are saturated, as are all solutions within the saturated pond. Due to sensible heat exchange with the regenerator feed, the dilute solution is heated somewhat to become the Donor Solution. This heating is desirable to prevent precipitation on either side of the membranes in the PRO permeator.

*ITC/Solar already has considerable experience in successful operation of bottom-heated saturated ponds. We have used them extensively to simulate solar-heated saturated ponds.

**ITC/Solar is, it is believed, the first to propose the use of saturated ponds in this manner.

Fig. 7. OHP Heat Engine Using Stratification as the Unmixing Technique

Solutions

R = Receiver	Dil = Dilute
M = Mixed	F = Flushing
S = Saturated Pond Feed	D = Donor
	Reg. Fd = Regenerator Feed

Fig. 8. Phase Diagram For OHP Heat Engine Using Stratification

The Donor Solution enters the low-hydraulic-pressure side of the permeator in which, as usual, permeate passes from the low- to the high-hydraulic-pressure side, forming the Mixed Solution at T_{inter} , a temperature intermediate between T_h and T_D , the Donor temperature. The Mixed Solution is depressurized through the hydroturbine as usual. After depressurization the Mixed Solution is joined by the Flushing Solution, also at T_{inter} , to form the Regenerator Feed. This stream is cooled to T_s in the regenerator to form the saturated pond feed, which is still slightly unsaturated to prevent precipitation in the regenerator. The cycle is now completed.

B. Salient Features of the OHP Heat Engine

1. Characteristics

The OHP heat engine, like any other heat engine, is a cyclical device, receiving heat as its input, and delivering work plus degraded (lower temperature) heat as its output. As a heat engine, it does not consume material resources. The cycle is closed; i.e., the engine does not require filtration or other pretreatment of any circulating streams prior to entering any of the operating units in the engine.

The OHP engine has at least the following operational units: a) PRO permeator, b) turbogenerator, c) two pumps, d) heat source, e) heat sink, and f) a device for separating the unmixed solutions. If conjugation, precipitation, or stratification is used for unmixing, a heat regenerator may be included as an operating unit to improve thermal efficiency.

Since the function of the heat source and the heat sink is only to unmix the Mixed Solution, low-grade heat sources, such as waste heat below 100°C , can be used to good advantage. If precipitation or stratification is used for unmixing, it appears that very low-grade heat sources, such as waste heat at $55^{\circ}\text{--}50^{\circ}\text{C}$, can be used. This is because appreciable osmotic pressure differences can be developed in solutions of solid solutes, the solubility of which increases strongly with temperature.

If conjugation is used for unmixing, it is directionally desirable that the temperature of the miscible region, at which the permeator is operated, be considerably different from the temperature of the two-phase region, in order to have appreciable osmotic pressure differences. Thus, conjugation may be more appropriate for high-temperature heat sources than for low-temperature ones.

If distillation is used for unmixing, the thermal efficiency is intrinsically lower than if conjugation or precipitation is used. This is due to two facts: first, with existing membranes the volatile species is limited to those having a relatively high latent heat of vaporization, like water; second, the direction of temperature differences between the distillate and the Still Feed rules out extensive recovery of latent heat by use of a regenerator.

The OHP engine utilizes a semipermeable membrane operating in the osmotic region known as Pressure-Retarded Osmosis (PRO). The rate of permeation through a given membrane is always lower in PRO than it would be in the well-established process of reverse osmosis. The lower permeation rate is largely due to a special effect in PRO, namely internal polarization in the porous substructure of the asymmetric membranes used. This special problem of internal polarization is discussed in detail in Appendix C.

The deleterious effect of internal polarization on permeation rate is proportional to membrane thickness. Hence, the hollow fiber geometry, for which membrane thickness is on the order of 25-30 microns, is preferable to the spiral-wound module geometry, in which flat sheets, having a thickness of 150-200 microns, are used.

2. Advantages

Calculations indicate that with a membrane having relatively modest transport properties, the OHP engine can convert waste heat or other low-grade heat sources below 100°C to electrical energy at a cost equal to 0.12 \$/kWh.

Useful power can be obtained with source/sink temperatures approaching as close as 55°/25°C, thus offering the possibility of developing economical bottoming cycles from the large sources of waste heat available at such temperature ranges.

The OHP engine is largely modular; i.e., the engine is increased or decreased in size largely by adding or subtracting discrete Pressure-Retarded Osmosis (PRO) permeator units and heat-exchanger units. Thus, although the energy cost described above is for a one-megawatt plant, it would not be much greater for a 0.1-megawatt plant, making the OHP engine especially suitable for decentralized power plants.

3. Disadvantage

The main disadvantage of the OHP heat engine is that the overall thermal efficiency will probably be less than 25 percent of Carnot efficiency. This is because: 1) the fractional mechanical efficiency of the engine (the ratio of useful energy obtained to potential energy, both referred to pressurized permeate), is only about half; 2) for maximum power output per unit area of membrane, the hydraulic pressure in the permeator is roughly half of the osmotic pressure difference across the membrane wall, which difference is, in effect, an expression of the free energy made available by the separation process.

C. Objectives of Project and Methodology

The general objective of this project was to investigate the utility of the OHP heat engine for producing economical electrical energy from waste heat or other low-grade thermal energy sources. To achieve this general objective required research on two interrelated sections of the engine: first, the Pressure-Retarded Osmosis permeator in which the free energy of mixing of the concentrated and dilute solutions is converted to potential mechanical energy as a pressurized liquid stream; and second, the thermal unmixer, in which the heat source and the heat sink are used to recover the original concentrated and dilute solutions prior to mixing again in the PRO permeator.

Thus, we were interested in finding the optimum combination of PRO permeator and thermal unmixing technique to produce the cheapest electrical energy in \$/kWh and with, if possible, the highest thermal efficiency. We carried out interrelated experiments on binary systems (solute and solvent chemical species), hollow fiber membrane materials, unmixing methods, and engine operating conditions. The experimental data were placed into calculation models developed to determine energy cost and thermal efficiency. These models served to point the way to further experimentation. Thus, there was a great deal of interaction and iteration on the various tasks as the project progressed.

In one of the initial tasks, analytical models were developed for analyzing the performance of OHP heat engines, the two figures of merit considered being the cost of electrical energy produced in \$/kWh and the thermal efficiency, i.e., the ratio of net electrical energy output to thermal energy input. Because the details of the flow scheme depend primarily on the method of unmixing the permeator effluent into dilute and concentrated solutions, separate mathematical models had to be developed. Models were developed for the conjugation and distillation methods of unmixing. The precipitation and stratification techniques were considered only in the later stages of the project because of the ready availability of commercial membranes which could handle the aqueous electrolyte binary system chosen, and models were not developed.

The two analytical models for conjugation and distillation were applied in simplified screening analyses to obtain approximate energy costs and thermal efficiencies for candidate binary systems. If not all of the relevant data were available for a candidate binary, assumptions of the missing data were made, usually on the optimistic side, and the analysis completed. By this means less desirable binaries were eliminated, and the binaries having more potential were selected for experimental testing.

Then necessary physical chemical data such as osmotic pressure, liquid-vapor equilibrium data, and phase diagrams of conjugating systems were obtained for selected binary systems by experimentation. Osmotic pressure data and liquid-vapor equilibrium data were also supplied by Tulane

University under a subcontract by application of the analytical technique known as UNIFAC. Further information on this technique and Tulane's scope of work is contained in Appendix F.

Membranes were then acquired and tested with the most promising binaries; a considerable number of different membranes are available commercially and were acquired for this purpose by ITC/Solar. Table I lists the commercial membranes acquired and tested by ITC/Solar. Membrane testing was also carried out by Gulf South Research Institute (GSRI), who was also supposed to develop new membranes since most commercially available membranes are made for desalinizing brines. Further information on the scope of work for GSRI is contained in Appendix E.

The tests on membranes included reverse osmosis (RO), osmosis, and Pressure-Retarded Osmosis (PRO) experiments with promising binaries, frequently after extended immersion in solutions of the binaries. The membranes were examined as flat sheets (RO and osmosis) and as hollow fiber permeators (RO, osmosis, and PRO). The reverse osmosis tests constituted a means for obtaining transport properties of solvent and solute as a function of the membrane skin (whereas in PRO, the transport properties can be a function of the porous substructure as well). The main purpose of testing flat-sheet material was that it provided an inexpensive means for determining the effect of prolonged contact of the binary components with relatively cheap membrane material, prior to contact with relatively more expensive hollow fiber permeators.

With the data obtained from the membrane tests and the physical chemical data on the binaries, it was then possible to obtain more realistic estimates of energy costs and thermal efficiency. These estimates were made with analytical models similar to the simplified screening models developed initially but further refined for more accurate estimation. An optimization procedure was developed for rapidly determining optimal designs for a given configuration.

As a final task in the project, a design for a working model was developed.

TABLE I
TYPES OF MEMBRANES TESTED

Membrane Designation	Fabricator	Total Thickness Microns	Type of Backing	Flat Sheet (FS) or Hollow Fiber (HF)	Composition of Membrane
FT-30	Filmtec	55	None	FS	Asymmetric composite, undisclosed composition
UOP-PA-300	Universal Oil Products	160	Paper	FS	Asymmetric composite, polyethyleneimine skin, polysulfone substructure
UOP-CA-85	Universal Oil Products	210	Fabric	FS	Asymmetric, cellulose acetate
GSRI-CA-85	Gulf South Research Inst.	75	No backing	FS	Asymmetric, cellulose acetate
DP-PA-B9	Du Pont	280	Fabric	FS	Asymmetric, polyamide
DP-PA-B9 or -B10	Du Pont	28		HF	Asymmetric, polyamide
FRL	Fiber Research Laboratory	83		HF	Composite polysulfone, furan skin
CTA	Dow	25		HF	Asymmetric, cellulose triacetate
ABC-PBIL	Abcor (Teijin)	280	Nonwoven polyester	FS	Asymmetric, poly-benzimidazole
CEL-PBI	Celanese	150	No backing	FS	Asymmetric poly-benzimidazole
GSRI-CA-Dense	Gulf South Research Inst.	10	No backing	FS	Homogeneous, cellulose acetate
UOP-CAB	Universal Oil Products	215	No backing	FS	Asymmetric, cellulose acetate butyrate
ENV-135	Envirogenics	220	Dacron	FS	Cellulose acetate, cellulose triacetate blend
ENV-203	Envirogenics	210	Dacron	FS	Cellulose acetate, cellulose triacetate blend
ENV-214	Envirogenics	210	Dacron	FS	Cellulose acetate, cellulose triacetate blend
ENV-235	Envirogenics	205	Dacron	FS	Cellulose acetate, cellulose triacetate blend
BM-1-T	Berghof	270		FS	Not stated
BM-0.5	Berghof	50		FS	Not stated
BM-0.5-C	Berghof	40		FS	Not stated

III. SUMMARY AND DISCUSSION OF RESULTS

A great deal of the work on this project consisted of experimental testing on candidate chemical species and semipermeable membranes. The detailed data which were obtained are included and discussed in the Appendix. Appendix A contains the data on chemical species and membranes taken by ITC/Solar. The mathematical models which were developed are presented in Appendix B. Discussion of internal polarization in the structure of a semipermeable membrane and its influence on permeation through a membrane in Pressure-Retarded Osmosis is presented in Appendix C. The experimental data collected by Gulf South Research Institute are contained in Appendix E, and the results of the calculations done by Tulane University with the thermodynamic correlation for activity coefficients UNIFAC are in Appendix F.

The following sections give a summary of the work and a discussion of the status of the development of each unmixing method or type of OHP heat engine as the result of work in this project.

A. Unmixing by Conjugation

On the basis of experimentally- and UNIFAC-obtained osmotic pressure data, it was found that binary mixtures unmixed by conjugation usually gave undesirably low osmotic pressure differences between the Donor and Receiver Solutions. The low osmotic pressures occurred because, within the temperature limits imposed by about 95°C as a waste heat source and 25°C as a heat sink, the miscible region is quite close to the two-phase region, and the binary therefore always exhibits a large positive deviation from ideality (i.e., the activity coefficients of the two chemical species are significantly greater than one). This problem is particularly acute with conjugating systems having a lower critical solution temperature. The only way to obtain high osmotic pressures within these temperature limits is with wide phase diagrams with wide separation of the conjugate solutions so that they would contain nearly zero and nearly 100 percent concentration of the solvent at the unmixing temperature. The best examples of binaries with such curves are amines and water,

such as methyldiethyl amine/water, a binary system having a lower critical solution temperature. However, this and similar amines are toxic and difficult to handle.

1. Conjugating Systems Having an Upper Critical Solution Temperature

The system methanol/hexane was examined extensively by both ITC/Solar and GSRI because a good membrane separation is possible between alcohols and hydrocarbons. However, as explained above, the osmotic pressure was low. Furthermore, a number of available flat-sheet membranes were attacked by methanol, except for the B-9 flat-sheet membrane. The B-9 hollow fiber collapsed under the combination of methanol and hydraulic pressure but did retain its semipermeability characteristics. On the other hand, the B-10 hollow fiber appeared to withstand collapsing, but its semipermeability characteristics were destroyed. Methanol also attacked the semipermeability characteristics of the FRL fiber.

The binary ethyl acetate/ethylene glycol had an adequate osmotic pressure difference, and the model indicated that this binary would give adequately cheap power (0.12 \$/kWh) and a thermal efficiency of 4 percent with a membrane having a reasonably good permeation coefficient of $0.003 \text{ m}^3/\text{m}^2 \text{ day atm}$. The results of these calculations and the results of other calculations on the most promising binaries found for all methods of unmixing are shown in Table II. However, all membranes were damaged by ethyl acetate.

2. Conjugating Systems Having a Lower Critical Solution Temperature

As shown in Table II, the binary system water/1-methyl piperidine showed adequate osmotic pressure differences and an energy cost of 0.24 \$/kWh at 4 percent thermal efficiency, providing as usual that an adequate membrane could be found and that its permeation coefficient would be 0.003. However, with the PA-300, CA-85, and PBI flat-sheet membranes, the reverse osmosis permeation coefficient was quite low, and with the B-9 flat-sheet membrane, the coefficient declined at a rate indicating chemical attack of the membrane.

Aside from the above problems, 1-methyl piperidine, like other amines, is toxic. This problem would be avoided with the system water/propoxypropanol

TABLE II

ONE MEGAWATT OHP HEAT ENGINE-
 PERFORMANCE OF BINARY SYSTEMS (Page 1 of 4)

Binary System	Unmixing Technique	Heat Source and Heat Sink Temperatures, °C	Maximum and Minimum Cycle Temperatures, °C	Assumed Permeation Coefficient $\frac{m^3}{m^2 \text{ day atm. and Thermal Efficiency, \%}}$	Permeator Surface m^2 and no. of 8" Du Pont Modules	Heat Transfer Surface for Heat Source, Heat Sink, and Regenerator, m^2	Mechanical Efficiency, %, and Surface Power $watt/m^2$	Unit Capital Cost, \$/kW, and Unit Energy Cost, \$/kWh
Ethyl Acetate Ethylene Glycol	Conjugation UCST	$\frac{100}{25}$	$\frac{65}{35}$	$\frac{0.003}{4.0}$	$\frac{75000}{140}$	$\frac{1485}{6140}$ 19100	$\frac{53}{13}$	$\frac{3300}{0.12}$
Methanol Ethylene Glycol	Distillation	$\frac{100}{25}$	$\frac{85}{35}$	$\frac{0.001}{0.44}$	$\frac{51000}{94}$	$\frac{15600}{21000}$ No Reg.	$\frac{53}{20}$	$\frac{3200}{0.11}$
Water N-Methyl Piperidine	Conjugation LCST	$\frac{100}{25}$	$\frac{90}{35}$	$\frac{0.003}{4.0}$	$\frac{94000}{170}$	$\frac{3730}{4900}$ 14400	$\frac{59}{11}$	$\frac{6900}{0.24}$

Notes:

- 1) Shell-side hydraulic pressure, always 100 atmospheres
- 2) Assumed overall heat transfer coefficient, $(3.7)(10)^5 \text{ cal/hr m}^2 \text{ } ^\circ\text{C}$
- 3) Assumed pump, turbine, and generator efficiencies, 0.90, 0.80, 0.95
- 4) All calculations for 1 megawatt plant
- 5) Assumed membrane and heat transfer surface cost, $\$/m^2$: 10,50

TABLE II
ONE MEGAWATT OHP HEAT ENGINE-
PERFORMANCE OF BINARY SYSTEMS (Page 2 of 4)

Binary System	Service	Solvent/Solute			Separators		
		Total Amount Used, Kg	Cost, \$/Kg	Throughput Rate in Separator, Kg/min	Linear Velocity in Separator, m/min	Total Volume Needed, m ³	Number of Separators Needed, (Note 8)
Ethyl Acetate Ethylene Glycol	Waste Heat	$(0.70)(10)^5$ $(2.5)(10)^5$	0.50 0.53	$(0.18)(10)^5$ $(0.62)(10)^5$	2.1 7.2 (Note 6)	80 (Note 7)	11
Methanol Ethylene Glycol	Waste Heat	$(0.78)(10)^5$ $(0.51)(10)^5$	0.14 0.53	$(0.10)(10)^5$ $(0.065)(10)^5$	200 (Vapor) (Note 10)	465 (Note 9)	60
Water 1-Methyl Piperidine	Waste Heat	$(1.5)(10)^5$ $(3.9)(10)^5$	0 25	$(0.15)(10)^5$ $(0.24)(10)^5$	3.8 6.1 (Note 6)	39 (Note 7)	5

Notes: (cont'd)

- 6) Based on number of separators and assumption that approximate liquid density is one gm/cm³
- 7) For one minute residence time of liquid
- 8) Each separator is assumed to be 10 meters high and one meter in diameter
- 9) For three second residence time of vapor
- 10) Assumed maximum permissible vapor velocity

TABLE II

ONE MEGAWATT OHP HEAT ENGINE-
PERFORMANCE OF BINARY SYSTEMS (Page 3 of 4)

Binary System	Floor Area Required, m ²				Total (Note 14)
	Heat Exchangers, Triple Tier (Note 11)	Separators (Note 12)	Permeators, Double Tier (Note 13)	Turbines	
Ethyl Acetate Ethylene Glycol	230	22	35	10	370
Methanol Ethylene Glycol	300	120	24	10	570
Water 1-Methyl Piperidine	190	10	43	10	320

Notes: (concluded)

- 11) Allowing 40/1 ratio of heat exchanger to floor area
- 12) Allowing 2 square meters for each separator
- 13) Allowing 1/2 square meter for each permeator
- 14) Allowing 25% for instrumentation, etc.

TABLE II

ONE MEGAWATT OHP HEAT ENGINE -
GENERAL COMMENTARY ON BINARY SYSTEMS (Page 4 of 4)

<u>Binary System</u>	<u>Unmixing Technique</u>	<u>Safety Problems</u>	<u>Compatibility With Present Membranes</u>	<u>Costs</u>	<u>Availability</u>	<u>Other Comments</u>
Ethyl Acetate Ethylene Glycol	Conjugation UCST	Ethyl Acetate Quite Flammable	Poor	Both species Reasonable	Both species Readily Available	Requires use of membrane at temperature above ambient.
Methanol Ethylene Glycol	Distillation	Methanol is toxic but widely handled	Poor	Both species are cheap	Both species readily available	Inherently very low thermal efficiency. Also separator may be large and expensive because of high volumetric flows of vapor (distillation only)
Water 1-Methyl Piperidine	Conjugation LCST	1-Methyl Piperidine is toxic	Mediocre	1-Methyl Piperidine is expensive	1-Methyl Piperidine is not a high-production chemical	
Water Disodium Phosphate (DSP)	Precipitation or Stratification	None	Good	Both species Reasonable	DSP readily Available	Requires use of membrane at temperature above ambient (55°C)

(POP), which was extensively tested at ITC/Solar and GSRI. The osmotic pressure was examined by several experimental techniques and by the UNIFAC method, and it was finally concluded that the osmotic pressure differences were too low, as with most other conjugating binaries. Furthermore, the aqueous POP solution attacked every membrane tested.

3. Status of Development

- i. Ethyl acetate/ethylene glycol is the most promising conjugating binary system. A membrane should be developed for this binary, and in particular for ethyl acetate.
- ii. With most known conjugating binaries, it is difficult to generate adequate osmotic pressure differences.
- iii. No membrane is available for any conjugating binary tested.

B. Unmixing by Distillation

1. Research and Development

In the OHP heat engine using distillation for unmixing, it is desirable that the permeable or solvent species should also be the volatile one (to achieve a high degree of purity in the Donor Solution). Because existing membranes are polar and/or hydrogen-bonding, it was decided that the effort on distillation unmixing in this project should be devoted to a study of permeating species which are polar and/or hydrogen-bonding (to permeate through a polar membrane, the permeating species should preferably be polar). This created somewhat of a dilemma because such species usually have a high latent heat of vaporization, which contributes to a low thermal efficiency. Low-molecular-weight alcohols, ketones, and chlorocarbons were considered as permeants. The nonpermeating, i.e., solute species, were of two types as described below.

a. Nonpolar and/or Non-Hydrogen-Bonding Solutes

One means of securing good rejection of the solute species by the membrane is to use a nonvolatile solute of opposite chemical properties, i.e., one having nonpolar and/or non-hydrogen-bonding groups. The following distillation binary systems were given a screening analysis with the initial mathematical model:

acetone/n-dodecane, acetone/tetradecane, methylene chloride/n-nonane, and methylene chloride/n-dodecane. These screening analyses indicated that these binary systems have low surface power (watts per square meter of membrane surface) and low mechanical efficiency. Both of these effects are due partially to unmixing at atmospheric pressure, but mostly to high molecular weight of the solute resulting in high circulation rates.

b. Polar and/or Hydrogen-Bonding Solutes

The rejection of polar and/or hydrogen-bonding solutes, i.e., solutes having the same groups as the solvent, was also considered on the assumption that their difference in size from the solvent would enable their rejection. Thus ethylene glycol and glycerol were considered as solutes, with methanol and ethanol as solvents.

It was calculated that binary mixtures of methanol/ethylene glycol would give very high osmotic pressure differences when unmixed by distillation, because the solutions are virtually ideal in the thermodynamic sense, as determined both experimentally and by UNIFAC calculations. Thus the energy cost was calculated from the analytical model to be reasonably low, 0.11 \$/kWh, on the assumption that a membrane resistant to the organic species could be found, and that its permeation coefficient A would be $0.001 \text{ m}^3/\text{m}^2 \text{ day atm}$, a reasonable value. On the other hand the thermal efficiency was also very low, 0.44 percent, due to the aforementioned high latent heat of vaporization of methanol, a polar and hydrogen-bonding permeant (see Table II).

Membrane tests were made with pure methanol on B-9, B-10, and FRL fibers. As discussed in the section on conjugation, none of these fibers was adequate with methanol. A number of flat-sheet membranes were also tested with methanol, and none was adequately resistant except the B-9 flat-sheet membrane, which subsequently failed in an osmosis test with methanol/ethylene glycol.

2. Status of Development

As a result of this work on distillation, the following conclusions can be drawn:

- i. Distillation offers the possibility of low energy costs because of the high osmotic pressures developed.
- ii. No membrane is available for any binary system considered thus far.
- iii. The thermal efficiency is too low with solvents considered to date because of their high latent heat of vaporization. This high latent heat is a consequence of choosing polar and hydrogen-bonding solvents, i.e., those which will permeate existing membranes. Nonpolar and/or non-hydrogen-bonding solvents would be more appropriate, but the use of these solvents would require development of new membranes.

C. Unmixing by Precipitation

As discussed above, it has not been possible thus far to find membranes for those promising binary systems which employ distillation or conjugation for unmixing. The problem is primarily that of obtaining a membrane which will resist attack by the organic species used. This is understandable because present-day membranes, which are all organic, are usually made to resist aqueous electrolyte solutions rather than organic species.

The precipitation (and stratification) method of unmixing offers the opportunity of using such aqueous electrolyte solutions, thereby obtaining a ready-made match of the binary system with existing membranes, although at somewhat elevated temperatures in the permeator. Although the precipitation method alleviates the problem of matching a membrane to a binary system, it does possess the problem of handling slurries and possibly of coating heat-transfer surfaces with solid precipitate. A further problem is that of the heat of solution of the salt used. For example, disodium phosphate heptahydrate, discussed below, has a heat of solution of 12,000 calories per gram mole of this salt. Although this heat of solution is negative, as desired to maintain a good temperature difference in the regenerator between the dissolving and crystallizing solute, it would be better if the heat of solution were zero.

Because the stratification method of unmixing, discussed below, possesses the advantages of precipitation without the above disadvantages due to phase change, we concentrated on examining the stratification method.

D. Unmixing by Stratification

1. Research and Development

Existing membranes, described above for use in the precipitation method of unmixing, are also applicable to stratification. In addition, as previously mentioned, the stratification method of unmixing has been extensively tested at ITC/Solar in connection with operation of bottom-heated saturated ponds. It is clear from those results that, because there is no phase change, stratification is a simple and effective unmixing technique and one which offers the possibility of minimizing the required heat-transfer surface and maximizing thermal efficiency.

Testing on the stratification method was confined to aqueous disodium phosphate (DSP) solutions. This solute has a very steep increase in solubility between 20° and 50°C, above which the increase is slow. Thus an important advantage of using DSP solutions is that the operating temperature of the permeator can be as low as 55°C, which should enable the use of several available commercial membranes.

The osmotic pressure differences were determined experimentally. The maximum osmotic pressure difference between saturated solutions at 28° and 50°C is about 290 atmospheres, and the osmotic pressure of the Donor Solution, 60 atmospheres, which intensifies internal polarization problems (see Appendix C).

The water/DSP system was tested with DP-PA-B9, UOP-CA-85, UOP-PA-300 and ABC-PBIL membranes. Of these, the PBIL membrane seemed best, largely because of its stability in continuous contact with hot, concentrated DSP solutions.

2. Status of Development

For economic power production by the stratification method, binaries must be used which will have a lower osmotic pressure at the low cycle temperature and a higher ratio of high to low osmotic pressure. This requirement can be met by some binaries, for example aqueous potassium

alum, but cycle temperatures between 30° and 90°C must be used instead of 30°-55°C, as in the design of the working model. The use of such higher temperatures may require further membrane development, either of new membranes or of high-temperature-resistant varieties of existing membranes. Because of its simplicity and other advantages cited above, the stratification method of unmixing should be extensively investigated further:

IV. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1. As the result of the work on this project, it was found that the OHP heat engine is technologically feasible and should be able to produce power economically from low temperature heat sources. However, a number of technological problems must be overcome before such a system can be fully developed.
2. The work with the four possible methods of unmixing revealed that each method has advantages and disadvantages. The work did not indicate which method is superior and should be developed further in preference to the others.
3. The conclusions reached about distillation are:
 - a. Distillation offers the possibility of low energy costs because of the high osmotic pressures developed.
 - b. No membrane is available for any binary system considered thus far.
 - c. The thermal efficiency is low with solvents considered to date because of their high latent heat of vaporization. This high latent heat is a consequence of choosing polar and hydrogen-bonding solvents, i.e., those which will permeate existing membranes.
4. The conclusions reached about conjugation are:
 - a. Ethyl acetate/ethylene glycol is the most promising conjugating binary system.
 - b. With most known conjugating binaries, it is difficult to generate adequate osmotic pressure differences.

c. No membrane is available for any conjugating binary tested. Ethyl acetate, being a good solvent, appeared to attack the membranes worked with particularly aggressively.

5. The precipitation method of unmixing offers the opportunity of using aqueous electrolyte solutions, thereby obtaining a ready-made match of the binary system with existing membranes, although at somewhat elevated temperatures in the permeator. While the precipitation method alleviates the problem of matching a membrane to a binary system, it does possess the problem of handling slurries and possibly of coating heat-transfer surfaces with solid precipitate.
6. Testing on the precipitation method was confined to aqueous disodium phosphate solutions. This binary was tested successfully at 50°-55°C with three different commercially available membranes. For economic power production by the precipitation method, binaries must be used which will have a lower osmotic pressure at the low cycle temperature and a higher ratio of high to low osmotic pressure. This requirement can be met by some binaries, for example aqueous potassium alum, but cycle temperatures between 30° and 90°C must be used instead of 30°-55°C, as in the working model. The use of such higher temperatures may require further membrane development, either of new membranes or of high-temperature-resistant varieties of existing membranes.
7. The membrane tests for the precipitation method of unmixing are also applicable to stratification. In addition, the stratification method of unmixing with a saturated pond was tested at ITC/Solar and was successful. It is clear from these results that, because there is no phase change, stratification is a simple and effective unmixing technique and one which offers the possibility of minimizing the required heat-transfer surface and maximizing thermal efficiency.

B. Recommendations

1. Because no one unmixing method proved itself to be superior, it is recommended that further work be done on all four methods.
2. Further identification of suitable solutes for precipitation and stratification should be done, as well as experimentation with membranes.
3. Materials-handling problems associated with the precipitation method should be studied to determine if this method has merit.
4. Further testing should be done with saturated ponds with appropriate binary systems for stratification.
5. In the further development of distillation systems, one promising direction is the identification of nonpolar volatile permeate species. However, for this type of compound, a new type of membrane must be developed.
6. Because ethyl acetate/ethylene glycol has been identified as the most promising conjugating binary, a suitable membrane should be developed.
7. To identify more promising conjugating binaries and to predict their properties, a thermodynamic model for these systems should be developed.
8. When the preceding recommendations have been carried out, sufficient information and analyses should be available on which to base a comparative analysis of the four unmixing methods. The most appropriate system should then be chosen for further development.
9. When the most feasible design of the system has been established, applications and market analyses should be carried out.

V. APPENDIX

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APPENDIX A

RESULTS AND DISCUSSION OF UNMIXING METHODS

I. UNMIXING BY CONJUGATION

A. Binaries Having an Upper Critical Solution Temperature

A survey was made of conjugating binary systems having an upper critical solution temperature (UCST). The binary systems found in this survey were examined for their conformance with the following criteria:

- 1) The UCST should be between 40° and 60°C. Above the UCST the binary should be a single solution; below the UCST the binary should separate into two solutions, one rich in solvent and the other rich in solute.
- 2) The density difference between the Donor and Receiver Solutions should be at least 0.05 gms/cm³ so that the separation in the separator can easily be effected by gravity.
- 3) The binary system should give high power output per unit area of the membrane (areal power) at 50 to 100 atm hydraulic pressure. The upper limit of hydraulic pressure is fixed by the fact that most membranes cannot withstand pressures higher than 100 atm and some cannot withstand more than 50 atm. As a guide for comparison, salt-water systems give about 5 watt/m² power at a hydraulic pressure of 50 atm.
- 4) Species used in the binary should have good safety properties.
- 5) These species should not be too expensive.

Six binaries with an UCST were considered as candidates for unmixing by conjugation. These were succinonitrile/water, succinonitrile/benzene, furfural/cyclopentane, ethyl acetate/ethylene glycol, methanol/n-heptane, and dimethyl formamide/cyclohexane. Of these the first three binaries were rejected because of the toxicity or cost of one or both binary species. The other three binaries are discussed below.

1. Methanol/n-Heptane

a. Osmotic Pressure and Screening Analyses

Methanol/n-heptane was considered as a candidate binary system having an upper critical solution temperature of 51°C. The phase diagram was determined experimentally for this binary and found to be similar to that in the literature. The results are shown in Table A-I.

Liquid-vapor equilibrium data were obtained on the methanol/hexane* system (which has properties close to the desired methanol/n-heptane system) by means of the Othmer equilibrium still. These data were used to calculate the activity coefficient and the osmotic pressure of methanol over the entire range of methanol concentration in hexane. The results are shown in Figure A-1. The osmotic pressure values were disappointingly low, a pattern that was to be repeated for all conjugation mixtures. These results for methanol/hexane were largely confirmed by the UNIFAC calculations of Tulane (see Appendix F); see Figure A-2.

On the assumption that methanol/n-heptane data would be similar to those for methanol/hexane, the membrane areal power of the methanol/n-heptane system was calculated by means of the screening model and found to be only 0.70 watt/m² of membrane surface, which was much too low for an adequately low power cost. In other words, too much membrane area would be required for a given power output.

The value of surface power was based on a number of assumptions. Perhaps the most important of these assumptions was the value of the permeation coefficient, assumed to be 0.001 m³/m² day atm. However, even if the

*Hexane was used because it is an easily available compound similar in properties to n-heptane.

TABLE A-I

TEMPERATURES OF SEPARATION OF
MIXTURES OF METHANOL AND n-HEPTANE

<u>Weight Percent</u> <u>Methanol in n-Heptane</u>	<u>Temperature of</u> <u>Separation, °C</u>
3.0	27
5.0	31
10.0	44
19.0	52
35.0	52
55.0	48
66.0	35
75.0	28

FIGURE A-1

ACTIVITY AND OSMOTIC PRESSURE OF METHANOL IN MIXTURES WITH HEXANE

(Determined from Equilibrium Still Tests, 9-16 November 1978).

FIGURE A-2

ACTIVITY COEFFICIENTS OF METHANOL IN
METHANOL/HEXANE AND METHANOL/HEPTANE
SOLUTIONS AT 50°C

coefficient were increased by a factor of three, the surface power would be only $(3)(0.7) = 2.1$ watt/m², still considerably lower than desired.

b. Membrane Testing

i. Du Pont PA-B-9/B-10 Membranes

1) Flat-Sheet Membrane

A series of reverse osmosis, pressure flow, and osmosis tests was made with B-9 flat-sheet membrane (polyamide, fabricated by Permasep Division of Du Pont Corporation). The tests were made with 0.5 percent salt solutions, methanol/water solutions, pure methanol and pure hexane. Results are shown in Table A-II. The following conclusions were reached: 1) the membrane rejects hexane; 2) the methanol permeation coefficient is 0.016 m³/m² day atm, a little more than half that of water; and 3) for the highest flux the membrane should be changed gradually from water immersion to methanol immersion.

A B-9 membrane, conditioned as described in Test 6 of Table A-II, was given an osmosis test. A methanol/hexane mixture containing 96 wt.% methanol flowed on the skin side of the membrane and pure methanol on the other side. The permeation coefficient value* was only 0.002 m³/m² day atm as compared with 0.016 in Pressure Test 6 of Table A-II. This low result can probably be attributed to the thickness of the flat-sheet membrane (280 microns versus 28 microns for a hollow fiber) and internal polarization (see Appendix C). Thickness is an important factor in an osmosis test but not in a pressure flow test.

2) Hollow Fibers

Pressure flow tests were made on three different types of hollow fibers with pure methanol. For the Du Pont B-10 fiber the permeation coefficient was quite low (0.00015 m³/m² day atm), and the brine semipermeability of the fiber was completely destroyed by contact with methanol. With the B-9 fiber the semipermeability was retained after the methanol pressure flow test. On the other hand the combination of pressure differential and contact with methanol caused the fibers to collapse to a great extent.

*In this calculation the osmotic pressure was assumed to be the ideal value, 25 atmospheres, because of the high mol fraction of methanol.

TABLE A-II

REVERSE OSMOSIS AND PRESSURE TESTING OF B-9 PERMEATOR MEMBRANE WITH METHANOL/HEXANE

No.	Conditioning* and Type of Test	Solvent** Permeation Coefficient m ³ m ² day atm	Solute** Rejection %	Results and Conclusions
1	No conditioning. Control test with 0.5% salt.	0.021	95.5	
2	Without shutting down Test 1, changed to 60% methanol.	0.006	0	Permeation rate of 60% methanol much less than that in dilute brine (Test 1).
3	Without shutting down Test 2, returned to 0.5% salt solution.	0.013	95.8	Comparison with Test 1 indicates that 60% methanol solution decreased water permeation coefficient.
4	Fresh membrane soaked in methanol overnight, then tested in 0.5% salt solution.	0.013	96.6	Comparison with Test 3 indicates that 60% and 100% soak give same results.
5	Fresh membrane soaked in hexane overnight, then tested in 0.5% salt solution.	0.026	89.5	Comparison with Test 1 indicates that soaking in hexane changes salt rejection only.
6	Fresh membrane soaked 10 minutes each in 33/67 and 60/40 weight ratio of methanol/water, then stored in methanol one hour and tested in pure methanol.	0.016	-	Comparison with Test 2 indicates that gradual conditioning is better than sudden change of immersion liquid.
7	Fresh membrane conditioned as in Test 6, then conditioned ten minutes each in 33/67 and 60/40 weight ratio of hexane/methanol. Finally stored in hexane one hour and then tested in hexane.	0	-	The B-9 membrane rejects hexane.

*All membranes immersed in water prior to initial service.

**Hydraulic pressure 31-34 atmospheres.

Test dates 2-7 November 1978.

With the FRL permeator the permeation coefficient with methanol was lower than desired. Furthermore, both the rejection and the permeation coefficient in brine reverse osmosis were reduced by previous contact with methanol under pressure.

It was concluded that none of the three fibers, B-9, B-10, or FRL, was appropriate for methanol service in PRO.

ii. Other Membranes

The UOP-PA-300 membrane showed blisters when gradually changed from water to pure methanol immersion. In an attempted subsequent pressure flow test with pure methanol, it was clear that the methanol had caused membrane failure.

In other pressure flow tests with pure methanol, cellulose acetate membranes showed a gradual flux decline over a two-hour period (the permeation coefficient declining from an initial high value to a value between 0.010 and 0.020 $\text{m}^3/\text{m}^2 \text{ day atm}$, which continued to decline), indicating plasticization. The CEL-PBI membrane also declined, but at a low enough rate to indicate its possible utility with methanol (from 0.013 to 0.009 $\text{m}^3/\text{m}^2 \text{ day atm}$).

In another methanol/hexane osmosis test at an osmotic pressure of 25 atmospheres, the Envirogenics membrane, Env-214, gave a low permeation coefficient of 0.0002 $\text{m}^3/\text{m}^2 \text{ day atm}$.

Thus no appropriate membrane was found for the methanol/n-heptane system.

2. Ethyl Acetate/Ethylene Glycol

a. Osmotic Pressures and Screening Analyses

Boiling-point-elevation data were obtained on the system ethyl acetate/ethylene glycol to obtain the curve of osmotic pressure versus composition. The use of the boiling-point-elevation method entailed the assumption that the partial pressure of ethylene glycol is negligible compared to that of ethyl acetate. These data were used to calculate activity coefficients and osmotic pressure of ethyl acetate over the range of

ethyl acetate concentration. Results are shown in Figure A-3. These results were largely confirmed by the UNIFAC calculations of Tulane. Although the osmotic pressure values were lower than desired, the membrane surface power calculated from the screening model was 6 watt/m^2 , an acceptable value.

b. Membrane Testing

Cellulose acetate, cellulose acetate butyrate (CAB), PA-300, and B-9 flat-sheet membranes were all conditioned by changing gradually from water immersion to ethylene glycol immersion. All seemed satisfactory, according to visual examination, except the PA-300 membrane, which showed blisters. The immersion medium was then changed gradually from ethylene glycol to ethyl acetate. The PA-300 membrane showed a significant number of blisters, and all of the cellulose acetate membranes were dissolved. Only the B-9 membrane survived this test.

Pressure flow tests with ethyl acetate were made, using DP-PA-B9 and CEL-PBI membranes. Both membranes rejected ethyl acetate completely. Pressure flow tests with ethylene glycol are reported in the following section on distillation, but these two membranes also rejected ethylene glycol.

As a result of these conditioning and pressure flow tests with ethyl acetate and ethylene glycol, the commercially available membranes tested were found to be inadequate, namely: UOP-CA-75, UOP-CAB, UOP-PA-300, DP-PA-B9, CEL-PBI.

3. Dimethyl Formamide/Cyclohexane

The phase diagram for the binary dimethyl formamide/cyclohexane was determined experimentally by making up mixtures of given composition and raising the temperature to determine the point of complete miscibility. The data are listed in Table A-III.

According to the phase diagram, there will be 0.25 mole fraction of the solute cyclohexane in the Donor Solution. This concentration would give a high Donor Solution osmotic pressure, which would be deleterious for

FIGURE A-3

ACTIVITY AND OSMOTIC PRESSURE OF ETHYL ACETATE
IN MIXTURES WITH ETHYLENE GLYCOL

(Determined from Boiling-Point-Elevation Tests)

TABLE A-III

TEMPERATURES OF SEPARATION OF
MIXTURES OF DIMETHYL FORMAMIDE AND CYCLOHEXANE

<u>Weight Percent</u> <u>Dimethyl Formamide</u> <u>in Cyclohexane</u>	<u>Temperature of</u> <u>Separation</u> <u>°C</u>
10.0	<20
15.0	44
25.0	49
50.0	48
75.0	34
85.0	26
90.0	<20

two reasons: First, the osmotic pressure difference between the Donor and Mixed Solution would be low; second, there would probably be excessive internal polarization in the porous substructure of the asymmetric membrane because of contact with the Donor Solution passing through it (see Appendix C).

For these reasons no further work was done with this binary.

B. Binaries Having a Lower Critical Solution Temperature (LCST)

A survey was made of conjugating binary systems having a lower critical solution temperature. Candidate systems were chosen which had a LCST between 45° and 65°C and which conformed to the other criteria for candidate binaries with an UCST.

1. Water/1-Methyl Piperidine

a. Osmotic Pressures and Screening Analysis

By means of the vacuum still, the total pressures of water/1-methyl piperidine mixtures at 35°C were determined over the entire concentration range. From these data it was possible to obtain the activity coefficient of each species by means of the Duhem-Margules equation. Results are shown in Figures A-4 and A-5. The osmotic pressures were calculated from the activity coefficient data.

From the screening model the energy cost was calculated to be 0.24 \$/kWh with a thermal efficiency of 4.0 percent and the assumption of the existence of an appropriate membrane. However, aside from any questions of its compatibility with membranes, 1-methyl piperidine has the disadvantages of toxicity, high cost, and unpleasant odor.

b. Membrane Testing

Reverse osmosis testing was carried out with 2 mole % of 1-methyl piperidine in an aqueous solution. This concentration corresponded to an osmotic pressure of 33 atmospheres. Results are shown in Table A-IV.

In the testing of UOP-CA-85, UOP-PA-300, and CEL-PBI membranes, the permeation coefficient was on the order of only 7-15% of what it was

FIGURE A-4
EXPERIMENTAL DATA ON TOTAL PRESSURE
VS.

MOLE FRACTION 1-METHYL PIPERIDINE (MP)/WATER SOLUTIONS AT 35°C

FIGURE A-5
ACTIVITY COEFFICIENTS OF WATER AND 1-METHYL PIPERIDINE (MP)
IN SOLUTIONS AT 35°C

TABLE A-IV

REVERSE OSMOSIS TESTS WITH THE BINARY SYSTEM 1-METHYL PIPERIDINE (MP)/WATER

Membrane	Test No. with Same Membrane	Feed Composition			Hydraulic Pressure, P atm	A, Water Permeation Coefficient (Note 1)	Salt Rejection %	Time from Start of Test Minutes	Comments
		mole percent				m ³			
		H ₂ O	MP	NaCl		m ² day atm			
UOP-CA-85	1	100	0	0	70	0.0130	-	50	Steady flux
	2	98	2	0	70	0.00090	-	230	Declining flux (Note 2)
	3	99.84	0	0.16	70	0.0042	2	30	Steady flux
	1	99.84	0	0.16	51	0.015	95		
UOP-PA-300	1	98	2	0	69	0.0032	-	10	Declining flux
	2	99.84	0	0.16	70	0.021	83	30	Steady flux
	1	99.84	0	0.16	69	0.020	89	75	
CEL-PBI	1	98	2	0	69	0.0028	-	20	Declining flux
	2	99.84	0	0.16	69		not tested		Membrane cracked
	1	99.84	0	0.16	65	0.022	58	45	
DP-PA-89	1	98	2	0	69	0.020	-	30	Steady flux
	2	98	2	0	48	0.017	-	40	Flux declined
	3	98	2	0	48	0.0058	-	45	
	4	98	2	0	48	0.0055	-	50	
	5	98	2	0	69	0.014	-	55	
	6	98	2	0	69	0.0038	-	60	
	7	98	2	0	69	0.0052	-	65	
	8	99.84	0	0.16	70	0.015	32	70	Steady flux
	1	99.84	0	0.16	70	0.013	86	80	

Note 1: In the tests with 98 mole % water, the water permeation coefficient, A, is calculated on the assumption that $\pi = \pi_{\text{ideal}} = 33$ atm.
 $A = J/(P-33)$, where J is flux, m³/m² day.

Note 2: Membrane in contact with 93 and with 96 mole % water at 70 atmospheres hydraulic pressure a total of two hours before test with 98 mole % water.

with pure water or dilute salt solution. With the DP-PA-B9 membrane the permeation coefficient was at first $0.020 \text{ m}^3/\text{m}^2 \text{ day atm}$, as it should have been, but it declined over a 4-hour period to 0.0052. When the permeator was finally operated with a dilute brine, the coefficient returned to normal, but the rejection was only 32 percent as compared with a normal 86-90 percent.

2. Water/2-Butoxyethanol

a. Osmotic Pressures

Data on the osmotic pressure versus the composition in the miscibility region of water/butoxyethanol mixtures were obtained by the freezing-point-depression method. Results are shown in Figure A-6. By comparing the phase diagram with the osmotic pressure curve, it was seen that the maximum possible osmotic pressure is only 55 atmospheres, which is too low for PRO purposes. This is due to the fact that the minimum possible mole fraction of water in the two-phase region is 82 mole percent, whereas it should be much lower.

b. Membrane Testing

i. DP-PA-B9 Membrane

1) Flat-Sheet Membrane

The DP-PA-B9 flat-sheet membrane gave an apparent permeation coefficient (see Appendix C) of only $0.0003 \text{ m}^3/\text{m}^2 \text{ day atm}$ in an osmosis test with water/2-butoxyethanol at an osmotic pressure of 40 atmospheres on the skin side and zero osmotic pressure on the porous substructure side, as shown in Figure A-7.

2) Hollow Fiber

In a PRO test with water/2-butoxyethanol (55 atmospheres osmotic pressure on the shell side--skin side--and zero osmotic pressure on the bore side--porous substructure side--with 14 and 6 atmospheres hydraulic pressure on the shell and bore side, respectively), the initial permeation coefficient of PA-B9 hollow fibers was $0.00065 \text{ m}^3/\text{m}^2 \text{ day atm}$, higher than with the flat-sheet membrane, as expected (see Appendix C).

FIGURE A-6

PROPERTIES OF INTEREST IN WATER/BUTOXYETHANOL
(BUTYL CELLOSOLVE) SOLUTIONS

FIGURE A-7

OSMOSIS TESTS WITH FRESH MEMBRANES
IN WATER/ALCOHOLIC ETHER SYSTEMS

However, the coefficient dropped to 0.00012 in 5½ hours, as shown in Figure A-8. In a brine reverse osmosis test after the PRO test, the rejection was only 66-79 percent compared to 84 percent before. Similarly, the RO permeation coefficient was 0.0028 m³/m² day atm compared to 0.0075 before. On the other hand, the bore-flow coefficient was not decreased by the PRO test.

It was concluded that the PRO test with water/2-butoxyethanol caused deterioration of the semipermeability characteristics of the B-9 fibers.

ii. UOP-PA-300 Membrane

The PA-300 membrane gave a permeation coefficient of 0.0008 m³/m² day atm in an osmosis test with water/2-butoxyethanol at an osmotic pressure of 40 atmospheres on the skin side and zero osmotic pressure on the porous substructure side (see Figure A-7). This osmosis test was repeated and amplified with osmotic pressures of 60 and 17 atmospheres on the skin and porous substructure sides, respectively. In this case, the permeation coefficient was only 0.00011 m³/m² day atm. The decrease in permeation coefficient is largely attributable to appreciable solute on the porous substructure side (see Appendix C). At any rate, the PA-300 membrane is not appropriate for PRO service with water/2-butoxyethanol.

3. Water/Propoxypropanol (POP)

Because it is difficult to obtain a pure isomer of propoxypropanol (1-n-propoxy-2-propanol or 2-n-propoxy-1-propanol), all experiments were performed with a 95/5 mixture by weight of 1-n-propoxy-2-propanol/2-n-propoxy-1-propanol. This mixture is fairly cheap and readily available.

a. Osmotic Pressures

The osmotic pressures for this system were also obtained by freezing-point-depression techniques. These data are shown in Figure A-9. The phase diagram was determined also. The maximum osmotic pressure with water/POP was 160 atmospheres, higher than with water/butoxyethanol, largely due to the fact that the minimum mole fraction of water in the two-phase region is 67 mole percent (at 90°C), considerably lower than the 82 mole percent with water/2-butoxyethanol. The composition-temperature data for the phase diagram are shown in Table A-V.

FIGURE A-8

PRESSURE-RETARDED OSMOSIS WITH
DU PONT B-9 FIBERS AND BUTOXYETHANOL/WATER AS THE BINARY SYSTEM

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Conditions

- 1) Shell-side: 82 mole % H_2O , osmotic pressure 60 atm, hydraulic pressure 14 atm.
- 2) Bore-side: water at hydraulic pressures varying from 5 to 6.5 atm.

FIGURE A-9
 PROPERTIES OF INTEREST IN WATER/PROPOXYPROPANOL* SYSTEMS

* 95/5 wt. ratio, $\frac{1\text{-n-propoxy-2-propanol}}{2\text{-n-propoxy-1-propanol}}$

TABLE A-V

TEMPERATURES OF SEPARATION OF
MIXTURES OF PROPOXYPROPANOL* AND WATER

<u>Weight Percent</u> <u>POP in Water</u>	<u>Temperature of</u> <u>Separation, °C</u>
10.0	miscible up to 90
11.0	70.0
20.0	38.8
30.0	31.8
40.0	30.8
50.0	32.0
60.0	34.2
70.0	44.2
74.0	56.4
75.0	59.8
76.0	68.0
77.0	miscible up to 90

*95/5 mixture by weight of 1-n-propoxy-2-propanol
and 2-n-propoxy-1-propanol.

The osmotic pressure values were somewhat suspect because they were obtained at temperatures below 0°C, i.e., below freezing. This is considerably below the operating temperature of 30°C, which is close to the two-phase region. Solutions in the miscible region but close to the two-phase region are much less ideal, and tend to have a much lower osmotic pressure than solutions further away from the two-phase region.

Boiling-point-elevation tests under vacuum and in the region of 35°C indicated that there was no osmotic pressure for either butoxyethanol or POP solutions. This latter result was supported by the UNIFAC calculations of Tulane. Subsequent reverse osmosis tests with aqueous POP solutions on B-9 membranes indicated that at relatively low concentrations of POP, the freezing-point-depression osmotic pressures of 25 atmospheres are realistic. See Figure A-10. However, tests with B-10 hollow fibers in higher concentrations of POP indicated that the real values of higher osmotic pressures were only half as high as those obtained by freezing-point-depression techniques.

b. Membrane Testing

Reverse osmosis and osmosis tests were made with dilute brine solutions before and after conditioning various membranes to immersion in a concentrated aqueous POP solution. Results are shown in Tables A-VI and A-VII. DP-PA-B9 and FT-30 membranes were adequate according to these tests. With the ABC-PBIL membrane it appeared that the porous substructure had been affected by immersion in POP solution. The cellulose acetate (CA) membranes were definitely damaged by contact with the POP solutions. The UOP-PA-300 membrane appeared adequate in the reverse osmosis test but was not tested in brine osmosis after immersion in POP solutions because of relatively poor performance in the brine osmosis test before immersion.

On the other hand results with the UOP-PA-300 membrane were better than those of all the above membranes in an osmosis test with 82 mole % POP (98 atmospheres osmotic pressure according to the freezing-point-depression tests), the membranes having previously been soaked in a similar solution for 2 days. The coefficient was $0.00075 \text{ m}^3/\text{m}^2 \text{ day atm}$, which is not

FIGURE A-10

ESTIMATION OF OSMOTIC PRESSURE OF
10 WEIGHT PERCENT POP/WATER SOLUTION

(Du Pont B-9 Flat-Sheet Membrane Used)

TABLE A-VI

EFFECT OF IMMERSION IN AQUEOUS PROPOXYPROPANOL (POP)
SOLUTIONS¹ ON REVERSE OSMOSIS PERFORMANCE IN DILUTE BRINE²

Membrane Designation	Water Permeation Coefficient $\text{m}^3/\text{m}^2 \text{ day atm}$			Rejection, percent			Comments
	Before Immersion (3)	After Immersion (3)	Percent Change	Before Immersion (3)	After Immersion (3)	Percent Change	
DP-PA-B9	0.0215	0.018	-16	91.7	94.4	+2.9	<u>Very good results.</u> Rejection actually improved by immersion.
ABC-PBIL	0.025	0.025	0	88.0	88.4	+0.4	<u>Very good results.</u> Essentially no change in performance of immersed membrane.
FT-30	0.032	0.051	+58	98.6	95.7	-2.9	<u>Good results.</u> Slight decline in rejection but phenomenal increase in permeation coefficient. Best membrane performance after immersion, but more affected than DP-PA-B9 by immersion.
UOP-PA-300	0.025	0.032	+28	97.5	92.2	-5.4	<u>Good results.</u> Somewhat of a decline in rejection but increase in permeation coefficient.
UOP-CA-85	0.0155	0.043	+178	95.1	35	- 63	<u>Poor results.</u> The skin of the membrane was definitely damaged by immersion in POP.

(1) The propoxypropanol was a mixture of 95 wt. % 1-n-propoxy-2-propanol, and 5 wt. % 2-n-propoxy-1-propanol. Immersion was in water, 40 wt. % POP 15 minutes, 75 wt. % POP 60 minutes, 40 wt. % POP 15 minutes, finally storage in water.

(2) 5000 ppm NaCl brine, nominally 50 atmospheres hydraulic pressure.

(3) Average of two samples.

TABLE A-VII

EFFECTS OF IMMERSION IN AQUEOUS PROPOXYPROPANOL (POP)
SOLUTIONS¹ ON OSMOSIS PERFORMANCE IN DILUTE BRINE²

<u>Membrane Designation</u>	<u>Apparent Permeation Coefficient</u> <u>m³/m² day atm</u>		<u>Percent Change</u>	<u>Comments</u>
	<u>Before Immersion</u>	<u>After Immersion</u>		
FT-30	0.0094	0.017	+ 81	<u>Excellent results.</u> The osmosis permeation coefficient has been increased significantly by the immersion conditioning in POP. Increase is similar to increase in RO coefficient after immersion.
DP-PA-B9	0.0036	0.0041	+ 14	<u>Good results.</u> Osmosis permeation coefficient after immersion equal to or better than coefficient before immersion. This result is qualitatively similar to result with RO coefficient after immersion.
ABC-PBIL	0.0085	0.0050	- 41	<u>Mediocre results.</u> Osmosis permeation coefficient after immersion worse than before immersion, but membrane still seems acceptable for use in osmosis or PRO with POP/H ₂ O. This result in contrast to result with RO coefficient after immersion because in that case coefficient did not change.

- (1) The propoxypropanol was a mixture of 95 wt % 1-n-propoxy-2-propanol, and 5 wt % 2-n-propoxy-1-propanol. Immersion was in water, 40 wt % POP 15 minutes, 75 wt % POP 60 minutes, 40 wt % POP 15 minutes, finally storage in water.
- (2) Water on porous substructure side, NaCl brine having 25 atmospheres osmotic pressure on the skin side.

very high, but about 4 times better than the next best, that for DP-PA-R9, which was only 0.00019. However, when a POP solution having 25 atmospheres osmotic pressure was introduced on the porous substructure side (as would occur in PRO practice) of the UOP-PA-300 membrane, the coefficient dropped to an unacceptably low value of $0.00015 \text{ m}^3/\text{m}^2 \text{ day atm}$ due to internal polarization (see Appendix C).

An FRL fiber was physically weakened by contact under pressure with aqueous POP solutions.

II. UNMIXING BY DISTILLATION

A. Nonpolar and/or Non-Hydrogen-Bonding Solutes

It was decided at the outset of the studies on distillation that the solvent, i.e., the permeable species, should also be the volatile species. It was also decided that the solvent should be polar and/or hydrogen bonding because of the fact that existing membranes preferentially pass these species. Therefore, to obtain good rejection, it appeared at first that the solute (nonpermeating) species should necessarily have opposite properties, i.e., be nonpolar and/or non-hydrogen bonding, in addition to being nonvolatile.

Binary systems considered were acetone/n-dodecane, acetone/tetradecane, methylene chloride/n-nonane, and methylene chloride/n-dodecane. These were evaluated by means of the distillation screening model. The surface power was found to be relatively low even with the optimistic assumption that in the PRO permeator the real osmotic pressures would equal the ideal osmotic pressures, i.e., those based on Raoult's Law.

The low surface power values are caused by the low mechanical efficiency of the system. This low mechanical efficiency occurs to a certain extent because of the difficulty in distillation of conducting the unmixing at the high permeator hydraulic pressures. However, the mechanical efficiency was especially low with the solutes used (i.e., those having the properties stated above) because of their high molar volume (high molecular weight relative to that of the solvent).

The high molar volume of the solute increases the circulation rate of the Receiver Solution, which, according to the flow diagram for distillation, must be pressurized in the Receiver Solution pump and depressurized in the turbine, both of which are considerably less than 100% efficient.

B. Polar and/or Hydrogen-Bonding Solutes

In an effort to improve the mechanical efficiency of the distillation process, solutes having a relatively low molecular weight were considered. These included ethylene glycol and glycerol, which, it was hoped, might

be rejected on the basis of size (steric hindrance) rather than on the basis of chemical properties.

1. Osmotic Pressures and Screening Analyses

Osmotic pressures of the methanol/ethylene glycol system were obtained by the boiling-point-elevation method. The results indicated very high osmotic pressures due to a virtually ideal solution.

Analyses were made with four distillation binaries, consisting of methanol or ethanol as solvents, and ethylene glycol or glycerol as solutes. These analyses indicated that the energy costs would be reasonable if a membrane were available--0.11 \$/kWh. However, the thermal efficiency was very low--less than one-half percent. This is due to two facts: first, the polar and/or hydrogen-bonding solvent--methanol or ethanol--has a high volumetric latent heat of vaporization (calories per unit volume), particularly in comparison with the gross volumetric useful energy output (calories or kilowatt-hours per unit volume of permeate); second, it is not possible to use a regenerator effectively to recover this latent heat because the Donor Solution produced by the distillation condenses at a temperature below the bubble point of the Still Feed; i.e., little or no latent heat can be transferred to the Still Feed.

2. Membrane Testing

Pressure flow tests with pure methanol were discussed in the preceding section on conjugation unmixing with binaries having an upper critical solution temperature.

Pressure flow tests were made with ethanol at 40 atmospheres hydraulic pressure. The results are shown in Figures A-11 and A-12. The UOP-CAB, UOP-PA-300, and CEL-PBI results were ambiguous in the sense that the permeation coefficient dropped considerably before leveling out. The UOP-CA-85 and DP-PA-B9 membranes gave low but relatively constant permeation coefficients on the order of 0.010 and 0.003 m³/m² day atm, respectively.

FIGURE A-11

PERMEATION COEFFICIENTS OF ETHANOL AT 41 ATMOSPHERES
AND AMBIENT TEMPERATURES IN CELLULOSE ACETATE (L-S)
MEMBRANES HEATED TO VARIOUS TEMPERATURES

FIGURE A-12

PERMEATION COEFFICIENTS OF ETHANOL AT 41 ATMOSPHERES
AND AMBIENT TEMPERATURE--MEMBRANES OTHER THAN CELLULOSE ACETATE

Note:

All membranes conditioned by immersion
as follows:

- 1) Water
- 2) 33/67, 67/33 weight ratio ethanol
to water, 15 minutes each
- 3) Pure ethanol

In pressure flow tests with ethylene glycol on flat-sheet membranes, the UOP-CAB membrane was plasticized, but the UOP-CA-75, DP-PA-B9, UOP-PA-300, and CEL-PBI membranes appeared possibly adequate with ethylene glycol. The results are shown in Figure A-13.

As a result of the conditioning and pressure flow tests with methanol and ethylene glycol, the following commercially available membranes were all found to be inadequate: UOP-CA-75, UOP-CAB, and UOP-PA-300. The DP-PA-B9 membrane was adequate in these tests. However, in an attempted osmosis test with 85 mole % methanol in ethylene glycol on the skin side and methanol on the porous substructure side, a differential head could not be supported across the membrane. Apparently the membrane was excessively plasticized by the solutions.

The CEL-PBI membrane also appeared adequate from the conditioning and pressure flow tests but could not be tested in osmosis because of its brittleness. In osmosis tests with methanol/ethylene glycol the permeation coefficients of DP-PA-B9 and ABC-PBIL membranes were quite low and decreased with increasing osmotic pressures (see Appendix C).

In summary, no appropriate membrane was found for methanol/ethylene glycol as a binary system appropriate for distillation unmixing.

FIGURE A-13
PERMEATION COEFFICIENTS OF ETHYLENE GLYCOL
AT 40 ATMOSPHERES AND AMBIENT TEMPERATURE

Note: All membranes conditioned by immersion as follows:
1) water
2) 33/67, 67/33 weight ratio ethylene glycol, 15 minutes each.
3) ethylene glycol

III. UNMIXING BY PRECIPITATION

With regard to the electrolytes and also the membranes to be used, precipitation and stratification are somewhat similar as unmixing methods. Because stratification appears to have some advantages over precipitation, as discussed in the SUMMARY AND DISCUSSION OF RESULTS, the detailed discussion on work accomplished will be given in the following section on stratification.

IV. UNMIXING BY STRATIFICATION*

In this technique a "saturated pond" is used, as discussed later in this section. The bottom of the pond is heated and the top cooled. This causes the pond feed to separate into a cool dilute low-density top (Donor) solution and a hot concentrated high-density bottom (Receiver) solution. The concentration increases monotonically from top to bottom and is saturated throughout. As with precipitation, the permeator is operated at the high cycle temperature. ITC/Solar was the first to conceive of using such ponds as unmixing devices for membrane permeators in energy conversion, and has tested them successfully for some time on another project.

The saturated pond unmixes without phase change, thus eliminating all the solids-handling problems associated with precipitation. As another benefit, any latent heat due to phase change is eliminated. It was planned to use the stratification method of unmixing in the operating model, as discussed in Appendix D.

A. Aqueous Disodium Phosphate Solutions

There are a number of aqueous electrolytes for which the solubility increases as desired within the maximum and minimum cycle temperatures of 30° and 90°C. Aqueous disodium phosphate (DSP) solutions were considered for initial study. Solutions of this electrolyte have a steep solubility curve in the range 30°-50°C. Therefore, membranes can be operated at 55°C, which is possible with existing membranes. A membrane-binary system can thus be made available for an operating model. Also, the use of heat sources at 55°-60°C is of interest in itself.

Because of the steep solubility curve, there is also a considerable change in osmotic pressure and density for DSP solutions. Thus, between the temperatures of 28° and 50°C, the osmotic pressure will change from 58 to 250 atmospheres, as shown in Figure A-14. A graph of solubility and density of saturated DSP solutions, as determined by experiment, is shown in Figure A-15.

*The membrane testing discussed in this section would also apply to precipitation.

FIGURE A-14
SOLUBILITY AND OSMOTIC PRESSURE OF
AQUEOUS DISODIUM PHOSPHATE SOLUTIONS

Figure A-15. SOLUBILITY AND DENSITY OF SATURATED DISODIUM PHOSPHATE SOLUTIONS IN WATER

B. Membrane Testing in DSP Solutions

1. Hollow Fiber Membranes

a. DP-PA-B9 Fiber

The hollow fiber version of the DP-PA-B9 membrane was tested with hot DSP solutions in PRO. In one test at 48°C with solutions having osmotic pressures of 126 and 22 atmospheres on the shell side (skin side) and bore side (porous substructure side), respectively, the permeation coefficient was $0.00065 \text{ m}^3/\text{m}^2 \text{ day atm}$ and was constant during the one-hour run. Both of these results were quite favorable to the use of B-9 membranes with the DSP/H₂O system, particularly since operation was at approximately 50°C. However, in reverse osmosis control tests made with dilute brine before and after the PRO run with DSP solution, the permeation coefficient and the rejection were both down somewhat in the final RO test, which indicated possible damage by the DSP solution. These results are shown in Table A-VIII.

2. Flat-Sheet Membranes

a. Screening Tests in DSP Solutions

Two series of screening tests were made with DSP solutions on flat-sheet membranes. One series consisted of osmosis tests at an elevated temperature (55°C) with 44.5% DSP on the skin side and 14.5% DSP on the porous substructure side, corresponding to saturation temperatures of 50° and 28°C and osmotic pressures of 250 and 58 atmospheres, respectively.

The other series of tests showed the effect on RO performance of soaking the membranes in a concentrated solution of DSP (44.5%) for 20 hours at an elevated temperature (55°-58°C). The RO tests were performed with 5000 ppm NaCl solutions at 55 atmospheres hydraulic pressure and ambient temperature. Results are discussed below.

i. Cellulose Acetate Membrane

The osmosis test was made with a UOP-CA-85 cellulose acetate membrane. The permeation coefficient declined from 0.00038 to $0.00026 \text{ m}^3/\text{m}^2 \text{ day atm}$ in 400 minutes.

Another CA-85 membrane was soaked 20 hours at 55°-58°C in 44.5 wt.% DSP. The pH was approximately 9. The RO test showed that both the permeation

TABLE A-VIII

RO AND PRO TESTS WITH AQUEOUS SODIUM CHLORIDE AND
DISODIUM PHOSPHATE (DSP) SOLUTIONS ON DU PONT B-9 FIBERS

Test No.	Type of Test	Tempera- ture, °C	Osmotic Pressure, Atmospheres		Hydraulic Pressure, Atmospheres		Water Permeation Coefficient $\frac{m^3}{m^2 \text{ day atm}}$	Binary System	Salt Rejection, Percent
			Shell Side	Bore- Side Inlet	Shell Side	Bore- Side Inlet			
1	RO	24	4	-	25	-	0.0078	NaCl/H ₂ O	90.9
2	PRO	25	170	0	16	18	0.0012 ⁽¹⁾	NaCl/H ₂ O	-
3	PRO	20	170	66	16	18	0.00033 ⁽¹⁾	NaCl/H ₂ O	-
4	RO	24	4	-	25	-	0.0063	NaCl/H ₂ O	91.8
5	RO	25	4	-	15	-	0.0062	NaCl/H ₂ O	87.3
6	RO	50	4	-	15	-	0.0094	NaCl/H ₂ O	87.3
7	PRO	47	126	0	15	14	0.0014	DSP/H ₂ O	-
8	PRO	48	126	22	15	14	0.00065 ⁽²⁾	DSP/H ₂ O	-
9	RO	20	4	-	26	-	0.0030	NaCl/H ₂ O	80.9

⁽¹⁾ Data taken over one hour. Coefficient appeared to be declining

⁽²⁾ Coefficient constant during the total run of one hour

coefficient and the percent rejection were decreased seriously. This was probably a result of the high pH, since cellulose acetate membranes are seriously attacked by alkaline solutions. Thus the cellulose acetate membrane did not appear suitable for DSP service.

ii. UOP-PA-300 Membrane

In the osmosis test the UOP-PA-300 membrane gave a constant but very low permeation coefficient of $0.00048 \text{ m}^3/\text{m}^2 \text{ day atm}$. This appears to be characteristic of presently available "composite" membranes. They seem to have porous substructures which are much denser than the integrally-made asymmetric membranes. The reverse osmosis test of the DSP-soaked membrane, which had been soaked for 20 hours, showed some deterioration, but this result was not conclusive because the pretest handling of the film was not exactly according to the manufacturer's recommendations. Nevertheless, the very low permeation coefficient would appear to preclude the use of the UOP-PA-300 membrane with DSP solutions.

iii. ABC-PBIL Membrane

This membrane gave a permeation coefficient in the osmosis test of $0.00022\text{--}0.00026 \text{ m}^3/\text{m}^2 \text{ day atm}$, which was constant over 150 minutes. In the reverse osmosis test of the DSP-soaked membrane, the permeation coefficient was slightly down, but the rejection was not affected.

These results generally confirmed published data to the effect that the PBIL membrane is good in alkaline (and acid) solutions and at elevated temperatures.

b. Further Testing of ABC-PBIL Membrane

It is reported above that the ABC-PBIL membrane performed satisfactorily in reverse osmosis after being soaked 20 hours at $55^\circ\text{--}58^\circ\text{C}$ in 44.5 wt.% disodium phosphate (DSP) solution. The soaking was repeated on a fresh membrane sample, but for 69 hours. After this soaking the membrane was given an osmosis test for 21 hours at 55°C with 44.5% DSP on the skin side and 14.5 wt.% on the porous substructure side, i.e., as before. The coefficient was constant at $0.00025 \text{ m}^3/\text{m}^2 \text{ day atm}$, the same as previously.

However, in the previous osmosis screening test, the membrane had not been given the soaking pretreatment discussed above. Furthermore, the duration of the previous osmosis test was only 150 minutes. Thus it was clear that the extended soaking period had not damaged the transport and semipermeability characteristics of the PBIL membrane used with DSP. Thus the PBIL membrane appears to be a good candidate for use with hot concentrated DSP solution.

C. Experiments on Saturated Pond for Unmixing

1. Experimental Set-Up and Procedure

A rectangular polypropylene tank (2' x 2' x 3' deep) with a plastic bottom was used for the disodium phosphate tests. A schematic diagram of this pond is shown in Figure A-16. In this pond a coiled heat exchanger made from 6.35-mm OD type L copper was used to heat the pond at the bottom. Two brine unmixing tests were conducted with this pond, which are discussed later in this section. An external bath and a pump were used for circulating hot water through the heat exchanger.

Temperature measurements in the pond were made by means of copper-constantan thermocouples hooked to a Digitrend digital temperature logging scanner. The Digitrend could scan temperature profiles automatically after a fixed time interval. A string of thermocouples was fixed on a stainless steel rod which was placed in the center of the pond. Thermocouples were also used for measuring the ambient air temperature, inlet and outlet water temperatures to and from the heat exchangers used for pond heating, and the temperature of various flow streams entering and leaving the pond during the unmixing tests.

To maintain a constant pond depth, a water bird bath was used at the top of the pond to provide a continuous supply of water to compensate for any evaporation from the pond surface. A bird bath is a very simple but accurate arrangement which works on the gravity feed principle to maintain a constant liquid level. Its working principle can be understood by referring to Figure A-16.

Figure A-16. SCHEMATIC DIAGRAM OF RECTANGULAR PLASTIC POND

The densities in the pond were measured very accurately in situ by means of a Troemner balance, which works on Archimedes' principle. In this set-up an epoxy-encapsulated plummet is lowered by means of a 0.13-mm diameter polyester thread to the point where the density is required. The weight loss of the plummet due to buoyancy of the surrounding solution is directly related to the density of the surrounding solution. This balance is capable of measuring the specific gravity up to ± 0.0001 .

For the unmixing tests the dilute and the concentrated disodium phosphate brine streams were withdrawn from the top and the bottom of the pond, respectively, by means of two adjustable-rate peristaltic pumps. These streams were mixed in a closed glass flask by means of a magnetic stirrer and heated before returning to the middle of the pond. The level where the mixed brine entered the pond was determined on the basis that the pond density and temperature at that level were equal to those for the mixed brine stream.

Heating of the mixed brine was done to make sure that the temperature of the mixed brine at the point where it entered the pond was equal to the temperature of the pond at that location. Thus, no convection current was generated because of a difference between the temperature of the mixed brine and the pond temperature at the point where this stream entered the pond. No pump was used on the return line because the pressure build-up from pumping the dilute and concentrated brines to the flask was sufficient to pump the mixed brine back into the pond. Tygon tubing (of 1/16" ID and 1/8" OD) was used for circulating all the streams. The concentrated brine stream was always maintained above the precipitation temperature by at least 5°C by heating this stream at the pond outlet by means of an electrical heating tape wound around the exit line.

2. Disodium Phosphate Pond Tests

a. Start-Up

The pond was started by filling half of it with 50°C water. The amount of disodium phosphate corresponding to the average solubility of the pond solution was calculated, weighed and placed in the pond. The

solution was stirred vigorously while the remaining water was added. The average solubility was calculated by taking the average of the solubilities corresponding to the surface and bottom temperatures. The bottom temperature inside the pond was maintained close to 55°C by adjusting the temperature of the heating bath. Data on temperature and density profiles were taken from time to time to determine the stratification in the pond. The pond reached a steady state after about 3 days. It therefore appeared that disodium phosphate can make a stable saturated pond.

b. Unmixing Tests

The results of two unmixing tests performed on the disodium phosphate saturated pond are discussed here. The apparatus for the unmixing test was comprised of copper tubes placed inside the pond at 2 cm and 76.5 cm below the surface for withdrawal of dilute and concentrated brine streams, respectively, in the first test. In the second test* the location of the dilute brine withdrawal port was changed to 4 cm below the surface of the pond. The mixed stream was heated before being returned to the pond at 31 cm and 21.75 cm below the pond surface during the first and second tests, respectively.

Before the first unmixing test was started, it was ascertained that the pond was fully saturated. This was done by measuring pond density and temperature at different levels and then confirming from Figure A-15 that the salt concentration corresponding to the actual density measurement was at least equal to or larger than the salt solubility at the measured temperature at that level. At the levels where this condition was not satisfied, salt crystal rods, prepared in a separate pond, were suspended in the pond.

In general, based upon Figure A-15, it was found that the pond was supersaturated at all levels. It is believed that complete saturation or supersaturation (depending upon the characteristics of the solute) of the pond is very necessary if it is to be used for brine unmixing.

*The second unmixing test was conducted under a different U.S. DOE contract (No. DE-AC05-78ET20471).

In the first unmixing test the dilute brine and concentrated brine flow rates were maintained at 62 cc/min and 100 cc/min, respectively. For these flow rates the net circulation time for the pond between the two withdrawal ports was 1.15 days or about 28 hours. This unmixing test was run continuously for 37.5 hours, thereby turning the pond over 1.35 time. After the test the pond was allowed to regenerate by itself while the heat was left on. Density and temperature profiles before, during, at the end of the unmixing, and 13 days after that are shown in Figures A-17 and A-18, respectively.

This unmixing was quite severe in the sense that the flow rates were so large that the entire pond was circulated in only about one day. The flow rates were so large that the pond could not maintain stable density and temperature profiles, and it began to mix, as shown in Figures A-17 and A-18. Consequently, the flow rates were turned off, and the pond was allowed to regenerate itself. The objective was to find the length of time required for self-stratification. This length of time should be the minimum net circulation time for the flow rate for unmixing to keep the pond stable. As is evident from Figures A-18 and A-17, the pond regenerated its original temperature and density profiles in a period of less than one week and two weeks, respectively. Since the thermal diffusivity of a salt solution is significantly larger than its salt diffusivity, the temperature profile is modified much more quickly than the density profile.

In the second unmixing test, while there was some excess salt at the bottom of the pond, no special care was taken to make sure that the pond was fully saturated at all levels. In this test the dilute and concentrated brine flow rates were initially set at 20 cc/min and 30 cc/min, but they later stabilized at 18 cc/min and 37.5 cc/min, respectively. At these flow rates the net circulation time for the pond between the two withdrawal ports (4 cm and 76.5 cm below the pond surface) was 3.6 days or 87 hours, which is about 3 times larger than that for the first unmixing test. Due to repeated salt precipitation in the dilute brine line, the test was stopped after about 80 hours, and the pond was allowed to unmix on its own.

Figure A-17. DENSITY PROFILES DURING THE FIRST UNMIXING TEST

Figure A-18. TEMPERATURE PROFILES DURING THE FIRST UNMIXING TEST

During the two-week period (3/21/79 to 4/4/79) following the mixing test, the pond was allowed to unmix by itself. However, there was no significant improvement either in the density or the temperature profile as in the first unmixing test. Since the pond was not fully saturated to begin with, not only did it not unmix, but also its stratification deteriorated during this test.

C. Discussion

The first unmixing test on disodium phosphate conclusively demonstrated that if the pond is fully saturated at each level it can be used to unmix the mixed brine into dilute and concentrated brines. For this solute a residence time of about two weeks brine unmixing should be adequate. Based upon the results of the second unmixing test, it is also evident that if the pond is not fully saturated, due to the presence of a convecting layer (uniform in density) in the pond, a complete unmixing may not be achieved.

APPENDIX B

MATHEMATICAL MODELS

I. PROCESS DESCRIPTION AND MATHEMATICAL MODEL FOR OHP HEAT ENGINE USING CONJUGATION FOR UNMIXING

Partially-miscible binary system with either Lower or Upper Critical Solution Temperature is used. Hydroturbine is on Donor Solution.

A. Flow Diagram of PRO Power Plant

Basis: One mol of separator feed. The Donor Solution consists of Dy mols of component 1 (the solvent, i.e. by definition the permeable component) and $D(1-y)$ mols of component 2 (the solute, i.e. nonpermeable component), i.e. a total of D mols where y is the mol fraction of component 1 in the Donor Solution. It is pumped at temperature $(T_{\text{cold}} + T_{\text{ch},1})$ in case of LCST Binary or at $(T_{\text{hot}} + T_{\text{ch},1})$ in case of UCST binary into the PRO permeator. T_{cold} is the minimum temperature to which the heat sink can cool either the Donor and Receiver solutions in case of LCST binary or separator feed in case of UCST Binary. T_{hot} is the maximum temperature to which the source can heat either the Separator Feed in case of LCST Binary, or Donor and Receiver Solutions in case of UCST Binary. $T_{\text{ch},1}$ is the temperature change in the hydroturbine, due to friction and isentropic expansion. The hydraulic pressure of the Donor Solution entering the permeator is $p_{D,\text{in}}$.

Some of the component 1 (but none of component 2) permeates through the wall of the membrane from the low to the high hydraulic pressure side. The amount of this permeate is designated as "Perm" in mols of component 1. At every point in the membrane system, $\Delta \Pi_{\text{wall}}$ is greater than Δp_{wall} , where $\Delta \Pi_{\text{wall}}$ and Δp_{wall} represent the osmotic and hydraulic pressure differences across the membrane wall.

After passing through the fiber wall, the permeate mixes with the pressurized Receiver Solution which has entered the permeator at the temperature T_{cold} in case of LCST Binary or T_{hot} in case of UCST Binary and a high hydraulic pressure, p_{high} . The Receiver Solution consists of Rx mols of Component 1 and $R(1-x)$ mols of Component 2, a total of R mols, where x is the mol fraction of Component 1.

The mixture of Permeate and Receiver Solution is called the Mixed Solution, which contains $(Rx + \text{Perm})$ mols of Component 1 and $R(1-x)$ mols of component 2, a total of $(R + \text{Perm})$ mols.

The temperature of the Mixed Solution and the Flushing Solution (to be discussed) is T_{inter} . This is the assumed temperature of the streams flowing within the interior of the PRO permeator and emerging from it, i.e., T_{inter} is calculated as if the streams mixed perfectly. The hydraulic pressure of the Mixed Solution is Vp_{high} where V is a number slightly less than one to allow for friction loss on the high pressure side of the permeator.

Pressurized mixed solution now mixes with the Flushing Solution, which is that part of the Donor Solution remaining after removal of the Permeate. The Flushing Solution contains $(Dy - \text{Perm})$ mols of component 1 and $D(1-y)$ mols of component 2, a total of $(D - \text{Perm})$ mols. The Flushing Solution is at zero pressure and T_{inter} as it leaves the permeator but is pressurized to Vp_{high} , i.e., the same pressure as the mixed solution, by the Flushing Solution pump and heated to $(T_{\text{inter}} + T_{\text{ch},2})$. $T_{\text{ch},2}$ is the temperature change in the Flushing Solution pump, due to friction and isentropic compression.

The Separator Feed, S , is a mixture of $(Rx + Dy)$ mols of component 1 and $[1 - (Rx + Dy)]$ mols of component 2. The pressure of the Separator Feed is Vp_{high} and the temperature of the mixture is assumed, for simplification, to be T_{inter} , i.e., the temperature of the Mixed Solution. This

assumption is acceptable because the Flushing Solution mass is small as compared to the Mixed Solution mass and because $T_{ch,2}$ is small.

The Separator Feed now passes through the regenerator where it either picks up or loses sensible heat to the Donor and the Receiver Solutions depending upon whether a LCST or UCST Binary is used.

The purpose of the regenerator is to reduce the heat loads on the heat source and the heat sink so that the thermal efficiency can be increased. Heat is received from the source at a higher temperature and rejected to the sink at a lower temperature, thus approaching more closely to Carnot conditions.

After passing through the regenerator, the Separator Feed is either at a temperature $(T_{hot} - T_{rise,source})$ in case of LCST Binary or at $(T_{cold} + T_{drop,sink})$ in case of UCST Binary, where $T_{rise,source}$ is the temperature rise in the heat source and $T_{drop,sink}$ is the temperature drop in the heat sink. The Separator Feed then passes through the heat source or the heat sink where it is either heated to T_{hot} or cooled to T_{cold} . It then enters the separator where it is divided into the Donor Solution and the Receiver Solution. These two solutions enter the regenerator separately where they are either cooled to a temperature of $(T_{inter} + T_{rise,source})$ or heated to $(T_{inter} - T_{drop,sink})$ depending upon whether a LCST or UCST Binary is used. The temperature is such that the drop in temperature of one stream is equal to the rise in temperature of the other stream, as required by the heat balance.

The Receiver Solution and Donor Solution enter the heat sink or source separately, and emerge at temperature T_{cold} or T_{hot} . The Receiver Solution then enters the permeator at p_{high} . The Donor Solution, still at p_{high} , is depressurized to a relatively low pressure, $p_{D,in}$, through the hydroturbine and then enters the permeator. This completes the cycle.

B. Log Mean Driving Pressure and Permeation Rate

Across any point in the membrane wall, we will have the requirement that:

$$\Delta \pi_{\text{wall}} > \Delta p_{\text{wall}} \quad (1)$$

The difference between $\Delta \pi$ and Δp will vary throughout the PRO permeator. Under these conditions we determine J , the permeation flux, $\text{m}^3/\text{m}^2 \text{ day}$ from the log mean driving pressure, atm:

$$\text{LMDP} = \frac{(\Delta \pi_{\text{RF}} - \Delta p_{\text{RF}}) - (\Delta \pi_{\text{MD}} - \Delta p_{\text{MD}})}{\ln \frac{(\Delta \pi_{\text{RF}} - \Delta p_{\text{RF}})}{(\Delta \pi_{\text{MD}} - \Delta p_{\text{MD}})}} \quad (2)$$

where the subscripts RF and MD refer to the osmotic and hydraulic driving pressures across the membrane wall, between Receiver and Flushing Solutions on the one hand and between the Mixed and Donor Solutions on the other.

It should be kept in mind that log mean averages assume linear changes in the quantities considered. This is probably not the case here, but further refinement does not seem to be in order at this time.

However, $\Delta p_{\text{RF}} = p_{\text{high}}$ and $\Delta p_{\text{MD}} = V p_{\text{high}} - p_{\text{D,in}}$. We now make the simplifying assumption that the pressure loss, in the receiver and mixed solution loop is approximately 2%, and that in the donor and flushing solution loop is 4% based on the design of hollow fibers. Thus $V = 0.98$ and $p_{\text{D,in}} = 0.04 p_{\text{high}}$, so that Eq. 2 becomes:

$$\text{LMDP} = \frac{(\Delta \pi_{\text{RF}} - p_{\text{high}}) - (\Delta \pi_{\text{MD}} - 0.94 p_{\text{high}})}{\ln \frac{\Delta \pi_{\text{RF}} - p_{\text{high}}}{\Delta \pi_{\text{MD}} - 0.94 p_{\text{high}}}} \quad (3)$$

C. Osmotic Pressures

1. Donor Solution and Receiver Solution

We know from solubility data of the partially-miscible binary system the values of the mol fractions y and x of the solvent in the Donor and Receiver Solutions. For mol fractions y and x , we can determine experimentally the partial pressures of Component 1 in the Donor and Receiver Solutions and finally the osmotic pressures. The values of the osmotic pressures, Π_D and Π_R , are then, in atm,

For LCST Binary

$$\Pi_D = - \frac{(82.06)(T_{\text{cold}})}{MW_1/\rho_1} \ln \frac{p_{1D}}{p_1^0} \quad (4A)$$

$$\Pi_R = - \frac{(82.06)(T_{\text{cold}})}{MW_1/\rho_1} \ln \frac{p_{1R}}{p_1^0} \quad (5A)$$

and for UCST Binary,

$$\Pi_D = - \frac{(82.06)(T_{\text{hot}})}{MW_1/\rho_1} \ln \frac{p_{1D}}{p_1^0} \quad (4B)$$

$$\Pi_R = - \frac{(82.06)(T_{\text{hot}})}{MW_1/\rho_1} \ln \frac{p_{1R}}{p_1^0} \quad (5B)$$

where

MW_1 = molecular wt of solvent

ρ_1 = density of solvent at temperature of permeator, gm/cm^3 .

p_1^0 = vapor pressure of component 1 at permeator temperature, atm.

p_{1D} = partial pressure of component 1 in Donor Solution at composition y , atm.

p_{1R} = partial pressure of component 1 in Receiver Solution at composition x , atm.

and 82.06 is the gas constant, $\text{cm}^3 \text{atm/mol}^\circ\text{K}$. It is assumed that $T_{\text{ch},1}$ and $T_{\text{ch},2}$ are negligible as compared to T_{cold} or T_{hot} and molar volume of the solvent is equal to MW_1/ρ_1 .

2. Mixed Solution and Flushing Solution

The mol fractions of component 1 in the Mixed Solution and in the Flushing Solution will depend on the values of D, R, and Perm. We have assumed a separator feed of one mol so that:

$$D + R = 1 \quad (6)$$

The ratios R/Perm and D/Perm can be adjusted arbitrarily by adjusting the outputs of the circulation pump and the hydroturbine. Therefore we say:

$$R/\text{Perm} = W \quad (7)$$

$$D/\text{Perm} = Z \quad (8)$$

where W and Z are arbitrary numbers greater than zero.

Solving between Eqs. 6, 7, and 8, we have:

$$\text{Perm} = 1/(W + Z) \quad (9)$$

$$R = W/(W + Z) \quad (10)$$

From Eqs. 6, 9, and 10 and the mol fractions of component 1 in the Mixed Solution and Flushing Solution, i.e., $(Rx + \text{Perm})/(R + \text{Perm})$ and $(Dy - \text{Perm})/(D - \text{Perm})$, we may say that the mol fractions, N, are:

$$N_{1M} = (Wx + 1)/(W + 1) \quad (11)$$

$$N_{1F} = (Zy - 1)/(Z - 1) \quad (12)$$

From the consideration of the fact that π_M must be greater than π_D , we may say that

$$(Wx + 1)/(W + 1) < y \quad (13)$$

This is the guide for selecting the value of W . From Eq. 12, it is clear that Z must be greater than $1/y$:

$$Z > 1/y \quad (14)$$

For the mol fractions N_{1M} and N_{1F} as determined by Eqs. 11 and 12 we can determine experimentally the partial pressures (p_1) of component 1 and finally the osmotic pressure (π):

$$\pi_M = - \frac{(82.06)(T_{\text{cold}})}{MW_1/\rho_1} \ln (p_{1M}/p_1^0) \quad (15A)$$

$$\pi_F = - \frac{(82.06)(T_{\text{cold}})}{MW_1/\rho_1} \ln (p_{1F}/p_1^0) \quad (16A)$$

and for UCST Binary

$$\pi_M = - \frac{(82.06)(T_{\text{hot}})}{MW_1/\rho_1} \ln (p_{1M}/p_1^0) \quad (15B)$$

$$\pi_F = - \frac{(82.06)(T_{\text{hot}})}{MW_1/\rho_1} \ln (p_{1F}/p_1^0) \quad (16B)$$

For the case we have no experimental data, we will use Raoult's Law ($N = p_1/p_1^0$) for calculating osmotic pressure.

3. Osmotic Pressure Differences Across Fiber Wall

The osmotic pressure difference across the membrane wall and between the Receiver Solution and Flushing Solution is given by Eq. 5 and Eq. 16:

For LCST Binary

$$\Delta\pi_{RF} = - \frac{(82.06) T_{cold}}{(MW_1/\rho_1)} \ln (p_{1R}/p_{1F}) \quad (17A)$$

For UCST Binary

$$\Delta\pi_{RF} = - \frac{(82.06) T_{hot}}{MW_1/\rho_1} \ln (p_{1R}/p_{1F}) \quad (17B)$$

Similarly for the Mixed Solution and the Donor Solution, the osmotic pressure difference is given by Eq. 4 and Eq. 15:

For LCST Binary

$$\Delta\pi_{MD} = - \frac{(82.06) T_{cold}}{MW_1/\rho_1} \ln (p_{1M}/p_{1D}) \quad (18A)$$

For UCST Binary

$$\Delta\pi_{MD} = - \frac{(82.06) T_{hot}}{MW_1/\rho_1} \ln (p_{1M}/p_{1D}) \quad (18B)$$

Note that in Eqs. 17 and 18 the terms after $\ln$ must be less than 1 in order that π will be greater than zero.

D. Permeate Flux, $\text{m}^3/\text{m}^2 \text{ Day}$

From Eqs. 17 and 18 and any arbitrarily selected value of p_{high} , we can obtain the log mean driving pressure (LMDP) by use of Eq. 2 or Eq. 3. Conversely, for any arbitrarily chosen value of log mean driving pressure, the value of p_{high} can be obtained. In either case we obtain the solvent permeation flux, $\text{J m}^3/\text{m}^2 \text{ day}$:

$$J = (A)(\text{LMDP}) \quad (19)$$

where A is the solvent permeation flux constant, $\text{m}^3/\text{m}^2 \text{ day atm.}$

E. Volumetric and Mass Flows

1. Volumetric Flows, cm^3

$$\text{Volume Permeate, } \text{Perm}_V = (\text{MW}_1/\rho_1) (\text{Perm}) \quad (20)$$

$$\text{Volume Receiver Solution, } R_V = (\text{Molar vol}_R)(R) \quad (21)$$

$$\text{Volume Donor Solution, } D_V = (\text{Molar vol}_D)(D) \quad (22)$$

where the term molar vol refers to the experimentally measured molar volume, cm^3/mol , at the temperature of the permeator.

With regard to the Flushing Solution, we assume that the volumes comprising it are additive, i.e.,

$$\text{Volume Flushing Solution} = D_V - \text{Perm}_V \quad (23)$$

In the absence of experimental data on molar volumes, we may calculate the volumetric flows as follows:

$$R_V' = R_x (\text{MW}_1/\rho_1) + R (1-x) (\text{MW}_2/\rho_2) \quad (24)$$

$$D_V' = D_y (\text{MW}_1/\rho_1) + D (1-y) (\text{MW}_2/\rho_2) \quad (25)$$

$$M_v' = \text{Perm}_v + R_v' \quad (26)$$

where the subscript 2 refers to the solute.

2. Mass Flows, Grams

$$R_G = R_x (MW_1) + R(1 - x)(MW_2) \quad (27)$$

$$S_G = (R_x + D_y)(MW_1) + (1 - [R_x + D_y])(MW_2) \quad (28)$$

$$D_G = D_y (MW_1) + D(1 - y) MW_2 \quad (29)$$

Eq. 29 is a check on Eqs. 27 and 28 since:

$$D_G = S_G - R_G \quad (30)$$

F. Mechanical Efficiency and Mechanical Losses

In an idealized plant, the net energy delivery (NED), $\text{cm}^3 \text{ atm}$, would be $(p_{\text{high}})(\text{Perm}_v)$. However, due to inefficiencies such as losses in rotating components, and to frictional losses in the various streams, the net energy delivery (NED) will be:

$$\text{NED} (\text{cm}^3 \text{ atm}) = (p_{\text{high}})(\text{Perm}_v)(\text{ME}) \quad (31)$$

$$\text{NED} (\text{cal}) = (0.024)(p_{\text{high}})(\text{Perm}_v)(\text{ME}) \quad (32)$$

where ME is the mechanical efficiency of the plant, calculated below, and 0.024 is $\text{cal}/\text{cm}^3 \text{ atm}$.

The energy input to the Flushing Solution pump, $\text{cm}^3 \text{ atm}$, is given by:

$$\text{Energy in/}_{FP} = V p_{\text{high}} (D_v - \text{Perm}_v) / E_{FP} \quad (33)$$

where E_{FP} is the fractional efficiency of the Flushing Solution pump.

The energy input to the Receiver Solution pump, $\text{cm}^3 \text{ atm}$, is:

$$\text{Energy in/}_{RP} = p_{\text{high}} (1-V)(R_v) / E_{RP} \quad (34)$$

where E_{RP} is the fractional efficiency of the Receiver Solution pump.

The energy output from the hydroturbine is:

$$\text{Energy out/}_{ht} = (V p_{\text{high}} - p_{D,\text{in}})(D_v)(E_{ht}) \quad (35)$$

Where E_{ht} is the hydroturbine efficiency.

Since the Flushing Solution pump is directly coupled to the hydroturbine, the energy delivered to the generator is given by the difference between Eq. 33 and Eq. 35. The energy delivered by the generator is the same except that generator efficiency, E_g , must be taken into account. Finally, some of the generator output goes to the Receiver Solution pump (Eq. 34) so that the net energy delivery from the plant is given by:

Net energy delivery = NED =

$$[E_g] [(V p_{\text{high}} - p_{D,\text{in}})(D_v)(E_{ht}) - (V p_{\text{high}})((D_v - \text{Perm}_v) / E_{FP})] - [p_{\text{high}} (1-V)(R_v) / E_{RP}] \quad (36)$$

The fractional mechanical efficiency, ME, is given by dividing both sides of Eq. 36 by $P_{high} \text{ Perm}_V$:

$$\frac{NED}{(P_{high})(\text{Perm}_V)} = ME = \left(\frac{D_V E_g}{\text{Perm}_V} \right) (V E_{ht} - \frac{P_{D,in} E_{ht}}{P_{high}} - \frac{V}{E_{FP}}) + \frac{E_g V}{E_{FP}} - \frac{R_V}{\text{Perm}_V} \left(\frac{1-V}{E_{RP}} \right) \quad (37)$$

The following efficiencies and other values are considered attainable and appropriate:

$$E_g = 0.95; \quad E_{ht} = 0.80; \quad E_{RP} = E_{FP} = 0.90$$

$$P_{D,in}/P_{high} = 0.04; \quad V = 0.98$$

When these terms are placed in Eq. 37 we have:

$$ME = 1.034 - 0.32 D_V / \text{Perm}_V - 0.022 R_V / \text{Perm}_V \quad (38)$$

For the case no measured molar volumes are available:

$$ME = 1.034 - 0.32 D_V' / \text{Perm}_V - 0.022 R_V' / \text{Perm}_V \quad (39)$$

G. Calculation of T_{inter}

T_{inter} is calculated from a heat balance around the permeator. If we consider T_{inter} , which appears in two streams, as the base temperature, and also assume equality for the specific heats of all streams entering and leaving the permeator we have:

For LCST Binary:

$$(T_{\text{cold}} - T_{\text{inter}})(R_G) = (T_{\text{inter}} - T_{\text{cold}} - T_{\text{ch},1})(D_G) \quad (40)$$

Solving for T_{inter} :

$$T_{\text{inter}} = T_{\text{cold}} + T_{\text{ch},1} \left(\frac{D_G}{D_G + R_G} \right) \quad (41)$$

On neglecting $T_{\text{ch},1}$ in comparison to T_{cold} one gets:

$$T_{\text{inter}} = T_{\text{cold}} \quad (42)$$

Similarly for UCST Binary:

$$(T_{\text{hot}} - T_{\text{inter}})(R_G) = (T_{\text{inter}} - T_{\text{hot}} - T_{\text{ch},1})(D_G) \quad (43)$$

$$\text{or } T_{\text{inter}} = T_{\text{hot}} + T_{\text{ch},1} \left(\frac{D_G}{D_G + R_G} \right) \quad (44)$$

and on neglecting $T_{\text{ch},1}$ in comparison to T_{hot} again one can write:

$$T_{\text{inter}} = T_{\text{hot}} \quad (45)$$

H. Heat Added and Removed, Thermal Efficiency

From first law of thermodynamics:

$$\text{Heat in } (Q_{\text{hot,actual}}) = \text{Work } (W_o) + \text{Heat out } (Q_{\text{cold,actual}}) \quad (46)$$

Where

$Q_{\text{hot,actual}}$ = Heat added by the source per mol of separator feed, cal/gm mol.

$Q_{\text{cold,actual}}$ = Heat removed in the heat sink = $c_p S_G (\Delta T)_{\text{sink}}$ (47)

W_o = Work done by the system =

$$(0.024)p_{\text{high}} \text{Perm}_v \text{ME} \quad (48)$$

c_p = Specific heat of Separator Feed, cal/gm $^{\circ}$ K

ΔT = Temperature drop in the heat sink, $^{\circ}$ K

0.024 = Conversion factor, cal/cm 3 atm.

$$\text{Thus } Q_{\text{hot,actual}} = (0.024) p_{\text{high}} \text{Perm}_v \text{ME} + c_p S_G (\Delta T)_{\text{sink}} \quad (49)$$

The overall thermal efficiency T_E will be given by:

$$T_E = \frac{\text{NED (cal)}}{Q_{\text{hot,actual}}} \quad (50)$$

By substituting Eqs. 37, 47 and 48 in Eq. 50, we have:

$$T_E = \frac{(0.024)p_{\text{high}} \text{Perm}_v \text{ME}}{(0.024)p_{\text{high}} \text{Perm}_v \text{ME} + c_p S_G (\Delta T)_{\text{sink}}} = \frac{1}{1 + [41.67 \frac{c_p S_G (\Delta T)_{\text{sink}}}{p_{\text{high}} \text{Perm}_v \text{ME}}]} \quad (51)$$

I. Unit Cost of Energy Conversion

Unit cost of energy conversion is divided into following five sections:

1. Cost due to Generator and Turbine
2. Cost due to Heat Transfer Equipment
3. Cost due to Membrane Modules
4. Cost due to Pumps, Separator, Pipings and other Auxiliary Equipment.
5. Cost due to Chemicals Holdup.

Method of calculating energy cost due to each of these components from the initial investment on each component is discussed in the Appendix. This method is known as the Discounted Cash Flow Analysis method. We have taken 21 years as the life of all the equipments and chemicals except membrane modules which have been assumed to be changed every three years. Furthermore, assumed return on investment after taxes is 15%, Federal Income Tax 48%, 90% on-stream time, and annual cost of maintenance is 2% of initial investment. The expression for the unit energy cost due to components discussed in sections 1, 2, 4 and 5 as given in Appendix A (Eq. 17) is:

$$C_{np} = \frac{0.2362}{E} (I_{np}) = 29.96 \times 10^{-6} \left(\frac{I_{np}}{P} \right) \quad (52)$$

Where

C_{np} = Unit cost of energy due to individual components 1, 2, 4 and 5, replaced every 21 years, \$/kWh.

I_{np} = Initial cost of the individual component, \$

E = Number of kWh in a year = $(24 \times 365 \times 0.9) P = 7884 P$

P = Net Power output from the plant, kW.

The expression for calculating cost due to membrane modules as given in Appendix A (Eq. 18) is:

$$C_3 = 0.4813 \left(\frac{I_m}{E} \right) = 61.05 \times 10^{-6} \left(\frac{I_m}{P} \right) \quad (53)$$

Where

C_3 = Unit cost of energy due to membrane modules, replaced every 3 years, \$/kWh.

I_m = Initial cost of the membrane modules, \$.

Method of Calculation

Initial investment on each of the components discussed above and finally the energy cost due to these components is given in the following Sections:

1. Cost Due to Generator and Hydroturbine

Total power produced by hydroturbine (P_1) is:

$$P_1 = (2.8 \times 10^{-8}) \dot{D}_v (V_{p_{high}} - P_{D,in}) E_{ht} \quad (54)$$

Where 2.8×10^{-8} is kWh/cm³ atm.

and P_1 = Power produced by hydroturbine, kW.

$\dot{D}_v$ = vol. flow rate of Donor, cm³/hr.

The installed cost of Generator and Turbine based on total power output from hydroturbine can be written (Ref. Report No. 280378, Eq. III-9) as:

$$I_1 = 202,000 (0.001 E_g P_1)^{0.7}$$

$$\text{or } I_1 = 1605 (E_g P_1)^{0.7} \quad (55)$$

From Eq. 52 unit cost of energy due to Generator and Hydroturbine can be written as:

$$C_1 = 29.96 \times 10^{-6} \left(\frac{I_1}{P} \right) \quad (56)$$

2. Cost Due to Heat-Transfer Equipment

For the purpose of preliminary cost calculation, it is assumed that there is no regenerator.

Expressions for calculating heat transfer area of source (A_{source}) and sink (A_{sink}) in m^2 can be written as:

$$A_{\text{source}} = \frac{Q_{\text{hot,actual}}}{U(\text{LMDT})_{\text{source}}} \left(\frac{\dot{S}_G}{S_G} \right) \quad (57)$$

$$\text{and } A_{\text{sink}} = \frac{Q_{\text{cold,actual}}}{U(\text{LMDT})_{\text{sink}}} \left(\frac{\dot{S}_G}{S_G} \right) \quad (58)$$

Where

$(\text{LMDT})_{\text{source}}$ = Log mean temperature in the source, $^{\circ}\text{K}$.

$(\text{LMDT})_{\text{sink}}$ = Log mean temperature in the sink, $^{\circ}\text{K}$.

$\dot{S}_G$ = Mass flow rate of separator feed, gm/hr .

U = overall heat transfer coefficient of the source and the sink, $\text{cal/hr}^{\circ}\text{K} \cdot \text{m}^2$.

$Q_{\text{cold,actual}}$ and $Q_{\text{hot,actual}}$ can be calculated from Eqs. 47 and 49.

$$\text{Total cost of heat transfer surface } (I_2) = (A_{\text{source}} + A_{\text{sink}}) C_h \quad (59)$$

where

$$C_h = \text{Unit cost of heat transfer surface, } \$/\text{m}^2. \quad (59)$$

From Eq. 52 unit cost of energy due to heat transfer surface can be written as:

$$C_2 = 29.96 \times 10^{-6} \left(\frac{I_2}{P} \right) \quad (60)$$

3. Cost Due to Membrane Modules

$$\text{Total membrane area } (A_m) = \frac{P}{P_W} \quad (61)$$

Where

P = Net power output from the plant, kW

P_W = Net power produced per unit area of membrane.

= ME (total power produced per unit area of membrane), kW/m².

A_m = membrane area, m².

Expression for total power produced by membrane modules is:

$$\frac{P_W A_m}{ME} = J A_m P_{high} \quad (62)$$

By substituting the value of J from Eq. 19 in Eq. 62, one gets:

$$P_W = A(LMDP) P_{high} ME \quad (63)$$

Assuming $A = 0.001 \text{ m}^3/\text{m}^2 \text{ day atm} = 4.1667 \times 10^{-5} \text{ m}^3/\text{m}^2 \text{ hr atm}$,

the expression for P_W can now be written as:

$$P_W = (4.1667 \times 10^{-5})(0.028)(LMDP)P_{high} ME$$

or

$$P_W = 1.1667 \times 10^{-6} LMDP (P_{high}) ME \quad (64)$$

where 0.028 is kWh/m³ atm.

From Eq. 3 one can see that the LMDP is a function of osmotic pressures of the Mixed and Flushing solutions. These osmotic pressures are functions of concentrations of the solutions, which in turn depend on Z and W. Therefore one can say that LMDP is a function of Z and W in addition to P_{high} . Furthermore, mechanical efficiency of the plant (ME) can be expressed in terms of Z and W as shown below:

$$\frac{D_v}{Perm_v} = \frac{Dy (\text{Molar vol of solvent}) + D(1-y)(\text{molar vol of Solute})}{Perm (\text{molar vol of solvent})}$$

or

$$\frac{D_v}{Perm_v} = \frac{D}{Perm} \left[y + (1-y) \left(\frac{\text{Molar vol of Solute}}{\text{Molar vol of Solvent}} \right) \right] \quad (65)$$

For practical purposes one can assume

$$\text{Molar vol} = \frac{\text{Molecular wt.}}{\text{Density}} \quad (66)$$

Eq. 65 can now be rewritten as:

$$\frac{D_v}{Perm_v} = \frac{D}{Perm} \left[y + (1-y) \left(\frac{MW_1}{MW_2} \right) (\rho_2/\rho_1) \right] = K_1 Z \quad (67)$$

where

$$K_1 = y + (1-y) \left(\frac{MW_1}{MW_2} \right) (\rho_2/\rho_1) \quad (68)$$

Similarly

$$\frac{R_v}{Perm_v} = \frac{R}{Perm} \left[x + (1-x) \left(\frac{MW_1}{MW_2} \right) (\rho_2/\rho_1) \right] = K_2 W \quad (69)$$

where

$$K_2 = x + (1-x) \left(\frac{MW_1}{MW_2} \right) (\rho_2/\rho_1) \quad (70)$$

Eq. 38 can now be rewritten as:

$$ME = 1.034 - 0.32K_1Z - 0.022 K_2W \quad (71)$$

From Eqs. 3, 64 and 71, one can see that P_W is a function of p_{high} , Z and W , and thus these variables have to be optimized in order to get maximum power output per unit area of membrane and consequently lower energy cost due to membrane. Since Z and W are appearing linearly and separately in the mechanical efficiency expression, and p_{high} (LMDP) is a monotonic function of Z and W (i.e., it increases continuously with both Z and W), power output per unit area of membrane (P_W) can be optimized by optimizing Z and W , only one at a time while calculating the optimum value of p_{high} such that P_W is maximum. In this way the three-dimensional optimization problem is reduced into two problems, each of which is two dimensional.

For any combination of Z and W , the optimum value of p_{high} can be obtained from an expression obtained by partially differentiating P_W with respect to p_{high} , $\left(\frac{\partial P_W}{\partial p_{high}}\right)$, and then equating this derivative to zero. The final expression for calculating optimum value of p_{high} can be written as:

$$\ln \left[\frac{\Delta\pi_{RF} - p_{high}}{\Delta\pi_{MD} - 0.94 p_{high}} \right] = \frac{p_{high} (\Delta\pi_{RF} - \Delta\pi_{MD} - 0.06 p_{high})(0.94 \Delta\pi_{RF} - \Delta\pi_{MD})}{(\Delta\pi_{RF} - p_{high})(\Delta\pi_{MD} - 0.94 p_{high})(\Delta\pi_{RF} - \Delta\pi_{MD} - 0.12 p_{high})} \quad (72)$$

Eq. 72 is to be solved by trial and error in order to get the optimum value of p_{high} for a chosen combination of Z and W . In case of no friction losses and expansion in the turbine to zero pressure, Eq. 72 can be written as:

$$\ln \left(\frac{\Delta \pi_{RF} - p_{high}}{\Delta \pi_{MD} - p_{high}} \right) = \frac{p_{high} (\Delta \pi_{RF} - \Delta \pi_{MD})}{(\Delta \pi_{RF} - p_{high})(\Delta \pi_{MD} - p_{high})} \quad (73)$$

where

$$\Delta \pi_{RF} = \pi_R - \pi_F$$

$$\text{and } \Delta \pi_{MD} = \pi_M - \pi_D$$

Once p_{high} is known, LMDP is calculated from Eq. 3, and ME from Eq. 71, and finally P_W is calculated from Eq. 64. First, W is kept constant and Z is varied and a plot of P_W against Z is made. From this plot optimum value of Z corresponding to maximum value of P_W is obtained. Then Z is kept constant at the optimum value and W is varied. Again a plot of P_W against W is made, and from this plot optimum value of W corresponding to maximum value of P_W is obtained. This way optimum values of all three variables, namely Z , W and p_{high} , is determined. In case the optimum value of p_{high} is higher than the value recommended by membrane manufacturers as the maximum pressure to which the membrane can withstand, p_{high} is fixed at this limiting value of pressure while Z and W are optimized for this fixed value of p_{high} . Once Z , W and p_{high} are known along with LMDP, P_W and ME from Eqs. 3, 64 and 71, the membrane area is calculated from Eq. 61. From the area of membrane modules, the initial cost of the membrane modules (I_m) is calculated as:

$$I_m = A_m C_m \quad (74)$$

where

$$C_m = \text{Unit cost of membrane modules, } \$/\text{m}^2.$$

and finally energy cost due to membrane module from Eq. 53 is:

$$C_3 = 61.05 \times 10^{-6} \left(\frac{I_m}{P} \right) \quad (75)$$

4. Cost Due to Pumps, Separator, Piping and Auxiliary Equipment

Total cost due to pumps etc. is assumed to be equal to the initial cost of the membrane modules, i.e., equal to I_m . Thus the energy cost due to pumps etc. from Eq. 52 is:

$$C_4 = 29.96 \times 10^{-6} \left(\frac{I_m}{P} \right) \quad (76)$$

5. Cost Due to Chemicals Holdup

Holdup inside membrane modules and heat exchangers is calculated from their sizes while the separator size and its holdup is calculated from the residence time needed for separation of receiver and donor solutions. Finally all the holdups are added and the actual holdup is determined by taking 20% more than the total holdup calculated in order to take into account the holdup in pumps, pipe lines etc. The total cost of the holdup can be written as:

$$I_5 = C_{\text{solvent}} W_{\text{solvent}} + C_{\text{solute}} W_{\text{solute}} \quad (77)$$

where

C_{solvent} = unit cost of solvent, \$/kg.

C_{solute} = unit cost of solute, \$/kg.

W_{solvent} = wt. of the solvent, kg.

W_{solute} = wt. of the solute, kg.

Again the energy cost due to chemicals from Eq. 52 is:

$$C_5 = 29.96 \times 10^{-6} \left(\frac{I_5}{P} \right) \quad (78)$$

6. Unit Cost of Energy, \$/kWh

Unit cost of energy conversion from Eqs. 56, 60, 75, 76 and 78 is:

$$C = C_1 + C_2 + C_3 + C_4 + C_5 = \frac{29.96 \times 10^{-6}(I_1 + I_2 + I_m + I_5)}{P} + \frac{61.05 \times 10^{-6}(I_m)}{P} \quad (79)$$

J. NOMENCLATURE

A	= Solvent permeation flux constant, $\text{m}^3/\text{m}^2 \text{ day atm.}$
A_m	= Membrane area, m^2 .
A_{sink}	= Heat transfer area of the heat sink, m^2 .
A_{source}	= Heat transfer area of the heat source, m^2 .
AOC	= Fractional annual operating cost based on initial investment.
c_p	= Specific heat of separator feed, $\text{cal/gm } ^\circ\text{K.}$
C	= Unit cost of energy, $\$/\text{kWh.}$
C_h	= Unit cost of heat transfer surface, $\$/\text{m}^2$.
C_m	= Unit cost of membrane area, $\$/\text{m}^2$.
C_{np}	= Unit cost of energy due to nonperiodic investment, $\$/\text{kWh.}$
C_p	= Unit cost of energy due to periodic investment, $\$/\text{kWh.}$
C_1	= Unit cost of energy due to hydroturbine and generator, $\$/\text{kWh.}$
C_2	= Unit cost of energy due to heat transfer equipment, $\$/\text{kWh.}$
C_3	= Unit cost of energy due to membrane modules, $\$/\text{kWh.}$
C_4	= Unit cost of energy due to pumps, separator, pipelines, etc., $\$/\text{kWh.}$
C_5	= Unit cost of energy due to chemicals holdup, $\$/\text{kWh.}$
D	= Moles of donor solution per mol of separator feed, gm mol/gm mol.
D_G	= Mass of donor solution per mol of separator feed, gm/gm mol.
D_v	= Volume of donor solution per mol of separator feed, $\text{cm}^3/\text{gm mol.}$
D_v^i	= Volume of donor per mol of separator feed on the basis of ideal solution, $\text{cm}^3/\text{gm mol.}$
$\dot{D}_v$	= Volume flow rate of donor solution, $\text{cm}^3/\text{hr.}$
E	= Number of net kWh generated in a year, kWh/yr.

E_{FP}	= Flushing solution pump efficiency.
E_g	= Generator efficiency.
E_{ht}	= Hydroturbine efficiency.
E_{RP}	= Receiver solution pump efficiency.
i	= Fractional after-tax rate of return.
I	= Initial Investment, \$.
I_e	= Initial investment, excluding membrane modules, \$.
I_m	= Initial investment in membrane modules, \$.
I_{np}	= Initial investment in a nonperiodic component, \$.
I_p	= Initial investment in a periodic component, \$.
I_1	= Initial investment in hydroturbine and generator, \$.
I_2	= Initial investment in heat transfer equipment.
I_4	= Initial investment in pumps, separator, pipelines etc., \$.
I_5	= Initial investment in chemicals holdup, \$.
IT	= Fractional investment tax credit.
J	= Solvent permeation flux, m^3/m^2 day.
K_1	= Constant defined by Eq. 68.
K_2	= Constant defined by Eq. 70.
$LCST$	= Lower critical solution temperature, $^{\circ}C$.
$LMDP$	= Log mean driving pressure, atm.
$(LMDT)_{sink}$	= Log mean driving temperature in the sink, $^{\circ}K$.
$(LMDT)_{source}$	= Log mean driving temperature in the source, $^{\circ}K$.
M_v	= Vol of mixed solution per mol of separator feed on the basis of ideal solution, cm^3/gm mol.
ME	= Mechanical efficiency of the plant.
MW_1	= Molecular weight of the solvent, gm/gm mol.
MW_2	= Molecular weight of the solute, gm/gm mol.
N	= mol fraction in the liquid phase.
NED	= Net energy delivery, $cm^3 atm$.

$NED (cal)$ = Net energy delivery, cal.
 N_{1F} = Mol fraction of solvent in the flushing solution.
 N_{1m} = Mol fraction of solvent in the mixed solution.
 OHP = Osmo Hydro PowerTM.
 p = Pressure, atm.
 P_D = Hydraulic pressure of the donor solution entering the permeator, atm.
 P_F = Hydraulic pressure of the flushing solution leaving the permeator, atm.
 P_m = Hydraulic pressure of the mixed solution leaving the permeator, atm.
 P_R = Hydraulic pressure of the receiver solution entering the permeator, atm.
 $P_{D,in}$ = P_D
 P_{high} = P_R
 p_1 = Partial pressure, atm.
 p_1^0 = Vapor pressure of solvent, atm.
 p_{1m} = Partial pressure of solvent in the mixed solution, atm.
 p_{1R} = Partial pressure of solvent in the receiver solution, atm.
 P = Net power output from the plant, kW.
 $Perm$ = Moles of permeate per mol of separator feed.
 $Perm_v$ = Volume of permeate per mol of separator feed, $cm^3/gm\ mol$.
 PRO = Pressure retarded osmosis.
 P_w = Power per unit area of membrane times mechanical efficiency of the plant, kW/m^2 .
 P_1 = Hydroturbine Power output, kW.
 $Q_{cold,actual}$ = Heat rejected per mol of separator feed in the sink, $cal/gm\ mol$.
 $Q_{hot,actual}$ = Heat input per mol of separator feed in the source, $cal/gm\ mol$.
 R = Moles of receiver solution per mol of separator feed.

R_G	= Mass of receiver solution per mol of separator feed, gm/gm mol.
R_V	= Volume of the receiver solution per mol of separator feed, $\text{cm}^3/\text{gm mol}$.
R'_V	= Vol of receiver solution per mol of separator feed on the basis of ideal solution, $\text{cm}^3/\text{gm mol}$.
S_G	= Molecular weight of the separator feed.
$\dot{S}_G$	= Massflow rate of separator feed, gm/hr.
T_{cold}	= Temperature of the outgoing stream from the sink, $^{\circ}\text{C}$.
$T_{\text{ch},1}$	= Temperature change in the Hydroturbine due to friction and isentropic expansion, $^{\circ}\text{C}$.
$T_{\text{ch},2}$	= Temperature change in the flushing solution pump due to friction and isentropic compression, $^{\circ}\text{C}$.
$T_{\text{drop},\text{sink}}$	= Temperature drop in the sink, $^{\circ}\text{C}$.
T_E	= Thermal efficiency.
T_{hot}	= Temperature of the outgoing stream from the source, $^{\circ}\text{C}$.
T_{inter}	= Temperature of the streams, flowing within the interior of the PRO permeator, $^{\circ}\text{C}$.
$T_{\text{rise},\text{source}}$	= Temperature rise in the source, $^{\circ}\text{C}$.
U	= Overall heat transfer coefficient of the heat source and heat sink, $\text{cal/hr } ^{\circ}\text{K m}^2$.
UCST	= Upper critical solution temperature $^{\circ}\text{C}$.
V	= Fractional friction loss towards high pressure side of the permeator.
W	= Ratio of the moles of receiver solution to moles of permeate per mol of separator feed.
W_0	= Work done by the system, cal.
x	= Mol fraction of solvent in the receiver solution.
X	= Any year.
y	= Mol fraction of solvent in the donor solution.
Z	= Ratio of moles of donor to moles of permeate per mol of separator feed.
ΔP_{wall}	= Hydraulic pressure difference across the membrane wall, atm.

Δp_{MD}	$= (p_M - p_{D,in}), \text{ atm.}$
Δp_{RF}	$= (p_R - p_F), \text{ atm.}$
Π	$= \text{Osmotic pressure, atm.}$
Π_D	$= \text{Osmotic pressure of the donor solution, atm.}$
Π_F	$= \text{Osmotic pressure of the flushing solution, atm.}$
Π_M	$= \text{Osmotic pressure of the mixed solution, atm.}$
Π_R	$= \text{Osmotic pressure of the receiver solution, atm.}$
$\Delta \Pi_{wall}$	$= \text{Osmotic pressure difference across the membrane wall, atm.}$
$\Delta \Pi_{MD}$	$= (\Pi_M - \Pi_D), \text{ atm.}$
$\Delta \Pi_{RF}$	$= (\Pi_R - \Pi_F), \text{ atm.}$
$(\Delta T)_{sink}$	$= \text{Temperature drop in the sink, } ^\circ K.$
ρ_1	$= \text{Density of the solvent, gm/cm}^3.$
ρ_2	$= \text{Density of the solute, gm/cm}^3.$
∂	$= \text{Partial differential operator.}$

II. PROCESS DESCRIPTION AND MATHEMATICAL MODEL FOR OHP HEAT ENGINE USING DISTILLATION FOR UNMIXING

A. Flow Diagram of PRO Power Plant

Basis: One mol of separator feed per hour. The Donor Solution consists of Dy mols/hr of component 1 (the solvent, i.e. by definition the permeable component) and $D(1-y)$ mols/hr of component 2 (the solute, i.e. nonpermeable component), i.e. a total of D mols/hr where y is the mol fraction of component 1 in the Donor Solution. It is pumped at temperature $(T_c + \Delta T_3)$ into the PRO permeator. T_c is the minimum temperature to which the heat sink can cool the Donor and the Receiver Solutions. ΔT_3 is the temperature change in the Donor Solution pump, due to friction and isentropic compression. The hydraulic and osmotic pressures of the Donor Solution entering the permeator are p_D and π_D respectively.

Some of the component 1 (but none of component 2) permeates through the wall of the membrane from the low to the high hydraulic pressure side. The amount of this permeate is designated as "Perm" in mols/hr of component 1. At every point in the membrane system $\Delta \pi_w$ is greater than Δp_w , where $\Delta \pi_w$ and Δp_w represent the osmotic and hydraulic pressure differences across the membrane wall.

After passing through the fiber wall, the permeate mixes with the pressurized Receiver Solution which has entered the permeator at high hydraulic pressure, p_R , and at the temperature $(T_c + \Delta T_4)$, where ΔT_4 is the temperature change in the Receiver Solution pump, due to friction and isentropic compression. The Receiver Solution consists of Rx_R mols/hr of component 1 and $R(1-x_R)$ mols/hr of component 2, a total of R mols/hr, where x_R is the mol fraction of component 1.

FIGURE B-2

DIAGRAM OF OHP HEAT ENGINE
USING DISTILLATION AS AN UNMIXING TECHNIQUE

The mixture of Permeate and Receiver Solution is called the Mixed Solution, which contains $(Rx_R + \text{Perm})$ mols/hr of component 1 and $R(1-x_R)$ mols/hr of component 2, a total of $(R + \text{Perm})$ mols/hr.

The temperature of the Mixed Solution and the Flushing Solution (to be discussed) is T_m . This is the assumed temperature of the streams flowing within the interior of the PRO permeator and emerging from it; i.e., T_m is calculated as if the streams mixed perfectly. The hydraulic pressure of the Mixed Solution is Vp_R where V is a number slightly less than one to allow for friction loss on the high pressure side of the permeator.

The mixed solution is depressurized to atmospheric pressure through the hydro-turbine. The temperature of the Mixed Solution leaving the hydro-turbine is $(T_m + \Delta T_1)$, where ΔT_1 is the temperature change in the hydro-turbine, due to friction and isentropic expansion. The depressurized Mixed Solution then mixes with the Flushing Solution, which is that part of the Donor Solution remaining after removal of the Permeate. The Flushing Solution contains $(Dy - \text{Perm})$ mols/hr of component 1 and $D(1-y)$ mols/hr of component 2, a total of $(D - \text{Perm})$ mols/hr. The Flushing Solution is at atmospheric pressure and T_m as it leaves the permeator.

The Separator Feed is a mixture of $(Rx_R + Dy)$ mols/hr of component 1 and $[1 - (Rx_R + Dy)]$ mols/hr of component 2. The Separator Feed is at atmospheric pressure and its temperature is $(T_m + \Delta T_2)$, where ΔT_2 is the temperature change in the Flushing Solution stream due to mixing with the Mixed Solution stream.

The Separator Feed now passes through the regenerator where it picks up sensible and latent heat from the Donor Solution and sensible heat from

the Receiver Solution. The purpose of the regenerator is to reduce the heat loads on the heat source and the heat sink so that the thermal efficiency can be increased. In addition heat is received by the source at a higher temperature and rejected to the sink at a lower temperature, thus approaching more closely to Carnot conditions.

After passing through the regenerator, the Separator Feed is at a temperature $(T_h - \Delta T_{hr})$, where ΔT_{hr} is the temperature rise of the Separator Feed in the heat source. The Separator Feed then passes through the heat source where it is heated to T_h . T_h is the maximum temperature to which the heat source can heat the separator feed. It then enters the separator where it is divided into Donor Solution vapor and Receiver Solution liquid. These two fluids enter the regenerator separately where they are cooled. The Donor Solution emerging from the regenerator is at T_s .

The Receiver Solution and Donor Solution enter the heat sink separately, and emerge at temperature T_c . The Receiver Solution then enters the receiver pump at atmospheric pressure, which increases the hydraulic pressure to p_R and pumps the receiver solution into the permeator. The Donor Solution at atmospheric pressure enters the donor pump, which increases the hydraulic pressure to p_D and pumps the Donor Solution into the permeator. This completes the cycle.

B. Log Mean Driving Pressure

Across any point in the membrane wall, we will have the requirement that:

$$\Delta \Pi_w > \Delta p_w \quad (1)$$

The difference between $\Delta\pi_w$ and Δp_w will vary throughout the PRO permeator. Under these conditions we determine J , the permeation flux $m^3/m^2 \text{ hr}$, from the log mean driving pressure, atm:

$$LMDP = \frac{(\Delta\pi_{RF} - \Delta p_{RF}) - (\Delta\pi_{MD} - \Delta p_{MD})}{\ln \frac{(\Delta\pi_{RF} - \Delta p_{RF})}{(\Delta\pi_{MD} - \Delta p_{MD})}} \quad (2)$$

where the subscripts RF and MD refer to the osmotic and hydraulic driving pressures across the membrane wall, between Receiver and Flushing Solutions on the one hand and between the Mixed and Donor Solutions on the other.

It should be kept in mind that log mean averages assume linear changes in the quantities considered. This is probably not the case here, but further refinement does not seem to be in order at this time.

However, $\Delta p_{RF} = (p_R - 1)$ and $\Delta p_{MD} = Vp_R - p_D$. We now make the simplifying assumption that the pressure loss in the receiver and mixed solution loop is approximately 2%, and that in the donor and flushing solution loop is 4% of P_h based on the design of hollow fiber modules. Thus $V = 0.98$ and $(p_D - 1) = 0.04 p_h$, so that Eq. 2 becomes:

$$LMDP = \frac{(\Delta\pi_{RF} - p_h) - (\Delta\pi_{MD} - 0.94 p_h + 0.02)}{\ln \frac{\Delta\pi_{RF} - p_h}{\Delta\pi_{MD} - (0.94 p_h - 0.02)}} \quad (3)$$

where P_h is the hydraulic pressure difference across the membrane wall in the permeator and is equal to $(p_R - 1)$ in the present case.

C. Osmotic Pressures

1. Donor Solution and Receiver Solution

For the Receiver Solution the sum of the partial pressures of each binary component is equal to the still pressure p_s :

$$p_s = p_{1,h} \gamma_{1R,h} x_R + p_{2,h} \gamma_{2R,h} (1-x_R) \quad (4)$$

where:

$\gamma_{1R,h}$ and $\gamma_{2R,h}$ are the activity coefficients of component 1 and component 2 at their respective mol fractions in the Receiver Solution and at still temperature T_h .

$p_{1,h}^\circ$ and $p_{2,h}^\circ$ are the vapor pressures, atm, of pure components 1 and 2 at temperature T_h .

Eq. 4 solves to:

$$x_R = \frac{p_s - p_{2,h}^\circ \gamma_{2R,h}}{p_{1,h}^\circ \gamma_{1R,h} - p_{2,h}^\circ \gamma_{2R,h}} \quad (5)$$

The mol fraction of component 1 in the distillate vapor is equal to its partial pressure divided by the still pressure:

$$y = p_{1,h}^\circ \gamma_{1R,h} x_R / p_s \quad (6)$$

Eq. 6 is substituted into Eq. 5 to eliminate x and to get an expression for y as:

$$y = \frac{p_s - p_{2,h}^\circ \gamma_{2R,h}}{p_s} \frac{p_{1,h}^\circ \gamma_{1R,h}}{p_{1,h}^\circ \gamma_{1R,h} - p_{2,h}^\circ \gamma_{2R,h}} \quad (7)$$

However, we choose species 1 to be much more volatile than species 2, i.e.,

$$p_{1,h}^{\circ} \gg p_{2,h}^{\circ}$$

Thus we can say that

$$y = \frac{p_s - p_{2,h}^{\circ} \gamma_{2R,h}}{p_s} \quad (8)$$

We now condense the distillate vapor at still pressure, p_s . This pressure must be compatible with the composition of the condensate, i.e., the Donor Solution, at condensate temperature. Condensation is completed in the regenerator such that the liquid leaving the regenerator is just saturated at T_s . For this purpose, a driving temperature of about 5°C is arranged between the Separator Feed and the Donor Solution.

For the saturated Donor Solution leaving the regenerator at temperature T_s , we can write:

$$p_{1,s}^{\circ} \gamma_{1D,s} y + p_{2,s}^{\circ} \gamma_{2D,s} (1-y) = p_s \quad (9)$$

where:

$\gamma_{1D,s}$ and $\gamma_{2D,s}$ are the activity coefficients of components 1 and 2 at their respective mol fractions in the Donor Solution and at saturation temperature, T_s .

$p_{1,s}^{\circ}$ and $p_{2,s}^{\circ}$ are the vapor pressures, atm, of pure component 1 and component 2 at temperature T_s .

Because $p^{\circ}_{1,s} \gg p^{\circ}_{2,s}$ and $y \gg (1-y)$ we can say:

$$p^{\circ}_{1,s} \gamma_{1D,s} y = p_s \quad (10)$$

Eq. 10 is substituted into Eq. 8 in order to eliminate p_s , and is then written as a quadratic equation:

$$y^2 - y + (p^{\circ}_{2,h} \gamma_{2R,h} / p^{\circ}_{1,s} \gamma_{1D,s}) = 0 \quad (11)$$

This is solved to give:

$$y = \frac{1 + \sqrt{1 - (4)(p^{\circ}_{2,h} \gamma_{2R,h} / p^{\circ}_{1,s} \gamma_{1D,s})}}{2} \quad (12)$$

From a knowledge of y as obtained from Eq. 12, we can find p_s from Eq. 10, then x_R from Eq. 6. Note from Eq. 12 that for any real value of y :

$$p^{\circ}_{1,s} \gamma_{1D,s} > 4 p^{\circ}_{2,h} \gamma_{2R,h} \quad (13)$$

The osmotic pressures of the Donor Solution and the Receiver Solution can be calculated from $\gamma_{1D} y$ and $\gamma_{1R} x_R$ where γ_{1D} and γ_{1R} are the activity coefficients of component 1 at the respective mol fractions and at the interior temperature, T_m , because the osmotic pressures (driving forces) of interest are within the permeator:

$$\pi_D = - \frac{(0.08206)(T_m)}{MW_1 / \rho_1} \ln (\gamma_{1D} y) \quad (14)$$

$$\pi_R = - \frac{(0.08206)(T_m)}{MW_1 / \rho_1} \ln (\gamma_{1R} x_R) \quad (15)$$

where:

0.08206 is the gas constant, $(\text{m}^3)(\text{atm})/(\text{kg mol})(^\circ\text{K})$, and MW_1/ρ_1 is the molar volume of component 1, $\text{m}^3/\text{kg mol}$, at T_m . MW_1 is the molecular weight of component 1, kg/kg mol , and ρ_1 is the density of component 1 at T_m , kg/m^3 .

γ_{1D} and γ_{1R} are the activity coefficients of Component 1 at its respective mol fractions, in the two solutions and at T_m .

2. Mixed Solution and Flushing Solution.

The mol fractions of component 1 in the Mixed Solution and in the Flushing Solution will depend on the values of D, R, and Perm. We have assumed a separator feed of one mol/hr so that:

$$D + R = 1 \quad (16)$$

The ratios R/Perm and D/Perm can be adjusted arbitrarily by adjusting the outputs of the circulation pump and the hydroturbine. Therefore we say:

$$R/\text{Perm} = W \quad (17)$$

$$D/\text{Perm} = Z \quad (18)$$

where W and Z are arbitrary numbers greater than zero.

Solving between Eqs. 16, 17, and 18 we have:

$$\text{Perm} = 1/(W + Z) \quad (19)$$

$$R = W/(W + Z) \quad (20)$$

From Eqs. 16, 19, and 20 and the mol fractions of component 1 in the Mixed Solution and Flushing Solution, i.e., $(Rx_R + \text{Perm})/(R + \text{Perm})$ and $(Dy - \text{Perm})/(D - \text{Perm})$, we may say that the mol fractions are:

$$x_M = (Wx_R + 1)/(W + 1) \quad (21)$$

$$x_F = (Zy - 1)/(Z - 1) \quad (22)$$

From Eq. 22, it is clear that: $Z > 1/y$ (23)

Also, from consideration of the fact that π_M must be greater than π_D , we may say that:

$$(W x_R + 1)/(W + 1) < y \quad (24)$$

The osmotic pressures of the two solutions are:

$$\pi_M = - \frac{(0.08206)(T_m)}{MW_1/\rho_1} \ln [(\gamma_{1M})(W x_R + 1)/(W + 1)] \quad (25)$$

$$\pi_F = - \frac{(0.08206)(T_m)}{MW_1/\rho_1} \ln [(\gamma_{1F})(Zy - 1)/(Z - 1)] \quad (26)$$

where γ_{1M} and γ_{1F} are the activity coefficients of component 1 at its respective mol fractions in the two solutions and at T_m .

3. Osmotic Pressure Difference Across Fiber Wall

The osmotic pressure difference between the Receiver Solution and the Flushing Solution is given by:

$$\Delta\pi_{RF} = \text{Eq. 15} - \text{Eq. 26} \quad (27)$$

or, if the partial pressures are known at the mol fractions of the Receiver and Flushing Solutions:

$$\Delta\pi_{RF} = - \frac{(0.08206)(T_m)}{MW_1/\rho_1} \ln \frac{P_{1R}}{P_{1F}} \quad (28)$$

Similarly:

$$\Delta\pi_{MD} = \text{Eq. 25} - \text{Eq. 14} \quad (29)$$

or

$$\Delta\pi_{MD} = - \frac{(0.08206)(T_m)}{MW_1/\rho_1} \ln \frac{P_{1M}}{P_{1D}} \quad (30)$$

D. Permeate Flux, $m^3/(m^2)(hr)$

From Eqs. 27 and 29 (or 28 and 30) and any arbitrarily selected value of p_h , we can obtain the log mean driving pressure (LMDP) by use of Eq. 2 or Eq. 3. Conversely, for any arbitrarily chosen value of log mean driving pressure, the value of p_h can be obtained. In either case we obtain the solvent permeation flux, J in $m^3/(m^2)(hr)$:

$$J = (A)(LMDP) \quad (31)$$

where A is the solvent permeation flux constant, $\text{m}^3/(\text{m}^2)(\text{hr})(\text{atm})$.

E. Volumetric and Mass Flows

1. Volumetric Flow Rates, m^3/hr

$$\text{Volume Permeate, Perm}_V = (\text{MW}_1/\rho_1) (\text{Perm}) \quad (32)$$

$$\text{Volume Receiver Solution, } R_V = (\text{Molar vol}_R)(R) \quad (33)$$

$$\text{Volume Donor Solution, } D_V = (\text{Molar vol}_D)(D) \quad (34)$$

where the term molar vol refers to the experimentally measured molar volume, $\text{m}^3/\text{kg mol}$, at the temperature of the permeator.

With regard to the Flushing Solution, we assume that the volumes comprising it are additive, i.e.,

$$\text{Volume Flushing Solution} = D_V - \text{Perm}_V \quad (35)$$

In the absence of experimental data on molar volumes, we may calculate the volumetric flows as follows:

$$R_V' = R x_R (\text{MW}_1/\rho_1) + R (1-x_R) (\text{MW}_2/\rho_2) \quad (36)$$

$$D_V' = D y (\text{MW}_1/\rho_1) + D (1-y) (\text{MW}_2/\rho_2) \quad (37)$$

$$M_V' = \text{Perm}_V + R_V' \quad (38)$$

where the subscript 2 refers to the solute.

2. Mass Flow Rates, kg/hr

$$R_G = R x_R (\text{MW}_1) + R (1 - x_R) (\text{MW}_2) \quad (39)$$

$$S_G = (Rx_R + Dy)(MW_1) + [1 - (Rx_R + Dy)](MW_2) \quad (40)$$

$$D_G = Dy (MW_1) + D (1 - y) MW_2 \quad (41)$$

Eq. 41 is a check on Eqs. 39 and 40 since:

$$D_G = S_G - R_G \quad (42)$$

F. Mechanical Efficiency and Mechanical Losses

In an idealized plant, the net power delivery (P_m), (m^3) (atm)/hr, would be $(p_h)(Perm_V)$. However, due to inefficiencies such as losses in rotating components, and to frictional losses in the various streams, the net power delivered (P_m) will be:

$$P_m (m^3 \text{ atm/hr}) = (p_h)(Perm_V)(ME) \quad (43)$$

$$P_k (\text{kcal/hr}) = (24)(p_h)(Perm_V)(ME) \quad (44)$$

where ME is the mechanical efficiency of the plant, calculated below, and 24 is kcal/(m^3)(atm).

The power input to the receiver pump, m^3 atm/hr, is given by:

$$\text{Power in/}_{rp} = p_h R_v / E_{rp} \quad (45)$$

where E_{rp} is the fractional efficiency of the receiver pump.

The power input to the donor pump, (m^3)(atm)/hr, is:

$$\text{Power in/}_{dp} = D_v(p_D-1)/E_{dp} \quad (46)$$

where E_{dp} is the fractional efficiency of the donor pump.

The energy output from the hydroturbine is:

$$\text{Power out/}_{ht} = (Vp_R-1) E_{ht} (\text{Perm}_v + R_v) \quad (47)$$

where E_{ht} is the fractional efficiency of the hydroturbine.

Since the receiver pump is directly coupled to the hydroturbine, the power delivered to the generator is given by the difference between Eq. 47 and Eq. 45. The power delivered by the generator is the same except that generator efficiency, E_g , must be taken into account. Finally, some of the generator output goes to the donor pump (Eq. 46) so that the net power delivered from the plant (to the busbar) is given by:

$$\text{Net power delivered} = P_m =$$

$$[E_g][(Vp_R-1) E_{ht} (\text{Perm}_v + R_v) - (p_h R_v/E_{rp})] - [p_D-1][D_v/E_{dp}] \quad (48)$$

The fractional mechanical efficiency is given by dividing both sides of Eq. 48 by $p_h \text{Perm}_v$:

$$\frac{P_m}{(p_h)(\text{Perm}_v)} = ME = \left(\frac{R_v}{\text{Perm}_v}\right) \left(E_g V E_{ht} - \frac{E_g}{E_{rp}}\right) + E_g V E_{ht} - \left(\frac{1}{E_{dp}}\right) \left(\frac{p_D-1}{p_h}\right) \left(\frac{D_v}{\text{Perm}_v}\right) \quad (49)$$

In Eq. 49 it is assumed that $V_{p-1} = V_{p_h}$. The following efficiencies and other values are considered attainable and appropriate:

$$E_g = 0.95; E_{ht} = 0.80; E_{rp} = E_{dp} = 0.90$$

$$(p_D - 1)/p_h = 0.04; V = 0.98$$

When these terms are placed in Eq. 49 we have:

$$ME = 0.745 - 0.311 R_V / \text{Perm}_V - 0.044 D_V / \text{Perm}_V \quad (50)$$

For the case where the measured molar volumes are not available:

$$ME = 0.745 - 0.311 R'_V / \text{Perm}_V - 0.044 D'_V / \text{Perm}_V \quad (51)$$

G. Calculation of T_m

T_m is calculated from the heat balance around the permeator. If we consider T_m , which appears in two streams, as the base temperature, and also assume that the specific heats of all streams entering and leaving the permeator are equal, we have:

$$(T_c + \Delta T_4 - T_m)(R_G) = (T_m - T_c - \Delta T_3)(D_G) \quad (52)$$

Solving for T_m :

$$T_m = T_c + \Delta T_3 \left(\frac{D_G}{R_G + D_G} \right) + \Delta T_4 \left(\frac{R_G}{R_G + D_G} \right) \quad (53)$$

On neglecting ΔT_3 and ΔT_4 in comparison to T_c , we have:

$$T_m = T_c \quad (54)$$

H. Heat Added and Removed, Thermal Efficiency

From first law of thermodynamics:

$$\text{Heat in} = \text{Work} + \text{Heat out} \quad (55)$$

The donor solution leaving the still must be condensed and cooled while receiver solution will simply be cooled in the regenerator and heat sink. As the donor vapor is in equilibrium with the receiver liquid in the still at temperature T_h , Donor vapor will condense at Temperature T_h in the regenerator. An expression for the heat removed from the donor and receiver solutions in the regenerator can therefore be written as:

$$q_r = \lambda_D D_G + c_p S_G (T_h - T_s) \quad (56)$$

where

q_r = Heat removed in the regenerator from the donor and receiver solutions, kcal/(kg mol)(hr).

λ_D = Latent heat of vaporization of the donor stream, kcal/kg.

c_p = Specific heat of separator feed, kcal/(kg)(°C).

The temperatures of the donor and receiver streams coming out of the regenerator are assumed to be both equal to T_s for the purpose of preliminary calculations of the heat balance. However, the exact temperatures of the two streams may be different depending upon the design of the regenerator based on economics. An expression for the heat removed in the sink can now be written as:

$$q_c = S_G c_p (T_s - T_c) \quad (57)$$

where

q_c = Heat removed in the sink from the donor and receiver solutions, kcal/(kg mol)(hr).

Heat added in the source can not be calculated directly from the temperature difference because unmixing occurs, requiring additional heat. Instead, the heat which must be added in the source is calculated from the first law of thermodynamics. If one assumes that most of the work lost in the cycle due to inefficiencies in the rotating components is dissipated through friction and appears as a rise in temperature of the corresponding fluid streams, except the work lost as heat in the electrical generator and electrical motor used to drive the Donor Solution pump, then the expression for heat added in the source can be written as:

$$q_h = P_k + q_c + q_l \quad (58)$$

Where

q_h = Heat added in the source, kcal/(kg mol)(hr).

q_l = work losses in the electrical generator and electrical motor, kcal/(kg mol)(hr).

P_k and q_c can be calculated from Eqs. 44 and 57.

Now the expression for thermal efficiency can be written as:

$$TE = \frac{P_k}{q_h} \quad (59)$$

By substituting the values of P_k and q_h from Eqs. 44, 57 and 58 into Eq. 59, we get:

$$TE = \frac{(24)(p_h)(perm_v)(ME)}{c_p S_G (T_s - T_c) + (24)(p_h)(perm_v)(ME) + q_l} \quad (60)$$

$$\text{or } TE = \frac{1}{1 + \frac{c_p S_G (T_s - T_c) + q_l}{(24)(p_h)(perm_v)(ME)}} \quad (61)$$

I. Unit Cost of Energy Conversion

Unit cost of energy conversion is divided into the following five sections:

1. Cost due to Generator and Turbine
2. Cost due to Heat Transfer Equipment
3. Cost due to Membrane Modules
4. Cost due to Pumps, Still, Pipings and other Auxiliary Equipment.
5. Cost due to Chemicals Holdup.

The method of calculating the energy cost due to each of these components from the initial investment on each component is discussed in Appendix A. This method is known as the Discounted Cash Flow Analysis method. We have taken 21 years as the life of all the equipments and chemicals except membrane modules which have been assumed to be changed every three years. Furthermore, the assumed return on investment after taxes is 15%, Federal Income Tax 48%, on-stream time 90%, and annual cost of maintenance is 2% of initial investment. The expression for the unit energy cost due to components discussed in sections 1, 2, 4 and 5 as given in Appendix A (Eq. 17) is:

$$C_{np} = \frac{0.2362}{E} (I_{np}) = 29.96 \times 10^{-6} \left(\frac{I_{np}}{P} \right) \quad (62)$$

Where

C_{np} = Unit cost of energy due to individual components
1, 2, 4 and 5, replaced every 21 years, \$/kWh.

I_{np} = Initial cost of the individual component which
does not need periodic replacement, \$.

E = Number of kWh in a year = $(24 \times 365 \times 0.9) P = 7884 P$

P = Net Power output from the plant, kW.

The expression for calculating the cost due to membrane modules as given in Appendix A (Eq. 18) is:

$$C_3 = 0.4813 \left(\frac{I_m}{E} \right) = 61.05 \times 10^{-6} \left(\frac{I_m}{P} \right) \quad (63)$$

Where

C_3 = Unit cost of energy due to membrane modules, replaced every 3 years, \$/kWh.

I_m = Initial cost of the membrane modules, \$.

Method of Calculation

Initial investment on each of the components discussed above and finally the energy cost due to these components is given in the following Sections:

1. Cost Due to Generator and Hydroturbine

Total power produced by hydroturbine (P_1) is:

$$P_1 = (0.028) V p_h E_{ht} (Perm_v + R_v) \quad (64)$$

Where 0.028 is kWh/(m³)(atm).

and P_1 = Power produced by hydroturbine, kW.

R_v = Vol. flow rate of Receiver, m³/(kg mol)(hr).

$Perm_v$ = Vol flow rate of permeating fluid, m³/(kg mol)(hr).

The installed cost of Generator and Turbine based on total power output from hydroturbine can be written (Ref. Report No. 280378, Eq. III-9) as:

$$I_1 = 202,000 (0.001 E_g P_1)^{0.7}$$

$$\text{or } I_1 = 1605 (E_g P_1)^{0.7} \quad (65)$$

From Eq. 52 the unit cost of energy due to the Generator and Hydro-turbine can be written as:

$$C_1 = 29.96 \times 10^{-6} \left(\frac{I_1}{P} \right) \quad (66)$$

2. Cost Due to Heat-Transfer Equipment

For the purpose of preliminary cost calculations, it is assumed that the donor solution coming out of the regenerator is liquid at $(T_m + 5)^\circ\text{C}$.

Furthermore, from Eq. 54 we can write:

$$T_s = T_m + 5 = T_c + 5 \quad (67)$$

For the purpose of preliminary calculations, q_1 , which appears in Eq. 58, will be neglected. The expressions for the heat transferred in the sink, source and the regenerator on the basis of one mol of separator feed/hr can now be rewritten as:

$$q_c = c_p S_G (T_s - T_c) = 5c_p S_G \quad (68)$$

from Eqs. 44, 58 and 68,

$$q_h = 5c_p S_G + (24) p_h (\text{Perm}_v)(\text{ME}) \quad (69)$$

and from Eqs. 56 and 67,

$$q_r = \lambda_D D_G + c_p S_G (T_h - T_c - 5) \quad (70)$$

where

$$q_r = \text{Heat transferred in the regenerator, kcal/(kg mol)(hr).}$$

Now the expressions for calculating heat transfer area of source (A_h), sink (A_c), and regenerator A_r in m^2 can be written as:

$$A_h = \frac{q_h}{U(\text{LMDT})_h} = \frac{5c_p S_G + (24)p_h (\text{Perm}_v)(\text{ME})}{U(\text{LMDT})_h} \quad (71)$$

$$A_c = \frac{q_c}{U(\text{LMDT})_c} = \frac{5 c_p S_G}{U(\text{LMDT})_c} \quad (72)$$

$$\text{and } A_r = \frac{q_r}{U(\text{LMDT})_r} = \frac{\lambda_D D_G + c_p S_G (T_h - T_c - 5)}{U(\text{LMDT})_r} \quad (73)$$

Where

$(\text{LMDT})_h$ = Log mean temperature difference in the source, °C.

$(\text{LMDT})_c$ = Log mean temperature difference in the sink, °C.

$(\text{LMDT})_r$ = Log mean temperature difference in the regenerator, °C.

U = overall heat transfer coefficient of the source, sink, and regenerator, kcal/(hr)(°C)(m²).

Expression for $(\text{LMDT})_r$ can now be approximated as:

$$(\text{LMDT})_r = \frac{(T_h - T_r) - 5}{\ln[(T_h - T_r)/5]} \quad (74)$$

Where T_r = temperature of separator feed at exit of regenerator, °C.

If one assumes that all the separator feed is vaporized in the regenerator, then T_r can be calculated from the expression for the temperature rise of the separator feed in the source, which can be approximated as:

$$T_h - T_r = \frac{q_h}{c_{pv} S_G} = \frac{5 c_p S_G + (24) p_h (\text{Perm}_v)(\text{ME})}{c_{pv} S_G} \quad (75)$$

Where

c_{pv} = Heat capacity of the separator feed in the vapor phase, kcal/(kg)(°C).

Total cost of heat transfer surface I_2 :

$$I_2 = (A_h + A_c + A_r) c_h \quad (76)$$

where

C_h = Unit cost of heat transfer surface, $\$/m^2$.

From Eq. 62 the unit cost of energy due to heat transfer surface can be written as:

$$C_2 = 29.96 \times 10^{-6} \left(\frac{I_2}{P} \right) \quad (77)$$

3. Cost Due to Membrane Modules

The net power delivered by the plant is calculated from Eq. 43:

$$P_m = p_h (\text{Perm}_v)(\text{ME}) \quad (43)$$

The volumetric rate of permeate can be calculated from Eq. 31 and the total membrane area A_m :

$$\text{PERM}_v = J A_m \quad (78)$$

$$\text{PERM}_v = A(\text{LMDP}) A_m \quad (79)$$

The net power produced per unit area of membrane can be calculated by combining Eqs. 43 and 78:

$$P_w = (0.028) p_h A(\text{LMDP})(\text{ME}) \quad (80)$$

Where 0.028 is $\text{kWh}/(\text{m}^3)(\text{atm})$.

Assuming $A = 0.001 \text{ m}^3/(\text{m}^2)(\text{day})(\text{atm}) = 4.1667 \times 10^{-5} \text{ m}^3/(\text{m}^2)(\text{hr})(\text{atm})$,

the expression for P_W in kW/m^2 can now be written as:

$$P_W = (4.1667 \times 10^{-5})(0.028)(\text{LMDP})p_h (\text{ME})$$

or

$$P_W = 1.1667 \times 10^{-6} (\text{LMDP})p_h (\text{ME}) \quad (81)$$

Where P_W is net power produced per unit area of membrane, kW/m^2 .

From Eq. 3 one can see that the LMDP is a function of the osmotic pressures of the Mixed and Flushing Solutions. These osmotic pressures are functions of concentrations of the solutions, which in turn depend on Z and W. Therefore one can say that LMDP is a function of Z and W in addition to p_h . Furthermore, the mechanical efficiency of the plant (ME) can be expressed in terms of Z and W as shown below:

$$\frac{D_v}{\text{Perm}_v} = \frac{Dy (\text{Molar vol of solvent}) + D(1-y)(\text{Molar vol of solute})}{\text{Perm} (\text{Molar vol of solvent})}$$

$$\text{or } \frac{D_v}{\text{Perm}_v} = \frac{D}{\text{Perm}} [y + (1-y) \frac{(\text{Molar vol of solute})}{(\text{Molar vol of solvent})}] \quad (82)$$

For practical purposes we can assume

$$\text{Molar vol} = \frac{\text{Molecular wt.}}{\text{Density}} \quad (83)$$

Eq. 82 can now be rewritten as:

$$\frac{D_v}{\text{Perm}_v} = \frac{D}{\text{Perm}} [y + (1-y) \left(\frac{\text{MW}_1}{\text{MW}_2} \right) (\rho_2/\rho_1)] = K_1 Z \quad (84)$$

where

$$K_1 = y + (1-y) \left(\frac{\text{MW}_1}{\text{MW}_2} \right) (\rho_2/\rho_1) \quad (85)$$

Similarly

$$\frac{R_v}{\text{Perm}_v} = \frac{R}{\text{Perm}} [x_R + (1-x_R)\left(\frac{MW_1}{MW_2}\right)(\rho_2/\rho_1)] = K_2 W \quad (86)$$

where

$$K_2 = x_R + (1-x_R)\left(\frac{MW_1}{MW_2}\right)(\rho_2/\rho_1) \quad (87)$$

Eq. 50 can now be rewritten as:

$$ME = 0.745 - 0.311K_1Z - 0.044 K_2W \quad (88)$$

From Eqs. 3, 81 and 88, we can see that P_W is a function of p_h , Z and W , and thus these variables have to be optimized in order to get maximum power output per unit area of membrane and consequently lower energy cost due to the membrane. Since Z and W are appearing linearly and separately in the mechanical efficiency expression, and p_h (LMDP) is a monotonic function of Z and W (i.e., it increases continuously with both Z and W), power output per unit area of membrane (P_W) can be optimized by optimizing Z and W , only one at a time while calculating the optimum value of p_h such that P_W is maximum. In this way the three-dimensional optimization problem is reduced to two problems, each of which is two dimensional.

For any combination of Z and W , the optimum value of p_h can be obtained from the expression obtained by partially differentiating P_W with respect to p_h , $\left(\frac{\partial P_W}{\partial p_h}\right)$, and then equating this derivative to zero. The final expression for calculating the optimum value of p_h can be written as:

$$\ln \left[\frac{\Delta\pi_{RF} - p_h}{\Delta\pi_{MD} - 0.94 p_h + 0.02} \right] = \frac{p_h (\Delta\pi_{RF} - \Delta\pi_{MD} - 0.06 p_h + 0.02)(0.94 \Delta\pi_{RF} - \Delta\pi_{MD} - 0.02)}{(\Delta\pi_{RF} - p_h)(\Delta\pi_{MD} - 0.94 p_h + 0.02)(\Delta\pi_{RF} - \Delta\pi_{MD} - 0.12 p_h + 0.02)} \quad (89)$$

Eq. 89 is to be solved by trial and error in order to get the optimum value of p_h for a chosen combination of Z and W . In the case of no frictional losses and expansion in the turbine to atmospheric pressure, Eq. 89 can be written as:

$$\ln \left(\frac{\Delta \Pi_{RF} - p_h}{\Delta \Pi_{MD} - p_h} \right) = \frac{p_h (\Delta \Pi_{RF} - \Delta \Pi_{MD})}{(\Delta \Pi_{RF} - p_h)(\Delta \Pi_{MD} - p_h)} \quad (90)$$

where

$$\Delta \Pi_{RF} = \Pi_R - \Pi_F$$

$$\text{and } \Delta \Pi_{MD} = \Pi_M - \Pi_D$$

Once p_h is known, LMDP is calculated from Eq. 3, and ME from Eq. 88, and finally P_W is calculated from Eq. 81. First, W is kept constant, Z is varied, and a plot of P_W against Z is made. From this plot the optimum value of Z corresponding to the maximum value of P_W is obtained. Then Z is kept constant at the optimum value and W is varied. Again, a plot of P_W against W is made, and from this plot the optimum value of W corresponding to the maximum value of P_W is obtained. In this way optimum values of all three variables, namely Z , W and p_h , are determined. In case the optimum value of p_h is higher than the value recommended by membrane manufacturers as the maximum pressure which the membrane can withstand, p_h is fixed at this limiting value of pressure while Z and W are optimized. Once Z , W and p_h are known along with LMDP, P_W and ME from Eqs. 3, 81 and 88, the membrane area is calculated from P_W and P . From the membrane area of the modules, the initial cost of the membrane modules (I_m) is calculated as:

$$I_m = A_m C_m \quad (91)$$

where

C_m = Unit cost of membrane modules, $\$/m^2$.

and finally the energy cost due to membrane modules from Eq. 63 is:

$$C_3 = 61.05 \times 10^{-6} \left(\frac{A_m C_m}{P} \right) \quad (92)$$

4. Cost Due to Pumps, Still, Piping and Auxiliary Equipment

Total cost due to pumps, etc. is assumed to be equal to the initial cost of the membrane modules, i.e., equal to I_m . Thus the energy cost due to pumps, etc. from Eq. 62 is:

$$C_4 = 29.96 \times 10^{-6} \left(\frac{I_m}{P} \right) \quad (93)$$

5. Cost Due to Chemicals Holdup

Holdup inside membrane modules and heat exchangers is calculated from their sizes while the still size and its holdup are calculated from the residence time needed for separation of receiver and donor solutions. Finally, all the holdups are added, and the actual holdup is determined by taking 20% more than the total holdup calculated in order to take into account the holdup in pumps, pipe lines, etc. The total cost of the holdup can be written as:

$$I_5 = C_{s1} W_{s1} + C_{s2} W_{s2} \quad (94)$$

where

C_{s1} = unit cost of solvent, $\$/kg$.

C_{s2} = unit cost of solute, $\$/kg$.

W_{s1} = wt. of the solvent, kg.

W_{s2} = wt. of the solute, kg.

Again the energy cost due to chemicals from Eq. 62 is:

$$C_5 = 29.96 \times 10^{-6} \left(\frac{I_5}{P} \right) \quad (95)$$

6. Unit Cost of Energy, \$/kWh

The unit cost of energy conversion from Eqs. 66, 77, 92, 93 and 95 is:

$$C = C_1 + C_2 + C_3 + C_4 + C_5 = \frac{29.96 \times 10^{-6} (I_1 + I_2 + I_m + I_5)}{P} + \frac{61.05 \times 10^{-6} (I_m)}{P} \quad (96)$$

J. NOMENCLATURE

- A = Solvent permeation flux constant, $m^3/(m^2)(hr)(atm)$.
 A_c = Sink heat transfer area, m^2 .
 A_h = Source heat transfer area, m^2 .
 A_m = Membrane area, m^2 .
 A_r = Regenerator heat transfer area, m^2 .
 AOC = Fractional annual operating cost based on initial investment.
 c_p = Specific heat of separator feed, $kcal/(kg)(^\circ C)$.
 c_{pv} = Specific heat of separator feed in the vapor phase, $kcal/(kg)(^\circ C)$.
 C = Unit cost of energy, $$/kWh.
 C_h = Unit cost of heat transfer surface, $$/m².
 C_m = Unit cost of membrane area, $$/m².
 C_{np} = Unit cost of energy due to nonperiodic investment, $$/kWh.
 C_p = Unit cost of energy due to periodic investment, $$/kWh.
 C_{s1} = Unit cost of component 1 (solvent), $$/kg.
 C_{s2} = Unit cost of component 2 (solute), $$/kg.
 C_1 = Unit cost of energy due to hydroturbine and generator, $$/kWh.
 C_2 = Unit cost of energy due to heat transfer equipment, $$/kWh.
 C_3 = Unit cost of energy due to membrane modules, $$/kWh.
 C_4 = Unit cost of energy due to pumps, still, pipelines, etc., $$/kWh.
 C_5 = Unit cost of energy due to chemicals holdup, $$/kWh.
 D = Donor solution flow rate, $kg\ mol/(kg\ mol)(hr)$.
 D_G = Mass flow rate of donor solution, $kg/(kg\ mol)(hr)$.
 D_v = Volumetric flow rate of donor solution, $m^3/(kg\ mol)(hr)$.
 D'_v = Volumetric flow rate of donor solution on the basis of an ideal solution, $m^3/(kg\ mol)(hr)$.$$$$$$$$$$$$

E = Number of net kWh generated in a year, kWh/yr.
 E_{dp} = Donor solution pump efficiency.
 E_g = Generator efficiency.
 E_{ht} = Hydroturbine efficiency.
 E_{rp} = Receiver solution pump efficiency.
 i = Fractional after-tax rate of return.
 I = Initial investment, \$.
 I_e = Initial investment, excluding membrane modules, \$.
 I_m = Initial investment in membrane modules, \$.
 I_{np} = Initial investment in nonperiodic component, \$.
 I_p = Initial investment in periodic component, \$.
 I_1 = Initial investment in hydroturbine and generator, \$.
 I_2 = Initial investment in heat transfer equipment, \$.
 I_4 = Initial investment in pumps, still, pipelines, etc., \$.
 I_5 = Initial investment in chemicals holdup, \$.
 IT = Fractional Investment tax credit.
 J = Solvent permeation flux, $m^3/m^2 \cdot hr$.
 k_1 = Constant defined by Eq. 85.
 k_2 = Constant defined by Eq. 87.
 $LMDP$ = Log mean driving pressure, atm.
 $(LMDT)_c$ = Log mean driving temperature in the sink, °C.
 $(LMDT)_h$ = Log mean driving temperature in the source, °C.
 $(LMDT)_r$ = Log mean driving temperature in the regenerator, °C.
 M'_V = Volumetric flow rate of mixed solution on the basis of an ideal solution, $m^3/(kg \text{ mol})(hr)$.
 ME = Mechanical efficiency of the plant.
 MW_1 = Molecular weight of component 1 (solvent), kg/kg mol.
 MW_2 = Molecular weight of component 2 (solute), kg/kg mol.
 n = Life of the plant in years.

OHP = Osmo-Hydro PowerTM
 p = Hydraulic pressure, atm.
 p_D = Hydraulic pressure of the donor solution entering the permeator, atm.
 p_F = Hydraulic pressure of the flushing solution leaving the permeator, atm.
 p_h = Hydraulic pressure difference across the membrane wall in the permeator, atm.
 p_M = Hydraulic pressure of the mixed solution leaving the permeator, atm.
 p_R = Hydraulic pressure of the receiver solution entering the permeator, atm.
 p_s = Still pressure, atm.
 p_1 = Partial pressure of component 1, atm.
 p_{1D} = Partial pressure of component 1 in donor solution, atm.
 p_{1F} = Partial pressure of component 1 in flushing solution, atm.
 $p_{1,h}^o$ = Vapor pressure of component 1 at temperature T_h , atm.
 $p_{2,h}^o$ = Vapor pressure of component 2 at temperature T_h , atm.
 p_{1M} = Partial pressure of component 1 in the mixed solution, atm.
 p_{1R} = Partial pressure of component 1 in receiver solution, atm.
 $p_{1,s}^o$ = Vapor pressure of component 1 at temperature T_s , atm.
 $p_{2,s}^o$ = Vapor pressure of component 2 at temperature T_s , atm.
 P = Net power output from the plant, kW.
 P_m = Net power output from the plant (m^3)(atm)/(kg mol)(hr).
 P_k = Net power output from the plant, kcal/(kg mol)(hr)
 P_W = Net power per unit area of membrane, kW/m².
 P_1 = Hydroturbine power output, kW.

Perm = Flow rate of permeate, $\text{kg mol}/(\text{kg mol})(\text{hr})$.
 Perm_v = Vol flow rate of permeate, $\text{m}^3/(\text{kg mol})(\text{hr})$.
 PRO = Pressure retarded osmosis.
 q_c = Rate of heat output rejected in the sink, $\text{kcal}/(\text{hr})(\text{kg mol})$.
 q_h = Rate of heat input in the source, $\text{kcal}/(\text{hr})(\text{kg mol})$.
 q_l = Work losses in the electrical generator and electrical motor, $\text{kcal}/(\text{hr})(\text{kg mol})$.
 R = Flow rate of receiver solution, $\text{kg mol}/(\text{kg mol})(\text{hr})$.
 R_G = Mass flow rate of receiver solution, $\text{kg}/(\text{kg mol})(\text{hr})$.
 R_v = Volumetric flow rate of receiver solution, $\text{m}^3/(\text{kg mol})(\text{hr})$.
 R'_v = Volumetric flow rate of receiver solution on the basis of an ideal solution, $\text{m}^3/(\text{kg mol})(\text{hr})$.
 S_G = Mass flow rate of separator feed, $\text{kg}/(\text{kg mol})(\text{hr})$.
 T = Fractional tax rate.
 T_c = Minimum temperature to which sink cools the incoming stream, °C.
 T_h = Maximum temperature to which the source heats the incoming stream, °C.
 T_m = Temperature of the streams flowing within the interior of the PRO permeator, °C.
 T_r = Temperature of separator feed at exit of regenerator, °C.
 T_s = Temperature of the saturated donor solution at exit of regenerator, °C.
 TE = Thermal efficiency of the plant.
 U = Overall heat transfer coefficient of the heat source, heat sink and regenerator, $\text{kcal}/\text{hr } ^\circ\text{C m}^2$.
 V = Fractional friction loss towards high pressure side of the permeator.
 W = Ratio of the moles of receiver solution to moles of permeate.

- W_{s1} = Weight of component 1 (solvent) in the chemicals holdup, kg.
 W_{s2} = Weight of component 2 (solute) in the chemicals holdup, kg.
 x = Mole fraction of component 1 (solvent) in the receiver solution.
 x_F = Mole fraction of component 1 (solvent) in the flushing solution.
 x_M = Mole fraction of component 1 (solvent) in the mixed solution.
 X = Any year.
 y = Mole fraction of component 1 (solvent) in the donor solution.
 Z = Ratio of the moles of donor solution to moles of permeate.

Greek

- γ_{1D} = Activity coefficient of component 1 in the donor solution at temperature T_m .
 $\gamma_{1D,s}$ = Activity coefficient of component 1 in the donor solution at temperature T_s .
 γ_{1R} = Activity coefficient of component 1 in the receiver solution at temperature T_m .
 $\gamma_{1R,h}$ = Activity coefficient of component 1 in the receiver solution at temperature T_h .
 $\gamma_{2D,s}$ = Activity coefficient of component 2 in the donor solution at temperature T_s .
 $\gamma_{2R,h}$ = Activity coefficient of component 2 in the receiver solution at temperature T_h .
 Δp_{MD} = $p_M - p_D$
 Δp_{RF} = $p_R - p_F$
 Δp_w = Hydraulic pressure difference across the membrane wall, atm.
 ΔT_{hr} = Temperature rise in the heat source, °C.
 ΔT_1 = Temperature change in the hydroturbine due to friction and isentropic expansion, °C.

- ΔT_2 = Temperature change in the flushing solution stream due to mixing with mixed solution stream, °C.
 ΔT_3 = Temperature change in the donor solution pump, °C.
 ΔT_4 = Temperature change in the receiver solution pump, °C.
 λ_D = Latent heat of vaporization of donor solution, kcal/kg.
 π_D = Osmotic pressure of the donor solution entering the permeator, atm.
 π_F = Osmotic pressure of the flushing solution at permeator exit, atm.
 π_M = Osmotic pressure of the mixed solution at the permeator exit, atm.
 π_R = Osmotic pressure of the receiver solution entering the permeator, atm.
 $\Delta \pi_{MD} = \pi_M - \pi_D$
 $\Delta \pi_{RF} = \pi_R - \pi_F$
 $\Delta \pi_W$ = Osmotic pressure difference across the membrane wall, atm.
 ρ_1 = Density of component 1 (solvent), kg/m³.
 ρ_2 = Density of component 2 (solute), kg/m³.
 ∂ = Partial differential operator.

III. MODEL FOR ECONOMIC ANALYSIS

A. Introduction

The economic analysis of OHP systems and their component parts has been carried out with the Discounted Cash Flow financing Method. The procedure, described here, is based upon the calculation of annual equivalent costs for the various cash flows using exact equations rather than approximations. Of course, the accuracy of the final answers is still influenced by the accuracy of the estimated costs used as input data and the validity of the assumptions, but at least any error due to procedure is eliminated.

B. Discounted Cash Flow Analysis Method

Any financial analysis uses as basic input the results of the cost analysis of a project. These costs are then combined and analyzed depending upon the method of financing to determine the revenue required per unit product over the project lifetime to produce the desired rate of return on invested capital under the applicable tax conditions.

In the discounted cash flow analysis method, cost of each component responsible in the final cost of the product is calculated as if that component cost is borne today. Discounted cash flow in any year X means, the present value of the cash which will be flowing in the year X . Finally, in this analysis total discounted flows over the whole life of the project are added and equated to zero, and the value of the unknown variable is calculated from this equation.

It is assumed here that this kind of power plant will be owned by an industry having low-temperature waste heat available at no cost and the power generated by the plant will be used to supplement the energy requirement of the industry. As the cost of the power generated can be deducted against taxable income as expenses in case this plant was not built, the net value of the power to the industry will be equal to the value of the power generated minus taxes on this value.

The required project data are:

1. Initial Investment (I)--This investment is divided into two parts, namely Depreciable Investment and Non-Depreciable Investment.

a. Depreciable Investment--This includes investment for equipment and building etc.; interest during construction and startup if included.

b. Non-Depreciable Investment--This includes land and working capital.

Total discounted cash flow due to initial investment over the life of the project means the present value of the initial investment and that is equal to $-I$. Any cash which is flowing out of the company, i.e., the cash to be spent, is taken as negative while any cash which is flowing into the company is taken as positive.

2. Net rate of return (i) after taxes on the investment.

3. Period of investment (n) for analysis purposes for the whole project or a piece of equipment.

4. Periodic Investment--This includes investment made in replacing an equipment or a piece of equipment during the life of the project (e.g., membrane modules every 3 years).

Discounted cash flow due to investment in X-th year will be:

$$\text{Discounted cash flow due to investment in X-th year} = \frac{-I_p}{(1+i)^X} \quad (1)$$

where

I_p = investment made in the year X.

i = fractional rate of return after taxes.

5. Investment Tax Credit (IT)--a tax credit is given by the government on investment at a fractional rate (IT) at the end of the year investment is made. Discounted cash flow in the year X, due to this tax credit will be:

$$\text{Discounted cash flow due to tax credit on investment made in the year, X} = \frac{(IT)(I_p)}{(1+i)^{1+X}} \quad (2)$$

and discounted cash flow due to tax credit on initial investment =

$$\frac{(IT)(I)}{(1+i)} \quad (3)$$

where I = Initial Investment

IT = Fractional investment tax credit

6. Annual Operating Cost (AOC) - As the annual operating cost is deductible against taxable income, the expression for the discounted cash flow due to annual operating cost in the year X, will be:

$$\begin{aligned} &\text{Discounted cash flow due to annual operating cost in the year X} \\ &= - \frac{(AOC)(1-T)(I)}{(1+i)^X} \quad (4) \end{aligned}$$

where

AOC = fractional annual operating cost based on initial investment.

T = fractional tax rate.

7. Cash flow due to depreciation--the depreciation is deductible against taxable income. Method of depreciation used is assumed to be sum-of-the-years-digits for the whole project except membrane modules. For membrane modules straight line method of depreciation is assumed. The expression for fractional depreciation allocation in X-th year by the method of sum-of-the-years-digits can be written as:

$$\begin{aligned} &\text{Fractional depreciation allocation in X-th year} \\ &= \frac{(n+1-X)}{(1/2)(n^2+n)} \end{aligned} \quad (5)$$

and the expression for the discounted cash flow due to tax savings on depreciation in the X-th year can be written as:

By straight line method

$$\begin{aligned} &\text{Discounted cash flow due to depreciation in X-th year} \\ &= \left(\frac{T}{3}\right) \frac{I}{(1+i)^X} \end{aligned} \quad (6)$$

By sum-of-the-years-digits

$$\begin{aligned} &\text{Discounted cash flow due to depreciation in X-th year} \\ &= \frac{(T)(n+1-X)}{(1/2)(n^2+n)} \frac{I}{(1+i)^X} \end{aligned} \quad (7)$$

8. Value of the Power Generated--As explained earlier the net value of the power generated will be equal to the value of the power generated minus the tax on this value. The expression for discounted cash flow due to power generated in the X-th year will be:

$$\begin{aligned} &\text{Discounted cash flow due to power generated in X-th year} \\ &= \frac{(1-T) EC}{(1+i)^X} \end{aligned} \quad (8)$$

Where

E = Energy generated in X-th year, kWh/year.

C = Unit cost of energy, \$/kWh.

The sum of all the discounted flows over the life of the project will be equal to zero, and from the expressions obtained any unknown quantity can be determined.

The calculation of unit cost of energy obtained from OHP heat engine proceeds as follows:

1. Initial Investment--it is divided into two parts as follows:
 - a. Depreciable Investment--This is equal to the initial cost of the membrane modules plus the cost of the rest of the equipment, while the interest during construction and startup is neglected.
 - b. Non-Depreciable Investment--This is assumed to be negligible as compared to depreciable investment. The expression for total discounted flow due to initial investment over the life of the project can therefore be written as:

$$\begin{aligned} &\text{Discounted cash flow due to initial investment} \\ &= -I_e - I_m \end{aligned} \quad (9)$$

where

I_m = initial investment in membrane modules

I_e = initial investment in the rest of the equipment except
membrane modules

2. Net rate of return (i) after taxes on investment is assumed to be 15%, i.e., $i = 0.15$

3. Period of investment (n) for analysis purposes is divided into two parts. The membrane modules assumed to be replaced every three years while rest of the equipment every 21 years, i.e., total life of the project is equal to 21 years.

4. Periodic Investment--Since the membrane modules have to be changed every three years, a periodic investment equal to the cost of the membrane modules has to be made at an interval of 3 years. The expression for total discounted cash flow due to this periodic investment over the life of the project can therefore be written as:

Total discounted cash flow due to periodic investment in
membrane modules in 21 years

$$= - \frac{I_m [(1+i)^{18} - 1]}{(1+i)^{18} [(1+i)^3 - 1]} = - 1.7647 I_m \quad (10)$$

where the cost of membrane replacement every three years is taken same as at the time when the plant was built; i.e., the effect of inflation on the cost of membrane modules is not considered. In fact, it can be assumed that the cost of membrane modules may not rise due to advances in the technology of producing them.

5. Investment Tax Credit--A tax credit of 10% on investment is assumed. The expression for the total discounted cash flow due to tax credit in 21 years can be written as:

$$\begin{aligned}
 &\text{Total discounted cash flow in 21 years due to tax credit on investment} \\
 &= \text{cash flow due to tax credit on (initial investment +} \\
 &\quad \text{periodic investment)} \\
 &= \frac{0.1 (I_e + I_m)}{(1+i)} + \frac{0.1 I_m}{(1+i)} \frac{[(1+i)^{18}-1]}{(1+i)^{18}[(1+i)^3-1]} \quad (11) \\
 &= 0.087 I_e + 0.2404 I_m
 \end{aligned}$$

6. Annual Operating Cost--The annual operating cost is assumed to be equal to 2% of initial investment, i.e., $AOC = 0.02$, and a tax rate of 48%, i.e., $T = 0.48$, is assumed. The expression for total discounted cash flow due to annual operating cost in 21 years can now be written as:

$$\begin{aligned}
 &\text{Total discounted cash flow due to annual operating cost in} \\
 &\quad \text{21 years} \\
 &= - (AOC)(1-T)(I_e + I_m) \frac{[(1+i)^n-1]}{i (1+i)^n} = - 0.0657 (I_e + I_m) \quad (12)
 \end{aligned}$$

7. Cash flow due to Depreciation--membrane modules are depreciated by straight line method while the rest of the equipment by sum-of-the-years-digits method. The expression for total discounted cash flow due to depreciation in 21 years

$$\begin{aligned}
 &= \left(\frac{T}{3}\right) I_m \left[\frac{(1+i)^n-1}{i(1+i)^n}\right] + T(I_e) \left[\frac{n - \frac{1}{i} + \frac{n}{(1+i)^n-1}}{(1/2)(n^2 + n)}\right] \left[\frac{(1+i)^n-1}{i(1+i)^n}\right] \\
 &= 1.01 I_m + 0.2035 I_e \quad (13)
 \end{aligned}$$

8. Value of the Power Generated--At a tax rate of 48% the expression for total discounted cash flow due to power generated in 21 years will be:

$$\begin{aligned} & \text{Total discounted cash flow due to power generated in 21 years} \\ & = (1-T)EC \frac{[(1+i)^{21}-1]}{i(1+i)^{21}} = 3.2825 EC \end{aligned} \quad (14)$$

When the sum of all discounted cash flows in 21 years is equated to zero one gets:

$$\begin{aligned} & -0.7752 I_e - 1.58 I_m + 3.2825 EC \\ \text{or } EC & = 0.2362 I_e + 0.4813 I_m \end{aligned} \quad (15)$$

$$\text{or } C = \frac{0.2362 I_e + 0.4813 I_m}{E} \quad (16)$$

Where

I_e = initial investment on all the components which do not need periodic replacement.

and I_m = initial investment on membrane modules which need replacement every three years.

Cost of individual components in the unit cost of energy can be determined by making use of equation similar to Eq. (16). The expression for unit cost of energy (C_{np}) due to components which have not to be replaced during the life of the equipment can be written as:

$$C_{np} = 0.2362 \left(\frac{I_{np}}{E} \right) \quad (17)$$

and the expression for unit cost of energy (C_p) due to components which have to be changed periodically (e.g., membrane modules every 3 years) can be written as:

$$C_p = 0.4813 \left(\frac{I_p}{E} \right) \quad (18)$$

Where

C_{np} = unit energy cost due to component which does not have to be changed periodically, \$/kWh.

C_p = unit energy cost due to component which has to be changed periodically, \$/kWh.

I_{np} = cost of the component which does not have to be changed periodically, \$.

I_p = cost of the component which has to be changed periodically, \$.

APPENDIX C

PERMEATION THROUGH SEMIPERMEABLE MEMBRANES DURING OSMOSIS OR PRESSURE-RETARDED OSMOSIS

In PRO there may be appreciable osmotic pressures on both sides of the membrane. These pressures can create internal polarization problems (discussed below) in the porous substructure of the asymmetric membranes used, particularly with the flat-sheet membranes used in the spiral-wound module since these membranes are thicker than hollow fibers. Furthermore, flat-sheet membranes have an extra thickness of backing material for strength.

This belief was supported by the following series of experiments. Four different types of flat-sheet membranes were tested in osmosis* with a sodium chloride brine, having either 25 (close to the osmotic pressure of seawater) or 75 atmospheres osmotic pressure, on the skin side of the membrane and water on the porous substructure side. A third osmosis test was made with 75 and 25 atmospheres osmotic pressure on the skin and porous substructure sides, respectively. The results are shown in Table C-I, along with the reverse osmosis results with a low-salinity feed brine. As can be seen, there is a progressive decrease in the water permeation coefficient as follows:

$$A_{\text{reverse osmosis}} > A_{\text{osmosis 75/0}} > A_{\text{osmosis 75/25}} > A_{\text{osmosis 75/25}}$$

*Osmosis may be considered as PRO at the limit of zero hydraulic pressure.

TABLE C-I

OSMOSIS PERFORMANCE OF SEVERAL ASYMMETRIC FLAT-SHEET MEMBRANES
WITH NONZERO OSMOTIC PRESSURE ON THE POROUS SUBSTRUCTURE SIDE

Membrane Designation	Membrane Thickness microns	Type of Backing	Average Water Permeation Coefficient, $\text{m}^3/\text{m}^2\text{-day-atm}$			
			Reverse Osmosis	Osmosis (25/0) [†]	Osmosis (75/0) [†]	Osmosis (75/25) [†]
ABC-PBIL	250	Reemay	0.025	0.0085	0.0031	0.0011
UOP-CA-85	210	Fabric	0.015	0.0069	0.0035	0.0011
FT-30	55	None	0.032	0.0094	-	-
FT-30 (untreated)	140	Reemay	0.032*	-	0.0014	0.00037
FT-30 (treated)	140	Reemay	0.032*	-	0.0028	0.00060
ENV-214	210	Fabric	0.0099	0.0072	0.0026	0.0011

All RO tests were done with NaCl at $\pi = 4$ atm and $\Delta p = 50$ atm.

+ The two numbers in parentheses give the osmotic pressures on the skin side and the porous substructure side, respectively.

* This result is for an unbacked FT-30 membrane but should be the same for the backed membrane.

Source: G. D. Mehta, "Further Results on the Performance of Present-Day Osmotic Membranes in Various Osmotic Regions," Submitted to J. Membrane Science, October 1980.

These results can all be explained on the basis of internal polarization. During osmosis (or PRO) solvent must pass through both the porous substructure and the skin of the asymmetric membrane by diffusion, whereas in reverse osmosis the passage through the porous substructure is by the relatively low-resistance mechanism of laminar flow. In PRO the diffusive flow is hindered by the presence of dissolved solute (i.e., the nonpermeable species) in the porous substructure. The higher this concentration of solute, the greater is the impedance to solvent diffusion in the porous substructure. Solute concentration in the porous substructure is enhanced by high solute concentration on either the skin or porous substructure side of the membrane.

The resistance offered by this internal polarization effect is also proportional to the porous substructure thickness. This effect is shown in Table C-II in which membranes similar in chemical structure but different in thickness were tested in osmosis or PRO. As can be seen, the ratio of osmosis coefficient to reverse osmosis coefficient was much higher for the B-10 hollow fiber with a 28-micron total thickness than for a B-9 flat sheet having a 280-micron thickness. Because of the strong effect of membrane thickness, hollow fibers are probably more appropriate for PRO than are spiral-wound modules, which use the relatively thick flat-sheet membranes.

The nature of the porous substructure also affects the magnitude of the internal polarization effect. "Composite" membranes usually have appreciably lower permeation coefficients in osmosis or PRO than asymmetric membranes, which are integrally formed.* This is due to the denser porous substructure of the composite membrane.

The adverse effect of internal polarization in osmosis or PRO was in evidence many times during this investigation, as indicated by the numerous citations in the text.

*With composite membranes the skin is laid down after completion of fabrication of the porous substructure. The skin may differ chemically from the porous substructure.

TABLE C-II

OSMOSIS AND PRO PERMEATION COEFFICIENTS FOR WATER
PERMEATING INTO SODIUM CHLORIDE BRINE SOLUTIONS

Fabricator and Number	Membrane		Osmotic Process	Skin-Side* Osmotic Pressure, atm	Permeation Coefficient, $\frac{m^3}{m^2 \text{ day atm}}$	Ratio, Osmosis Coefficient Reverse Osmosis Coefficient
	Chemical Type	Geometry and Wall Thickness, Microns				
Du Pont B-9	Polyamide	Flat Sheet, 280	Osmosis	28	0.0055	0.25
				80	0.0024	0.11
				250	0.0007	0.03
Du Pont B-10	Polyamide	Hollow Fiber, 28	PRO	25	0.0013	1.00
				100	0.00070	0.54
				200	0.00065	0.50
				300	0.00047	0.30

*Water was used on the porous substructure side in each test.

The influence of internal polarization in osmosis or PRO has been discussed earlier by Lonsdale* and by Mehta and Loeb.**

* Bend Research, Incorporated, "Membrane Research for Salinity Gradient Energy Production" Final Report to Department of Energy, Contract No. EG-77-C-05-5525, 16 August 1978.

**Mehta, G.D., and Loeb, S., "Internal Polarization in the Porous Substructure of a Semipermeable Membrane Under Pressure-Retarded Osmosis," Journal of Membrane Science, 4, 261-265 (1978).

APPENDIX D

DESIGN OF WORKING MODEL

As part of this project, the design of a small working model of an OHP heat engine was developed.

I. DESIGN CHARACTERISTICS

The permeator may be of the spiral-wound module type because commercially available modules of this geometry, in which flat-sheet membranes are used, can be modified for PRO service much more easily than commercially available modules having the hollow fiber module geometry. It was planned to use a module containing 15 square meters of membrane surface. The membrane may be of the ABC-PBIL type, with an estimated permeation coefficient of $0.00025 \text{ m}^3/\text{m}^2 \text{ day atm}$. The Teijin Company (Japan), which makes the membrane, agreed to supply the membrane to UOP, and the latter agreed to fabricate the PBIL membrane into a module for PRO service. However, the membrane could not be available until after the project was scheduled to be concluded.

The module was to be operated at about 55°C , with feeds of 44.5 wt.% DSP on the skin side and 14.5 wt.% DSP on the porous substructure side. These represent saturation concentrations expected from the 50°C bottom and 28°C top of the saturated stratified pond to be used for unmixing.

The working model was to possess almost all of the operating components of the full-scale OHP heat engine. The exception was to be the turbo-generator, which is difficult to obtain on such a small scale. The turbine was to be replaced by a back-pressure regulator. Thus there would be no actual power generation. However, the potential power output would be calculated from the permeation rate into the high-pressure side of the permeator.

The hydraulic pressure on the high-pressure side of the permeator was to be on the order of 30 atmospheres, which is somewhat less than the pressure capability of the membrane at ambient temperature, but considered appropriate at the operating temperature of 55°C.

II. FLOW DIAGRAM

Figure D-1 shows the flow diagram for the working model. The circulation rates were determined by the permeation rate through the 15-square-meter membrane and by the relative rates of the Donor and Receiver Solutions. These rates were chosen to provide the highest average osmotic driving pressure in the permeator, consistent with an adequate mechanical efficiency for a full-scale unit.

III. THERMAL DUTY OF HEAT-TRANSFER UNITS

A. Thermal Duty of Heat Source

It is necessary to calculate the free energy of unmixing in the saturated pond to determine the theoretical minimum required duty of the heat source in the stratified pond. The change in free energy is given by:*

$$\Delta F = aRT (n_{2D} \ln N_{2D}/N_{2F} + n_{2R} \ln N_{2R}/N_{2F}),$$

where ΔF is the rate of free energy change, $\text{cm}^3 \text{ atm/min}$, the term a is the number of ions resulting from disassociation of the solute, n_{2D} and n_{2R} are the rates of production of the Donor and Receiver Solutions, moles/min, and N_{2D} , N_{2R} , and N_{2F} are the mole fractions of the Donor, Receiver, and (pond) Feed solutions respectively. The term R is the gas constant, $82 \text{ cm}^3 \text{ atm/mole } ^\circ\text{K}$, and T is the absolute temperature, $^\circ\text{K}$.

The molar flow rates and the mole fractions are determined from the flow diagram, and the temperature was assumed to be 328°K . The value of the term a was estimated to be 2 from experimentally obtained osmotic pressure data on various concentrations of DSP. From all of these data the free energy rate of unmixing in the pond was found to be ~ 38 watts.

The free energy rate of unmixing is equal to the maximum power possible in an ideal reversible cycle, where the maximum power is related to the

*The expression is strictly appropriate only for isothermal processes.

FIGURE D-1

WORKING MODEL OF OHP HEAT ENGINE
FLOW DIAGRAM FOR 15-SQUARE-METER
ABC - PBIL SPIRAL MODULE

1. P and π are hydraulic and osmotic pressures, atm.
2. gm/min and cm³/mn refer to total solution flow rates.
3. Pressure approximately zero if not shown.
4. Temperature in degrees Centigrade.
5. DSP is Disodium Phosphate

minimum heat input through the Carnot efficiency if the unmixing were done by an ideal reversible system.* The actual heat input will be greater than the minimum heat input because of heat losses from the pond and system irreversibilities.

When all these effects were taken into account, the thermal duty of the pond heat source was found to be 628 watts of which 377 watts was estimated to be lost to the atmosphere by the pond. From the flow diagram the heat input to the Receiver Heater was calculated to be 113 watts to raise the Receiver Solution 5° above saturation temperature. The heat sink then must handle $28 + 6 + 628 + 113 - 377 = 398$ watts, where the Receiver and Donor pumps add 28 and 6 watts, respectively.

B. Heat Balance

The regenerator thermal duty was based on assuming countercurrent flow with a 5°C minimum approach. This means that the Donor Solution emerges from the regenerator at a temperature of 44°C, 16° higher than at the top of the pond. The sensible heat addition fixes the thermal duty (all internal) of the regenerator at 603 watts.

Figure D-2 gives the heat balance of the plant.

C. Sizing of Heat-Transfer Units

The heat-transfer units were sized from the familiar equation for the area:

$$A = Q/U\Delta T$$

where A is the area in square meters, ΔT is the average temperature difference, Q is the heat-transfer rate in calories/hr, and U is the overall heat-transfer coefficient, assumed to be $(3.7)(10)^5$ cal/hr m² °K. The heat-transfer area actually to be used should be some multiple of that obtained from the above calculation.

Figure D-2 gives the area of each heat-transfer unit.

<p>*I.e., minimum heat input in Carnot cycle =</p>	$\frac{\text{Maximum Work}}{\text{Fractional Carnot Efficiency}}$	$=$	$\frac{\text{Free Energy of Unmixing}}{\text{Fractional Carnot Efficiency}}$
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FIGURE D-2

WORKING MODEL OF OHP HEAT ENGINE
HEAT BALANCE AND AREA OF HEAT-TRANSFER UNITS

IV. INSTRUMENTATION DETAILS

Figure D-3 illustrates the instrumentation details. The thermocouples and pressure gauges are desirable for measuring performance and also for operating purposes, e.g., preventing plugging by precipitation. The difference in flow through the two rotameters gives the permeation rate. Permeation rate times hydraulic pressure difference is gross power, expected to be about 10 watts.

The flow rate in the Donor loop will be controlled by partial by-passing around the Donor pump, that in the Receiver loop by controlling the pump speed.

FIGURE D-3

WORKING MODEL OF OHP HEAT ENGINE
INSTRUMENTATION DETAILS

Notes:

1. PRO permeator, spiral module type, 15 m², ABC - PBIL membrane.
2. Saturated pond, 2'L, 2'W, 3'H, heated at bottom by hot water, cooled at top by cold water.
3. Regenerator

SYMBOLS

APPENDIX E

EXPERIMENTAL WORK ON MEMBRANES BY GULF SOUTH RESEARCH INSTITUTE

The overall objectives of this work were: (i) to identify, develop and fabricate membranes including hollow fiber minipermeators for the different chemical binary systems and (ii) to develop a prototype permeator using the most promising membrane.

However, since most of the chemical binaries were new and had not been used before with the osmotic membranes, most of the experimental work was directed towards testing different flat-sheet membranes in pervaporation,* reverse osmosis, osmosis and under hydraulic pressure conditions. Because of failure to arrive at a working system--an appropriate binary system with a compatible membrane--hollow fiber minipermeators and prototype permeators were not developed.

The results of experimental testing of various chemical binary systems with different flat-sheet membranes is summarized below.

I. METHANOL/HEXANE (upper critical conjugating binary)

A. Dense Cellulose Acetate Membrane

A pervaporation test at 25°C on a 4-micron thick membrane indicated that the separation factor α (methanol/hexane) drops from 2,000 for a 1% (by weight) MeOH solution to about 100 for a 9% MeOH solution, while the total flux through the membrane was approximately constant at about 12 kg/m² day.

*In pervaporation tests, the membrane is flushed with the binary mixture feed solution on the skin side and a vacuum is pulled on the porous substructure side. The separation factor α is determined by measuring the composition of solutions on the feed and the product sides:

$$\alpha \text{ (solute/solvent)} = \frac{(\text{product/feed})^{\text{solute}}}{(\text{product/feed})^{\text{solvent}}}$$

B. Asymmetric Cellulose Acetate Membrane

1) Pressure tests with pure methanol gave a hydraulic permeability coefficient of about $2.8 \text{ kg/m}^2 \text{ day atm}$ at 25 atm. The flux was almost constant as the hydraulic pressure was gradually increased to 90 atm. However, when the pressure was slowly relaxed to 25 atm, the flux was only $10 \text{ kg/m}^2 \text{ day}$, corresponding to a permeability coefficient of $0.4 \text{ kg/m}^2 \text{ day atm}$. This result occurred apparently because the membrane was plasticized by methanol and compacted at the high hydraulic pressure.

2) A pressure test at 900 psi with pure n-hexane gave a starting hydraulic permeability coefficient of about $4.2 \text{ kg/m}^2 \text{ day atm}$, which gradually dropped to $3.5 \text{ kg/m}^2 \text{ day atm}$ after 90 minutes and was still falling.

A similar test with another membrane gave no permeate when the hydraulic pressure was gradually increased to 90 atm.

3) A pervaporation test at 25°C indicated that the separation factor α (methanol/hexane) dropped from about 40 to 5 (and was still falling) while the permeate flux increased from 48 to $132 \text{ kg/m}^2 \text{ day}$ (and was rising) as the methanol concentration in the feed solution was increased from 2 to 11 weight percent.

4) A pressure test at 900 psig with 5% mixture of methanol in n-hexane gave a starting hydraulic permeability coefficient of $17 \text{ kg/m}^2 \text{ day atm}$, which gradually dropped to $11 \text{ kg/m}^2 \text{ day atm}$ after 80 minutes and was still falling. The separation factor α (methanol/hexane) was about 1.5. The drop in the permeability coefficient is primarily attributed to the plasticization by methanol and resulting hydraulic compaction.

5) A reverse osmosis test employing a feed solution of 4.5% methanol in n-hexane at 90 atm gave a flux of $2.2 \text{ kg/m}^2 \text{ day}$ and a separation factor α (methanol/hexane) of 97; the product was an 82% methanol solution. Below 90 atm no detectable flux was obtained.

6) Pervaporation tests with various feed solutions at 25°C showed that the flux increased from 3 to 14 kg/m² day while the separation factor α (methanol/hexane) dropped from 66,000 to 500 as the methanol content in the feed solution increased from 0.2% to 6%. Pervaporation tests with 0.15% methanol solutions at higher hydraulic pressures showed a permanent damage to the membrane, which was reflected by a drop in flux as the pressure was slowly decreased from 50 atm to zero. The separation factor in these tests was constant at 66,000 at 0, 25 and 50 atm.

7) Results of reverse osmosis tests employing a feed solution of 7% methanol are summarized below. Once again, it is evident that contact with methanol at high hydraulic pressures damages the membrane permanently.

Test No.	Applied Pressure atm	Flux kg/m ² day	Separation Factor α (methanol/hexane)
1	25.0	45	28.5
2	49.0	65	12.0
3	67.5	69	4.75
4	87.5	75	2.25
5	67.5	47	1.38
6	49.0	33	1.25
7	25.0	13	1.10

8) The results of the osmosis experiment at 45°C with methanol on the skin side and hexane on the porous substructure side showed that the osmotic flux decreased from about 42 to 6 kg/m² day in about two hours and was constant for the next hour. This test also showed that methanol permeated preferentially over hexane across the membrane.

9) A pervaporation experiment at 50°C indicated that the permeate flux dropped from 135 to 15 kg/m² day while the separation factor decreased from 7×10^{14} to a very low value as the methanol concentration in the feed solution was gradually increased from about 5 to 65%.

These flux values were higher by a factor of 10 than in the pervaporation experiment at 25°C.

In conclusion, it can be said that (i) cellulose acetate membrane permeates methanol preferentially over n-hexane; (ii) the membrane is plasticized by contact with methanol; (iii) the membrane is permanently damaged at high hydraulic pressures, particularly when in contact with solutions containing 4% methanol or higher; and (iv) the flux and the separation factor are greater at higher temperatures.

II. BENZENE/CYCLOHEXANE (distillation)

The variation of osmotic pressure with the composition of benzene/cyclohexane mixtures is shown in Figure E-1.

A. Dense Cellulose Acetate Membrane

Pervaporation tests with a 17-micron cellulose acetate alloy membrane designated CAD/PPN-II using a 50/50 weight percent mixture of benzene and cyclohexane were conducted as shown in Table E-I. From these tests it is evident that as the upstream pressure is increased from 1 to 28 atm the separation factor decreases.

The permeate flux for this binary at 1 atm upstream hydraulic pressure and at 25°C was lower than that for methanol/hexane primarily because the membrane had a greater thickness.

B. Asymmetric Cellulose Acetate Membrane

1) The membrane was annealed in water for 15 minutes at 91°C. At 600 psi pressure with 1% NaCl solution as feed, this membrane gave a salt rejection of 99% and a flux of 26 kg/m² day. However, the membrane performed poorly in pervaporation with 55/45 (by weight) benzene/cyclohexane solution at 25°C. The separation factor $\alpha(B/CH)$ was 1.3, with a pervaporation flux of 3.5 kg/m² day.

2) The annealed cellulose acetate asymmetric membrane was used in a pervaporation test with a feed of benzene/cyclohexane 60/40 (by weight) at a reflux temperature $\approx 78^\circ\text{C}$. This gave a separation factor $\alpha(B/CH) \approx 20$ and flux = 1.5 kg/m² day. Hence, the effects of annealing in the feed solution at different temperatures were considered.

3) The cellulose acetate asymmetric membrane was first annealed in water at 91°C for 15 minutes and then in the feed solution of benzene/cyclohexane (55/45 by weight) at 50°C for 15 minutes. This membrane on pervaporation gave a separation factor of $\alpha(B/CH) \approx 10$ and a flux ≈ 0.99 kg/m² day.

FIGURE E-1
OSMOTIC PRESSURE VS. MOLE FRACTION OF
BENZENE IN CYCLOHEXANE AT 25°C

TABLE E-I

INFLUENCE OF APPLIED HYDRAULIC PRESSURE ON THE FEED SOLUTION IN
SEPARATION OF BENZENE/CYCLOHEXANE (3/1) WITH CAd/PPN-II ALLOY MEMBRANES

Experimental Order ^c	Temperature (C°)	Upstream Pressure (atm)	Downstream Pressure (atm)	Permeation Rate (kg/m ² day)	Benzene in Product (wt%)	Separation Factor
1	78	1	0.025 ^b	20.2	91	10.1
2	25	1	0.025 ^b	2.5	94	15.6
3	25	28	0.025 ^b	7.2	80	4.0
4	25	28	1	1.2	53	1.12
5	25	1	0.025 ^b	2.8	92	11.5

^aIsotropic, 17- μ m thick alloy membrane.

^bSeparation via pervaporation.

^cMembranes were allowed to equilibrate until steady-state permeation was reached.

III. ETHYL ACETATE/ETHYLENE GLYCOL (upper critical conjugating binary)

Figure E-2 shows the phase diagram for ethylene glycol/ethyl acetate, as determined by GSRI with reagent grade chemicals (as supplied by the manufacturers). This binary was found to interact with (swell or dissolve) most commercial membranes; severe difficulties were also encountered during attempts to run osmotic permeation tests with various novel membranes developed in this laboratory. The membranes were cast from

polyphenylene oxide (PPO)

ring-brominated phosphonylated-PPO (PPOBrP)

brominated PPO (PPOBr₂)

polystyrene phosphonate (PSP)

cellulose acetate (CA)

poly(vinylidene fluoride) (PVF₂)

polyvinyl acetate (PVAc)

alloys of PVF₂/PVAc

Ethyl acetate excessively swelled the membranes of PVF₂, PPO, PPOBrP, and PPOBr₂, which mechanically disintegrated while testing. All the other membranes dissolved in the binary system.

Crosslinked PVF₂ and hydrolyzed PVF₂/PVAc membranes were found to withstand treatment with ethyl acetate. Membranes were cast from a 15 wt% solution of PVF₂ in dimethyl formamide (DMF). The membranes were equilibrated with 1N NaOH solution for 24 hours, rinsed with deionized water, and dried. Membranes were also cast using a 15 wt% solution of PVF₂/PVAc (1/1) in DMF. These membranes were hydrolyzed for 24 hours with 1N NaOH solution, rinsed with deionized water, and dried.

1) Pervaporation experiments were conducted at 25°C on these membranes with 90% ethylene glycol in ethyl acetate solution. Crosslinked PVF₂ membrane (thickness $\approx 10 \mu\text{m}$) yielded a separation factor α (ethyl acetate/ethylene glycol) ≈ 100 with ethyl acetate permeating preferentially. The permeate flux was extremely low (1 kg/m² day).

Since the separation was less than that achieved by pervaporation at 78°C, the cellulose acetate membrane was first annealed in water at 91°C for 15 minutes and then in feed solution of benzene/cyclohexane (55/45) at 73-75°C for 15 minutes. Pervaporation with this membrane at 25°C resulted in a separation factor $\alpha(B/CH) \approx 19$ and a flux of 1.5 kg/m² day. It took 2-3 hours for the separation factor to increase from 4 to a steady-state value of approximately 19.

4) After annealing in water and a feed solution of benzene/cyclohexane (55/45), the membrane was tested for hydraulic permeability at pressures of 20, 50 and 95 atm for 3 hours each. No product could be collected at any of these applied pressures during the 3-hour period.

5) The effect of applied pressure on pervaporation separation and flux was tested for the azeotropic composition with cellulose acetate membrane annealed in water feed. The tests showed that the pervaporation flux increases as the applied pressure is gradually increased from atmospheric pressure to 95 atm. However, when the applied hydraulic pressure is gradually relaxed the flux at atmospheric pressure was only 0.4 kg/m² day. Similar results were noted for the separation factor. This hysteresis effect may be due to the compaction of the membrane. The separation factor decreases as the applied pressure on pervaporation is increased and may be due to the difference in the equilibrium solubility at the corresponding pressures.

FIGURE E-2.

**PHASE DIAGRAM FOR
ETHYL ACETATE/ETHYLENE GLYCOL* BINARY MIXTURE**

*Ethyl Acetate: MCB-EX240 (<0.25% water)
Ethylene Glycol: Mallinckrodt #5001 (<0.25% water)

Similar experiments with hydrolyzed PVF₂/PVAc membrane (thickness $\approx 10 \mu\text{m}$) resulted in a separation factor of $\alpha(\text{EA/EG}) \approx 30\text{-}40$, with ethyl acetate permeating preferentially. The pervaporation flux rate was higher for this membrane ($7.83 \text{ kg/m}^2 \text{ day}$). Both systems exhibited a rather high separation; the flux can be substantially increased by employing thinner membranes. Hence it was decided to pursue the study of membrane characteristics under hydraulic pressure-induced transport, e.g., reverse osmosis.

2) High-pressure reverse osmosis tests were conducted with 1 wt% NaCl solution. The results with dense, crosslinked PVF₂ membranes at elevated hydraulic pressures around 400 to 800 psi seemed to have an adverse effect on the transport rate. This observation indicates a deformation in the dense membrane substructure. The amorphous regions which are above the glass transition temperature "compact" under pressure, and mass transport is partially blocked.

Like the PVF₂ membrane, the results of high-pressure reverse osmosis with hydrolyzed PVF₂/PVAc membranes showed that these membranes are also permanently damaged at elevated hydraulic pressures.

3) Attempts were made to determine the hydraulic permeability constants of ethyl acetate, ethylene glycol, and the binary mixture through cross-linked PVF₂ membranes (thickness $\approx 10 \mu\text{m}$) at 10 atm pressure. Ethylene glycol, a strong nonsolvent for this membrane, did not permeate the membrane under the above conditions (i.e., flux through the membrane was nil). The flux of ethyl acetate through the membrane was high, and the membrane swelled excessively.

Similar experiments were conducted with hydrolyzed PVF₂/PVAc membranes (thickness $\approx 10 \mu\text{m}$). The hydraulic permeability coefficient for ethylene glycol dropped from an initial value of $350 \text{ kg/m}^2 \text{ day atm}$ to $175 \text{ kg/m}^2 \text{ day atm}$ within the first 20 minutes and remained at this value for the next hour.

Results of hydraulic permeability tests with an ethylene glycol/ethyl mixture (9/1 by weight) as feed showed a lower initial permeability coefficient ($A \approx 120 \text{ kg/m}^2 \text{ day atm}$), which reached a steady-state value of $\approx 20 \text{ kg/m}^2 \text{ day atm}$ within the first one hour. The system yielded a separation factor of $\alpha(\text{EA/EG}) \approx 1.2$ with ethyl acetate permeating the membrane preferentially.

Hydraulic permeability values for the pure ethyl acetate component were too high because of excessive swelling of the membrane. The permeability coefficient employing the binary mixture were lower than those of the pure ethylene glycol. The reason again is compaction of the substructure resulting from plasticization caused by the low fraction of ethyl acetate in the feed solution.

IV. WATER/BUTYL CELLOSOLVE (lower critical conjugating binary)

Since 2-butoxyethanol (butyl cellosolve) and water have different refractive indices, measurement of the refractive index was used to standardize the concentrations of the binary mixture.

A. Asymmetric Cellulose Acetate Membrane

1) Osmotic experiments were conducted with a cellulose acetate asymmetric membrane annealed at 91°C for 15 minutes in water. Preliminary experiments showed that water is transported through this membrane preferentially. Water was used on the skin side to determine the effect of the cellosolve on the porous support matrix. Initially pure solutions of known weight were kept on the two sides of the membrane and the concentrations and weights measured at different times. The membrane exhibited an initial water flux of $\approx 250 \text{ kg/m}^2 \text{ day}$ but stabilized to a steady-state value of $\approx 75 \text{ kg/m}^2 \text{ day}$ in about 60 minutes.

2) Pervaporation experiments were conducted at 25°C with water/butoxyethanol mixtures of different composition. The separation factor $\alpha(\text{H}_2\text{O}/\text{BE})$ was high (450) at a low water concentration in butoxyethanol ($\approx 4 \text{ wt\%}$). The separation factor was lower (30) at a feed concentration of 32 wt% H_2O in butoxyethanol. The pervaporation flux showed an opposite trend. At low water concentration in the feed, the flux was low ($\approx 1 \text{ kg/m}^2 \text{ day}$), but at 32 wt% H_2O in butoxyethanol as the feed, the flux increased to $\approx 330 \text{ kg/m}^2 \text{ day}$. The effect of the concentration of the permeating species in the feed on the separation factor and flux is similar to that observed with the methanol/n-hexane system. Since this system exhibited a high separation and flux, a preliminary study of the membrane characteristics under hydraulic pressure-induced transport was conducted.

3) Hydraulic permeability measurements were conducted using pure solutions of water and 2-butoxyethanol with annealed cellulose acetate membranes at 20, 50, and 90 atm hydraulic pressures. The steady-state water permeability coefficient A had a value of about $6.2 \text{ kg/m}^2 \text{ day atm}$ and was approximately independent of pressure.

The steady-state hydraulic permeability of 2-butoxyethanol with annealed cellulose acetate membrane at 90 atm pressure was about $0.08 \text{ kg/m}^2 \text{ day atm}$. At 20 and 50 atm pressures the flux was negligible. The permeability of butoxyethanol is much lower than that of water under pressure.

Since the actual system of interest was n-propoxypropanol/water, further tests with this system were terminated.

V. WATER/PROPOXYPROPANOL (lower critical conjugating binary)

Membranes cast from the following polymers were tested with water/POP (propoxypropanol) binary mixtures:

- cellulose triacetate - dense
- cellulose acetate - asymmetric
- ethyl cellulose - asymmetric
- modified PPO - asymmetric and dense (nylon type modification)
- brominated and phosphonylated PPO - asymmetric.

Efforts with Tulane University were coordinated to test the ability of the UNIFAC method to predict experimental values of activity coefficients. Asymmetric cellulose acetate membrane was also evaluated in pervaporation with pressure for this binary system. An unpredicted change in performance occurred with higher pressures.

A. Cellulose Triacetate

Dense membranes were cast from a 5% solution of cellulose triacetate in dioxane to yield membranes $\approx 6 \mu\text{m}$ thick. Several sheets of these membranes were sent to ITC/Solar for evaluation. The membranes were tested with 0.2 wt% NaCl solution in reverse osmosis. The results showed a salt rejection of 60 to 99% and a permeate flux of 265 to zero $\text{kg/m}^2 \text{ day}$ at a hydraulic pressure of 95 and 20 atm, respectively. Treatment with POP/ H_2O (75/25 w/w) for 24 hours did not alter membrane transport characteristics. The results of reverse osmosis tests employing POP/ H_2O (75/25 w/w) as feed gave a separation factor $\alpha(\text{water/POP})$ of about 1.3 and a flux of about 15 $\text{kg/m}^2 \text{ day}$ at 100 atm. Separation of the feed solution by these cellulose triacetate (CTA) membranes is surprisingly poor.

Upon testing at ITC/Solar, some of the thin CTA films ($6 \mu\text{m}$) generated pinholes. Following this observation, carefully conducted reverse osmosis experiments with $6 \mu\text{m}$ CTA films proved that this thin material is too sensitive to pressure and in spite of its initially high salt rejection develops defects in the course of the experiment.

Based on the results with cellulose triacetate membranes, it can be concluded that salt rejection with NaCl solution is not necessarily a good indication of the expected behavior of the membrane in reverse osmosis with POP/H₂O solutions. Even though membrane salt separation characteristics (salt rejection and flux) did not deteriorate after exposure to POP solution, separation by reverse osmosis of POP/H₂O (75/25 w/w) remained very poor.

B. Cellulose Acetate

Asymmetric cellulose acetate membrane was annealed in water at 91°C for 15 minutes. Reverse osmosis with 1 wt% NaCl solution at 600 psi gave a salt rejection of 99% and a flux of 26 kg/m² day. The membrane was treated with a 60/40 (by weight) mixture of POP/H₂O for a day. In the subsequent reverse osmosis tests with 1 wt% NaCl solution at 600 psi, the membrane gave a salt rejection of 56% and a flux of 18.38 kg/m² day. The reduction in the salt rejection and flux is due to the morphological changes in the polymer membrane caused by interactions with POP.

Pressure tests with the treated annealed membrane with 60 wt% POP in water showed a decrease in the hydraulic permeability coefficient from 0.875 kg/m² day to 0.235 kg/m² day as the pressure was increased from 20 to 95 atm. This is most probably due to compaction of the membrane. The separation factor $\alpha(W/POP)$ increased from 1.5 at 20 atm to 3.0 at 95 atm.

Pervaporation using a treated, annealed, asymmetric cellulose acetate membrane without any applied pressure and 60 wt% POP in water as feed resulted in a flux of 34 kg/m² day and a separation factor $\alpha(W/POP) \approx 3.0$. The separation factor in pervaporation is the same as the value with hydraulic permeability tests at 95 atm pressure. With all binary systems tested before, the separation factor in pervaporation was several times higher than the separation factor due to hydraulic permeability. The strange behavior with this system may be due to the high vapor pressure of the permeating species (water). The permeating species may not be removed by vaporization fast enough to achieve a high separation.

C. Ethyl Cellulose

Membranes made of ethyl cellulose either swelled or dissolved completely when contacted with 75% POP solution in water for one hour.

D. Modified PPOBrØBr and PPOBrØBrP Membranes

Various surface-treated asymmetric membranes of PPOBrØBr, PPOBrØBrP, and blends of PPOBrØBr brominated to different levels were tested for possible use with the POP/H₂O binary mixture (10/90 by weight).

1) An asymmetric membrane of PPOBrØBr was prepared by casting an 18% solution of the polymer in dioxane on a glass plate and quenching in a mixture of acetone and water. Table E-II shows membrane casting variables. Reverse osmosis tests with 0.2 wt% NaCl solution on these membranes gave a salt rejection of 5 to 20% and a permeate flow of 3,000 to 10,000 kg/m² day at 500 psig. Reverse osmosis tests at 800 psig indicated that these membranes are damaged, as evidenced by a decrease in permeate flow, at elevated pressures.

All surface treatments were done on membranes cast with a thickness of 8 mils and evaporation time of 20 seconds.

The asymmetric PPOBrØBr membrane was treated with triethylamine by immersion for 15 minutes followed by rinsing with deionized water. The membrane had enormous flux with 0.2 wt% NaCl solution and gave almost no salt rejection. But after equilibration with a 10/90 POP/H₂O solution, the membrane had a flux of 4000 kg/m² day and a separation factor $\alpha(W/POP) \approx 1.22$ for reverse osmosis with 10/90 POP/H₂O feed at 20 atm pressure.

The PPOBrØBr (1.0) asymmetric membrane was surface treated on the skin side with 1,6-hexane diamine. The resulting membrane exhibited very little salt rejection and very high flux for reverse osmosis with 0.2% NaCl solution. The results of an osmotic test on this membrane with pure POP on the skin side and water on the support side gave an initial osmotic flux of 220 kg/m² day, which dropped to zero in one hour. In an osmosis test POP transported through the membrane selectively with little water diffusing through.

TABLE E-II
MEMBRANE CASTING VARIABLES

Polymer: PPOBrØBr (1.0) (8-12-77)
Solution: 18 wt% in dioxane

Membrane No.	Casting Thickness (mils)	Evaporation Time (seconds)
340-12-1	8	20
340-12-2	11	5
340-12-5	11	20

The PPOBrØBr asymmetric membrane was treated by immersion in 5% 1,6-hexane diamine in ethanol for 15 minutes followed by drying at ambient conditions. The results of the osmotic experiments with POP on the skin side and water on the support side showed that water is transported easily over the POP. Once again the osmotic flux dropped to very low values after two to three hours.

2) Asymmetric membranes of a 3:1 blend of PPOBrØBr (1.0) and PPOBrØBr (0.25) were prepared by a procedure similar to that used for the pure polymer. The asymmetric membrane was surface treated on the skin side with 1,6-hexane diamine. The resulting membrane has very little salt rejection and very high flux for reverse osmosis with 0.2 weight percent NaCl solution. After equilibration with the feed (10/90 POP/H₂O), the flux was still high but had a separation factor $\alpha(W/POP) \approx 1.29$ at 20 atm applied pressure. The results of osmosis experiments using POP on the skin side and water on the support side showed that the performance of this membrane is comparable to that of PPOBrØ (1.0) membrane in that POP is transported selectively over water.

The asymmetric membrane was treated by immersion in a solution of triethylamine in acetone and methanol. This membrane also gave very high fluxes during reverse osmosis trials with 0.2% NaCl solution. But after a three-hour treatment with 10/90 POP/H₂O, the hydraulic permeability coefficient A was 205 kg/m² day atm and the separation factor $\alpha(W/POP)$ was 1.30 during reverse osmosis with a feed of 10/90 POP/H₂O and 20 atm applied pressure.

The asymmetric membrane was surface treated on the skin side with 3.33% PVPy in ethanol to form a composite membrane. This membrane also gave little salt rejection and very high flux. The results of reverse osmosis experiments with 10/90 POP/H₂O showed that the hydraulic permeability coefficient A drops from a value of $A = 10.3$ kg/m² day atm to 20 atm applied pressure to a value $A = 4.3$ kg/m² day atm at 90 atm applied pressure. This shows that the membrane compacts under pressure, closing the pores due to defects in the membrane and thus increasing the effectiveness of separation. The separation factor $\alpha(W/POP)$ increased from 1.1 to 1.3 as the pressure was increased from 20 to 90 atm.

3) Asymmetric membranes of PPOBr ϕ BrP (0.75) were cast from a solution of the polymer in dioxane and acetic acid and quenched in water. The asymmetric membrane was hydrolyzed by treating the skin side with 1% NaOH solution overnight. The treated membrane was equilibrated in a solution of 10/90 (by weight) POP/H₂O for two days. To investigate the effect of hydrolysis and treatment with POP on the salt rejection and flux, reverse osmosis experiments with 0.2 wt% NaCl solution were conducted. Treatment with POP swelled the membrane and resulted in an increase in flux. Hydrolysis did not seem to have much effect on the flux and salt rejection. Pressure tests using a feed of 10/90 POP/H₂O with the POP-treated membrane showed that the membrane compacts in the presence of POP/H₂O solution. The separation factor α (water/POP) was very low (1.12-1.06) at all pressures between 20 and 95 atm.

Another membrane was hydrolyzed by treatment of the skin side with 1% HCl overnight. The treated membrane was equilibrated in a solution of 10/90 (by weight) POP/H₂O solution for two days. Reverse osmosis with 0.2 wt% NaCl solution showed that hydrolysis reduced the salt rejection a little but there was no effect on the flux. Treatment with POP/H₂O had a negative effect on the salt rejection but increased the flux due to swelling of the membrane. The effect of applied pressure on the permeability of this membrane with a feed of a 10/90 POP/H₂O solution showed that the hydraulic permeability coefficient dropped due to compaction of the membrane. The separation factor also dropped from a value of α (W/POP) = 3.6 at 20 atm to 1.25 at 95 atm applied pressure.

The asymmetric membrane was surface treated on the skin side with 1,6-hexane diamine and was equilibrated with 10/90 POP/H₂O solution for two days. Surface treatment with 1,6-hexane diamine reduced the flux and salt rejection at high pressures in reverse osmosis. Treatment with 10/90 POP/H₂O had little effect on the flux but reduced the salt rejection.

E. Modified PPO - Asymmetric and Dense (Nylon Type Modification)

Preliminary studies were done with 10 wt% POP, while later work was carried out with 75 wt% POP solution. Membranes made of PPOBr ϕ BrP either swelled or dissolved completely when treated with POP solution

(75 wt%) for one hour. Modifying the PPOBrØBrP membrane through cross-linking or treating with 1,6-hexane diamine did not change its susceptibility to the POP solution.

Since untreated PPOBrØBr (0.5) asymmetric membranes yielded very high fluxes with low salt rejection, 10- μ m dense membranes were cast. Reverse osmosis tests using a feed solution of 0.2 wt% NaCl showed that treatment with hexane diamine reduced the swelling behavior of this membrane in 75 wt% POP, apparently due to internal cross-linking. Results of reverse osmosis experiments using a 25 wt% POP solution in water, with a membrane that had been allowed to equilibrate with the feed solution for 2 hours, gave a separation factor $\alpha(\text{POP}/\text{W}) = 1.1$ to 2.5, with POP transported preferentially.

The same membrane, when treated with 75/25 (w/w) POP/H₂O for 24 hours, and run in reverse osmosis tests at 50 atm (75 wt% POP feed) yielded a separation factor $\alpha(\text{W}/\text{POP}) = 9$ and a flux of 140 kg/m² day. However, separation decreased and flux increased when the pressure was gradually increased to 100 atm. Water was preferentially transported in these cases.

Asymmetric membranes cast from PPOBrØBr were too open and gave low separation (even after modification).

In summary, of all the membranes tested, modified PPO membranes yielded the best separation. However, no membrane was developed which could tolerate high concentrations of POP in water solution for extended periods of time at 90 atm with decent separation factors.

VI. DISODIUM PHOSPHATE / WATER (Precipitation)

The sodium salt of phosphoric acid (Na_2HPO_4) was suggested by ITC/Solar for use in the precipitation method of unmixing in a PRO system. The electrical conductivity of an aqueous solution of this salt at 55°C was used to standardize the concentration of this binary mixture.

Brominated Polyphenylene Oxide Membrane

Asymmetric membranes of PPOBrP (374-56-2/3) were used for the osmotic tests at 55 - 57°C . Water was used on the skin side of the asymmetric membrane while the salt solution was used on the porous side. After the system had stabilized, the conductivity of the salt solution (and hence concentration) was determined at specified time intervals. Changes in volume on the two sides of the membrane were also determined.

During the course of these tests, it was observed that the concentration of the aqueous salt solution did not change appreciably as is evident from Table E-III. Hence different concentrations of the salt were used to generate varying osmotic pressure differences. The volumetric difference (ΔV) is the average of the volumetric differences in each of the reservoirs on the two sides of the membrane.

These tests showed that the water flux increases with an increase in the osmotic pressure difference between the two sides of the membrane. The osmotic permeability coefficient decreased from a value of $0.0038 \text{ m}^3/\text{m}^2 \text{ day atm}$ at 20 atm osmotic pressure difference to $0.0013 \text{ m}^3/\text{m}^2 \text{ day atm}$ at 160 atm osmotic pressure difference.

TABLE I - III
OSMOTIC EXPERIMENTAL RESULTS USING ASYMMETRIC PPOBr₄BrP MEMBRANES

Membrane Number	ΔT (min)	ΔV (ml)	Flux (kg/m ² day)	Concentration of Na ₂ HPO ₄ (wt%)	$\Delta \pi$ (atm)	Permeability Coefficient x 10 ³ (m ³ /m ² day atm)
2	15	9.2	189.73	39	~160	1.19
2	15	9.5	195.92	38		1.22
2	40	24.6	190.24	36		1.19
2	15	10.2	210.35	35		1.31
2	15	10.5	216.54	35		1.35
2	20	14.0	216.54	35		1.35
3	30	23.2	239.22	38	~160	1.50
3	15	10.8	222.72	36		1.39
3	15	9.6	197.98	37		1.24
3	15	10.5	216.54	35		1.35
3	15	11.8	243.35	34		1.52
3	30	22.8	235.90	32		1.42
2	15	8.6	177.35	20	80	2.22
2	15	8.2	169.11	20		2.11
2	15	7.6	156.7	20		1.96
2	15	8.4	173.34	20		2.12
3	15	8.6	177.35	20	80	2.22
3	15	7.4	148.6	20		1.94
3	15	8.6	177.35	20		2.22
3	15	8.2	169.11	20		2.11
2	15	5.4	111.36	10	40	2.78
2	15	5.0	103.11	10		2.58
2	15	5.3	109.30	10		2.73
3	20	6.9	106.72	10	40	2.66
3	15	4.9	101.05	10		2.53
3	15	5.0	103.11	10		2.58
2	15	3.6	74.24	6	20	3.71
2	15	3.5	72.17	5		3.66
2	15	3.6	74.24	5		3.71
3	15	3.7	76.3	5	20	3.82
3	15	3.4	70.1	5		3.55
3	15	3.6	74.24	5		3.71

APPENDIX F

ANALYTICAL WORK ON THERMODYNAMIC CORRELATIONS

BY TULANE UNIVERSITY

Tulane University was subcontracted to do analytical work with generalized thermodynamic correlations to provide physical chemical data on promising binary mixtures. The data to be provided included vapor-liquid equilibrium data, phase diagrams for conjugating binaries, and activity coefficients. By this means this work aided in identifying and evaluating candidate binaries. Tulane also provided analytical services to GSRI to help them evaluate membranes. This work was done in the Chemical Engineering Department at Tulane.

I. STATEMENT OF WORK

Tulane was to implement and refine its binary simulation program to calculate vapor-liquid and liquid-liquid multicomponent phase equilibrium data. The simulation program was to be based on state-of-the-art group contribution theory and, specifically, on the UNIFAC method of calculation. This work was to include:

- a. Implementation of the binary simulation program.
- b. Dissemination of the binary simulation program's specifications and capabilities to GSRI and InterTechnology/Solar. In particular this information was to include descriptive narration on the concept and method of calculation with comparison of calculated results to existing data.
- c. Adjustment of program calculations to best simulate vapor-liquid equilibrium necessary for distillative mixture calculations. The purpose of this effort was to investigate possible binaries which would utilize distillation separation techniques.

- d. Program calculations necessary for partially miscible mixture calculations. The purpose of this effort was to investigate possible binaries which could utilize liquid phase miscibility separation techniques.
- e. Additional program capabilities to include programming for osmotic pressure calculations possible for a chosen binary system.

In other tasks the binary simulation program was to be employed to initially investigate possible binary mixtures. Binary mixtures investigated were those suggested by GSRI and InterTechnology/Solar as well as those identified by Tulane. Specifically, this task was to include:

- a. Investigation of suggested binary mixtures with comparison, where possible, to existing experimental data. Both distillative and miscibility separation systems were to be investigated.
- b. Submission of findings to GSRI and InterTechnology/Solar.

It was anticipated that a significant effort would be required to discover a suitable membrane for a given binary system. This task specifically included:

- a. Investigation of systems similar to candidate systems should the candidate system be determined infeasible in membrane application.
- b. Investigation of systems compatible with existing membrane technology.

II. DISCUSSION OF THE UNIFAC CORRELATION*

A. The Group Contribution Concept

A large part of process design is concerned with separation processes. Many of these are diffusional operations of the phase-contacting type, e.g., distillation, absorption, and extraction. Rational design of such separation processes requires a quantitative understanding of phase equilibrium in multicomponent mixtures as expressed through vapor-liquid fugacity coefficients and liquid-phase activity coefficients. At low or modest pressures fugacity coefficients can be estimated easily; however, except for very simple mixtures, experimental mixture data are required to calculate activity coefficients.

Since the number of liquid mixtures commonly experienced is quite large, it is not likely that the necessary experimental data will always be available for every mixture, particularly at the required state conditions. It is therefore desirable to correlate the limited experimental data in such a way as to enable a confident prediction of activity coefficients in those mixtures where little or no experimental data exist. For non-electrolyte mixtures a procedure for establishing such a correlation is provided by the concept of group contributions.

In any group contribution method the basic idea is that, whereas there are thousands of chemical compounds of interest, the number of functional groups which constitute these compounds is much smaller (e.g., n-propanol is composed of one CH_3 group, one CH_2 group and one CH_2OH group). Therefore, if the assumption is made that the activity coefficient of component i in a mixture is the sum of contributions made by the molecule's functional groups, a possible technique can be obtained for correlating the activity coefficient γ_i in a variety of mixtures in terms of a much smaller number of parameters which characterize the contributions of individual groups.

Any group contribution method is necessarily approximate because the contribution of a given group in one molecule is not necessarily the

*A. Fredenslund, J. Gmehling, P. Rasmussen, "Vapor-Liquid Equilibrium Using UNIFAC," Elsevier, 1977.

same as that in another molecule. For example, the contribution of a carbonyl group in a ketone (e.g., acetone) cannot be expected to be the same as that of a carbonyl group in an organic acid (e.g., acetic acid). On the other hand, experience suggests that the contribution of a carbonyl group in, for example, acetone, is similar to the contribution of a carbonyl group in another ketone, e.g., 2-butanone.

Finally, accuracy of the correlation technique improves with increasing distinction between groups; in considering, for example, aliphatic alcohols, in a first approximation no distinction is made between the position of a hydroxyl group, but in a second approximation such a distinction is desirable. In the limit, as more and more distinctions are made, we recover the ultimate group: the molecule. In that event the advantage of the group contribution method is lost. For practical utility, a compromise must be reached. The number of distinct groups must remain small but not so small as to neglect significant effects of molecular structure on physical properties.

B. The UNIFAC Model

The UNIFAC method for calculation of activity coefficients is based on the group contribution concept. The basic aim of UNIFAC is to utilize existing phase equilibrium data for predicting phase equilibria of systems for which no data are available. The method entails the following: a suitable reduction of experimentally obtained activity coefficients, data to obtain parameters characterizing interactions between pairs of structural groups in nonelectrolyte systems, and use of these parameters to predict activity coefficients for other systems which have not been studied experimentally but which contain the same functional groups.

The fundamental assumptions of UNIFAC are:

1. The logarithm of the activity coefficient is assumed to be the sum of two contributions: a combinatorial part, essentially due to differences in size and shape of the molecules in the mixture, and a residual part,

essentially due to energy interactions. The distinction between these two kinds of contributions to the activity coefficients is necessary since the liquid-phase non-idealities caused by size and shape effects cannot be associated with group energetic interactions.

2. The contribution from group interactions, the residual part, is assumed to be the sum of individual contributions from each solute group in the solution less the sum of the individual contributions in the pure-component environment.
3. The individual group contributions in any environment containing groups of types 1, 2, ..., N are assumed to be only a function of group concentrations and temperature.

For the detailed equations comprising the UNIFAC method, the reader is referred to the recent text by Fredenslund, Gmehling and Rasmussen.

From the user's point of view, UNIFAC provides three advantages:

1. Flexibility: UNIFAC has a well-founded basis for establishing group sizes and shapes,
2. Simplicity: UNIFAC parameters are nearly independent of temperature over a relatively large temperature range (30-125°C),
3. Large Range of Applicability: UNIFAC parameters are now available for a considerable number of different functional groups.

As it stands, the UNIFAC method may be applied to nonelectrolyte multi-component mixtures removed from the critical point. Furthermore, all components must be condensable. The temperature range considered is typically 30° - 125°C. Finally, the UNIFAC method in its present state of development correlates more than 70% of the published vapor-liquid equilibrium data.

C. Phase-Equilibria Calculations

Phase equilibrium thermodynamics serves as the mathematical framework for providing quantitative information on phase behavior. Typically, a mixture is given with M components and two (or more) phases, and it is supposed that the two phases have reached an equilibrium state. Equilibrium thermodynamics enables one to answer the following question: If the mole fractions in Phase I ($x_1, \dots, x_M$) and the temperature T are known, what are the mole fractions in Phase II ($y_1, y_2, \dots, y_M$) and the pressure P ? To solve this problem, the condition for phase equilibria is used:

$$f_i^I = f_i^{II} \text{ for } i = 1, 2, \dots, M \quad (1)$$

where f_i is the fugacity of component i in phase I or II. There are M such relationships, where M is the total number of components in the mixture.

If Phase I is a vapor and II is a liquid, the following relation holds:

$$\frac{y_i}{x_i} = \frac{\gamma_i p_i^{\text{sat}} \phi_i^{\text{sat}}}{p \phi_i} \exp \left[\int_{p^{\text{sat}}}^P \frac{V_i^L}{RT} dP \right] \quad (2)$$

Here, nonideality in the vapor phase is characterized by ϕ_i and ϕ_i^{sat} , both readily calculated at low pressures (e.g., several atmospheres) using the virial equation of state, and γ_i accounts for nonideal liquid behavior and is calculated using the UNIFAC method.

If both phases are liquid (mole fractions given by x_i^I and x_i^{II}), equation (1) becomes:

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \quad (3)$$

where the UNIFAC method now provides γ_i^I and γ_i^{II} . The UNIFAC technique can predict phase splitting. For design of a liquid-liquid extraction cascade, one needs to know accurately the relative distribution of the solute(s) between the two liquid phases. It should be noted that since the solute mole fractions are often small, the relative error in the

predicted mole fractions--and hence in the solute distribution ratios--may be large. This problem is encountered by all methods for calculating activity coefficients, and the UNIFAC model is no exception.

D. Application of UNIFAC

Tulane applied the UNIFAC correlation to the calculation of physical chemical data for a number of potential binary mixtures. Most of these binaries were candidates for distillation unmixing. Calculations were also done for some conjugation candidates, but UNIFAC cannot predict the equilibrium data for conjugating binaries very well. A discussion of this situation and Tulane's attempt to develop a correlation specific for the purposes of this project is contained in the next section. Table F-I is a list of the binaries for which Tulane calculated activity coefficients during the course of the project, to show the range of the application of UNIFAC.

TABLE F-I

BINARY MIXTURES EVALUATED BY TULANE WITH UNIFAC

1. Methanol/Hexane
2. Ethyl Acetate/Ethylene Glycol
3. Heptane/Water
4. Hexane/Water
5. Ethanol/Water
6. Ethyl Benzyl Amine/Methanol
7. Ethyl Benzyl Amine/Glycerol
8. 1 - Methyl Piperidine/Water
9. Acetone/Ethylene Glycol
10. Methanol/Ethylene Glycol
11. Methanol/Glycerol
12. Ethanol/Glycerol
13. Ethanol/Ethylene Glycol
14. Benzene/Cyclohexane
15. 2-Propoxy-1-Propanol/Water

III. DISCUSSION OF ATTEMPTS TO DEVELOP A NEW CORRELATION FOR PARTIALLY MISCIBLE LIQUID SYSTEMS

The UNIFAC correlation at the present time does not work very well in predicting liquid-liquid equilibrium data for binary mixtures. The shortcomings of the program were brought to light by the methanol-hexane system, which predicted an unrealizable critical solution temperature; i.e., there was no agreement with experimental data in the critical temperature region. Agreement was good, however, with experimental data at low concentrations. The program works well for ternary systems, where temperature dependence has a relatively insignificant role, but fails for binary systems, where phase splitting is entirely due to temperature dependence. An effort was therefore made to develop a new correlation for equilibrium properties of liquid-liquid systems.

Binary liquid immiscibility can be represented exactly by the following thermodynamic expression:

$$\mu_i^I = \mu_i^{II} \quad (4)$$

where i is the index of components and the superscripts I and II denote the phase.

Now it has been established that:

$$\mu_i = \left(\frac{\partial G_i}{\partial n_i} \right)_{T, P} = RT \ln f_i \quad (5)$$

$j \neq i$

where f_i is the fugacity of component i .

$$\text{Thus } RT \ln f_i^I = RT \ln f_i^{II} \text{ or } f_i^I = f_i^{II} \quad (1)$$

But, for liquids, the nonideality is represented by the activity coefficient:

$$f_i = x_i \gamma_i f_i^\circ \quad (6)$$

which yields:

$$(x_i \gamma_i f_i^\circ)^I = (x_i \gamma_i f_i^\circ)^{II} \quad (7)$$

Since f_i^o is the standard-state fugacity, it can be chosen such that it is the same for both phases. Hence

$$(x_i \gamma_i)^I = (x_i \gamma_i)^{II} \quad (8)$$

It is therefore evident that an adequate representation of the activity coefficient is essential for the prediction of phase separation.

Further, if the overall homogeneous composition is specified, and the compositions of the two phases in equilibrium are desired, a calculation of the flash-distillation type can be performed. Let F be the total number of moles in the two phases and z_i be the composition of the solution before phase separation. Then

$$F = L^I + L^{II}$$

$$Fz_i = (Lx_i)^I = (Lx_i)^{II}$$

$$\text{or } Fz_i = (Lx_i)^I = (F - L^I)x_i^{II}$$

where L^I and L^{II} are the total moles in the two phases.

$$\text{But } x_i^{II} = x_i^I \frac{\gamma_i^I}{\gamma_i^{II}} = x_i^I K_i$$

where K_i = equilibrium constant = $\gamma_i^I / \gamma_i^{II}$

Substituting for x_i^{II} and dividing by F give:

$$z_i = x_i^I \left(\frac{L^I}{F} + \left(1 - \frac{L^I}{F}\right) K_i \right)$$

Defining $\theta = L^I/F$ and substituting give:

$$x_i^I = \frac{z_i}{(\theta + (1 - \theta)K_i)} \quad (9)$$

An iterative calculation can be employed to calculate x_i^I and θ . The above expression is very nonlinear, however, due to the appearance of activity coefficients in the form of K_i . Knowledge of x_i^I and K_i then allows us to calculate the composition of the other phase in equilibrium.

The preceding development and methodology have been applied to calculate liquid-liquid immiscibility for ternary systems with satisfactory results.

The governing factor in ternary systems is the composition of the homogeneous phase prior to phase separation. For such multicomponent systems temperature dependence of the activity coefficient is not necessary. In binary liquid systems, however, phase separation is totally governed by temperature. For such binary systems it has been our experience and those of previous workers (2) that two-parameter activity coefficients cannot represent liquid immiscibility adequately.

The most current expression for activity coefficients is due to Fredenslund, et al. (3), known as UNIFAC. To limit the complexity of the mathematical expression, only two parameters per binary pair were allowed. Of the various systems we have run so far, either the phase separation for a binary system is like that of previous two-parameter expressions, or nonexistent at all. UNIFAC was unable to predict phase separation for nitrobenzene/hexane and nitroethane/hexane systems.

Guggenheim has derived a semirigorous theory known as quasichemical approximation through statistical mechanics (4,5). The result for excess Gibbs free energy, g^E , in series form is given by:

$$\frac{g^E}{RT} = \left(\frac{w}{kT}\right) x_1 x_2 \left[1 - \frac{1}{2} \left(\frac{2w}{zkT}\right) x_1 x_2 + \dots\right] \quad (10)$$

where w = the interchange energy

k = Boltzman's constant

z = the co-ordination number.

The Gibbs free energy of mixing is given by:

$$\Delta g_{\text{mixing}} = RT [x_1 \ln x_2 + x_2 \ln x_1] + g^E \quad (11)$$

At the critical solution temperature, CST,

$$\frac{\partial^2 \Delta g_{\text{mixing}}}{\partial x^2} = \frac{\partial^3 \Delta g_{\text{mixing}}}{\partial x^3} = 0. \quad (12)$$

The critical solution temperature T^C is then given by

$$T^C = \frac{w}{kz[\ln z - \ln(z-2)]} \quad (13)$$

Eckert (6) calculated the binodal curve for methane/carbon tetrafluoride, and prediction was good compared to experimental data. It must, however, be borne in mind that the expression for g^E is highly symmetrical around $x = 0.5$. The quasichemical theory cannot predict the skewed binodal curves for highly nonideal, unequal-sized molecules. A similar treatment has been expounded by Kirkwood (7).

R. B. Parlin and H. Eyring (8) have treated a binary liquid mixture as composed of quasi-macro-crystalline regions of twelve or less molecules. An appropriate treatment of the partition function then yields:

$$\frac{T}{T^C} = 2 \frac{\ln(z/z-2)}{\ln \left[\frac{(x_1 + \frac{1}{z-2})(1-x_1 + \frac{1}{z-2})}{x_1(1-x_1)} \right]} \quad (14)$$

However, once again the treatment is for equal-sized molecules, and the binodal curve is symmetrical around $x_1 = 0.5$ as is evident from the denominator of the right-hand side:

Hildebrand (9,12) has combined the Flory-Huggins equation entropy correction

$$R \ln x_2 = R [\ln \phi_2 + (1 - V_2/V_1) \phi_1] \quad (15)$$

with the heat term given by the van Laar-Scatchard-Hildebrand equation for a regular solution as

$$\ln a_2 = \ln x_2 + (v_2 \phi_1^2 / RT) (\delta_1 - \delta_2)^2 \quad (16)$$

to obtain

$$RT \ln (a_2 / \phi_2) = V_2 \phi_1^2 (\delta_1 - \delta_2)^2 + RT \phi_1 [1 - V_2/V_1] \quad (17)$$

where

- a = activity
- V = molal volume
- δ = solubility parameter
- ϕ = volume fraction

and subscripts 1 and 2 refer to solvent and solute, respectively.

Hildebrand and Scott (11) give the relation:

$$RT^C = \frac{2x_1x_2 V_1^2 V_2^2}{(x_1V_1 + x_2V_2)^3} (\delta_1 - \delta_2)^2 \quad (18)$$

and

$$\left(\frac{x_2}{x_1}\right) = \frac{(V_1^2 + V_2^2 - V_1V_2)^{1/2}}{V_1 - (V_1^2 + V_2^2 - V_1V_2)^{1/2}} \quad (19)$$

It is evident that the size effect of the individual molecules has been incorporated into the theory to represent symmetrical as well as skewed binodal curves. The theory of regular solutions is, however, based on nonpolar species, and although attempts have been made to represent polar liquids by this theory, these attempts are only partially successful.

By analogy with the gas-liquid single-component critical point, scaling laws can be extended to the binary liquid-liquid critical solution region. Current descriptions of thermodynamic behavior in the neighborhood of the critical point rely on the scaling hypotheses, a summary of which is given by Rowlinson (7). Hall and Eubank (15) have applied a vapor density equation of the form

$$\Delta\rho_{rs} = \frac{1}{3} k_1 |\Delta T|^\beta + k_2 \Delta T + k_3 |\Delta T|^{1-\alpha} \quad (20)$$

where k_1 , k_2 , k_3 are material constants and α , β are scaling exponents. If we let $\Delta T \rightarrow 0$, the equation becomes:

$$\Delta\rho_{rs} = \frac{1}{3} k_1 |\Delta T|^\beta \quad (21)$$

By analogy, for a liquid-liquid system:

$$|x^I - x^{II}| = k_1 |T - T^C|^{1/3} \quad (22)$$

where T^C is the critical solution temperature and I and II are the phase superscript. This cubic equation has been found to fit most measurements in the range of 1 - 30°C for $|T - T^C|$. Unfortunately, the equation gives only tie-line information, and additional information is required to fix the phase diagram. For twelve mixtures with upper critical solution

temperatures and four with lower critical solution temperatures, Cox and Herrington (16) give the relationship:

$$\ln \left(\frac{x_1^I x_2^C}{x_2^I x_1^C} \right) = \beta |T - T^C|^{1/3} = \ln \left(\frac{x_2^{II} x_1^C}{x_1^{II} x_2^C} \right) \quad (23)$$

where once again I and II represent phases and x_i^C represents the critical composition. This relationship gives a linear plot of

$$\ln \left(\frac{x_1^I x_2^C}{x_2^I x_1^C} \right) \text{ with respect to } |T - T^C|^{1/3}$$

If, instead of representing both phases by the same constant β , two different constants are employed, the representation is improved significantly. In regions close to the critical solution temperature, the relationship reduces to the scaling laws (17). Equation (23) has been found to be equally valid for mixtures with either a LCST or an UCST.

In our investigation it appeared that the best representation of binary liquid immiscibility is obtained by the Cox-Herrington expressions. In the event that critical compositions as well as the critical solution temperature are known, only one additional point must be known to calculate the constant β and generate the binodal curve. However, most all the investigators of critical solution temperatures employ techniques that do not determine critical compositions simultaneously. Francis (18,19) has compiled critical solution temperatures of numerous binary mixtures, but hardly any critical compositions are available.

Attempts were therefore made to correlate the critical compositions in terms of the critical solution temperature. In the first attempt the logarithm of the ratio of the smaller mole fraction with respect to the larger mole fraction was plotted against the infinite-dilution activity coefficients, using previously published data. A straight-line correlation was obtained for this plot. "Large" and "small" in the above case were determined by the value of the molar volume. The molar volumes and the infinite-dilution activity coefficients were calculated at the critical solution temperature.

In the second attempt the group $\ln \left[\frac{x_S^C \gamma_S^\infty}{x_L^C \gamma_L^\infty} \right]$ was plotted against $\ln \left[\frac{V_L}{V_S} \right]$

where the subscripts S and L again signify small and large, determined by the value of the molar volume at the critical solution temperature. The correlation again was a straight line.

In both cases the infinite-dilution activity coefficients were calculated using UNIFAC, which, in contrast to most other activity-coefficient correlations, predicts these values rather well. Thus, if the value of the critical solution temperature is known and the critical constants (P_C , T_C , V_C , Z_C) are available, both the infinite-dilution activity coefficients as well as the molar volumes can be calculated. Then, the appropriate value of the x_i^C can be calculated from the correlations presented above.

One additional point on the binodal curve is necessary for the evaluation of the constant β ; UNIFAC was employed to do this. Preliminary results were encouraging. It must be mentioned that all the data points on the two graphs were for compounds containing carbon, hydrogen and oxygen.

Although this work produced encouraging results, additional work would be necessary to make this empirical correlation useful. A significant extension of the theory of UNIFAC is necessary before it would be possible to predict with any degree of certainty the entire phase diagram of a partially miscible binary mixture from only a knowledge of pure component properties and molecular interactions. Such work was outside the scope of this project.

IV. BIBLIOGRAPHY

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