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THE ROLE OF SPENT SHALE IN OIL SHALE PROCESSING AND THE
MANAGEMENT OF ENVIRONMENTAL RESIDUES

By
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August 1980

Work Performed Under Contract No. AC20-79LC10020

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THE ROLE OF SPENT SHALE IN OIL SHALE PROCESSING
AND THE MANAGEMENT OF ENVIRONMENTAL RESIDUES

FINAL TECHNICAL REPORT
FOR THE PERIOD JANUARY 1979 - MAY 1980

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A proposal entitled "The Role of Spent Shale in Oil Shale Processing and the Management of Environmental Residues," was submitted to the United States Department of Energy - Laramie Energy Technology Center on May 18, 1977. The work outlined in the proposal was to begin September 1, 1977 and continue for a three year period. The amount requested to carry out this study was \$270,029. After receiving favorable reviews on the proposal, the study was initiated on January 12, 1979.

This project was divided into three primary tasks. The first task was to investigate the properties of spent shale that had been retorted in both a combustion retort as well as an inert atmosphere. The results from the first portion of this task (retorting in an inert atmosphere) was then to be used in carrying out the second task, which was to study the sorptive properties of the spent shale. The third primary task was to conduct studies to develop methods for treating water produced during retorting.

The proposal under which this work was to be carried out was for a period of three years. However, because of the nature of the contract, funding to continue this study was not available after the first year of the project. A no-cost extension to the contract was approved by the Laramie Energy Technology Center so that the maximum amount of work could be achieved with the first year funding. The period for the no-cost extension ended May 15, 1980.

The proposed program schedule for the full three year project are shown in Appendix A. The scope of work for the first year as agreed upon by Dr. David Farrier, Project Officer, is as follows.

Task 1 (Analysis of Spent Shale)

A small oil shale retort will be designed and constructed to produce spent shale comparable to that produced in the in situ process. The temperature and atmosphere in the retort and receiver will be controllable. The retort will be capable of operation to 1000°C. The spent shale produced in the retort will be analyzed for mineral composition and characterized according to the type shale, retorting temperature, retorting time, porosity, surface area, and particle size. Forty-eight retorting runs will be made to characterize the oil shale. Two types of shale will be retorted at 8 temperatures and at 3 different retorting times in an inert atmosphere. In addition to making x-ray analyses to characterize the shale according to mineral composition, the porosity and surface area will be measured on all 48 samples.

Task 2 (Adsorption of Gases on Spent Shale)

The adsorption of H_2S on spent shale produced in an inert atmosphere will be studied. This will include the measurement of adsorption and desorption curves at three temperatures on all shale samples. The adsorption data will be correlated in terms of known adsorption models. Diffusion coefficients will be calculated from the breakthrough curves.

Task 3 (Clean up of Retort Water)

Hot gas stripping of retort water will be studied in a desorption apparatus packed with Berl saddles. A model retort water containing ammonium carbonates will be studied to determine the desorption rates of NH_3 and CO_2 . Mass transfer coefficients will be calculated for the model retort water. Stripping of the actual retort water will be carried out during the final quarter of the first year.

Task 4 (Adsorption of Aliphatic Acids from Aqueous Solutions)

The removal of single solute aliphatic acids from dilute aqueous solutions will be studied using activated carbon as the adsorbent. In particular, five pure component systems (acetic acid, propionic acid, n-butyric acid, n-hexanoic acid, and n-heptanoic acid) will be investigated.

Task 5 (Multi-Solute Adsorption of Aliphatic Acids)

Multi-solute adsorption of aliphatic acids from dilute aqueous solutions onto activated carbon will be studied. A competitive adsorption model will be developed to predict bi-solute equilibrium data.

All of the above tasks have been completed and the results of each study will be presented here in the final report. Since each of these tasks were very lengthy, only the most important results will be summarized in the body of this report. The results for Tasks 1 and 2 are combined since the adsorption of gases on the spent shale is related to the properties of the shale. Details of each task are provided in the attached theses.

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PART I

TASKS 1 AND 2

RETORTING EXPERIMENTS AND ADSORPTION OF GASES ON SPENT SHALE

SUMMARY

The adsorption of hydrogen sulfide on retorted oil shale was studied at 10, 25, and 60°C using a packed bed method. Equilibrium isotherms were calculated from the adsorption data and were modeled by the Langmuir, Freundlich, and Polanyi equations. The isosteric heat of adsorption was calculated at three adsorbent loadings and was found to increase with increased loading. A calculated heat of adsorption less than the heat of condensation indicated that the adsorption was primarily due to Van der Waals' forces. Adsorption capacities were also found as a function of oil shale retorting temperature with the maximum uptake occurring on shale that was retorted at 750°C.

INTRODUCTION

The recovery of oil from shale by in situ retorting eliminates mining a portion of the shale and the pollution problem that accompanies the disposal of large quantities of spent shale. In situ processing of oil shale is based on the initiation of combustion or introduction of heat into the formation which results in the decomposition of kerogen into bitumen that is subsequently converted to oil, residual carbon, hydrocarbon gases, and combustion products. Although retorting begins at about 350°C, temperatures of the in situ oil shale retorting process may exceed 1000°C. At the temperatures at which retorting is carried out, the complex mineral structure of the shale also undergoes change. The extent of these mineral reactions depends not only on temperature but also on how long the mineral has been heated. In addition to studies of raw shale, several investigators have studied a variety of experimental retorting conditions and determined what effects these conditions had on the pyrolytic products (1-7). Even though the literature is replete with studies of how various minerals found in shale react under different experimental conditions, except for the work of Smith (8) and Campbell (9), these studies were not directed toward the retorting of shale, particularly by in situ methods. Since spent shale beds offer a possible means of disposing of retort water and certain undesirable combustion gases, studies of the spent shale become even more important. This study investigates the adsorption of hydrogen sulfide on oil shale retorted in nitrogen and the changes in the properties of shale that occur during retorting.

EXPERIMENTAL

The oil shale studied in this work was from the Green River formation and contained $13.5 \times 10^{-5} \text{ m}^3/\text{kg}$ (32.4 gal/ton) of oil as found by Fischer assay. The shale samples were prepared by collecting a large quantity of raw shale which was ground and mixed several times so that the effects of retorting conditions would not be masked by variations in the properties of the raw shale. The samples were sieved and the shale which passed a one-fourth inch screen but was collected on a one-eighth inch screen provided a homogeneous material for this study.

The retorting and production of spent shale was carried out in a 0.61 m long stainless steel retort with an inside diameter of 0.05 m. The retort was sealed with threaded caps that had been tapped at each end to allow for the removal of oil and combustion gases. This also provided a means of controlling the atmosphere inside the retort. Oil shale was packed in the retort which was sealed and placed in a furnace. Nitrogen was passed through the retort at a rate of $6.0 \times 10^{-3} \text{ m}^3/\text{h}$ to provide an inert atmosphere while retorting. The retort was then heated to the desired retorting temperature and the samples were retorted for a fixed period of time. Following retorting, the shale was subsequently cooled to ambient temperature while nitrogen continued to flow. The samples were analyzed for residual carbon, hydrogen, nitrogen, and sulfur. In addition to determining the surface area of each sample, an x-ray diffraction analysis was conducted to relate the effects of retorting temperature to the mineral content, surface area, and adsorptive capacity of the processed shale. Retorting was carried out for two hours at temperatures ranging from 250°C to 950°C.

The adsorption of hydrogen sulfide on spent shale was studied in packed beds, under steady flow conditions. The experimental apparatus was designed and constructed to utilize the ultraviolet detector to measure and record gas concentrations.

The column used in this study was prepared from a 1/2 inch OD stainless steel tube 7.5 inches in length. It was furnished with union reducers at both ends so that one end could be connected to the heating coil and the other end to a Beckman model 25 ultraviolet detector. Each end of the column contained a 1/4 inch section of pyrex glass wool to prevent small particles of spent shale from being carried away by the gas flow. Thermocouples were attached to both ends of the column to measure any temperature change in the gas stream that might result due to adsorption. The gas flow rate was continuously monitored with a rotameter type of flow measuring device which had been calibrated to experimental conditions. The flow rates were checked periodically with a soap bubble meter to insure steady flow. The desired temperature for the adsorption run was maintained constant by using a refrigeration-heating cycle water bath.

Spent shale obtained from the retorting process, in the size range 16 to 35 U.S. mesh, was packed into the column at a packing density of 1.56 g/cm^3 and the column was attached to the adsorption system and placed in the constant temperature bath. Pure nitrogen gas was passed through the packed bed to flush any impurities from the shale and to establish a base line. After the spent shale reached thermal equilibrium with the bath, a gas mixture of hydrogen sulfide in nitrogen was then started. The effluent gas concentration was continuously monitored until it became equal to the concentration of the inlet gas mixture. The resulting breakthrough curves were analyzed for the amount of gas adsorbed on the shale at equilibrium.

RESULTS AND DISCUSSION

Properties of Retorted Shale:

The oil shale samples were retorted at temperatures ranging from 250°C to 950°C for a retorting time of 2 hours. The chemical analyses of these samples are shown in Table 1. A comparison of the values given for mineral carbon indicates that retorting strongly influences the properties of the spent shale.

The total residual carbon decreased with increasing retorting temperature as did the weight percent of the residual organic carbon. The decomposition of the more stable organic compounds at higher temperatures accounts for the decrease of organic carbon. Further, it is readily seen that for retorting temperatures less than 650°C the weight percent of mineral carbon is about constant at 5%, but as the retorting temperature increased the percent mineral carbon also decreased. According to Jukkola, et al. (10), dolomite in oil shale begins to decompose below 565°C while the calcite begins to decompose from 620 to 650°C.

Diffraction scans were run on all samples of the richer shale and the results are given in Table 2. Semiquantitative estimates for the phases identified were made by relating the diffracted intensity for each phase to the total diffracted intensity for the whole sample. Since the starting composition (before heating) was the same for all eight samples, observed differences in the x-ray patterns are a direct result of the heating. The most noticeable of these differences is due to decomposition of the carbonate minerals in the upper range of temperatures. By 650°C, the dolomite $\text{CaMg}(\text{CO}_3)_2$ has started to break down, with evolution of CO_2 and formation of

periclase (MgO). By 750°C, breakdown of the calcite ($\text{CaCO}_3 + \text{heat} \rightarrow \text{CaO} + \text{CO}_2$) and formation of lime (CaO) is also evident. By 950°C, all of the carbonates are gone and new silicates (melilite and pyroxene) are beginning to form at the expense of feldspar, quartz, and the oxides from the carbonates. The zeolite mineral analcite also appears to break down in the upper 100-200 degrees of heating.

TABLE 1

Chemical Analysis of $13.5 \times 10^{-5} \text{ m}^3/\text{kg}$ Oil Shale Retorted for Two Hours

Retorting Temperature, °C	Weight Percent				Mineral	Organic
	Carbon	Hydrogen	Nitrogen	Sulfur	Carbon	Carbon
250	18.89	2.05	0.68	0.61	4.40	14.49
350	19.96	2.32	0.72	0.65	4.37	15.59
450	12.51	0.83	0.60	0.55	4.98	7.53
550	10.26	0.18	0.45	0.49	4.99	5.27
650	9.27	0.17	0.41	0.50	4.41	4.86
750	8.77	0.12	0.37	0.54	3.72	5.05
850	6.63	0.21	0.24	0.70	1.62	5.01
950	4.79	0.14	0.13	0.69	.62	4.17

The decrease in mineral carbon shown in Table 1 and the decrease in dolomite shown in Table 2 is consistent with the work of Jukkola, et al. (10). In view of the nonhomogeneous nature of the spent shale, the fact that calcite does not decrease with increasing temperature but disappears completely above 850°C is not in conflict with the results of Jukkola, et al. The presence of portlandite indicated for two samples in Table 2 is probably due to the strong tendency for lime to absorb atmospheric moisture.

TABLE 2

X-Ray Diffraction Analysis of $13.5 \times 10^{-5} \text{ m}^3/\text{kg}$ Shale Samples Retorted for Two Hours

Mineral*	Temperature, °C							
	250	350	450	550	650	750	850	950
Quartz	Major	Major	Major	Major	Major	Major	Major	Major-Moderate <850
Alkali Feldspars	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate <850
Dolomite	Major	Major	Major	Major	Major <550	Moderate	Minor	--
Calcite	Moderate	Moderate	Major-Moderate	Major-Moderate	Major-Moderate	Major-Moderate	Minor	--
Periclase	--	--	--	--	Minor	Minor-Moderate	Moderate	Moderate >850
Lime	--	--	--	--	--	--	Minor	Minor
Portlandite	--	--	--	--	--	--	Minor	Minor
Siderite	Minor	Minor	Minor	Minor	Trace	--	--	--
Muscovite	Trace	Trace	Trace	Trace	Trace	Trace	--	--
Analcite	Moderate	Moderate	Moderate	Moderate	Moderate	Moderate-Minor	Minor-Trace	Trace
Melilite	--	--	--	--	--	Minor	Minor	Moderate

*Major = >30%

Moderate = 10-30%

Minor = 3-10%

Trace = <3%

In a review article by Smith (8), it was noted that the presence of certain mineral compounds could be used as a guide for determining the temperature to which shale had been heated. For example, a shift in the d-spacing of analcite indicated that shale had been heated past 325°C. If calcite remains but dolomite is not present then the shale has been heated to 800°C. If calcite is absent then heating to 900°C has occurred. If X-ray analysis indicates the presence of diopside then the shale has been heated to 1100°C. The presence of calcite at 850°C and its disappearance at 950°C, as found in this study, is consistent with the guide suggested by Smith. However, he indicated that diopside first appeared if the shale had been heated above 1100°C. Although diopside is not shown in Table 2, the X-ray analysis indicated the presence of diopside at a retorting temperature of 950°C. It should be stressed that this could be the result of working with a nonhomogeneous material or possibly uneven heating inside the retort.

A BET surface area analysis was performed on the retorted shale samples and the results are given in Table 3. The maximum surface area was found to be $8.8 \times 10^3 \text{ m}^2/\text{kg}$ with the maximum occurring at a retorting temperature near 750°C. The decrease in surface area above 750°C, although not expected, can be attributed to sintering of the mineral structure. Tisot (3) measured the surface areas of two grades of raw shale. He found that both $11.9 \times 10^{-5} \text{ m}^3/\text{kg}$ (28.6 gal/ton) and $31.3 \times 10^{-5} \text{ m}^3/\text{kg}$ (75.0 gal/ton) shales had surface areas of about $4.0 \times 10^3 \text{ m}^2/\text{kg}$. In addition, Compton and Rowan (11) found the internal surface area for raw Anvil Points shale to be $1.5 \times 10^3 \text{ m}^2/\text{kg}$. In view of the larger surface areas found in this study and the changes in mineral structure as found in the diffraction studies, it is reasonable to assume that the larger area is due to the removal of organics from the matrix and to mineral reactions that occur at various retorting temperatures. On the

basis of the limited results presented herein, the increase in surface area with retorting temperature indicates that the retorting zones could possibly be used as disposal sites for either retort water or stack gases.

Breakthrough Curves and Isotherms:

Prior to initiating the isotherm studies, a comparison was made of the adsorption capacities of the various spent shale samples as a function of the shale retorting temperature. The capacity determination was carried out at 7°C using a sample gas containing 10,000 ppm hydrogen sulfide in dry nitrogen. The results given in Figure 1 show that the hydrogen sulfide uptake is a function of retorting temperature and the maximum uptake was found for shale that had been retorted at approximately 750°C. On the basis of the data presented in Tables 1 and 2, it is not clear why the maximum adsorption capacity should occur at this temperature. However, comparison of this result with Table 3 shows that the uptake of hydrogen sulfide on the shale is directly related to the available surface area as should be expected.

On the basis of the preliminary study, shale that had been retorted at 750°C was selected for the remainder of the adsorption studies. Experimental breakthrough curves were obtained at 10, 25, and 60°C for concentrations of 1000, 2000, 3000, 5000, 7000, and 10,000 ppm hydrogen sulfide in dry nitrogen gas. This was done in a packed bed of spent shale about 0.15 m long with the particle sizes ranging from 16 to 35 U. S. mesh and using a gas flow rate set at 4.02×10^{-3} (m³/h). Typical experimental breakthrough curves are shown in Figure 2. Replicate runs were made because of the nonhomogeneous nature of the spent shale and the average of those runs were used to plot the curves.

FIGURE 1. Adsorption of H_2S on Spent Shale at 7°C for Shale Retorted at Temperatures Ranging from 350 to 950°C.

FIGURE 2. Comparison of Experimental Breakthrough Curves for Concentrations of 1000, 2000, 3000, 5000, 7000, 10,000 ppm H_2 in Nitrogen at 25°C.

TABLE 3

BET Surface Area of $13.5 \times 10^{-5} \text{ m}^3/\text{kg}$ Oil Shale
Retorted for Two Hours

<u>Temperature, °C</u>	<u>BET Surface Area, m²/kg</u>
350	0.4×10^3
450	1.5×10^3
550	4.3×10^3
650	6.4×10^3
750	8.8×10^3
950	6.9×10^3

For each run the area under the breakthrough curve was determined and the concentration of adsorbate gas on the spent shale was calculated. The equilibrium isotherm data are shown in Table 4. These data were correlated with three models: Langmuir (12), Freundlich, and the Polanyi potential relationship (13,14). The Langmuir equation is represented as

$$q^* = \frac{Q_0 C^*}{1 + Q_1 C^*} \quad (1)$$

where Q_0 is the first Langmuir constant with units $\text{cm}^3 \text{ gas}/\text{cm}^3 \text{ solid}$ and Q_1 is the second Langmuir constant with the units used in this study of cm^3/g . The gas concentration, C^* , has units g/cm^3 and the equilibrium adsorbate concentration, q^* , has units g/cm^3 . The equilibrium data presented in Table 4 were correlated with the Langmuir equation which is given below for each temperature studied.

$$q^* = \frac{2.245 \times 10^3 C^*}{1 + 5.669 \times 10^5 C^*} \text{ for } 10^\circ\text{C} \quad (2)$$

$$q^* = \frac{2.761 \times 10^3 C^*}{1 + 8.556 \times 10^5 C^*} \text{ for } 25^\circ\text{C} \quad (3)$$

$$q^* = \frac{3.238 \times 10^3 C^*}{1 + 1.195 \times 10^6 C^*} \text{ for } 60^\circ\text{C} \quad (4)$$

The Langmuir equations are compared to the experimental data in Figure 3.

TABLE 4

Equilibrium Adsorption Data for Hydrogen Sulfide on Spent Shale**

Temperature	10°C		25°C		60°C	
ppm H ₂ S in nitrogen	C*	q*	C*	q*	C*	q*
	g. H ₂ S(10 ⁻⁵)	g. H ₂ S(10 ⁻²)	g. H ₂ S(10 ⁻⁵)	g. H ₂ S(10 ⁻²)	g. H ₂ S(10 ⁻⁵)	g. H ₂ S(10 ⁻²)
	cm ³ gas	cm ³ solid	cm ³ gas	cm ³ solid	cm ³ gas	cm ³ solid
1,000	0.142	0.188	0.143	0.188	0.145	0.181
2,000	0.284	0.210	0.286	0.200	0.289	0.187
3,000	0.426	0.264	0.429	0.241	0.434	0.222
5,000	0.711	0.324	0.715	0.274	0.723	0.236
7,000	0.995	0.357	1.001	0.294	1.013	0.245
10,000	1.422	0.396	1.429	0.345	1.447	0.299

** Data were taken at a gas pressure of 620 mm. Hg.

FIGURE 3. Equilibrium Isotherms for Adsorption of H₂S on Spent Shale at 10°C, 25°C, and 60°C Fit to the Langmuir Equation.

The equilibrium data were also correlated with the Freundlich isotherm equation

$$q^* = m(C^*)^{1/n} \quad (5)$$

where m and n are constants. The Freundlich equations are given below.

$$q^* = 19.2 \times 10^{-2} C^{*.347} \quad \text{for } 10^\circ\text{C} \quad (6)$$

$$q^* = 6.58 \times 10^{-2} C^{*.268} \quad \text{for } 25^\circ\text{C} \quad (7)$$

$$q^* = 2.85 \times 10^{-2} C^{*.209} \quad \text{for } 60^\circ\text{C} \quad (8)$$

A comparison of the experimental data with the Freundlich equation is presented in Figure 4. As shown in the figure, the Freundlich model provides a slightly better correlation of the experimental data than does the Langmuir model.

The Polanyi potential theory has been used to characterize multilayer adsorption. This model assumes that the adsorbent exerts a strong attractive force upon the gas in its vicinity and this attraction gives rise to adsorption. The attraction forces reaching out from the surface are such that the adsorbed layers that form on the surface are under compression. It is further assumed that the gas obeys the same equation of state in the adsorbed phase as it does in the gas phase and that one characteristic curve can be drawn to represent the uptake on the surface of the adsorbent at any temperature. For an equilibrium pressure P , the adsorption potential at the surface is given by

$$-\Delta G = RT \ln \frac{P_0}{P} \quad (9)$$

where P_0 is the saturation pressure of the adsorbate at the system temperature. The characteristic curve is shown in Figure 5. It is apparent that, for each gas, the data at all temperatures lie close to a single characteristic curve as required by the Polanyi theory. The consistency of the experimental data is demonstrated by this result.

FIGURE 4. Equilibrium Isotherms for Adsorption of H₂S on Spent Shale at 10°C, 25°C, and 60°C Fit to the Freundlich Equation.

FIGURE 5. Characteristic Curve for the Adsorption of H_2S on Spent Shale.

Heat of Adsorption:

The isosteric heat of adsorption at constant loading is represented by the equation

$$\Delta H_s = -R \left[\frac{\partial(\ln P)}{\partial(1/T)} \right]_{q^*} \quad (10)$$

Heats of adsorption were determined graphically from plots of $\log P$ vs. $1/T$ and were found to be of the same order of magnitude as the heat of condensation. The calculated values shown in Table 5 suggest that the hydrogen sulfide is held on the surface of the shale primarily by physical forces. Desorption curves obtained for each run by passing pure nitrogen through the packed bed at the adsorption temperature showed that less than 50 percent of the hydrogen sulfide was recovered during the same time period as adsorption. However, upon increasing the desorption temperature to about 40°C above the adsorbing temperature, more than 90 percent of the hydrogen sulfide could be removed from the shale.

TABLE 5

Heats of Adsorption at Different Loadings	
$\text{g. H}_2\text{S}$ $\text{cm}^3 \text{ solid}$	ΔH_s Kcal g mole
2.3×10^{-3}	1.39
2.5×10^{-3}	2.31
2.6×10^{-3}	3.50

The studies by Compton and Rowan (11) show that hydrogen sulfide and oxygen react at temperatures well below the hydrogen sulfide air ignition temperature when oil shale is present. The reaction products are solid sulfur-containing compounds, including elemental sulfur, and sulfur dioxide gas. Temperature and oxygen concentration strongly effect the steady state

product distribution. This effect may be due to the stoichiometry of the two competing reactions.

One-third of the oxygen is required when forming elemental sulfur, and it may be a favored product when O_2 is scarce. The results of studies on effects of temperature, carrier gas, shale sources or conditions, and hydrogen sulfide and O_2 concentration show that reaction rate is dependent on temperature for a constant amount of hydrogen sulfide reacted.

However, in the present study oxygen was not added to the spent shale and the only oxygen present was in the form of compounds. Because the heats of adsorption were relatively low, it may be assumed that the hydrogen sulfide was held on the surface by a combination of Van der Waals' forces and chemisorption.

CONCLUSIONS

Although the experimental adsorption data could be fit accurately with the Langmuir equations, a better fit was obtained with the Freundlich equation. The experimental data for all isotherms were reduced to a Polanyi type potential plot and were found to obey this type relationship relatively well. The fact that the data could be reduced to a single curve demonstrates the consistency of the data for all temperatures.

The desorption curves, which were obtained for each of the runs, showed that more than 90 percent of the hydrogen sulfide could be recovered. At the temperatures used in this work hydrogen sulfide is held on the surface primarily by Van der Waals' forces.

Since spent shale has been shown to adsorb hydrogen sulfide, the use of spent shale beds as a means of disposing of undesirable retort gases appears feasible. The extent to which hydrogen sulfide will ultimately be adsorbed depends on several factors including: the presence of other gases, the retorting atmosphere and the size of the shale in the retort. Thus, a prediction as to the effectiveness of the retort zone as a disposal site would be premature. Further adsorption studies of the retort product gases should be carried out using spent shale produced in a combustion retort.

NOMENCLATURE

C = gas phase concentration of hydrogen sulfide, (g/cm^3)

C_0 = inlet gas concentration of hydrogen sulfide, (g/cm^3)

C^* = equilibrium gas phase concentration of hydrogen sulfide, (g/cm^3)

ΔG = adsorption potential, $(\text{cal}/\text{g mole})$

ΔH_s = the isosteric heat of adsorption $(\text{Kcal}/\text{g mole})$

m = constant dependent on T in Freundlich equation

n = constant dependent on T in Freundlich equation

q^* = equilibrium concentration of adsorbed hydrogen sulfide, (g/cm^3)

Q_0 = first Langmuir constant $(\text{cm}^3 \text{ gas}/\text{cm}^3 \text{ solid})$

Q_1 = second Langmuir constant (cm^3/g)

P = pressure (mm Hg)

P_0 = the saturation pressure of pure adsorbate or vapor pressure (mm Hg)

R = gas constant

T = temperature

LITERATURE CITED

1. Stanfield, K. E., Frost, I. C., McAuley, W. S., and Smith, H. N. "Properties of Colorado Oil Shale," U. S. Bur. Mines Rept. Invest., 4825 (1951).
2. Carpenter, H. C., Tihen, S. S., Sohns, H. W., "Retorting Ungraded Oil Shale as Related to In Situ Processing," Preprints Petroleum Division, Am. Chem. Soc., 13, No. 2, F50 (1968).
3. Tisot, P. R., "Properties of Green River Oil Shale Determined From Nitrogen Adsorption and Desorption Isotherms," J. Chem. Eng. Data, 7, 405 (1962).
4. Tisot, P. R., "Alterations in Structure and Physical Properties of Green River Oil Shale by Thermal Treatment," J. Chem. Eng. Data, 12, 405 (1967).
5. Tisot, P. R., Sohns, H. W., "Structural Response of Rich Green River Oil Shales to Heat and Stress and its Relationship to Induced Permeability," J. Chem. Eng. Data, 15, 425 (1970).
6. Matzick, A., Dannenberg, R. O., "Bureau of Mines-Gas Combustion Retort for Oil Shale," U. S. Bur. Mines Rept. Invest. 5545, 1960.
7. Ward, J. C., "Water Pollution Potential of Spent Oil Shale Residues From Above Ground Retorting," Colorado State University, 1972.
8. Smith, J. W., "Thermal Analysis," 3, Proc. Third ICTA DAVOS, 605, 1971.
9. Campbell, J. H., "The Kinetics of Decomposition of Colorado Oil Shale: II Carbonate Minerals," UCRL-52089, Part 2, March 13, 1978.
10. Jukkola, E. E., Denilauler, A. J., Jensen, H. B., Barnett, W. I., Murphy, W.I.R., "Thermal Decomposition Rates of Carbonates in Oil Shale," Ind. Eng. Chem., 45, 2711 (1953).
11. Compton, L. E., Rowan, W. E., "Hydrogen Sulfide Removal From Retort Offgases Using Oil Shale," The Second Pacific Chemical Engineering Congress Proceedings, AIChE, 422, August 1977.
12. Langmuir, I., "The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum," J. Amer. Chem. Soc., 40, 1368 (1918).
13. Polanyi, M., Verh. Dtsch. Phys. Ges., 16, 1012 (1914).
14. Polanyi, M., Verh. Dtsch. Phys. Ges., 18, 55 (1916).

PART II

TASK 3

HOT GAS STRIPPING OF RETORT WATER

SUMMARY

The hot gas stripping of ammonia and carbon dioxide from retort water was studied in this section. These studies were carried out on a model retort water containing ammonium carbonates and on an in situ retort water, Omega-9, over a temperature range of 160-200°F. Mass transfer coefficients were calculated for both waters and the height of the transfer units were calculated. In addition, the pH of the Omega-9 retort water was modified to determine how the stripping rate was affected.

INTRODUCTION

The large quantity of water produced by in situ oil shale retorting processes poses a potential pollution problem of significant magnitude. Waters collected from experiments conducted in the Laramie NTU type simulated in situ retorts have been examined (1) and have been shown to contain large concentrations of organic and inorganic species that could pollute the environment if not removed prior to disposal of the water. A study by Cook (2) of water produced from the Tosco II process revealed the presence of a variety of organic materials that could also harm the environment. Further, Hubbard (3) studied the process water produced by the Bureau of Mines gas combustion retort operated at Rifle, Colorado, and the water produced from the in situ retorting process near Rock Springs, Wyoming. He found that the waste water produced by both processes contained essentially the same components although in different quantities. Hubbard suggested two slightly different schemes to treat the waste water. One was to first contact the water with lime followed by: activated carbon, a cation exchange resin, and finally an ion exchange resin. In his second scheme he suggested that the waste should first be contacted with activated carbon and then with lime and the ion exchange resins. He concluded that it may be possible to recover ammonia and ammonia salts in addition to purifying the water.

A number of other investigators have also studied various retort waters and have found essentially all the species identified in the work of Jackson et al. (1). Using the assumption of Harak, Long, and Carpenter (4), that one barrel of water is produced with each barrel of oil, a 50,000 barrel per day in situ process would produce 2352 acre feet of water annually. Consequently, the study of methods to treat retort water is very important to the development of a viable shale oil industry.

The most prevalent species found in the retort water are the ammonium ions and the carbonates. Because they are present in large quantities, 13,000 ppm ammonia and 45,000 ppm carbonates, they must be dealt with prior to the treatment of retort water by either adsorptive or ion exchange techniques. A search of the literature (5-19) revealed that the petroleum industry routinely uses hot gases, particularly steam and flue gases, to strip sour water containing H_2S and NH_3 . Because of the success of the petroleum industry in removing H_2S and NH_3 , the removal of ammonium ions and carbonates from retort water by hot gas stripping was studied.

EXPERIMENTAL

The equipment used in carrying out the experimental study consisted of a stripping column equipped with fluid handling devices, heat transfer equipment, and temperature and pressure monitoring sensors; a schematic of the apparatus is shown in Figure 1. The liquid feed was introduced into the column with a variable speed diaphragm type metering pump and the flow rate was measured with a rotameter. Prior to entering the column, the feed water flows through a three zone electrical resistance furnace where it was heated to the desired temperature.

The gas system was set up for two types of gases; one was steam supplied by a miniature steam generator, the second was a bottled gas, such as compressed nitrogen or air. The gas flowed through an electrical resistance furnace where heat was transferred into a twenty foot long section of tightly coiled stainless steel tubing. From the furnace, the stripping gas passed through a rotameter and was injected into the bottom of the column where it flowed upward, countercurrent to the downward flowing liquid feed. The gas

exited from the top of the tower and passes through a small water cooled heat exchanger, then through two water traps and finally was vented to the atmosphere. The stripped water flowed from the bottom of the column, through another small heat exchanger and was collected for subsequent analysis.

Temperature measurements were made by inline thermocouple connections at all inlet and outlet ports on the column as well as on the heat exchangers. Control of the inlet temperatures of the gas and liquid streams was made by two separate temperature controllers. The temperatures were read to ± 2 degrees Fahrenheit from a digital readout device connected in parallel to a millivolt recorder. The absolute pressure was monitored with a pressure transducer connected to a digital millivolt output device.

The column itself was constructed of heavy wall, two inch NPS glass pipe made up in six sections of varying lengths for a total length of nine and one half feet; the sections were flanged together using a teflon type gasket material. The packing height could be varied by using one of four different liquid injection ports along the column. The gas entered the bottom of the column just above the point at which the liquid exited. The gas passed upward through the irrigated packing and was removed from the top of the column. Connections from the 1/4 inch stainless steel tubing and the 3/8 inch glass column ports were made by a combination of flexible stainless steel hose and a special teflon reducing union. In order to obtain representative data, the column diameter was approximately eight times greater than the packing size. Consequently, the two inch column used in this study was packed with 1/4 inch Intalox saddles. To decrease water entrainment, four inches of Pyrex glass wool was packed into the top of the column. Because of the ineffectiveness of dry packing in distributing the liquid feed across the column, a flow distributor was installed in all liquid inlets.

FIGURE 1

Water flow rates were varied from 432 to 1296 lb/hr-ft² and the gas rates were varied from 155 to 676 lb/hr-ft². The gas to liquid ratios varied from 18 to 155. The column was maintained at a constant temperature for each run; the stripping temperature was set at either 160, 180, or 200°F. The packed height available for stripping could be set at: 7.21, 4.42, 2.92, or 0.62 feet by changing the position of the water feed. Flooding characteristics of the two inch column were such that the approach to flooding varied from 30 to 60 percent.

Two types of water were studied in this work: a simulated retort water containing only ammonium bicarbonate and Omega-9 retort water. The concentrations for NH₃ and HCO₃ in the simulated retort water varied from 11,000 to 13,000 ppm for NH₃ and from 15,000 to 21,000 ppm for HCO₃. Its pH of 7.8-8.0 was the natural value of the solution. The effects of several key variables on the desorption rates of ammonia and carbon dioxide from the simulated retort water and Omega-9 were measured using the bench scale stripper column. These were: the effects of liquid and gas flow rates, the temperature of the stripping gas and retort water, and packing height. The effects of pH, lime addition, and comparisons between actual and simulated retort water were investigated.

RESULTS

The experimental results are organized and classified according to the column inlet process conditions. The initial concentrations for the model compound system of total ammonia and carbon dioxide were essentially constant with average values of 11,000-13,000 ppm by weight NH₃ and 15,000-21,000 ppm by weight total CO₂ respectively. The initial quantity of carbon dioxide

varied somewhat due to loss of CO_2 from the open storage container. However, frequent samples were taken so that the column inlet concentration were always known. The composition of the untreated Omega-9 retort water feed remained essentially constant at 4200 ppm HN_3 and 7500 ppm CO_2 .

The column was operated isothermally at one of three temperatures: 160° , 180° , or 200°F . The inlet liquid flow rate was varied between 0.5 and 3.5 gallons per hour, corresponding to 200 to 1500 lb/hr-ft^2 of column cross section, with most of the column runs being made at 1.0, 2.0, and 3.0 gallons per hour or 432, 864, and 1296 lb/hr-ft^2 respectively at each of the three temperatures. Runs were also made at various inlet gas rates with the liquid flow rate and inlet temperatures fixed. Further treatment of the feed solution by changing the initial pH over a range of pH 3-11 and by the addition of lime were additional parameters evaluated in the experimental program.

Model Retort Water:

The experimental results are organized according to temperature and liquid flow rate beginning with the lowest temperature. Concentrations of the two major species were plotted in semilog fashion as functions of column height, with the slopes of these curves giving the stripping rates. These figures were arranged in order of increasing liquid rates and increasing temperatures. The experimental data points were fitted with a least squares fit to give the effluent concentrations with respect to height. The temperature, gas and liquid flow rates, and deviation between the experimental data and curve fits are given in Table 1.

Table 1

Deviations of Individual Curve Fits from Average

Fit as a Function of Gas

Rate

Temp °F	RUN	L lb/hr	G ft ²	NH ₃ PPM	CO ₂ PPM	%DEV NH ₃	%DEV CO ₂
160	9	432	153	9,630	13,810	-0.9	1.4
160	4	432	177	8,845	14,800	-0.0	8.7
160	11	432	427	10,815	12,140	11.3	-10.9
160	3	432	455	8,570	13,710	-1.5	0.7
160	8	864	312	10,790	15,270	-0.5	4.5
160	2	864	315	10,885	13,945	0.5	-4.5
160	5	1296	328	11,825	15,145	0	0
180	15	432	322	7,835	9,405	6.5	-6.3
180	16	432	421	7,600	10,690	3.3	6.4
180	17	432	577	6,640	10,035	-9.8	0.0
180	29	864	324	6,825	9,360	-9.5	-3.0
180	35	864	338	7,844	9,225	4.1	-4.4
180	27	864	585	7,945	10,355	5.4	7.4
180	32	1296	316	8,695	12,590	-2.6	1.2
180	33	1296	623	9,150	12,280	2.6	-1.2
200	28	432	404	2,520	3,655	-3.8	0.5
200	20	432	484	2,720	3,620	3.8	-0.5
200	30	864	356	2,905	3,910	-5.8	-7.3
200	24	864	644	3,270	4,525	5.8	7.3
200	31	1296	352	5,405	7,995	-2.4	2.2
200	25	1296	621	5,665	7,655	2.4	-2.2
				NH ₃	CO ₂		
Maximum deviation				11.3	8.7		
Minimum deviation				-9.8	-10.9		
Average positive deviation				4.6	4.0		
Average negative deviation				-4.6	-4.5		

The figures showing the experimental data are arranged in order of increasing liquid flow rates, with the concentrations profiles shown as a function of the inlet gas rate to the column. Figures 2 and 3 give the effluent concentrations of CO_2 and NH_3 at the lowest inlet liquid rate studied, 432 lb/hr-ft^2 , and various gas rates ranging from 153 to 445 lb/hr-ft^2 respectively. The computer summaries of the raw data may be found in Appendix C showing concentration and flow rate profiles as a function of height. Figures 4 and 5 are at the same temperature as the previous two figures but with an inlet liquid rate of 864 lb/hr-ft^2 and a gas rate of approximately 315 lb/hr-ft^2 . Figures 6 and 7 show the concentration profiles at a liquid rate of $1,296 \text{ lb/hr-ft}^2$ and a gas rate of 328 lb/hr-ft^2 . The effects of the liquid flow rate on the rate of stripping are shown in Figures 8 and 9 for CO_2 and NH_3 respectively. The individual curves shown in these two figures are least squares curve fits of runs made at varying gas rates and at a constant liquid rate. The two illustrations are composites of Figures 2 through 7. Note that as the liquid rate decreased from 1296 to 432 lb/hr-ft^2 a steady decrease in the effluent concentration resulted at each column height. For the range of conditions studied at 160°F , the amount of ammonia removed at the tallest column height ranged from approximately 8 percent at the high liquid rate to an average of 47 percent removal for the low liquid rate of 432 lb/hr-ft^2 . The same trends were noted for the carbonate removals, where between 18.5 and 47 percent of the entering CO_2 was stripped out of solution.

The data presented in the previous figures can be used to determine the controlling resistance to mass transfer. If the data taken at various gas rates show a definite trend with the slopes decreasing as the gas rate increases, then the process has a gas film resistance. If, on the other hand,

the slopes decrease as the liquid rate increases, then the liquid phase resistance is predominate. At the conditions used in this study, a single solute system of CO_2 in water would be entirely liquid phase controlled due to the very steep slope of the equilibrium curve. At room temperature, the absorption of NH_3 into aqueous solution is considered to be primarily gas phase controlled; but, as the temperature is increased, the solubility of NH_3 decreases and the transfer process becomes increasingly dependent on the liquid phase resistance.

With the multisolute system considered here, the mass transfer process is coupled with reaction and the NH_3 and CO_2 transfer rates are functions primarily of the liquid phase resistances, temperature, and the reaction kinetics. The gas phase conditions should have at best only a minor effect on the transfer unit heights. This effect is illustrated in Figures 2 and 3 where the data for both CO_2 and NH_3 at various gas rates ranging from 155 to 455 lb/hr-ft² fall on single curves. Within the experimental accuracy of this data, no gas phase dependence is indicated.

The results of nine column runs made at 180°F are shown in Figures 10 through 17. At a liquid rate of 432 lb/hr-ft², 77 percent of the ammonia and 74 percent of the carbonates were desorbed. As shown in the above figures, the effluent concentrations are not a function of the gas flow rate. The effect of the liquid rate on the effluent concentrations is much more pronounced; at 180°F and 320 lb/hr-ft² gas rate, the CO_2 concentration increased by about 50 percent with a corresponding 100 percent in the liquid rate. As the liquid rate increases, the effect becomes smaller. For example at the same 180°F conditions as above, over a liquid flow rate range of 864-1296 lb/hr-ft² (50 percent increase), the effluent CO_2 concentration increases

by about 30 percent. Comparing the 160°F curves with those at 180°F shows that even at high liquid rates, the 20°F increase in the temperature permits much higher removals of both components.

Seven runs carried out at 200°F are shown in Figures 18-25. The lowest effluent ammonia concentration of 345 ppm, reflecting a 97 percent removal, was found at a 432 lb/hr-ft² inlet liquid rate and 155 SCF/gal gas/liquid ratio. The carbon dioxide concentration dropped from 17,150 ppm CO₂ to only 490 ppm or 97 percent CO₂ stripped from solution. Higher stripping rates were found in all of the 200°F runs for both species of interest. Figures 26-31 show the effects of temperature on the stripping rates as a function of liquid flow rate. By lowering the temperature from 200°F to 180°F or by about 10 percent, the effluent concentration at the 7.2 feet column height increases by a factor of 5.4 for CO₂ (770 to 4160 ppm) and by a factor of 6 for NH₃ (500 to 3000 ppm). The percentage increase in effluent concentration resulting from lowering the temperature from 180°F to 160°F is not as dramatic, although the magnitude of the increase is still approximately the same (3000 to 6650 ppm NH₃ and 4160 to 8300 ppm CO₂).

MODEL COMPOUND EFFLUENT CONCENTRATIONS

160°F AND 432 LB/HR-FT² LIQUID RATE

Figure 2

MODEL COMPOUND EFFLUENT CONCENTRATIONS

160°F AND 432 LB/HR-FT² LIQUID RATE

Figure 3

MODEL COMPOUND EFFLUENT CONCENTRATIONS

160°F AND 864 LB/HR-FT² LIQUID RATE

Figure 4

MODEL COMPOUND EFFLUENT CONCENTRATIONS

160°F AND 864 LB/HR-FT² LIQUID RATE

Figure 5

MODEL COMPOUND EFFLUENT CONCENTRATIONS

160°F AND 1296 LB/HR-FT² LIQUID RATE

Figure 6

MODEL COMPOUND EFFLUENT CONCENTRATIONS

160°F AND 1296 LB/HR-FT² LIQUID RATE

Figure 7

Figure 8

MODEL COMPOUND EFFLUENT CONCENTRATIONS

LIQUID RATE DEPENDENCE AT 160°F

Figure 9

MODEL COMPOUND EFFLUENT CONCENTRATIONS

183°F AND 432 LB/HR-FT² LIQUID RATE

Figure 10

MODEL COMPOUND EFFLUENT CONCENTRATIONS

180°F AND 432 LB/HR-FT² LIQUID RATE

Figure 11

Figure 12

Figure 13

MODEL COMPOUND EFFLUENT CONCENTRATIONS

180°F AND 1296 LB/HR-FT² LIQUID RATE

Figure 14

Figure15

Figure 16

MODEL COMPOUND EFFLUENT CONCENTRATIONS

LIQUID RATE DEPENDENCE AT 180°F

Figure 17.

MODEL COMPOUND EFFLUENT CONCENTRATIONS

200°F AND 432 LB/HR-FT² LIQUID RATE

Figure 18

MODEL COMPOUND EFFLUENT CONCENTRATIONS

200°F AND 432 LB/HR-FT² LIQUID RATE

Figure 19

Figure 20

MODEL COMPOUND EFFLUENT CONCENTRATIONS
200°F AND 864 LB/HR-FT² LIQUID RATE

Figure 21

MODEL COMPOUND EFFLUENT CONCENTRATIONS
200°F AND 1296 LB/HR-FT² LIQUID RATE

Figure 22

Figure 23

Figure 24

MODEL COMPOUND EFFLUENT CONCENTRATIONS

LIQUID RATE DEPENDENCE AT 200°F

Figure 25

MODEL COMPOUND EFFLUENT CONCENTRATIONS

TEMPERATURE DEPENDENCE AT 432 LB/HR-FT² LIQUID RATE

Figure 26

MODEL COMPOUND EFFLUENT CONCENTRATIONS

TEMPERATURE DEPENDENCE AT 432 LB/HR-FT² LIQUID RATE

Figure 27.

Figure 28

MODEL COMPOUND EFFLUENT CONCENTRATIONS

TEMPERATURE DEPENDENCE AT 864 LB/HR-FT² LIQUID RATE

Figure 29

MODEL COMPOUND EFFLUENT CONCENTRATIONS

TEMPERATURE DEPENDENCE AT 1296 LB/HR-FT² LIQUID RATE

Figure 30

MODEL COMPOUND EFFLUENT CONCENTRATIONS

TEMPERATURE DEPENDENCE AT 1296 LB/HR-FT² LIQUID RATE

Figure 31

Omega-9 Retort Water:

Experimental stripping rates of NH_3 and CO_2 from Omega-9 retort water were measured in the same manner as the model compound system. The concentration profiles for the two major species were obtained as functions of temperature, liquid and gas flow rates, and column height. In addition, the effects of changing the initial pH and lime addition were investigated. Perhaps the most striking difference between the observed concentrations for the simulated water and the retort water was the leveling out of the CO_2 values as the column height increased. This phenomenon was most pronounced under high stripping rate conditions, i.e., low liquid rates and high temperatures. The CO_2 concentration appears to level out at about 1600-1700 ppm even at the lowest liquid rate and the highest temperature of 200°F. Figures 32-39 illustrate these effects.

Comparison of the Omega-9 retort water curves with the data of the model compound system reveals that the quantity of CO_2 removed at 180°F is approximately equal over the 7 feet column height. At a liquid rate of 432 lb/hr-ft², about 5000 ppm CO_2 is removed from both waters, although the retort water initial concentration is half that of the model compound system. At liquid flow rates of 864 and 1296 lb/hr-ft², the comparison of the two types of water illustrates the same phenomenon, with lesser quantities of CO_2 removed in both cases as the liquid rate is increased. Note also that at the higher liquid rates, the Omega-9 water profile for CO_2 is linear on the semi-log plot as was the case for the simulated retort water. The linear nature of the semi-log plots can probably be observed as long as the effluent CO_2 concentration remains above 1700 ppm.

It is difficult to directly compare the curves for ammonia for the two waters although the trends for each appear to be the same. One important observation that can be made is that in a number of samples at the low liquid rate of 432 lb/hr-ft² and both 180 and 200°F, no detectable ammonia was found. These results are shown in Figures 37 and 39. This is an encouraging point because it demonstrates that there is no lower concentration limit for removal of ammonia in the Omega-9 water as was found for the CO₂ removal. It is not known if this trend for ammonia removal holds for other retort waters.

It is difficult to graphically compare the stripping rates because the initial retort water NH₃ composition was about 4200-4300 ppm or one-third that of the simulated retort water. The NH₃ stripping rates for the Omega-9 water appear to be greater than for the model system. But, since the internal liquid and gas compositions are not directly comparable, it would be more meaningful to delay comparison until the transfer unit heights are compared in the data analysis section.

OMEGA-9 RETORT WATER EFFLUENT CONCENTRATIONS
180°F AND 432 LB/HR-FT² LIQUID RATE

Figure 32

OMEGA-9 RETORT WATER EFFLUENT CONCENTRATIONS

180°F AND 364 LB/HR-FT² LIQUID RATE

Figure 33

OMEGA-9 RETORT WATER EFFLUENT CONCENTRATIONS
180°F AND 1296 LB/HR-FT² LIQUID RATE

Figure 34

OMEGA-9 RETORT WATER EFFLUENT CONCENTRATIONS
180°F AND 1296 LB/HR-FT² LIQUID RATE

Figure 35

OMEGA-9 RETORT WATER EFFLUENT CONCENTRATIONS

200°F AND 432 LB/HR-FT² LIQUID RATE

Figure 36

OMEGA-9 RETORT WATER EFFLUENT CONCENTRATIONS

200°F AND 432 LB/HR-FT² LIQUID RATE

Figure 37

OMEGA-9 RETORT WATER EFFLUENT CONCENTRATIONS

200°F AND 1296 LB/HR-FT² LIQUID RATE

Figure 38

OMEGA-9 RETORT WATER EFFLUENT CONCENTRATIONS

200°F AND 1296 LB/HR-FT² LIQUID RATE

Figure 39

Omega-9 Retort Water pH Adjustment and Lime Treatment:

To further investigate different processing conditions for ammonia and carbon dioxide removal, the effects of changing the initial pH of the Omega-9 water and of the addition of calcium hydroxide were observed at a fixed liquid rate and temperature. The experimental values found for these studies appear in Figures 40-44. The beginning graph of this series is a titration curve for determining the quantity of sulfuric acid or caustic soda required to obtain a given pH value. The titration curves dramatically illustrate the highly buffered nature of the retort water. A large quantity of acid or base is required to significantly alter the pH. Note that at a pH of 6, the acidity curve drops off sharply, indicating that CO_2 is being directly liberated from solution. This effect was noted when adding sulfuric acid to the water because the retort water foamed quite violently as the CO_2 desorbed from solution. No noticeable effect was found as the pH was raised above the initial value of pH 8.4.

Figures 41 and 42 give the effluent concentration of CO_2 and NH_3 respectively at various pH values. The curve for CO_2 at pH 3.3 was not shown because no CO_2 was detected in the initial solution and in the bottoms after acidification. At the two upper column heights (4.42 and 7.21 feet), approximately 100 ppm CO_2 was present in the effluent, indicating that some CO_2 had been absorbed from the hot air stripping gas. The pH of these two effluent samples were above 7; thus absorption was possible. In the feed solution and the first column height effluent, the pH was well below 6 so that CO_2 uptake in the liquid phase could not occur. The curve for an initial pH of 6 indicated most of the CO_2 was liberated in dropping from an untreated concentration of about 7500 ppm down to 750 ppm, a drop by a factor of 10.

TITRATION CURVES FOR OMEGA-9 RETORT WATER

Figure 40

pH ADJUSTED OMEGA-9 RETORT WATER EFFLUENT CONCENTRATIONS

200°F AND 1296 LB/HR-FT² LIQUID RATE

Figure 41

pH ADJUSTED OMEGA-9 RETORT WATER EFFLUENT CONCENTRATIONS
200°F AND 1296 LB/HR-FT² LIQUID RATE

Figure 42

LIME TREATED OMEGA-9 RETORT WATER EFFLUENT CONCENTRATIONS

200°F AND 1296 LB/HR-FT² LIQUID RATE

Figure 43

LIME TREATED OMEGA-9 RETORT WATER EFFLUENT CONCENTRATIONS
200°F AND 1296 LB/HR-FT² LIQUID RATE

Figure 44.

This curve also showed a leveling out at about 100 ppm signifying that a stripping gas containing almost no CO_2 would be required to completely desorb all of the CO_2 from solution. The corresponding curves for NH_3 illustrates the phenomena of no ammonia removal in the acidic range as expected. At lower pH values all the free ammonia is converted into NH_4^+ ions which must be reconverted to NH_3 before stripping can take place.

As the pH is increased above the original value of the water, the opposite effects should take place. The CO_2 is more difficult to remove and the NH_3 becomes easier. At values of 9.7 and 10.0, essentially no CO_2 was removed; but, the NH_3 desorption process took place at increasingly rapid rates. In fact at pH 10.0, only 13 ppm NH_3 were detected at the 7.21 feet column height compared with 145 ppm at corresponding conditions for the untreated Omega-9 water. Because of the dichotomy involved in either raising or lowering the pH from the initial value of about pH 8.4, it is difficult to ascertain which, if either, of these two methods should be undertaken without some idea of the economic factors involved in building a commercial tower. One advantage to lowering the pH, in addition to the increased stripping rates for CO_2 , is the fact that no foaming in the column was observed at either of the two acidic pH values studied.

Lime treatment of the Omega-9 water did not appear to have any significant effect on either the CO_2 or NH_3 species. Similar stripping rates for the lime treated water and the untreated water were noted. The addition of a 10 percent excess calcium hydroxide did not precipitate a noticeable quantity of calcium carbonate or affect the NH_3 stripping curves. The use of sulfuric acid and lime did lighten the chocolate brown color of the water and the sulfuric acid treatment precipitated a very small quantity of dark brown or black material of unknown composition.

DATA ANALYSIS

The use of the experimental data as presented in the previous section is limited to prediction of the effluent concentration profiles at similar conditions to those studied. Since the use of transfer unit heights or mass transfer coefficients is of much more utility in the design of commercial towers than concentration profiles, the calculation of overall liquid phase transfer unit heights, determined from the overall mass transfer coefficients, was made for each column run. These calculations were performed by the computer program given in Appendix C. Because the overall coefficients or transfer unit heights include both gas and liquid phase resistances simultaneously, it is difficult to correlate these overall values as functions of the column parameters. The liquid flow rate, in addition to the liquid transport coefficients such as viscosity and diffusivity, are all factors that must be included in any correlation attempt. If the overall transfer unit heights could be separated into their individual constituents, the individual transfer unit heights would depend only on their own phase property values rather than on both liquid and gas phase conditions simultaneously. The principal difficulty in obtaining the individual liquid or gas phase transfer units is that the interfacial concentrations must be obtained. Except in limiting cases, the conditions will not usually be known for the Omega-9 water.

Since the transfer unit heights calculated are not representative of those obtained for purely physical stripping of a single component from aqueous solution, it is difficult to separate the overall coefficients into their individual components. The effect of the kinetic processes occurring in the liquid phase is to decrease the quantity of free solute well below the total bulk solute concentrations.

A type of correlation method was needed to fit the experimental transfer unit heights that included both liquid and gas phase properties since individual heights could not be obtained. This correlation was made using the bulk concentration driving forces incorporated into the numerical value of the transfer height. The use of the bulk driving force ($X_B - X_B^*$) eliminates the need to calculate the free CO_2 in solution at process conditions, a calculation that would depend strongly on the quality of the water treated. The total bulk concentration may be measured directly by titration of a given water sample regardless of additional contaminants that could affect the free solute concentration. A further advantage to a transfer unit height utilizing the ($X_B - X_B^*$) driving force is that it may be used directly for design purposes. A simple correlation utilizing the liquid phase Reynold's Numbers and the liquid phase Schmidt Number is proposed to correlate the experimental data at each of the three temperatures for CO_2 . The form of the correlation is as follows:

$$H_{\text{TOL}} \approx H_{\text{TL}} = \alpha \left(\frac{L}{a_t \mu_L} \right)^\beta \left(\frac{\mu_L}{\rho D_L} \right)^{1/2} \quad (1)$$

where α and β are correlation parameters determined for each component at each of the three temperatures. Note that the quantity L in the Reynold's Number is the mass flow rate per unit empty cross sectional area of the column for the liquid phase. The viscosity, density, and diffusivity terms should be readily obvious. The " a_t " term in the liquid Reynold's Number is the total surface area per unit volume of packing. This quantity is available in the literature for the 1/4 inch Intalox saddles used in this study. The interfacial area for this size and type of packing does not appear in the open literature and so it could not be used in this correlation without an

extensive series of experimental measurements over the range of liquid and gas flow rates used in this study. The interfacial area is undoubtedly a more meaningful parameter; but, for a given packing this should not be of major significance.

The transfer unit height correlations for ammonia were the same as for CO_2 with an additional term added to account for the column height dependence exhibited by the ammonia system. The correlation, expressed by equation (2), is given by

$$H_{\text{TOL}} = \alpha \left(\frac{L}{a_t L} \right)^{\beta} \left(\frac{\mu_L}{\rho D_L} \right)^{1/2} \left(\frac{Z}{Z_R} \right)^{\delta} \quad (2)$$

This correlation also utilizes the total driving force $(X_A - X^*_B)$. The column height dependence cannot be explained by the mass transfer process alone since the equilibrium curve is linear as is the operating line in the dilute region. The two lines are sufficiently far apart that experimental error could not be the cause of a steady, definite decrease in the transfer unit height as the column height increases. This phenomenon can be explained in terms of a liquid phase reaction effect dependent on the contact time as represented by the column height. Examination of the fraction of free ammonia to the total concentration of NH_3 as a function of column height demonstrates that as the column height increases, the ratio or fraction increases. The effective driving force becomes larger and ammonia is more readily liberated from solution. It can be shown that the reason for the increased fraction of free ammonia at greater column heights is that as the solution becomes more dilute, the nature of the dissociation equilibria is such that the relative amount of free ammonia becomes greater.

The experimental values of the transfer unit heights are shown for three temperatures in Figures 45 and 46 for CO_2 and NH_3 respectively. Figure 46 contains the values for a column height of about 2.8 feet which most nearly stayed constant over the experimental program, during which the packing was changed several times. The average values of the experimental data at various gas rates and constant liquid rates were plotted to reduce crowding of the data points and to provide a clearer picture of the correlation. The values of the exponents were obtained from a nonlinear regression analysis computer program and are listed in Table 2. The magnitude of the Reynold's Number exponents are slightly higher than typical values for physical mass transfer obtained from the literature of about 0.5. The larger exponent is more indicative of transfer rates with chemical reaction, suggesting greater dependence on the liquid rate.

Transfer unit heights were also determined for the Omega-9 retort water as functions of the liquid and gas flow rates at two temperatures. The transfer heights obtained were of the same order of magnitude as those found for the model compound system, but the numerical value for the Omega-9 water was in general, higher for CO_2 and lower for NH_3 . This trend might be expected, particularly for the CO_2 data since the retort water contains a number of cations besides the ammonia ion. These other componenets such as calcium, magnesium, sodium, and potassium cannot be stripped from aqueous solution and serve to tie up the carbonate species and make it more difficult for CO_2 to be desorbed. On the other hand, the ammonia species are more easily decomposed without the complexing effects of the carbonate species and hence, more easily removed from solution.

Because ammonia is so soluble, even at the temperatures used in this study, the transfer rates for carbon dioxide are slower than for physical

desorption. The CO_2 cannot be removed from solution at a rate faster than the ammonia because only a small fraction of the total CO_2 in solution is in the molecular form. As the ammonia is converted to the free form and desorbs from solution, by stoichiometry 0.5-1.0 times that much CO_2 can be removed. The ammonia cannot be removed as quickly as for physical desorption alone since more than half of the total ammonia concentration is in an ionic form which must be converted to free NH_3 before stripping can take place. The reaction rates in solution are extremely rapid at these temperatures keeping the forms of the ionic species in a state of pseudo-equilibrium at all times. This is not to say that the liquid and gas phases are in equilibrium but that the ionic species are in chemical equilibria in solution. A more detailed discussion of the height of a transfer unit for Omega-9 retort water is presented in Appendix C.

Table 2
Correlation Coefficients for Liquid Film Transfer
Unit Heights

$$H_{TOL} = \alpha \left(\frac{L}{a_t \mu_L} \right)^\beta \left(\frac{\nu_L}{\rho_L D_L} \right)^{1/2} \left(\frac{Z}{Z_R} \right)^\delta$$

	<u>T, °F</u>	<u>α</u>	<u>β</u>	<u>δ</u>	<u>STD DEV, FT.</u>
CO ₂	160	0.775	0.961	0	2.44
	180	0.733	0.328	0	0.93
	200	0.192	0.735	0	0.48
NH ₃	160	0.395	1.830	-0.075	2.72
	180	0.457	0.582	-0.133	1.29
	200	0.145	0.755	-0.138	0.42

Note: Z_R or reference height was chosen as 10.0 feet. Transfer heights based on $(X_A - X_A^*)$ or $(X_B - X_B^*)$ driving forces.

MODEL COMPOUND SYSTEM

CO₂ TRANSFER UNIT HEIGHT CORRELATIONS

Figure 45

MODEL COMPOUND SYSTEM

 NH_3 TRANSFER UNIT HEIGHT CORRELATIONS

Figure 46

LITERATURE CITED

1. Jackson, L. P., Poulson, R. E., Spedding, T. J., Phillips, T. E., and Jensen, H. B., "Characteristics and Possible Roles of Various Waters Significant to In Situ Oil-Shale Processing," Proc. of Colo. Sch. of Mines Environmental Oil shale Symp. (Oct. 1975).
2. Cook, E. W., "Organic Acids in Process Water from Green River Oil Shale," Chem. and Ind., No. 1, 485 (1971).
3. Hubbard, A. B., "Method for Reclaiming Waste Water from Oil Shale Processing," ACS Div. of Fuel Chemistry, Preprint 16, No. 1, 21 (1971).
4. Harak, A. E., Long, Jr., A., Carpenter, H. C., "Preliminary Design and Operation of a 150-Ton Oil-Shale Retort," Colorado School of Mines Quart., 64, No. 4, 41 (1970).
5. Peoples, R. F., Krishman, P., and Simonsen, R. N., "Nonbiological Treatment of Refinery Wastewater," J. Water Pol. Fed., 44, 2120 (Nov. 1972).
6. Kostenbader, P. D., and Flecksteiner, J. W., "Biological Oxidation of Coke Plant Weak Liquor," J. Water Pol. Fed., 2, Part 1 (Feb. 1969).
7. Hart, J. S., "An Improving Wastewater Quality," Water and Sewage Works, 1W20 (Sept. - Oct. 1970).
8. Annessen, R. J., and Gould, G. D., "Sour Water Processing Turns Problem into Paydirt," Chemical Engineering, 67 (March 22, 1971).
9. Klett, R. J., "Treat Sour Water for Profit," Hydrocarbon Processing, 97 (Oct. 1972).
10. Finneran, J. A., and Whelchel, P. H., "Recovery and Reuse of Aqueous Effluent from a Modern Ammonia Plant," Proc. Ind. Process Design Workshop, 109, AIChE (San Francisco, CA., March 31 - Feb. 2, 1970).
11. Mavrovic, I., "Recovery of Nitrogen Compounds from Effluents in Urea and Ammonia Plants," Proceedings Workshop on Industrial Process Design for Pollution Control, Vol. 7, 1 (New Orleans, LA., Oct. 15 - 17, 1974).
12. Suhr, L. G., and Kepple, L., "AWT Plant gets Tough with Ammonia," Water and Wastes Eng., 26 (March 1975).
13. Resen, L., "Sour-Water Stripping Unit," The Oil and Gas J., 138 (March 12, 1956).
14. Elkin, H. F., and Henderson, G. R., "Waste Treatment at Sun Oil's Sarnia Refinery," Can J. Chem. Eng., 129 (Oct. 1957).
15. Hull, C. D., "How Conoco Treats Waste Water," Oil and Gas J., 73 (Dec. 8, 1958).

16. Ewing, R. C., "Shell Refinery uses Pollution-abatement Units," Oil and Gas J., 62 (March 8, 1971).
17. Brunet, M. J., and Parsons, R. H., "Mobile Solves Fouling Problems in Sour-Water Strippers," Oil and Gas J., 62 (Nov. 20, 1972).
18. Rodrigues, D. G., "Sour Water Strippers: Its Design and Application," AIChE Symp. Ser., 70, No. 136, 667 (1974).
19. Beychok, Mr. R., "The Design of Sour Water Strippers," Proc. of the 7th World Pet. Cong. 1967, 9, 313 (Pub. 1968).

PART III

TASK 4

ADSORPTION OF ALIPHATIC ACIDS FROM
AQUEOUS SOLUTIONS

SUMMARY

The radioisotope technique was applied to study the removal of aliphatic acid contaminants found in by-product waters of fossil fuel conversion processes at three difference temperatures. Five pure component systems (acetic acid, propionic acid, n-butyric acid, n-hexanoic acid, and n-heptanoic acid) were investigated at three different temperatures, 278, 298, and 313 K, by using activated carbon as the adsorbent. The results were modeled by a three parameter adsorption isotherm equation.

INTRODUCTION

In recent years, the adsorption of organic contaminants from aqueous solution was studied primarily by chromatographic techniques and the uptake was calculated from the invariant adsorption equation (3,8). Several different systems have been reported for different adsorbents at different temperatures (1,2,3,4,6,7,9,10,11,12,13). However, only a few systems have been studied over wide concentration ranges. Among those works mentioned above, Hansen, Fu, and Bartell (3), Hansen and Craig (2), Linner and Gortner (4), and Parkash (6) presented experimental data for the adsorption of aliphatic acids on various types of activated charcoal over moderate concentration ranges. This study presents the adsorption data of five carboxylic acids at three different temperatures obtained over a wide concentration range by using radioactive tracer techniques. Analytical sensitivity can be improved by the use of radioactive tracer techniques with an expected $10^3 - 10^6$ increase in sensitivity over conventional spectroscopic or chromatographic quantitation methods (5). The amount of uptake can be determined by counting the radioactivity of the solution after the equilibrium is reached. Neither the assumption of very dilute solution is using the invariant adsorption equation (7,14), nor the surface excess calculation (12) are needed when using this method. The data obtained is important for developing theoretical adsorption models applicable to wide concentration ranges.

EXPERIMENTAL

The major experimental apparatus used in this study was a Beckman Instrument Company liquid scintillation counter, model LS-9000. All of the organic acids were obtained from Pfaltz Bauer, Inc. The purities were 99+% as determined by a chromatographic analysis. Radioactive acetic acid, propionic acid, and n-butyric acid were obtained from the Radiochemical Center, Amersham, England, whereas n-hexanoic acid and n-heptanoic acid were obtained from ICN Pharmaceutical, Inc. The lignite-based activated carbon was obtained from Darco Company, Denver, Colorado. A 20 x 40 mesh material with a total surface area of 667 m²/g was used.

The activated charcoal was washed and heated at 428 K for nine hours prior to use. The concentrations of acetic, propionic and n-butyric acids varied from 1 ppm to 5000 ppm. The concentration of n-hexanoic acid varied from 100 ppm to 2500 ppm, and the concentration of n-heptanoic acid varied from 100 ppm to 2000 ppm.

The radioanalytical approach used in these adsorption experiments involved the addition of a small mass (less than 1 μ g) of high specific activity radioactive solute to each of the stock solutions of solute made up at varying concentrations. This imparted a uniform and high solute specific activity to each of the stock solutions with negligible change to the final solute concentration. This method provides an equally sensitive and accurate radioanalysis for determining solute concentrations at both high and low levels. The net result is that the overall statistical variance and accuracy of the results obtained are the same over the entire concentration range.

After preparing the radioactive solutions, samples of five milliliters were taken before and after equilibration with the activated carbon. To count the radioactivity, 1 ml (out of 5 ml) of each sample was mixed with 12 ml of

Dimilume-30, Packard Inst. Co. Ninety-five milliliters of each samples solution was shaken with 0.5 g of activated carbon in a shaker bath set at either 278, 298, or 313K, for 48 hours to reach equilibrium. Samples were placed in the liquid scintillation counter and dark adapted for at least 30 minutes prior to counting. Counting was performed in a wide open ^{14}C window and continued until a 2-sigma count rate error of .1% or less was achieved. Random coincidence monitoring was used to insure that the contribution of counting events not due to radioactivity disintegrations, e.g., chemiluminescence, was less than 0.2%. The counting efficiency was determined for each sample and was used to compute the absolute activity as disintegrations per minute (DPM). Efficiency corrections were made by instrumental measurement of the Compton edge inflection point (a Beckman modification of the external standardization method) and determination of the counting efficiency was made from a calibration curve previously obtained from a series of water quenched ^{14}C standards prepared in Dimilume. Final DPM values were corrected by subtraction of background count rate.

RESULTS AND DISCUSSION

The experimental adsorption data are presented in Tables 1 through 5. A direct comparison of this work was made with the study of Parkash (6) at 278 K. For an equilibrium concentration of 0.1M, the uptake of the various acids in this study is about 37 percent greater than the uptake found by Parkash for the same absorbent. The greater uptake found in this work can be attributed to the more extensive pretreatment of the carbon prior to beginning the study. An examination of the adsorption data shows that the adsorption of

lower aliphatic acids from aqueous solutions increases with increasing chain length. This result agrees with Traube's rule, i.e. the addition of CH_2 group to the aliphatic acid molecule reduces its solubility in water.

The experimental data were fitted with a three parameter empirical equation proposed by Radke and Prausnitz (7)

$$\frac{1}{q} = \frac{1}{aC_f} + \frac{1}{bC_f^\beta} \quad (1)$$

where q is the uptake of the solute by the solid, m mole/g, C_f is the final concentration of the solute in the solution, mole/l, and β is constrained to be less than one. The data were fitted to within 1% using the parameters given in Table 6. The broad range of the experimental data are shown in Figures 1, 2, and 3 with the curve fit given by equation (1).

In the dilute solution limit, equation (1) will give a straight line and the parameter "a" becomes the Henry's constant. As shown in Table 6, the parameter "a" decreases with increasing temperature and increases with increasing molecule size as expected.

Table 1. Adsorption Isotherm Data of Acetic Acid

278 K		298 K		313 K	
$q, \frac{\text{m.mole}}{\text{g}}$	$C_f, \frac{\text{mole}}{\text{l}}$	$q, \frac{\text{m.mole}}{\text{g}}$	$C_f, \frac{\text{mole}}{\text{l}}$	$q, \frac{\text{m.mole}}{\text{g}}$	$C_f, \frac{\text{mole}}{\text{l}}$
1.60	7.46×10^{-2}	1.23	7.69×10^{-2}	1.06	7.78×10^{-2}
1.14	3.61×10^{-2}	8.83×10^{-1}	3.70×10^{-2}	8.04×10^{-1}	3.74×10^{-2}
6.83×10^{-1}	1.33×10^{-2}	5.47×10^{-1}	1.41×10^{-2}	4.58×10^{-1}	1.43×10^{-2}
4.38×10^{-1}	5.98×10^{-3}	3.65×10^{-1}	6.52×10^{-3}	2.84×10^{-1}	6.84×10^{-3}
2.71×10^{-1}	2.74×10^{-3}	2.29×10^{-1}	2.96×10^{-3}	1.75×10^{-1}	3.25×10^{-3}
1.35×10^{-1}	9.56×10^{-4}	1.16×10^{-1}	1.06×10^{-3}	8.10×10^{-2}	1.24×10^{-3}
7.50×10^{-2}	4.40×10^{-4}	6.98×10^{-2}	5.04×10^{-4}	4.25×10^{-2}	5.10×10^{-4}
1.73×10^{-2}	7.58×10^{-5}	1.50×10^{-2}	7.77×10^{-5}	1.16×10^{-2}	1.06×10^{-4}
1.62×10^{-3}	6.01×10^{-6}	2.68×10^{-3}	9.00×10^{-6}	1.58×10^{-3}	8.34×10^{-6}

Table 2. Adsorption Isotherm Data of Propionic Acid

278 K		298 K		313 K	
$q, \frac{\text{m.mole}}{\text{g}}$	$C_f, \frac{\text{mole}}{\text{l}}$	$q, \frac{\text{m.mole}}{\text{g}}$	$C_f, \frac{\text{mole}}{\text{l}}$	$q, \frac{\text{m.mole}}{\text{g}}$	$C_f, \frac{\text{mole}}{\text{l}}$
1.88	5.77×10^{-2}	1.30	2.71×10^{-2}	1.60	5.63×10^{-2}
1.55	2.71×10^{-2}	8.80×10^{-1}	8.79×10^{-3}	1.28	2.63×10^{-2}
1.00×10^{-1}	8.98×10^{-3}	5.72×10^{-1}	3.80×10^{-3}	8.03×10^{-1}	9.30×10^{-3}
6.40×10^{-1}	3.39×10^{-3}	3.55×10^{-1}	1.51×10^{-3}	4.95×10^{-1}	4.15×10^{-3}
3.94×10^{-1}	1.41×10^{-3}	1.70×10^{-2}	5.00×10^{-4}	3.10×10^{-1}	1.75×10^{-3}
1.80×10^{-1}	3.81×10^{-4}	8.95×10^{-2}	2.10×10^{-4}	1.56×10^{-1}	5.61×10^{-4}
9.46×10^{-2}	1.78×10^{-4}	2.02×10^{-2}	2.80×10^{-5}	8.50×10^{-2}	2.28×10^{-4}
2.07×10^{-2}	2.62×10^{-5}	---	---	2.00×10^{-2}	3.60×10^{-5}
2.57×10^{-3}	2.06×10^{-6}	---	---	2.40×10^{-3}	8.22×10^{-7}

Table 3. Adsorption Isotherm Data of Butyric Acid

278 K		298 K		313 K	
$q, \frac{\text{m.mole}}{\text{g}}$	$C_f, \frac{\text{mole}}{\text{l}}$	$q, \frac{\text{m.mole}}{\text{g}}$	$C_f, \frac{\text{mole}}{\text{l}}$	$q, \frac{\text{m.mole}}{\text{g}}$	$C_f, \frac{\text{mole}}{\text{l}}$
2.72	9.70×10^{-2}	2.43	1.00×10^{-1}	1.93	1.04×10^{-1}
2.05	4.66×10^{-2}	1.87	4.75×10^{-2}	1.65	4.80×10^{-2}
1.62	2.04×10^{-2}	1.42	2.12×10^{-2}	1.39	2.11×10^{-2}
1.11×10^{-1}	6.30×10^{-3}	9.24×10^{-1}	6.50×10^{-3}	8.45×10^{-1}	6.92×10^{-3}
7.04×10^{-1}	1.98×10^{-3}	6.57×10^{-1}	2.22×10^{-3}	5.96×10^{-1}	2.54×10^{-3}
4.30×10^{-1}	5.70×10^{-4}	4.08×10^{-1}	6.38×10^{-4}	3.77×10^{-1}	8.55×10^{-4}
1.95×10^{-1}	1.11×10^{-4}	1.98×10^{-1}	1.48×10^{-4}	1.84×10^{-1}	1.66×10^{-4}
1.03×10^{-1}	2.87×10^{-5}	1.00×10^{-1}	4.10×10^{-5}	9.72×10^{-2}	5.66×10^{-5}
---	---	3.11×10^{-2}	5.44×10^{-6}	2.09×10^{-2}	3.62×10^{-6}

Table 4. Adsorption Isotherm Data of Hexanoic Acid

278 K		298 K		313 K	
$q, \frac{\text{m.mole}}{\text{g}}$	$C_f, \frac{\text{mole}}{\text{l}}$	$q, \frac{\text{m.mole}}{\text{g}}$	$C_f, \frac{\text{mole}}{\text{l}}$	$q, \frac{\text{m.mole}}{\text{g}}$	$C_f, \frac{\text{mole}}{\text{l}}$
1.72	1.25×10^{-2}	1.66	1.28×10^{-2}	1.56	1.33×10^{-2}
1.30	2.32×10^{-3}	1.20	2.30×10^{-3}	1.08	2.90×10^{-3}
7.66×10^{-1}	2.80×10^{-4}	7.19×10^{-1}	3.72×10^{-4}	7.04×10^{-1}	6.05×10^{-4}
3.90×10^{-1}	3.87×10^{-5}	4.00×10^{-1}	6.45×10^{-5}	3.92×10^{-1}	8.87×10^{-5}
---	---	1.62×10^{-1}	7.16×10^{-6}	1.62×10^{-1}	1.02×10^{-5}

Table 5. Adsorption Isotherm Data of Heptanoic Acid

278 K		298 K		313 K	
$q, \frac{\text{m.mole}}{\text{g}}$	$C_f, \frac{\text{mole}}{\text{l}}$	$q, \frac{\text{m.mole}}{\text{g}}$	$C_f, \frac{\text{mole}}{\text{l}}$	$q, \frac{\text{m.mole}}{\text{g}}$	$C_f, \frac{\text{mole}}{\text{l}}$
1.76	6.13×10^{-3}	1.60	6.96×10^{-3}	1.47	7.10×10^{-3}
1.31	1.31×10^{-3}	1.19	1.73×10^{-3}	1.09	1.97×10^{-3}
6.97×10^{-1}	1.76×10^{-4}	6.90×10^{-1}	2.13×10^{-4}	6.30×10^{-1}	2.49×10^{-4}
4.10×10^{-1}	2.65×10^{-5}	3.60×10^{-1}	2.55×10^{-5}	3.40×10^{-1}	4.03×10^{-5}
---	---	---	---	1.41×10^{-1}	6.22×10^{-6}

Table 6. Parameters of Equation (1)

Aliphatic Acid	Temperature K	a	b	β
Acetic	278	0.2811	0.2743	0.4288
	298	0.2357	0.2181	0.4155
	313	0.1324	0.1706	0.4602
Propionic	278	0.8827	0.5202	0.3404
	298	0.8594	0.4024	0.3895
	313	0.7138	0.3377	0.4144
n-Butyric	278	9.0113	0.5620	0.3462
	298	6.7248	0.5010	0.3457
	313	3.0223	0.4921	0.3133
n-Hexanoic	278	72.0000	1.0265	0.2260
	298	52.4989	0.9349	0.2444
	313	43.4166	0.8185	0.2547
n-Heptanoic	278	111.3755	1.1626	0.2487
	298	70.0420	1.0411	0.2286
	313	46.7134	0.9278	0.2446

Figure 1. Adsorption Isotherms at 278 K

Figure 2. Adsorption Isotherms at 298 K

Figure 3. Adsorption Isotherms at 313 K

LITERATURE CITED

1. Fritz, W., Schluender, E. U., Chem, Eng, Sci., 29, 1279 (1974).
2. Hansen, R. S., Craig, R. P., J. Phys, Chem., 58, 211 (1954).
3. Hansen, R. S., Fu, Y., Bartell, F. E., J. Phys. Colloid. Chem., 53, 769 (1949).
4. Linner, E. R., Gortner, R. A., J. Phys. Chem., 39, 35 (1935).
5. Neame, K. D., Homewood, C. A., "Liquid Scintillation Counting," John Wiley & Sons, New York, N.Y. (1974).
6. Parkash, S., Carbon, 12, 37 (1974) Pergamon Press, England.
7. Radke, C. J., Prausnitz, J. M., Ind. Eng. Chem. Fundam., 11 (4), 445 (1972).
8. Radke, C. J., Prausnitz, J. M., AIChE J., 18, (4), 761 (1972).
9. Sircar, S. Myers, A. L., AIChE J., 17, 186 (1971).
10. Sircar, S., Myers, A. L., J. Phys. Chem., 74 (14), 2823 (1970).
11. Sircar, S., Myers, A. L., Molstad, M. C., Trans. Farad. Soc., 66 (9), 2354 (1970).
12. Sircar, S., Novosad, J., Myers, A. L., Ind. Eng. Chem. Fundam., 11 (2), 249 (1972).
13. Smith, H. A., Hurley, R. S., J. Phys. and Coll. Chem., 53, 1409 (1949).
14. Young, D. M., Crowell, A. D., "Physical Adsorption of Gases," p. 375, Butterworths, London (1952).

PART IV

TASK 5

MULTI-SOLUTE ADSORPTION OF ALIPHATIC ACIDS

SUMMARY

The radioisotope technique was used to study the competitive adsorption of organic acids from dilute aqueous solution onto activated carbon at 278 and 298 K. A competitive adsorption potential theory was developed in this study and used to predict bi-solute equilibrium data. The calculated values were compared with both experimental data and the values predicted by the ideal adsorbed solution theory. It was found in this study that the competitive adsorption potential theory gives slightly better results than those calculated by the ideal adsorbed solution theory.

INTRODUCTION

Due to the growing concern for potential carcinogenic, mutagenic and teratogenic compounds found in drinking water and the associated impact of developing alternate energy sources, the removal of biologically resistant organic contaminants from water has become more important in recent years. The organic contaminants found in by-product water of synthetic fuel processes are mainly aliphatic organic acids, and phenol and its derivatives.

The adsorption of organic acids from aqueous solution has been studied primarily by chromatographic or spectroscopic techniques over moderate and high concentration ranges. The adsorption data of aliphatic acids from dilute aqueous solution (less than 1% by weight) are not readily available in the literature.

This work presents the adsorption data of bi-acid solutions by using radioactive tracer techniques. A new competitive adsorption potential theory was developed to predict adsorption of completely miscible organic acids from dilute aqueous solutions onto activated carbon. In studying competitive adsorption of organic acids from dilute aqueous solutions, three acid mixtures: (a) acetic and propionic acid, (b) acetic and butanoic acid, and (c) propionic and butanoic acid were investigated. This was done at 278 and 298 K over three decades in concentrations. In all these studies, activated carbon was used as the adsorbent because of its high capacity for removing organic contaminants from aqueous solution.

LITERATURE REVIEW

Experimental Work:

Numerous pertinent studies of adsorption using carbon have been reported in the literature by different investigators. The monograph by Kipling (1965) provides an excellent review on the adsorption at the liquid-solid interface for research done prior to 1965. The adsorption of organic acids from aqueous solution has been carefully studied by Linner and Gortner (1), Hansen and co-workers (2 - 6), and Smith and Hurley (7).

Linner and Gortner studied the adsorption onto decolorizing carbon of thirty-one acids, differing in most cases in chemical configuration. The experiments were conducted at essentially room temperature which varied from 22°C to 30°C; the equilibrium concentrations were determined by titrimetric methods. Hansen and co-workers studied the homologous normal aliphatic acids from acetic acid to heptanoic acid at 25°C on three non-porous carbons: Spheron-6, Graphon, and Acheson Graphite (DAG-1). The results were analyzed interferometrically. Smith and Hurley studied the adsorption of acetic, capric, palmitic, and stearic acids onto six different carbon blacks at 25°C. Concentrations were determined volumetrically using methanolic sodium hydroxide and phenolphthalein as an indicator. All of their work, however, was devoted to single-solute systems only.

Since 1970, granular and powered activated carbons have been widely used to remove organic contaminants from water. Also, researchers have extended their experimental studies to multi-solute systems. Manes and co-workers (8, 9) studied the adsorption of acrylamide, benzamide, benzoic acid, coumarin, glucose, methionine, phthalide, p-nitrophenol, thiourea, urea and valine at 25°C and the final concentrations were determined by U.V. spectrophotometry. Parkash (10) studied the adsorption of homologous

aliphatic acids, from formic acid to n-caproic acid on four activated carbons at 25°C over a concentration range 0.02M to 0.20M. Radke and Prausnitz (11, 12) reported the adsorption data for dilute aqueous solutions containing acetone and propionitrile, and p-chlorophenol and p-cresol at 25°C using activated carbon as the adsorbent. In their work, the equilibrium concentrations were measured by a gas chromatograph with a flame ionization detector. The bi-solute mixture of p-nitrophenol and phenol was thoroughly studied by Fritz and Schluender (13) at 20°C who also determined the concentrations by U.V. spectrophotometry.

Previous Theoretical Models:

In addition to these new experimental data, four competitive adsorption models have been proposed by different investigators. All these models require only that the single-solute adsorption isotherm be known. In the waste water treatment problem, a competitive adsorption model based solely on single-solute isotherms is essential in determining the bed life of an adsorbent. Several models based on fundamental thermodynamic principles have been developed to predict the uptake of each solute from multi-solute mixtures. Butler and Ockrent (14) proposed a competitive Langmuir model that found limited success because of thermodynamic inconsistency as indicated by Jain and Snoeyink (15). Radke and Prausnitz (12) developed the thermodynamic formulation for adsorption of multi-solute mixtures from dilute aqueous solutions by direct extension of the method proposed by Myers and Prausnitz (16). A simplified model based on the same concepts and using the approach taken by Radke and Prausnitz has recently been proposed by Digiano, et al. (17). The method of Radke and Prausnitz is often referred to as the ideal adsorbed solution theory. The application of this model depends on the ease with which the spreading pressure can be evaluated. In order to overcome this

difficulty, Digiano et al. suggest that if the individual single-solute isotherms can be expressed in some simple form, then the ideal adsorbed solution theory can be extended easily to an n-component system without evaluating the spreading pressures.

The application of the above model is limited primarily to the dilute concentration range. To overcome this shortcoming, Minka and Myers (18) proposed a method to predict the surface excess over the entire composition range in terms of the system variables. These variables are: the energy of immersion of the adsorbent, the capacity of the adsorbent at saturation, and the activity coefficients in the bulk and adsorbed phases. Minka and Myers assumed that the total uptake of the solutes can be determined from the individual pore capacity for the liquid solutes. The pore capacity is given by the amount adsorbed from the vapor of the liquid solute at saturation. Unfortunately, most organic contaminants found in waste water have low vapor pressures which makes this determination difficult.

Using the Polanyi adsorption potential theory as a basis, Manes and co-workers extended gas phase adsorption theory to the liquid phase. The modified potential theory was used to predict the adsorption of organic liquids and solids from trace to saturated concentrations for partially miscible bi-solute and tri-solute aqueous mixtures. The major disadvantage of their method is that it cannot be applied to the case where the solutes are completely soluble in the solvent. When applying this method, an adjusted adsorbate volume factor must be used. Although Rosene and Manes gave some explanations about the physical meaning of the adjusted adsorbate volume factor, this factor appears to be little more than a correction factor so that the model will fit the experimental data. Also, the potential theory for partially miscible liquids is not thermodynamically rigorous.

where $\bar{V}_i$ and $\bar{V}_j$ are the partial molar volumes of solutes i and j respectively. In the above treatment, the adsorption of water is small and can be neglected because of its very low adsorption potential per unit volume on activated carbon as shown by Wohleber and Manes (21, 22). Thus Eq. 11 becomes

$$dn_j = -\frac{\bar{V}_i}{\bar{V}_j} dn_i \quad (12)$$

The adsorption of any solute occurs whenever the following criteria is satisfied

$$\epsilon_i > RT \ln \frac{x_{i\phi}}{x_{iB}} \quad (13)$$

The equality holds when equilibrium is reached. The driving force, on a per mole basis, for adsorption of single solute i is thus

$$-\Delta\bar{G}_i = \epsilon_i - RT \ln \frac{x_{i\phi}}{x_{iB}} \quad (14)$$

The condition $\Delta G < 0$ is the criterion for any solute to be adsorbed in a given element of adsorption space. In a bi-solute system, the displacement of the j^{th} solute by the i^{th} solute will occur in a given element of adsorption space when

$$d(\Delta G) = \Delta\bar{G}_i dn_i + \Delta\bar{G}_j dn_j < 0 \quad (15)$$

Substituting Eqs. 12 and 14 into Eq. 15 gives

$$\frac{1}{\bar{V}_i} \frac{d(\Delta G)}{dn_i} = -\frac{\epsilon_i}{\bar{V}_i} + \frac{RT}{\bar{V}_i} \ln \frac{x_{i\phi}}{x_{iB}} + \frac{\epsilon_j}{\bar{V}_j} - \frac{RT}{\bar{V}_j} \ln \frac{x_{j\phi}}{x_{jB}} \quad (16)$$

Since $x_{i\phi} + x_{j\phi} = 1.0$, Eq. 16 can be rearranged to give

$$\frac{\epsilon_i}{\bar{V}_i} - \frac{RT}{\bar{V}_i} \ln \frac{x_{i\phi}}{x_{iB}} < \frac{\epsilon_j}{\bar{V}_j} - \frac{RT}{\bar{V}_j} \ln \frac{x_{j\phi}}{x_{jB}} \quad (17)$$

where the equality holds when equilibrium is reached. Equation 17 can thus be solved to yield values for $x_{i\phi}$ and $x_{j\phi}$. The calculational procedure is similar to that for the prediction of competitive adsorption of partially miscible solutes as presented by Rosene and Manes. The complete procedure is illustrated as follows:

NEW COMPETITIVE ADSORPTION POTENTIAL THEORY

The purpose of the present work is to overcome these shortcomings mentioned above so that the adsorption potential theory can be applied to predict competitive adsorption from totally miscible liquid mixtures. Since the method of Rosene and Manes (19, 9) cannot be used to predict competitive adsorption data for completely soluble solutes in water, a new competitive adsorption potential theory has been developed. The main assumption is that the total adsorbed volume space can be determined from the more strongly adsorbed component as though it were adsorbed singly from aqueous solution. The individual adsorbed volume spaces can be determined from basic thermodynamics. However, the sum of the individual adsorbed volume spaces must be equal to the total adsorbed volume space. Then the uptake of each component can be obtained by dividing the individual adsorbed volume space by its corresponding molar volume.

If a mixture of solutes is in equilibrium with an adsorbent, the chemical potential of solute i in the adsorbed phase is equal to that in the bulk liquid phase. Thus

$$\mu_{i\phi} = \mu_{iB} \quad (1)$$

where the subscripts ϕ and B indicate the adsorbed phase and the bulk phase respectively. The chemical potentials for the two phases are

$$\mu_{i\phi} = \mu_{i\phi}^{\circ} + RT \ln a_{i\phi} \quad (2)$$

$$\mu_{iB} = \mu_{iB}^{\circ} + RT \ln a_{iB} \quad (3)$$

in which a_i is the activity of solute i .

Following the work of Hansen and Fackler (20), the adsorption potential of single solute i from aqueous solution is given by

$$\mu_{i\phi}^{\circ} - \mu_{iB}^{\circ} = -\epsilon_i \quad (4)$$

Thus the potential can be written as

$$\epsilon_1 = RT \ln \frac{a_1}{a_{1B}} \quad (5)$$

The standard state of the liquid phase is chosen to be the infinitely dilute solution at the mixture temperature. The activity is expressed as

$$a_{1B} = x_{1B} \gamma_{1B} \quad (6)$$

where x_{1B} and γ_{1B} are the mole fraction and activity coefficient of solute 1 in the bulk liquid phase respectively. In very dilute solutions, γ_{1B} can be assumed to equal to 1.0. Thus

$$a_{1B} = x_{1B} \quad (7)$$

Assuming that the adsorbed phase forms an ideal solution

$$f_{1\phi} = x_{1\phi} f_{1\phi}^0 \quad (8)$$

in which $f_{1\phi}^0$ is the fugacity of single solute 1 when it adsorbs singly from dilute solution at the temperature and total solute concentration as that of the mixture and $x_{1\phi}$ is the solvent free mole fraction of solute 1 in the adsorbed phase. A similar treatment, in which the adsorbed phase was treated as though it were solvent free, was also used by Radke and Prausnitz. The activity is thus given as

$$a_{1\phi} = \frac{f_{1\phi}}{f_{1\phi}^0} = x_{1\phi} \quad (9)$$

Using this approach, Eq. 5 becomes

$$\epsilon_1 = RT \ln \frac{x_{1\phi}}{x_{1B}} \quad (10)$$

Paralleling the treatment of Hansen and Fackler (20), Rosene and Manes let $\Delta\phi'$ be an infinitesimal volume increment enclosed between two equipotential surfaces ϕ and $\phi + \Delta\phi$. At equilibrium, for infinitesimal mass transfer between the liquid in $\Delta\phi'$ and the bulk solution, the change in $\Delta\phi'$ can be considered as invariant. Thus

$$d(\Delta\phi') = \bar{V}_1 dn_1 + \bar{V}_j dn_j = 0 \quad (11)$$

1. Plot the adsorbed volume V_{ads} versus $\epsilon/\bar{V}$ for each single solute from its corresponding adsorption isotherm (see curves i and j in Figure 1).

$V_{i ads}$ is defined as the product of the molar volume of solute i and the moles of solute i adsorbed. ϵ_i is equal to $RT \ln \frac{x_{i\phi}}{x_{iB}}$. The adsorption potential of the solute i in the solvent $x_{i\phi}$ is assumed to be equal to 1 because of the very low adsorption potential of water on activated carbon.

2. For a given set of (x_{iB}, x_{jB}) , try an assumed value of $x_{i\phi}$ and use this value to calculate $\frac{RT}{\bar{V}_i} \ln \frac{x_{i\phi}}{x_{iB}}$.

3. Shift curve i to the left by an amount equal to $\frac{RT}{\bar{V}_i} \ln \frac{x_{i\phi}}{x_{iB}}$ (see curve i' in Figure 1).

4. The adsorption of component j will occur whenever

$$\frac{RT}{\bar{V}_j} \ln \frac{x_{j\phi}}{x_{jB}} = \frac{\epsilon_j}{\bar{V}_j} - \frac{\epsilon_i}{\bar{V}_i} + \frac{RT}{\bar{V}_i} \ln \frac{x_{i\phi}}{x_{iB}} \quad (18)$$

The dashed line in Figure 1 shows the right hand side of Eq. 18.

5. Enter $\frac{RT}{\bar{V}_j} \ln \frac{x_{j\phi}}{x_{jB}}$ on the abscissa of Figure 1, point D, and find its corresponding ordinate C on the dashed line. This ordinate gives the volume of component j adsorbed. The volume of component i adsorbed is represented by the distance (B-C). If $C > B$, then the surface excess of component i is a negative value equal to $B-C$. This is contrary to the explanation of Rosene and Manes who indicated that component i would be excluded. The fact that the surface excess is negative for component i does not mean that it is not adsorbed. It means only that the percent of solute in the adsorbed phase is less than its value in the bulk phase. This results from the strong adsorption of the solvent molecules relative to the solute molecules.

Figure 1 Schematic diagram of competitive adsorption potential theory

6. Check to determine if the assumed x_j value is equal to that given by

$$x_{j\phi} = \frac{\frac{C}{\bar{V}_j}}{\frac{C}{\bar{V}_j} + \frac{(B-C)}{\bar{V}_1}} \quad (19)$$

If the value calculated by Eq. 19 is not equal to the assumed value, steps 2 through 6 should be repeated until the assumed and calculated values are equal.

RESULTS AND DISCUSSION

The single-solute adsorption data used in these calculations were obtained in a previous study carried out by Wang et al. (23). Figures 2 and 3 give the adsorbate volumes, $V_{ads} = q_1 \times \bar{V}_1$, versus $\frac{T}{\bar{V}_1} \log \frac{1}{x_{iB}}$, for the acids adsorbed singly from aqueous solutions at 278 and 298 K respectively. The experimental results of the individual adsorption of bi-solute organic acids are compared in Tables 1 through 6 with values predicted by the new model. The average errors shown in the tables are taken to be the absolute errors compared with the experimental data. The predicted uptakes as found by the method proposed in this study are compared with experimental values and with values predicted by the method of Radke and Prausnitz. In all of the calculations, the partial molar volumes of solutes are assumed to be equal to their molar volumes at the specified system temperatures. This is a reasonable assumption since the adsorbed phase is essentially pure solute.

Figures 4 through 15 show the predicted results for different mixtures at the specified system temperatures. The solid lines are the interpolated single solute isotherms, dotted lines are calculated from the potential theory as modified in this study, and the dashed lines represent values calculated by

the method of Radke and Prausnitz. The experimental data are shown by the black points. Thirty-six experimental mixture points were measured over a two-decade range in solute concentration and surface loading. However, only one point per calculated line is shown because of the difficulty in controlling the final equilibrium concentration, especially for completely miscible systems.

The experimental error of the bi-solute studies is estimated to be 4%. The average deviation between predicted and experimental loadings ranged from 4.4% to 14.4% for uptake of the individual components and from 2% to 11% for the total uptake of both components. The average error between the predicted and experimental loading is greater than the 4% estimated experimental error. This could be the result of several factors including the pH effects and the non-ideal behavior of the adsorbed phase. The errors in using the ideal adsorbed solution model are possibly due in part to the extrapolation error introduced when evaluating the spreading pressure in the very low concentration region. However, as shown in Tables 1 through 6, and in Figures 4 through 15, the errors do not appear to be systematic.

Figures 4 through 15 show that the potential theory generally predicts lower adsorption in the high concentration range and higher adsorption in the lower concentration range than does the method of Radke and Prausnitz. The higher adsorption in the lower concentration range is probably due to the effect of neglecting the adsorption potential of the solvent, which in this case is water. By the same argument the potential theory as presented here might be expected to predict higher adsorption uptakes even in moderate or high concentration ranges. As shown in Figures 4 through 15 this does not appear to be the case for all of the data. The disagreement again may be due to the pH effects, steric hinderance and/or chemisorption in the higher concentration range as suggested by Radke and Prausnitz.

Figure 2 Volume adsorbed versus adsorption potentials of acetic, propionic and n-butanoic acids at 278 K

Figure 3 Volume adsorbed versus adsorption potentials of acetic, propionic and n-butanoic acids at 298 K

Figure 4 Adsorption of acetic acid in the presence of propionic acid at 278 K

Figure 5 Adsorption of propionic acid in the presence of acetic acid at 278 K

Figure 6 Adsorption of acetic acid in the presence of n-butanoic acid at 278 K

Figure 7 Adsorption of n-butanoic acid in the presence of acetic acid at 278 K

Figure 8 Adsorption of propionic acid in the presence of n-butanoic acid at 278 K

Figure 9 Adsorption of n-butanoic acid in the presence of propionic acid at 278 K

Figure 10 Adsorption of acetic acid in the presence of propionic acid at 298 K

Figure 11 Adsorption of propionic acid in the presence of acetic acid at 298 K

Figure 12 Adsorption of acetic acid in the presence of n-butanoic acid at 298 K

Figure 13 Adsorption of n-butanoic acid in the presence of acetic acid at 298 K

Figure 14 Adsorption of propionic acid in the presence of n-butanoic acid at 298 K

Figure 15 Adsorption of n-butanoic acid in the presence of propionic acid at 298 K

Table 1 Competitive adsorption data for the mixture of acetic acid and propionic acid at 25° C

C_2^+	C_3	q_2^{exp}	q_2^*	q_2^{**}	q_3^{exp}	q_3^*	q_3^{**}	q_T^{exp}	q_T^*	q_T^{**}
mole/l	mole/l	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$
7.28×10^{-3}	4.52×10^{-3}	0.219	0.242	0.210	0.445	0.514	0.507	0.664	0.756	0.717
1.52×10^{-2}	4.69×10^{-3}	0.353	0.385	0.367	0.431	0.473	0.467	0.784	0.858	0.834
3.54×10^{-2}	1.45×10^{-2}	0.450	0.495	0.546	0.735	0.783	0.760	1.185	1.279	1.306
3.96×10^{-2}	2.34×10^{-2}	0.442	0.490	0.506	0.868	1.000	1.010	1.310	1.490	1.516
6.38×10^{-2}	1.51×10^{-2}	0.743	0.758	0.804	0.607	0.635	0.706	1.350	1.393	1.510
6.36×10^{-2}	2.30×10^{-2}	0.605	0.640	0.768	0.821	0.887	0.866	1.426	1.527	1.652
average error			8.1%	13.7%		9.9%	10.5%		9.2%	11.3%

* Radke & Prausnitz

** Potential Theory

+ Subscript 2,3 and 4 refer to acetic acid, propionic acid and n-butanoic acid respectively

Subscript T indicates total uptake of the solutes

Table 2 Competitive adsorption data for the mixture of acetic acid and n-butanoic acid at 25° C

C_2	C_4	q_2^{exp}	q_2^*	q_2^{**}	q_4^{exp}	q_4^*	q_4^{**}	q_T^{exp}	q_T^*	q_T^{**}
mole/l	mole/l	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$
7.31×10^{-3}	2.50×10^{-3}	0.194	0.196	0.192	0.605	0.589	0.644	0.799	0.758	0.836
1.15×10^{-2}	1.98×10^{-3}	0.327	0.355	0.314	0.588	0.579	0.602	0.905	0.934	0.899
3.98×10^{-2}	6.93×10^{-3}	0.397	0.480	0.472	0.842	0.750	0.853	1.239	1.230	1.325
4.01×10^{-2}	1.19×10^{-2}	0.413	0.420	0.454	0.975	0.994	1.028	1.388	1.414	1.482
6.32×10^{-2}	1.66×10^{-2}	0.659	0.549	0.594	1.170	1.050	1.160	1.829	1.595	1.754
6.30×10^{-2}	7.09×10^{-3}	0.690	0.690	0.699	0.751	0.675	0.788	1.441	1.365	1.487
average error			8.7%	7.9%		6.2%	3.6%		4.2%	4.4%

Table 3 Competitive adsorption data for the mixture of propionic acid and n-butanoic acid at 25° C

C_3	C_4	q_3^{exp}	q_3^*	q_3^{**}	q_4^{exp}	q_4^*	q_4^{**}	q_T^{exp}	q_T^*	q_T^{**}
mole/l	mole/l	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$
5.28×10^{-3}	3.02×10^{-2}	0.302	0.329	0.293	0.525	0.586	0.569	0.827	0.915	0.862
9.78×10^{-3}	3.13×10^{-3}	0.697	0.642	0.480	0.485	0.437	0.525	1.182	1.079	1.005
2.32×10^{-2}	7.94×10^{-2}	0.727	0.861	0.682	0.651	0.623	0.650	1.378	1.484	1.332
2.94×10^{-2}	1.29×10^{-2}	0.877	0.920	0.746	0.786	0.758	0.875	1.663	1.678	1.621
3.62×10^{-2}	3.75×10^{-3}	0.856	1.067	0.907	0.563	0.573	0.635	1.419	1.640	1.542
3.67×10^{-2}	1.83×10^{-2}	0.738	0.895	0.800	0.836	0.895	0.985	1.574	1.790	1.785
average error			14.4%	11.6%		6.4%	9.8%		9.6%	7.9%

Table 4 Competitive adsorption data for the mixture of acetic acid and propionic acid at 5°C

C_2^+	C_3	q_2^{exp}	q_2^*	q_2^{**}	q_3^{exp}	q_3^*	q_3^{**}	q_T^{exp}	q_T^*	q_T^{**}
mole/l	mole/l	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$
7.05×10^{-3}	4.11×10^{-3}	0.244	0.280	0.264	0.513	0.578	0.554	0.753	0.858	0.808
1.46×10^{-2}	4.31×10^{-3}	0.423	0.518	0.475	0.464	0.482	0.449	0.887	1.000	0.924
3.00×10^{-2}	1.03×10^{-2}	0.626	0.669	0.615	0.652	0.724	0.707	1.278	1.393	1.323
3.78×10^{-2}	1.62×10^{-2}	0.737	0.684	0.704	0.787	0.886	0.843	1.524	1.570	1.547
4.56×10^{-2}	1.06×10^{-2}	0.841	0.902	0.827	0.584	0.650	0.639	1.425	1.552	1.446
4.67×10^{-2}	2.26×10^{-2}	0.682	0.742	0.752	0.881	0.984	0.952	1.563	1.726	1.704
average error			11.2%	6.4%		10.5%	7.1%		9.6%	4.6%

Table 5 Competitive adsorption data for the mixture of acetic acid and n-butanoic acid at 5° C

C_2	C_3	q_2^{exp}	q_2^*	q_2^{**}	q_4^{exp}	q_4^*	q_4^{**}	q_T^{exp}	q_T^*	q_T^{**}
mole/l	mole/l	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$
7.29×10^{-3}	2.31×10^{-3}	0.214	0.219	0.245	0.640	0.674	0.578	0.854	0.893	0.823
1.49×10^{-2}	2.48×10^{-3}	0.373	0.447	0.405	0.608	0.593	0.569	0.981	1.070	0.974
3.83×10^{-2}	6.89×10^{-3}	0.633	0.665	0.669	0.850	0.836	0.804	1.483	1.496	1.473
3.93×10^{-2}	1.63×10^{-2}	0.465	0.512	0.528	1.220	1.220	1.194	1.685	1.732	1.722
6.25×10^{-2}	7.13×10^{-2}	0.792	0.855	0.880	0.804	0.670	0.781	1.595	1.525	1.661
6.28×10^{-2}	1.67×10^{-2}	0.727	0.726	0.757	1.150	1.144	1.105	1.877	1.870	1.862
average error			8.8%	9.6%		4.4%	5.1%		3.7%	2.0%

Table 6 Competitive adsorption data for the mixture of propionic acid
and n-butanoic acid at 5° C

C_3	C_4	q_3^{exp}	q_3^*	q_3^{**}	q_4^{exp}	q_4^*	q_4^{**}	q_T^{exp}	q_T^*	q_T^{**}
mole/l	mole/l	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$	$\frac{\text{m mole}}{\text{g}}$
5.12×10^{-3}	2.90×10^{-3}	0.321	0.374	0.367	0.539	0.665	0.569	0.860	1.039	0.936
9.70×10^{-3}	3.06×10^{-3}	0.724	0.738	0.571	0.498	0.474	0.491	1.220	1.212	1.062
2.30×10^{-3}	7.69×10^{-3}	0.765	0.851	0.816	0.708	0.799	0.670	1.473	1.650	1.486
2.92×10^{-2}	1.29×10^{-2}	0.917	1.000	0.816	0.793	0.836	0.881	1.710	1.836	1.697
3.48×10^{-2}	8.13×10^{-3}	1.165	1.226	1.116	0.615	0.557	0.640	1.780	1.783	1.756
3.58×10^{-2}	1.76×10^{-2}	0.886	1.000	0.870	0.980	0.979	1.004	1.866	1.979	1.874
average error			9.5%	9.9%		9.3%	5.0%		7.9%	4.7%

In contrast to the studies of Manes and co-workers, an adjusted adsorbate volume correction factor was not necessary in predicting bi-solute uptake. The reasons are twofold. First, the surface excess is zero when pure solute is used as indicated by Minka and Myers (18). Secondly, it is not possible at the present time to give a meaningful adjusted volume correction factor because of many-body effects and the unknown structure of the adsorbed liquid phase. The lack of quantitative information on intermolecular potentials, to say nothing of the complexity of a multi-layer phase of a dense-fluid adsorbate, is the main reason for not using the adjusted adsorbate volume factor.

A major difference between the method of Radke and Prausnitz and the adsorption potential theory is that it is the pore volume and not the surface area that plays the major role in the model presented in this work. It was indicated by Minka and Myers (18) that the surface area has no meaning for microporous adsorbents. In the adsorption potential, the multilayer character of the adsorbed phase is explained by the decay of the potential energy between the adsorbate molecules and the adsorbent as their separation distance increases. The significance of this approach is that it is not necessary to postulate a specific thickness for the adsorbed layer, since adsorption is considered as only a function of the adsorption potential at any distance from the adsorbing surface, Kipling (24). In the ideal adsorbed solution theory, the adsorbed phase is considered to be of zero thickness and the small pressure effect is neglected. In monolayer surface coverage or less, the concept of a zero-thickness adsorbed phase may be a good approximation. However, it cannot be applied to the case where multi-layer adsorption occurs. Radke and Prausnitz indicated that the adsorbed phase was determined according to the Gibbs dividing surface. The concept of Gibbs dividing

surface was originally developed to deal with the vapor-liquid interface or an immiscible liquid-liquid interface. For miscible liquid systems, it is not appropriate to apply the Gibbs dividing surface to treat the adsorption at a liquid-solid interface because there is no sharp density change in the liquid phase. A thorough discussion of this problem is given by Kipling (24) and by Defay et al. (25).

The application of the potential theory in this study is based on the assumptions that the bulk phase and adsorbed phase form an ideal solution. In addition, it was assumed that the amount of water adsorbed in the adsorption space near the surface can be neglected because of its low adsorption potential on activated carbon as substantiated by Wohleber and Manes. Thus, the application of the potential theory as presented here is limited to predicting adsorption in dilute solutions or for systems where the adsorption of the solvent is so low compared to the solute that it can be neglected even at potential surfaces somewhat removed from the solid surface. For more concentrated solutions, the activity coefficients must be introduced for both the bulk liquid phase and the adsorbed phase. Unfortunately, adsorbed-phase activity coefficients cannot be measured independently. Therefore, the proposed model can be more accurately utilized for dilute solutions.

CONCLUSIONS

A competitive adsorption potential theory was developed in this study to predict the bi-solute equilibrium data. The agreement between the calculated values and the experimental data is good. The success of the competitive adsorption potential theory indicates several important conclusions.

1. The model presented in this work provides a simple way to predict bi-solute equilibrium data if pure solute data are available.

2. The adjusted adsorbate volume factor is not necessary when the surface loading is not high. This is in contrast to the approach of Rosene and Manes.

3. The derivation of the model presented in this work is thermodynamically rigorous. It can be extended to more concentrated solutions provided the activity coefficients of the adsorbed and the bulk liquid phases are known or can be calculated.

4. The idea of finite adsorbed volume space occupied by adsorbates describes the actual physical system more closely than does the conventional Gibbs adsorption equation.

LITERATURE CITED

1. Linner, E. R., Gortner, R.A., J. Phys. Chem. 39, 35 (1935).
2. Hansen, R. S., Fu, Y., Bartell, F. E., J. Phys. Colloid Chem., 53, 769 (1949).
3. Hansen, R. S., Craig, R. P., J. Phys. Chem. 58, 211 634 (1953).
4. Hansen, R. S., Hansen, R. B., J. Phys. Chem. 59, 496 (1954).
5. Hansen, R. S., Miller, F. A., J. Phys. Chem. 58 (3), 193 (1954).
6. Graham, D., Hansen, R. S., J. Phys. Chem. 60 (8), 1153 (1956).
7. Smith, H. A., Hurley, R. B., J. Phys. Colloid Chem. 53, 1409 (1949).
8. Rosene, M.R., Ozcan, M., Manes, M., J. Phys. Chem. 80, 2586 (1976).
9. Rosene, M. R., Manes, M., J. Phys. Chem. 81, 1646 (1977).
10. Parkash, S. Carbon, 12, 37 (1974).
11. Radke C., J., Prausnitz, J. M., Ind. Eng. Chem. Fundam., 11 (4), 445 (1972).
12. Radke, C. J., Prausnitz, J. M. AIChE J. 18, 761 (1972).
13. Fritz, W., Schluender, E-U, Chem. Eng. Sci, 29, 1279 (1974).
14. Butler, J. a. V., Ockrent, C. J., J. Phys. Chem 34, 2841, (1930).
15. Jain, J. S., Snoeyink, V. L., J. Watter Pollut. Control Fed. 45, (1973).
16. Myers, A. L., Prausnitz, J. M., AIChE J., 11, 121 (1965).
17. Digiano, F. A., Baldauf, G., Frick, B., Sontheimer, H., Chem. Eng. Sci. 33, 1667-73 (1978).
18. Minka, C., Myers, A. L., AIChE J., 11, 121 (1973).
19. Rosene, M. R., Manes, M., J. Phys. Chem. 80, 953 (1976).
20. Hansen, R. S., Fackler, W., V. Jr., J. Phys. Colloid Chem., 53, 769 (1949).
21. Wohleber, D. A., Manes, M., J. Phys. Chem. 75, 61 (1971).
22. Wohleber, D. A., Manes M., J. Phys. Chem. 75, 3720 (1971).
23. Wang. S. W., Hines, A. L., Färrier, D. S., J. Chem. Eng. Data, 24 (4), 345 (1979).

24. Kipling, J. J., "Adsorption from Solutions of Non-Electrolytes" Academic Press (1965).
25. Defay, R., Prigogine, I., Bellemans, A., Everett, D. H., "Surface Tension and Adsorption" John Wiley, New York (1966).
26. Radke, C. J., Prausnitz, J. M., J. Chem. Phys. 57 (2), 714 (1972).

NOMENCLATURE

a = activity

C = concentration, mole/l

ϵ = adsorption potential, cal/g mole

f = fugacity

$\bar{G}$ = partial molar Gibbs free energy

n = moles of solutes adsorbed

ϕ = equipotential surface

ϕ' = volume space in the adsorbed phase, ml

q = uptake of the solutes, m mole/g solid

R = universal gas constant, cal/(g mole.K)

T = temperature, K

μ = chemical potential

$\bar{V}$ = partial molar volume, ml/mole

x = mole fraction

γ = activity coefficient

Subscripts and Superscripts

2 = acetic acid

3 = propionic acid

4 = butanoic acid

B = the bulk liquid phase

i = the i^{th} component

j = the j^{th} component

o = standard state

ϕ = adsorbed phase

T = total solutes

APPENDIX A

PROGRAM SCHEDULE

PROGRAM SCHEDULE AND PERSONNEL

The main research program is scheduled to be completed over a three year period. An approximate work completion schedule is given in the bar graph below.

The program will be directed by Dr. Anthony L. Hines who will be assisted by Dr. E. Dendy Sloan. The resumes of these individuals are attached. It is proposed to make use of the services of two graduate students throughout the course of this study.