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COMPARISON OF DILUENTS FOR TRIBUTYL PHOSPHATE

by

L. L. Burger
Chemical Research Section
Separations Technology Division

October 6, 1950

HANFORD WORKS
RICHLAND, WASHINGTON

Operated for the Atomic Energy Commission
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COMPARISON OF DILUENTS FOR TRIBUTYL PHOSPHATE

INTRODUCTION

The use of TBP as an extractant for uranium necessitates the addition of a diluent to obtain a solvent phase of suitable density and sufficiently low viscosity to be operable in the extraction columns employed. Other criteria in the choice of a diluent are its effect on distribution ratios of the particular inorganic compounds concerned, stability towards the chemical constituents of the various process streams and the flash point.

With the diluent restricted to non-polar substances such as hydrocarbons and certain chlorinated hydrocarbons, the variations in distribution ratio of uranyl nitrate has been shown to be insignificant. ⁽¹⁾ ⁽²⁾ ⁽³⁾ Likewise the distribution of fission products and hence decontamination has been shown ⁽⁴⁾ to be nearly constant for various diluents. The question of chemical stability has not been completely answered. However, olefins and aromatics would be expected to be more reactive than paraffin hydrocarbons. The remaining properties of interest are then the vapor pressure, density and viscosity.

This report summarizes a study of the composition and physical properties of a number of hydrocarbon diluents together with some generalizations regarding relations between these properties.

SUMMARY AND CONCLUSIONS

1. Aromatic and olefin content were below 1% by weight for most of the diluents examined. The highest content found was about 10% aromatic and 2% olefin. The naphthenic content was not determined.

2. Initial boiling points varied from 160°C. to 200°C. and final boiling points from 190°C. to 270°C. The ASTM boiling range indicated much more selective refining for several of the diluents than for others.

3. The flash points of the diluents ranged from 102°F. to 162°F. The flash point may be increased by more selective refining of the diluent.

4. Densities of the diluents at 25°C. varied from 0.754 to 0.804 g./cc.

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depending on average molecular weight and molecular structure. The density of any TBP-diluent mixture at 25°C. can be calculated from the density of the components by the equation

$$\rho_{\text{Mix}} = \phi_{\text{TBP}} (0.972) + \phi_{\text{Dil}} \rho_{\text{Dil}}$$

where ϕ_{TBP} and ϕ_{Dil} are the respective volume fractions of TBP and diluent.

5. The diluents examined varied in viscosity from 9 millipoises to 19 millipoises at 25°C. The viscosity of a 15% by volume solution of TBP in a low viscosity diluent is only slightly greater than that of the diluent. The viscosity, η , in millipoises of a TBP - diluent mixture can be calculated from the expression

$$\log \eta_{\text{Mix}} = \phi_{\text{TBP}} (1.345 + 0.36 \phi_{\text{TBP}}) + \phi_{\text{Dil}} \log \eta_{\text{Dil}}$$

6. The physical properties of the two phase system, TBP in diluent-aqueous, have been correlated with the physical properties of the diluents.

7. All of the materials investigated would behave as a satisfactory diluent for TBP. In practical operation flash point restrictions eliminate a number of the commercially available diluents. In addition, optimum operating efficiency for a specific solvent extraction column design would probably warrant a more narrow bracketing of properties such as viscosity and density.

EXPERIMENTAL

Densities and refraction indices were determined at 25°C. by conventional procedures. The viscosity was determined at 25°C. using an ostwald viscometer with the kinetic energy correction applied to the data. The boiling range was determined in accordance with ASTM D-86-30 while the flash point was that given by the Tag closed-cup method, ASTM D-56-36.

The aromatic content was obtained from the volume change on washing with a $\text{H}_2\text{SO}_4 - 2\text{O}_5$ mixture (ASTM D-875-46T). Due to the method of measurement, an aromatic content of less than 1% is not very significant. The aromatic content was also checked by measuring the index of refraction by the following procedure: The index was measured for the untreated diluent and again after treatment to constant index with activated silica. The per cent aromatic is then

given approximately by

$$\% = \frac{n_D^{25}(\text{untreated}) - n_D^{25}(\text{treated})}{1.4900 - n_D^{25}(\text{treated})} 100$$

where 1.4900 is the index of a typical aromatic in the diluent boiling range. By this method, which is subject to errors arising from molecular weight differences and the presence of other constituents such as olefins, Stoddard Solvent was found to give 2.6%, Shell Spray Base 1.1%, and Varsol 10% aromatics, in reasonable agreement with 1.8, 1.0 and 9.1% respectively by the H_2SO_4 method. Silica gel adsorption of aromatics has been discussed in more detail by Mair. ⁽⁵⁾ Ultra-violet absorption spectra is a more sensitive technique and strong absorption bands may appear from 230 m μ to 390 m μ characteristic of the aromatic type. In the event that small amounts of aromatic constituents should appear more important than they now seem, ultra-violet absorption studies should be extended.

Olefin content determinations are somewhat less satisfactory. As determined by the bromine number the results may be either higher or lower than the actual olefin content depending on, among other things, the location of the double bond, the extent of chain branching, the concentration of both the olefin and the bromine, ⁽⁶⁾ ⁽⁷⁾ and the reaction time. Experiments based on ASTM D-875-46T and modifications of this procedure designed to give more accurate values at lower concentrations indicated clearly that concentration and time factors were too great to give reproducible results. Bromination of side chains was probably the greatest error.

The iodine number is somewhat less objectionable in this respect ⁽⁸⁾ and a modification of ASTM D-460-46 using large samples was used to obtain the values listed in Table I. Infrared absorption methods have been used for determination of olefins ⁽⁹⁾ but are in general not accurate below 1-2%. 0.50 4

The remaining data in Table I are the aniline point and the Kauri-butanol number. These rather arbitrary properties are based on the partial miscibility of the substance tested with particular organic substances and were carried out

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Table I

PHYSICAL PROPERTIES OF PURE DILUENTS

Diluent	Density 25°C. g./cc.	Index Refraction n_D^{25}	Viscosity 25°C millipoise	Boiling Range and Mid-point °C.	Flash Point Tag closed-cup °F.	Aromatic Content %	Iodine Number	Aniline Point °F	Kauri- Butanol Value
Union Insecticide Base	0.8037	1.4444	16.1	175-269, (229)	133	0.9	1.13	164	30.2
Standard Oil Special Grade "B"	0.7918	1.4382	14.5	179-263, (217)	145	0.2	0.11	164	27.9
Standard Oil "C"	0.7933	1.4386	14.9	181-263, (220)	143	1.4	0.07	164	29.1
Deo Base (Sonneborn Co., N. Y. C.)	0.7804	1.4344	17.3	198-269, (225)	162	<1.0	0.02	177	25.0
Shell Spray Base	0.8038	1.4435	19.0	193-260, (232)	150	<1.0	0.42	166	35.7
AMSCO 149-92 Br	0.7741	1.4339	11.7	172-242, (200)	119	7.0	1.22	150	30.1
AMSCO 125-90 W	0.7570	1.4226	14.1	186-199, (190)	133	<1.0	0.49	186	25.1
Penn. Ref. Co. "Super Sol"	0.7543	1.4217	9.6	162-(198), (185)	127	1.9	0.04	167	28.6
Gulf B. T. "Varsol"	0.7606	1.4271	8.9	165-198, (177)	111	9.1	1.07	150	31.4
Shell Stod. Solv.	0.7765	1.4295	9.2	160-193, (168)	102	1.8	0.48	143	34.3
CCl ₄	1.5844	1.4603 ^{20°C.}	9.14	--	--	--	--	--	--
C ₁₀ H ₂₂	0.726	--	11.0	196	115	--	--	171	--
C ₁₂ H ₂₆	0.746	--	14.0	216	165	--	--	183	--

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using the ASTM procedures 1012-49T and D-50T, respectively. The Doctor test for sulfur, ASTM D-484-40, was negative for all the diluents listed.

The physical properties of mixtures of these diluents with tributyl phosphate were determined in the range of 5% to 50% by volume TBP. The solutions were then equilibrated with uranyl nitrate solutions and the viscosities and densities redetermined.

DISCUSSION

A. Chemical Composition

Most of the diluents studied were predominantly paraffinic in composition. Aromatic and olefinic hydrocarbons have been in most cases removed or greatly reduced by treatment by the manufacturer. The content of naphthenes may be higher depending on the source of the parent crude. Naphthenic content was not investigated in this survey. The aromatic and olefinic contents as found by analysis are listed in Table I. On the assumption that the average molecular weight is 150, the per cent olefin will be about 0.7 of the iodine number.

The aniline point, Kauri-butanol value (Kb), index of refraction and density are all related to the composition, being particularly influenced by the aromatic content. The aniline point, or temperature of miscibility with aniline, is lower if aromatic hydrocarbons are present. The Kauri-butanol value is based on the greater solubility of Kauri gum in aromatic hydrocarbons than in paraffins. A low Kb number, 25-26, indicates the probable absence of aromatic compounds while the number approaches 100 as the aromatic content increases. However, the correlation of Kb number and per cent aromatic as given in Table I is extremely poor and points to the nonspecificity of the determination. The same criticism can be given for the aniline point.

Density and index of refraction are likewise indications of chemical composition but both are nonspecific. The degree to which these measurements are useful may be evaluated by reference to Table II where a number of pure hydrocarbons are compared.

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TABLE II

PHYSICAL PROPERTIES OF TYPICAL PURE HYDROCARBONS

Compound	Density g./cc. 20°C.	Index of Refraction n_D^{20}	Boiling Point °F	Aniline Point °F
C ₈ n-paraffin	0.703	1.398	258	161
aromatic	0.867	1.497	282	< -22
olefin-1	0.720	1.409	250	90
cyclo-paraffin	0.784	1.431	256	--
C ₁₀ n-paraffin	0.730	1.412	345	171
aromatic	0.866	1.490	343	< -22
cyclo-paraffin	0.812	1.45	338	--
C ₁₂ n-paraffin	0.749	1.422	420	--
aromatic	0.86	1.490	406	--
C ₁₄ n-paraffin	0.764	1.436	484	--
aromatic	0.88	1.50	482	--
di phenyl denv.	1.00	1.58	500	--

Aniline point, Kb number, index of refraction, and density then have only qualitative significance and are effected by relative amounts of paraffins, olefins, cyclo-paraffins, aromatics and molecular weight. However, if a knowledge of the molecular weight is at hand, e.g., from boiling point, significant information as to composition can be obtained from each of these measurements.

The boiling ranges given by the ASTM distillation are illustrated in

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Figure 1. The distillation curves using an efficient fractionating column would be significantly different. However, the ASTM curves have comparative value for example indicating not only that the molecular weight ranges differ considerably among the various diluents but also that a much more selective refinement was achieved in the case of some diluents, e. g., "AMSCO 125-90 W" and "Super Sol".

B. Flash Points

The flash points of the diluents examined varied from 102°F. to 162°F. Safety considerations will probably set a temperature of about 130°F. as the lower limit, which would eliminate several of the materials in Table I. A pure C₁₁ or C₁₂ paraffin hydrocarbon would evidently meet this requirement. A study of pure hydrocarbons reveals that the flash point is reached when the vapor pressure, p_f , reaches 6-9 mm Hg. Using an arbitrary value, p_f , and assuming ideal solutions then the mixtures of pure hydrocarbons which will give a specified flash point can be found from the relation

$$p_f = \sum_i N_i p_i \quad (1)$$

where N_i is the mol fraction of component i having vapor pressure p_i . Conversely, the change in flash point with change in composition can be ascertained. The viscosity of an ideal solution can be calculated from the relation

$$\log \eta_m = \sum \log \eta_i \quad (2)$$

By comparison of viscosities and flash points of these mixtures with those of pure compounds an important generalization can be deduced: A mixture of two or more hydrocarbons will have a higher vapor pressure and thus a lower flash point than a pure hydrocarbon of the same viscosity. The practical application of this would seem to be simply that a narrow fractionation cut is desired for the diluent if a low viscosity-high flash point material is desired. The validity of this was tested by selectively removing by distillation 15% and 30% of the low boiling material from two of the diluents. The data are shown in Figure 2 where the dotted line represents an average trend of the viscosity-flash point

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relation. The flash point and viscosity of the residue from these fractionations are shown by heavy lines. It is apparent that the theoretical generalization is applicable and further that the flash point-viscosity relation can be significantly improved by fractional removal of the low boiling constituents.

A second consideration involves the change in flash point when the comparatively non-volatile TBP is added. Assuming again an ideal solution and that the flash point is reached when the vapor pressure of the hydrocarbon in the mixture reaches the vapor pressure of the pure hydrocarbon at its flash point, the Clapeyron equation relates the respective temperatures and pressures.

$$\log \frac{P_f}{P_o} = \log N = 2300 \left(\frac{1}{T_N} - \frac{1}{T_o} \right)$$

or approximately

$$\Delta T = - \frac{T_o^2}{2300} \log N \quad (3)$$

where T_o is the flash point of pure diluent in $^{\circ}\text{K}$ and T_N the flash point in $^{\circ}\text{K}$ of the mixture in which the mol fraction of diluent is N . The constant 2300 includes an arbitrary heat of vaporization of 11 K cal./mole. Table III lists some comparative data for two mixtures.

TABLE III

FLASH POINTS OF TBP-DILUENT MIXTURES

<u>Solution</u>	<u>Mol Fraction Diluent (N)</u>	<u>Flash Point Pure Diluent $^{\circ}\text{F.}$</u>	<u>Flash Point of Solution, $^{\circ}\text{F.}$</u>	
			<u>Obs.</u>	<u>Calc.</u>
15% TBP in Stodd. Solv.	0.88	102	106	106
25% TBP in Gulf B. T.	0.80	111	117	118

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C. Viscosity

Viscosities at 25°C. of the pure hydrocarbon diluents examined varied from 8.9 to 19.0 millipoises, which can be compared with the viscosity of carbon tetrachloride, 9.1 millipoises. The viscosity of pure TBP is 33.2 millipoises and rises to 39.9 millipoises on saturation with water, about 64 gm. H₂O/liter. The viscosity of a TBP diluent mixture can be computed from the relation

$$\log \eta_{\text{Mix}} = N_{\text{TBP}} \log \eta_{\text{TBP}} + N_{\text{Dil}} \log \eta_{\text{Dil}} \quad (4)$$

where N_{TBP} and N_{Dil} are the mol fractions of TBP and diluent in the mixture. Since the molecular weight is in general not accurately known, a more useful expression and one which is only slightly less sound theoretically involves the volume fraction, ϕ , in place of the mol fraction.

$$\log \eta_{\text{Mix}} = \phi_{\text{TBP}} \log \eta_{\text{TBP}} + \phi_{\text{Dil}} \log \eta_{\text{Dil}} \quad (5)$$

Since the form of the equations gives greater weight to the low viscosity component, i.e. the diluent, and since the diluent is present in greater amount than the TBP, the viscosity of the mixture approaches that of the diluent chosen.

Observed viscosities are lower by several per cent than those calculated from either of the above equations. The deviations from Equation (5) which arise from (1) non-ideality of the solution, (2) varying water content of the solution as a function of TBP concentration, and (3) the non-proportionality of ϕ and N , can be combined in an equation of the type

$$\log \eta_{\text{Mix}} = \phi_{\text{TBP}} (A + B \phi_{\text{TBP}}) + \phi_{\text{Dil}} \log \eta_{\text{Dil}} \quad (6)$$

where the "apparent viscosity" of TBP is included in the constant A. In Table IV are listed data for water-saturated TBP-diluent mixtures. The viscosity data were found to fit the equation

$$\log \eta_{\text{Mix}} = \phi_{\text{TBP}} (1.345 + 0.36 \phi_{\text{TBP}}) + \phi_{\text{Dil}} \log \eta_{\text{Dil}} \quad (7)$$

It will be seen from the table that the viscosities of 15% TBP mixtures studied vary from about 10 to 20 millipoises.

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The change in viscosity of these solvent mixtures when uranyl nitrate is dissolved is included in Table IV. It is significant that the coefficient of viscosity per mole of uranyl nitrate is greater the higher the solvent viscosity. This is illustrated by Figure 3 where viscosity is plotted as a function of uranyl nitrate concentration. Thus the choice of a low viscosity diluent becomes more important for 30% to 50% TBP mixtures than for 10% to 15% TBP.

D. Density

Densities of the diluents at 25°C. varied from 0.754 to 0.804 g./cc. reflecting, as discussed in a previous section, differences in aromatic and cyclo-paraffin content and molecular weight.

TABLE IV

PROPERTIES OF DILUENT-TBP MIXTURES SATURATED WITH H₂O

25°C.

<u>Solvent Mixture</u> <u>Vol. % TBP</u>	<u>Diluent</u>	<u>Density, ρ</u> <u>g./cc.</u>	<u>Viscosity, η</u> <u>millipoises</u>	<u>$\Delta \rho$/mole</u> <u>UO₂ (NO₃)₂</u>	<u>$\Delta \eta$/mole</u> <u>UO₂ (NO₃)₂</u>
5.1	CCl ₄	1.5539	9.5	0.26(0)	11
15.4	CCl ₄	1.4916	10.7	0.27	13
25.2	CCl ₄	1.4309	11.9	0.27(0)	15
40.5	CCl ₄	1.3387	14.8	0.27	21
15.0	Gulf B. T.	0.7919	10.4	0.33	12
25.1	Gulf B. T.	0.8126	11.8	0.33	15
39.5	Gulf B. T.	0.8453	14.7	0.33	21
15.0	Deo Base	0.8081	18.3	0.328	29
23.5	Deo Base	0.8206	19.4	0.33	31
46.0	Deo Base	0.8728	23.6	0.33	44
15.1	AMSCO	0.7860	15.5	0.334	23
	125-90W				
15.2	Shell Spray	0.8281	19.7	0.33	32
	Base				
15.1	Stodd. Solv.	0.8051	10.0	0.33	11

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The density of TBP at 25°C. varies from 0.9730 when water-free to about 0.9762 when water-saturated. The concentration of water in the TBP-diluent mixtures is found to be somewhat less than predicted by the mol fraction of TBP. Also there is a small expansion on mixing and to fit the data a lower "TBP density" was arbitrarily assumed. The expression

$$\rho_{\text{Mix}} = (0.9720) \phi_{\text{TBP}} + \rho_{\text{Dil}} \phi_{\text{Dil}} \quad (8)$$

fits all the experimental data at 25°C. within 0.2%. The equation agrees well with that found by Moore⁽⁴⁾ for the CCl₄-TBP system.

The density change as uranyl nitrate or nitric acid is added depends upon the original density of the solvent mixture. In a preliminary study of density and viscosity of TBP-diluent mixtures it was found that the following equation held for 15% TBP in Deo Base at 25°C. ⁽¹⁰⁾

$$\rho = 0.808 + 0.328 \frac{M_{\text{UO}_2(\text{NO}_3)_2}}{M_{\text{HNO}_3}} + 0.028 \frac{M_{\text{HNO}_3}}{M_{\text{HNO}_3}} \quad (9)$$

For 20% TBP in carbon tetrachloride Moore⁽⁴⁾ found a density coefficient for uranyl nitrate of 0.266 and a negligible nitric acid coefficient.

These results together with data obtained from the present work lead to the conclusion that the density coefficient for uranyl nitrate varies from about 0.334 per mole for low density mixtures, i.e., 15% TBP in AMSCO, to about 0.260 for high density mixtures, i.e., 15% TBP in CCl₄. The coefficient for nitric acid varies from about 0.029 per mol for the low density solvent to zero for 20% CCl₄ and becomes slightly negative at lower TBP concentrations in CCl₄. The density coefficients are included in Table IV.

E. Distribution of Uranyl Nitrate

The distribution coefficient of uranyl nitrate between the organic and aqueous phases does not vary significantly with the diluents employed in this study although the E_a^0 for uranium for the CCl₄-TBP system was perhaps slightly lower. Rehn and Slansky found little difference between the diluents CCl₄ and Deo Base in a countercurrent batch extraction study.⁽³⁾ Clagget⁽¹¹⁾ also found no differences in uranium distribution using the diluents Stoddard Solvent, Deo

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Base and Shell Spray Base.

F. Viscosity-Density Relations in the Two Phase System

The implicit relation of viscosity to the diffusion coefficient makes the former property of significance in the transfer of the solute through the bulk phases and across the interface. The size of drops formed on dispersion together with the rate of coalescence of the dispersed phases also involve the viscosity and density along with interfacial tension. Fundamental studies of these phenomena have been attempted ⁽¹²⁾ ⁽¹³⁾ but in general are too incomplete to be directly applicable to the present work.

One relation which would seem significant in countercurrent flow studies is the "Stokes' factor" or the ratio of the density difference between phases to the viscosity of the phase which is continuous. This factor, $\Delta\rho/\eta$, is according to Stoke's Law nearly proportional to the rate of fall or rise of dispersed drops. It is thus related to extraction behavior in determining the time the drop is in contact with the continuous phase and is also related to column flooding and throughput capacity in that the relative motion of the two phases determines the total flow. Thus a high $\Delta\rho/\eta$ would permit a high throughput. From the equations for density and viscosity for TBP-Diluent mixtures and from similar equations for aqueous solutions ⁽¹⁴⁾ the Stoke's factor can be computed for various two-phase systems. ⁽¹⁾

In Tables V and VI the Stokes factors are compared for various regions of interest in the extraction and stripping columns for both the HW #4 Metal Recovery flowsheet ⁽¹⁵⁾ and the ORNL #2 Purex flowsheet. ⁽¹⁶⁾ In the last two columns $\Delta\rho/\eta$ is computed for the solvent-aqueous system using a low density, low viscosity diluent, e. g., "Super Sol", contrasted with one of higher density and viscosity, e. g., Shell "Spray Base". Although this represents a comparatively narrow range in density and viscosity it will be seen that factors of two to three are found in comparing $\Delta\rho/\eta$ values of the two solvent mixtures for either the Metal Recovery system or Purex.

The use of carbon tetrachloride as a diluent produces an organic phase heavier than the aqueous phase and thus inverts the extraction column.

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TABLE V

COMPARISON OF STOKES' FACTORS FOR METAL RECOVERY SYSTEMSHW #4 FLOWSHEET12.5% TBP IN HYDROCARBONS

System	$\Delta \rho / \eta$	
	Low viscosity diluent $\rho_{RAX} = 0.785 \text{ g./cc.}$ $\eta_{RAX} = 11 \text{ millipoises}$	High viscosity diluent $\rho_{RAX} = 0.825 \text{ g./cc.}$ $\eta_{RAX} = 20 \text{ millipoises}$
RAS- $\Delta \rho$	0.26	0.22
RAU $\Delta \rho / \eta \text{ org.}$	0.022	0.0094
$\Delta \rho / \eta \text{ aq.}$	0.024	0.020
RAFS- $\Delta \rho$	0.46	0.42
"RXU" $\Delta \rho / \eta \text{ org.}$	0.035	0.016
$\Delta \rho / \eta \text{ aq.}$	0.029	0.026
RAW- $\Delta \rho$	0.43	0.39
RAX $\Delta \rho / \eta \text{ org.}$	0.039	0.020
$\Delta \rho / \eta \text{ aq.}$	0.031	0.028
RCF- $\Delta \rho$	0.22	0.18
RCU $\Delta \rho / \eta \text{ org.}$	0.018	0.0080
$\Delta \rho / \eta \text{ aq.}$	0.020	0.018
RCW- $\Delta \rho$	0.22	0.18
RCX $\Delta \rho / \eta \text{ org.}$	0.020	0.0090
$\Delta \rho / \eta \text{ aq.}$	0.024	0.020

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TABLE VI

COMPARISON OF STOKES FACTORS FOR PUREX SYSTEMSORNL #2 FLOWSHEET
30% TBP IN HYDROCARBONS

<u>System</u>		$\Delta \rho / \eta$	
		<u>Low viscosity diluent</u>	<u>High viscosity diluent</u>
		$\rho_{\text{IAX}} = 0.820 \text{ g./cc.}$	$\rho_{\text{IAX}} = 0.854 \text{ g./cc.}$
		$\eta_{\text{IAX}} = 12 \text{ millipoises}$	$\eta_{\text{IAX}} = 21 \text{ millipoises}$
IAS-	$\Delta \rho$	0.146	0.112
IAU	$\Delta \rho / \eta \text{ org.}$	0.0082	0.0032
	$\Delta \rho / \eta \text{ aq.}$	0.0133	0.010
IAFS-	$\Delta \rho$	0.348	0.314
	$\Delta \rho / \eta \text{ org.}$	0.018	0.0085
	$\Delta \rho / \eta \text{ aq.}$	0.023	0.021
IAW-	$\Delta \rho$	0.27	0.24
IAX	$\Delta \rho / \eta \text{ org.}$	0.022	0.011
	$\Delta \rho / \eta \text{ aq.}$	0.027	0.024
ICF-	$\Delta \rho$	0.143	0.110
ICU	$\Delta \rho / \eta \text{ org.}$	0.0087	0.0035
	$\Delta \rho / \eta \text{ aq.}$	0.014	0.011
ICW-	$\Delta \rho$	0.180	0.146
ICX	$\Delta \rho / \eta \text{ org.}$	0.015	0.0070
	$\Delta \rho / \eta \text{ aq.}$	0.020	0.010

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A solvent consisting of 10-15% TBP in carbon tetrachloride leads to $\Delta \rho / \eta$ values which are higher for stripping systems, e. g., RC column, and lower for the RA extraction system than those found with hydrocarbon systems. ⁽¹⁾

In a mixer-settler type of column operation both $\Delta \rho / \eta_{aq}$ and $\Delta \rho / \eta_{org.}$ are of interest while if a single continuous phase exists throughout the column then $\Delta \rho / \eta_{cont}$ is the significant factor. The throughput of a column should be limited by the lowest $\Delta \rho / \eta$ reached and flooding would be expected to commence at that point unless compensated by other factors such as larger drops.

G. CHEMICAL STABILITY

Although not of primary concern in this report the chemical stability should be mentioned. The small differences in decontamination found by Moore ⁽⁷⁾ among the various diluents suggests that under normal conditions of contact with aqueous solutions little reaction takes place. Further, evidence obtained at ORNL indicated that extraction coefficients for plutonium were unchanged when the TBP-hydrocarbon (Varsol) mixture was left in contact for two weeks with a radioactive feed solution 3 molar in nitric acid and 0.5 molar in uranyl nitrate. ⁽¹⁷⁾ It was also demonstrated that the solvent mixture could be recycled as much as 10 times without build-up of deleterious impurities. ⁽¹⁸⁾

On the other hand olefins and certain aromatics would be expected to show greater reactivity than paraffin hydrocarbons and Wagner ⁽¹⁹⁾ has shown that considerable nitration of the hydrocarbon diluent occurred when a mixture of TBP-AMSCO 149-92Br was contacted with nitric acid containing a little nitrous acid. A photochemical decomposition of various hydrocarbons in the presence of uranyl nitrate has also been observed but the extent of this reaction has not been investigated further.

It would appear then that under normal conditions of contact with the aqueous streams in a Purex or Metal Recovery process, no trouble would be experienced from diluent decomposition. Off-standard conditions could lead to reactions involving principally the aromatic and olefinic constituents of the hydrocarbon diluent.

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150 17
17
11
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050 05145 7824 18

Figure 2

Viscosity-Flash Point Relation
for Hydrocarbon Mixtures

Viscosity, Millipoises

20
19
18
17
16
15
14
13
12
11
10
9

- 1 Gulf BT
- 2 Stodd. Solv.
- 3 Stodd. Solv. less 10%
- 4 Stodd. Solv. less 30%
- 5 Penola High Flash Varsol
- 6 Super-Sol
- 7 Super-Sol less 30%
- 8 AMSCO 149-92 Br
- 9 Penola Naphtha
- 10 AMSCO 125-90W
- 11 Std Oil Base C
- 12 Std Oil Base B
- 13 Union Oil Base
- 14 Deobase
- 15 Shell Spray Base
- 16 n-decane
- 17 n-dodecane

110 120 130 140 150 160 170

Flash Point, °F

050 119

182 19

3697

03171228030