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PHYSICAL PROPERTIES OF
TRIBUTYLPHOSPHATE-DILUENT SOLUTIONS

By

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PHYSICAL PROPERTIES OF
TRIBUTYLPHOSPHATE-DILUENT SOLUTIONS

INTRODUCTION

Measurements of the physical properties of tributylphosphate (TBP)-diluent systems for diluents having plant application have been reported previously by Burger and Forsman⁽¹⁾. To understand better the interactions between TBP and the diluent, the measurements have now been extended to a wide variety of diluents. In addition, such measurements provide data essential for the understanding of the mechanism of an extraction process when TBP is used as an extractant.

The diluents used were mineral oil, Amsco 125-90W, dodecane, hexane, cyclohexane, benzene, n-octyl bromide, carbon tetrachloride, chloroform, and pentachloroethane. The properties measured were the activity coefficient for the cyclohexane system, solubility of TBP in water for all diluents, solubility of water in the organic phase and partial molal volumes for all diluents except mineral oil and Amsco, viscosity for the diluents hexane, dodecane, cyclohexane, and pentachloroethane, and diffusion coefficients of TBP in cyclohexane, dodecane, and pentachloroethane.

SUMMARY AND CONCLUSIONS

1. The solubility of TBP in water and of water in the TBP phase have been determined as a function of organic phase concentration for several different TBP-diluent mixtures.
2. There is no evidence that a definite TBP-H₂O complex of simple mole ratio exists in any of the TBP-diluent systems studied.
3. The very low solubility of TBP in water from solutions of TBP in chloroform and pentachloroethane confirm earlier indications that these diluents interact with TBP, presumably through the formation of hydrogen bonds.

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4. The activity coefficients for TBP in anhydrous cyclohexane solutions have been determined from freezing point lowering.
5. Viscosities at 25°C for both dry and water saturated solutions of TBP in diluents n-hexane, cyclohexane, n-dodecane, and pentachloroethane have been determined.
6. The viscosity data for the TBP-pentachloroethane system (wet and dry) show maxima at a mole ratio of one to one, suggesting a complex between TBP and pentachloroethane of this mole ratio.
7. The partial molal volume of TBP in the eight diluents investigated was constant up to a 0.75 volume fraction of TBP and very nearly equal to the molal volume of TBP.
8. The self-diffusion coefficient and the diffusion coefficient for TBP at various concentrations in the diluents n-dodecane, pentachloroethane and cyclohexane have been determined at 25°C.

EXPERIMENTAL

A. Methods

The technique used to determine the solubility of TBP in water using P-32 labeled TBP was essentially the same as that described by Burger and Forsman⁽¹⁾. The only change in procedure was to determine the concentration of TBP in the organic phase after contacting with water by counting a sample of appropriate size. This was particularly necessary for the more volatile diluents as appreciable evaporation of the diluent occurred during the equilibration with water.

The determination of water in the organic phase was made with Karl Fischer reagent. Equilibrations were made at room temperature, 24-26°C.

The viscosity was determined at 25°C using an Ostwald viscometer with a kinetic energy correction applied. The density was determined at 25°C with a pycnometer.

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The diffusion coefficient was determined by the method of Anderson and Saddington⁽²⁾. The capillary cells used were made from 1 cm lengths of precision bore capillary cemented with "Airolyte" cement to a glass base. The diameter of the bore was 0.0759 cm, and was uniform to ± 0.0001 cm. Temperature was controlled to $\pm 0.004^{\circ}\text{C}$. The capillary cells were immersed in the outer solution by a hydraulic system at a uniform rate.

Tributyl phosphate labeled with P-32 was used as tracer. The cell was filled with labelled solution. The capillary cell was then placed on the tray which was at such a level that when the jar containing the outer solution was screwed in place only the lower half of the capillary cell was immersed in the outer solution. Fifty milliliters of outer solution containing no tracer labelled TBP was used. After assembling the cell unit, the unit was immersed in the thermostat. Approximately one-half hour was allowed for temperature equilibrium to be obtained and then the capillary cell was totally immersed in the outer solution.

The concentration of the outer solution was adjusted so that its density was slightly less than that of the solution in the capillary cell to minimize convection. The concentration difference between the two solutions amounted to approximately one per cent. Diffusion was allowed to continue until from one-half to two-thirds of the tracer-labelled TBP had diffused from the capillary cell. According to the work of Burkell and Spinks⁽³⁾, this amount of diffusion from the capillary cell should lead to maximum accuracy. The capillary cell was raised from the outer solution, the cell unit taken from the thermostat and disassembled. The contents of the cell were pipetted onto a one-inch watch glass, the cell rinsed four times with cyclohexane, and the rinse solutions added to the solution on the watch glass and the solvent allowed to evaporate for one-half hour at room temperature. The cell was then filled with the same solution as used in the diffusion run and the contents of the cell transferred with a clean pipet to a watch glass and the cell rinsed four times. All

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rinse solutions were transferred to the watch glass. The watch glasses were placed on aluminum trays, covered with cellophane, and counted. The standard was counted immediately before and after the diffusion sample. Comparison of the counts for the two samples gave the concentration of labeled TBP remaining in the cell after diffusion. The results reported here are the average of six determinations at each concentration.

B. Materials

The unlabeled tributylphosphate used was vacuum-distilled prior to use. The P-32 labeled tributylphosphate was a sample kindly supplied by W. H. Baldwin of Oak Ridge National Laboratories. This latter material was washed with sodium carbonate solution and water and dried with anhydrous potassium carbonate before use.

The mineral oil sample was U. S. P. with a boiling point range indicating an average molecular weight corresponding to a C_{18} hydrocarbon.

The hexane and cyclohexane were obtained from Phillips Petroleum Co., and were of 99.1 mole per cent purity.

Pentachloroethane and dodecane were Eastman practical grades. The pentachloroethane was fractionated prior to use. The dodecane was used as received.

The n-octyl bromide was a sample prepared in this laboratory.

The other diluents were Merck reagent grade used without treatment.

RESULTS AND DISCUSSION

A. Solubility Relations in TBP-Diluent-Water Systems

The solubility of TBP in water from solutions of TBP and Amsco has been previously reported⁽¹⁾. Solubility values from Amsco solution have been redetermined in the present work, and it is seen from Figure 1, which presents the two sets of data graphically, that there is fair agreement. The value for 100% TBP is, however, somewhat higher than that

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reported previously. This solubility was determined five times, and the value of 0.44 g/l represents the average of these determinations. The solubility of TBP in water from solutions of the ten diluents studied are given in Table I. These data are presented graphically as Figure 1. In these presentations of the data the volume fraction indicated is the volume fraction of the dry TBP-diluent solution prior to contacting with water.

Water is soluble in TBP and in TBP-diluent solutions to an extent which requires that its presence in the organic phase not be overlooked when considering the equilibria between water and TBP-diluent mixtures. The concentration of water in Amsco solutions of TBP has been reported by Burger and Forsman⁽¹⁾. The solubility of water in the organic phase for all the other diluents given in Table I, with the exception of mineral oil, are given in Table II. The densities of these water saturated solutions as well as the densities of dry TBP diluent solutions are also given in Table II.

The data given in Table II allow the calculation of the mole fraction of the TBP in a diluent system saturated with water. These calculations were made, and a plot of TBP solubility in water against the mole fraction of TBP in the organic at equilibrium is given as Figure 2.

It is interesting to note that if the ratio moles H_2O /moles TBP is plotted against the volume fraction of TBP in the organic prior to saturation with water, the points for all the saturated hydrocarbon diluents fall on the same straight line.

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TABLE I
SOLUBILITY OF TBP IN H₂O (25°C) FROM DILUENT SOLUTIONS
 Solubility in g/l

Vol. % TBP(1)	Diluent									
	Mineral Oil	Amsco	Dodecane	Hexane	Cyclohexane	Benzene	Chloroform	Carbon Tetrachloride	Pentachloro- ethane	n-octyl Bromide
100	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44
71	0.373	0.328	0.341	0.215	0.247	0.100	0.098	0.199	0.200	0.316
59	---	---	---	---	0.193	---	---	---	---	---
54	---	---	---	---	---	---	0.040	0.113	---	---
50	0.328	0.285	0.277	---	---	---	---	---	0.078	0.210
40	---	---	---	---	---	0.037	---	---	---	---
34	---	---	---	---	0.118	---	---	---	---	---
32	---	---	---	0.148	---	---	0.023	---	---	---
30	---	---	---	---	---	---	---	0.044	---	---
25	0.296	0.242	0.244	---	---	---	---	---	0.025	0.107
22	---	---	---	---	---	0.023	---	---	---	---
17	---	---	---	---	---	---	---	0.030	---	---
16	---	---	---	0.090	---	---	---	---	---	---
12.5	0.257	0.179	0.197	---	0.095	0.014	---	---	---	0.058
11	---	---	---	---	---	---	0.010	---	---	---
10	---	---	---	0.069	---	---	---	---	---	---
7.7	---	---	---	---	---	---	---	0.012	---	---
6	0.184	0.111	0.130	---	0.075	---	0.010	---	---	0.030

(1) Dry basis, prior to contacting with water.

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TABLE II

DENSITY AND SOLUBILITY OF WATER IN TBP-DILUENT SYSTEMS

Dry Solutions		H ₂ O Saturated Solutions		
ϕ TBP (vol. fraction)	d^{25}	ϕ TBP	d^{25}	C_{H_2O} (g/l)
a. n-Hexane				
0.0246	0.6639	0.0246	0.6638	0.2
0.0497	0.6717	0.0495	0.6717	0.42
0.0838	0.6829	0.0837	0.6824	0.64
0.0998	0.6876	0.0997	0.6882	1.21
0.1495	0.7036	0.1493	0.7046	1.92
0.2487	0.7357	0.2453	0.7384	5.2
0.4990	0.8158	0.4909	0.8200	18.4
0.7500	0.8954	0.7248	0.9012	35.9
b. Cyclohexane				
0.01754	0.7754	0.0175	0.7756	<0.01
0.04038	0.7803	0.0403	0.7803	0.07
0.05070	0.7822	0.0506	0.7822	0.26
0.08294	0.7902	0.0828	0.7903	0.98
0.1376	0.7990	0.1373	0.7990	1.30
0.1757	0.8065	0.1751	0.8060	2.4
0.2415	0.8181	0.2405	0.8194	4.9
0.3391	0.8296	---	---	---
0.4972	0.8711	0.4891	0.8711	14.1
0.7448	0.9193	0.7184	0.9227	36.0
c. Dodecane				
0.0246	0.7520	0.0246	0.7508	0.24
0.0503	0.7572	0.0503	0.7564	0.62
0.0748	0.7623	0.0747	0.7619	0.99
0.0994	0.7678	0.0992	0.7676	1.57
0.1490	0.7783	0.1487	0.7790	2.21
0.2461	0.7999	0.2445	0.8006	5.8
0.4913	0.8545	0.4824	0.8576	18.1
0.7368	0.9102	0.7108	0.9136	35.5

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TABLE II (contd.)

Dry Solutions		H ₂ O Saturated Solutions		
ϕ TBP (vol. fraction)	d^{25}	ϕ TBP	d^{25}	C _{H₂O} (g/l)
d. Benzene				
0.0255	0.8753	0.0255	0.8753	1.21
0.0742	0.8805	0.0740	0.8801	2.00
0.0992	0.8828	0.0989	0.8826	2.67
0.1005	0.8777	0.1003	0.8776	1.64
0.1486	0.8877	0.1479	0.8876	4.11
0.2481	0.8982	0.2460	0.8979	7.0
0.4965	0.9227	0.4876	0.9236	17.5
0.7450	0.9469	0.7167	0.9488	37.9
e. n-Octyl bromide				
0.0251	1.1028	0.0251	1.1030	0.53
0.0497	1.0993	0.0497	1.0993	0.76
0.0741	1.0958	0.0741	1.0958	1.05
0.0993	1.0925	0.0992	1.0921	1.49
0.1488	1.0856	0.1484	1.0849	2.28
0.2488	1.0715	0.2475	1.0708	4.73
0.4967	1.0377	0.4896	1.0368	15.2
0.7454	1.0045	0.7211	1.0047	32.9
f. Carbon tetrachloride				
0.0247	1.5692	0.0247	1.5691	<0.1
0.0490	1.5538	0.0490	1.5538	<0.1
0.0740	1.5393	0.0739	1.5385	1.0
0.0991	1.5245	0.0991	1.5249	1.05
0.1481	1.4951	0.1477	1.4933	1.65
0.2479	1.4347	0.2467	1.4317	3.66
0.4961	1.2836	0.4896	1.2785	11.7
0.7480	1.1298	0.7251	1.1240	28.7
g. Chloroform				
0.0248	1.4611	0.0247	1.4608	1.55
0.0495	1.4482	0.0494	1.4480	1.87
0.0745	1.4361	0.0744	1.4345	2.03

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TABLE II (contd.)

Dry Solutions		H ₂ O Saturated Solutions		
ϕ TBP (vol. fraction)	d^{25}	ϕ TBP	d^{25}	C_{H_2O} (g/l)
g. Chloroform (contd.)				
0. 0992	1. 4239	0. 0990	1. 4224	
0. 1488	1. 3978	0. 1484	1. 3966	2. 36
0. 2481	1. 3487	0. 2468	1. 3452	2. 60
0. 4966	1. 2241	0. 4923	1. 2202	3. 54
0. 7442	1. 0983	0. 7321	1. 0984	6. 7
				18. 0
h. Pentachloroethane				
0. 0249	1. 6535	0. 0249	1. 6531	1. 05
0. 0493	1. 6369	0. 0492	1. 6363	1. 58
0. 0944	1. 6189	0. 0943	1. 6199	1. 41
0. 0992	1. 5993	0. 0991	1. 5987	1. 11
0. 1490	1. 5685	0. 1487	1. 5674	1. 33
0. 2590	1. 4989	0. 2585	1. 4979	1. 71
0. 5004	1. 3248	0. 4955	1. 3191	7. 3
0. 7516	1. 1479	0. 7328	1. 1446	25. 5

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Comparing the water solubility of TBP from the paraffin hydrocarbons, either on the volume fraction or mole fraction basis, it is seen that the water solubility increases with increasing molecular weight of the diluent. The difference between the curves for hexane and cyclohexane as well as the very low solubility of TBP from benzene solutions suggests that better correlation might be obtained on the basis of the molal volume or internal pressure, $\frac{\Delta E^v}{V}$, of the diluent. Values of the molal volume and internal pressures for those diluents for which data are available are given in Table III. The molal volume of the diluent is seen to qualitatively follow the observed differences in solubility of TBP from the various diluents. No simple relationship is evident between the internal pressure of the diluent and solubility of TBP in water.

TABLE III
MOLAL VOLUMES AND INTERNAL PRESSURES,
 $(\frac{\Delta E^v}{V})$ FOR VARIOUS DILUENTS AT 25°C

<u>Diluent</u>	<u>Molal Volume</u>	<u>$\frac{\Delta E^v}{V}$</u>
Dodecane	228.6	61.5
n-Hexane	131.5	52.8
Cyclohexane	108.6	67.9
Benzene	90.5	82.9
n-Octyl bromide	174.6	--
Carbon tetrachloride	97.1	58.2
Chloroform	80.8	--

The very low solubility of TBP in water from solutions of chloroform and pentachloroethane is not unexpected since both of these diluents possess a hydrogen atom capable of forming a hydrogen bond with tributylphosphate. In the use of pentachloroethane the low distribution coefficient for uranyl nitrate between water and TBP, in this diluent, also points to interaction between TBP and pentachloroethane. In the section on viscosity

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further evidence of interaction will be presented which suggests a one to one interaction between TBP and the diluent. Such an interaction would be expected to lower the activity of TBP in the organic phase leading to the lowered water solubility of the TBP observed.

B. Activity Coefficient of TBP from Solubility Data

In principle these solubility data may be used to calculate the activity and activity coefficient of TBP in the various diluents. The solubility of the diluents in the aqueous is sufficiently low that treating the aqueous phase as a two component system of TBP and H_2O is justified. The method of Colburn and Schoenborn⁽⁴⁾ was used to evaluate the constants in the van Laar equation

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{A}{B} \frac{X_1}{X_2}\right)^2}$$

where γ_1 is the activity coefficient of TBP, X_1 is the mole fraction of TBP, X_2 is the mole fraction of the diluent, A and B are constants. The values of the constants in the above equation were found to be $A = 4.29$, $B = 0.34$, giving an activity coefficient of 1.9×10^4 for TBP in water at saturation. Since the aqueous phase remains very dilute, it is easy to demonstrate by means of equations of the van Laar or Margules type that the activity coefficient of TBP in water will remain essentially constant over the entire range of concentrations of TBP in water. The activity coefficient evaluated in this way is only an approximation as this system is too unsymmetrical to expect the equations used to hold with any degree of accuracy. The activity of TBP in water saturated TBP, then, is 0.57, which is not unreasonable since its mole fraction is 0.492.

At the very low concentrations of TBP in the aqueous encountered here, it is evident that the activity of TBP in the aqueous phase is directly proportional to the concentration of TBP expressed as grams TBP per liter

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of solution. Figures 1 and 2, then, may be considered to be equivalent to plots of activities of TBP vs. the volume fraction and mole fraction of TBP, respectively, since the activity of TBP in both the organic and aqueous phases must be equal at equilibrium. For an ideal solution a plot such as Figure 2 should be a straight line provided the TBP exists as the same species in both phases. It is seen that none of the solutions studied give a linear plot. On the basis of the present data this may be interpreted as deviations from ideality and/or a difference in the distributing species in the two phases.

If an estimate of the activity coefficient of TBP in water-saturated TBP diluent solution is desired, the equation,

$$\frac{\gamma_{\text{TBP}}^I}{X_{\text{TBP}}^I} = \frac{(1.9 \times 10^4) (X_{\text{TBP}})}{X_{\text{TBP}}^I} \quad (2)$$

where the primes refer to the organic phase, may be applied.

C. Activity Coefficient of TBP in Cyclohexane Solutions

The activity of cyclohexane in TBP-cyclohexane solutions from the freezing point lowering was evaluated by means of the equation:

$$-\ln A_1 = (4.11 \times 10^{-3}) \Delta T_f + (2.96 \times 10^{-6}) \Delta T_f^2 \quad (3)$$

where ΔT_f is the freezing point lowering, and A_1 is the activity of cyclohexane. The constants in the equation are based on cryoscopic data obtained from the "2" tables of the American Petroleum Institute Research Project 44⁽⁵⁾. Molal activity coefficients of TBP were evaluated from the activity of the solvent using the "h" function of Randall and White⁽⁶⁾.

The freezing point lowering and molal activity coefficients for TBP are given in Table IV.

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TABLE IV

FREEZING POINT LOWERING AND MOLAL ACTIVITY COEFFICIENTS
AT THE FREEZING POINT FOR CYCLOHEXANE SOLUTIONS OF TBP

<u>Molality TBP</u>	<u>Freezing Point Lowering, $\Delta^\circ\text{C}$</u>	<u>$-\ln A_1 \times 10^3$</u>	<u>$\frac{m}{\gamma_2}$</u>
0.496	0.962	3.95	0.90
0.0962	1.774	7.30	0.82
0.1306	2.407	9.91	0.79
0.1457	2.552	10.51	0.75
0.2033	3.473	14.31	0.70
0.2773	4.402	18.15	0.62
0.5079	7.360	30.40	0.50
0.8486	11.013	45.62	0.39
2.408	22.21	92.74	0.23

Since the volume change of mixing of TBP and cyclohexane is small, an attempt was made to fit the data to the Hildebrand-Scatchard equation,

$$\ln A_1 = \ln \phi_1 + \phi_2 \left(1 - \frac{V_1}{V_2}\right) + V_1 \phi_2^2 (\delta_1 - \delta_2)^2 / RT. \quad (4)$$

where V_1 = molal volume TBP, V_2 = molal volume cyclohexane, ϕ_1 = volume fraction TBP, ϕ_2 = volume fraction cyclohexane. No heat of vaporization data for TBP were available so the term $(\delta_1 - \delta_2)^2$ was simply taken as an adjustable parameter. It was found, however, that no value of $(\delta_1 - \delta_2)$ could be found which give a fit to the experimental data. Attempts to fit the data to equations such as the van Laar and Margules equations were equally unsuccessful.

D. Viscosity

The viscosity at 25°C of both dry and water saturated solutions was measured for the diluents n-hexane, cyclohexane, n-dodecane, and penta-chloroethane. The equation

$$\log \eta_{\text{mix}} = X_{\text{TBP}} \log \eta_{\text{TBP}} + X_{\text{dil}} \log \eta_{\text{dil}} \quad (5)$$

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where X_{TBP} and X_{dil} are the mole fractions of TBP and diluent, respectively, does not represent the data for any of these systems, the error being as high as 20%. No better agreement was achieved by the use of the equation,

$$\log \eta_{\text{mix}} = \phi_{\text{TBP}} \log \eta_{\text{TBP}} + \phi_{\text{dil}} \log \eta_{\text{TBP}} \quad (6)$$

where ϕ_{TBP} and ϕ_{dil} are the volume fractions of TBP and diluent, respectively.

Burger and Forsman⁽¹⁾ found for diluents such as Amsco 125-90 W and Gulf BT that an equation of the type,

$$\log \eta_{\text{mix}} = \phi_{\text{TBP}} (A + B \phi_{\text{TBP}}) + \phi_{\text{dil}} \log \eta_{\text{dil}} \quad (7)$$

fit the viscosity data very well for water saturated solutions. For TBP solutions in n-hexane, cyclohexane, n-dodecane and pentachloroethane the data did not fit such an equation either for the dry or the water saturated solution. The best values that could be obtained for the constants A and B gave values for η_{mix} were several per cent different from the observed values.

The viscosity data for these systems is given in Table V. It will be noted that the viscosity of TBP-pentachloroethane solutions, both dry and water saturated, pass through a maximum at a volume fraction of TBP of about 0.7. This corresponds to a mole ratio of 1 to 1, indicating the interaction of TBP and pentachloroethane presumably by hydrogen bonding to form a 1 to 1 complex.

The fact that the viscosity of these solutions cannot be represented by equations of the type presented here is not surprising since these are not ideal solutions.

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TABLE V

VISCOSITY OF DRY AND WATER SATURATED TBP-DILUENT MIXTURES AT 25°C

n-Hexane			Dodecane			Cyclohexane			Pentachloroethane		
ϕ_{TBP} (dry basis)	η_{dry}^{25}	η_{sat}^{25}	ϕ_{TBP}	η_{dry}^{25}	η_{sat}^{25}	ϕ_{TBP}	η_{dry}^{25}	η_{sat}^{25}	ϕ_{TBP}	η_{dry}^{25}	η_{sat}^{25}
0.0246	3.09	3.09	0.0246	13.62	13.59	0.01754	8.85	8.86	0.0249	22.54	22.25
0.0497	3.25	3.26	0.0503	13.88	13.68	0.04038	9.01	9.03	0.0493	23.06	23.01
0.0838	3.39	3.41	0.0748	14.03	14.04	0.05070	9.06	9.05	0.0944	23.89	23.81
0.0998	3.50	3.53	0.0994	14.21	14.25	0.08294	9.34	9.34	0.0992	24.81	24.59
0.1495	3.81	3.88	0.1490	14.74	14.73	0.1376	9.70	9.68	0.1490	26.59	26.36
0.2487	4.63	4.84	0.2461	15.77	16.04	0.1757	10.04	10.10	0.2590	30.35	30.33
0.4990	7.97	8.94	0.4913	19.36	21.09	0.2415	10.67	10.91	0.5004	41.28	40.15
0.7500	15.25	18.33	0.7368	24.58	28.04	0.3391	11.40	---	0.7516	43.93	42.21
						0.4972	14.51	15.64			
						0.7448	21.19	24.07			

E. Partial Molal Volume

The partial molal volume of TBP in the diluents used was calculated for the dry solutions from the density data presented in Table II. In all cases the partial molal volume of TBP was found to be constant from 0 to 0.75 volume fraction and to differ but slightly from the molal volume of TBP. The partial molal volume of TBP in the various diluents used are given in Table VI. The constancy of the partial molal volume is somewhat unexpected in view of the large departures from ideal, as shown by the freezing point lowering, solubility, viscosity, etc.

TABLE VI

PARTIAL MOLAL VOLUME OF TBP IN VARIOUS DILUENTS AT 25°C

<u>Diluent</u>	<u>Partial Molal Volume TBP</u>	<u>Diluent</u>	<u>Partial Molal Volume TBP</u>
Dodecane	275.2	n-octyl bromide	275.3
Hexane	272.6	Carbon tetrachloride	273.6
Cyclohexane	274.5	Chloroform	275.3
Benzene	273.3	Pentachloroethane	273.0

Molal volume TBP = 273.7.

F. Diffusion

Of the various types of diffusion coefficient which can be defined⁽⁸⁾ and measured, a diffusion coefficient which involves no mass flow is probably of the greatest value for fundamental studies of solvent extraction. The capillary cell method of Saddington and Anderson provides such a diffusion coefficient. In this method the diffusion is followed by tracer techniques so that essentially no concentration gradient is present and no mass transport of solvent occurs. The diffusion coefficient evaluated by these methods is characteristic of TBP and does not necessarily equal that of the solvent.

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The diffusion coefficients at 25°C for TBP in cyclohexane, dodecane, and pentachloroethane and the self diffusion coefficient of TBP are given in Table VII. An inspection of Table VII shows that for a given solvent the product $D\eta$ is fairly constant. The low diffusion coefficient of TBP in pentachloroethane is apparently due in a large part to the higher viscosity of this diluent, as can be seen by the close agreement between the values of $D\eta$ for dodecane and pentachloroethane.

TABLE VII
DIFFUSION COEFFICIENTS OF TBP AT 25°C

Diluent	Volume Fraction TBP	$D \times 10^6$ (cm ² /sec)	$D\eta \times 10^6$ dyne
Cyclohexane	10.3	5.56 ± 0.17	51.7
Dodecane	10.0	4.88 ± 0.05	69.5
	32.5	4.27 ± 0.11	71.7
	58.0	3.24 ± 0.05	68.2
Pentachloroethane	10.4	2.73 ± 0.05	66.8
	29.7	2.08 ± 0.03	67.4
None	100	2.29 ± 0.01	76.0

For ideal solutions the Nernst-Einstein relation,

$$D\eta = \frac{kT}{6\pi r} \quad \text{relates the product } D\eta \text{ to the radius} \quad (8)$$

where r is the radius of the molecule considered as a sphere. The derivation of equation (8) requires that the dimensions of the diffusing particles be large compared to that of the solvent. In binary mixtures the product $D\eta$ may vary inversely as some average linear dimension of the molecules. The theory of absolute reaction rates gives a relation similar to equation (8). The constancy of the product $D\eta$ for the systems studied fits well with the observed constancy of the partial molal volumes of TBP and diluent.

The above considerations should apply only to ideal mixtures. It is surprising therefore that the product $D\eta$ is essentially constant for these TBP-diluent mixtures, which other evidence suggests are far from ideal.

The diffusion coefficient of uranyl nitrate is $5 \times 10^{-6} \text{ cm}^2/\text{sec}^{(9)}$, which is of the same order as the diffusion coefficient of TBP in dodecane. On the basis of the two-film theory of liquid-liquid extraction, this suggests that the rate of diffusion of TBP to the interface may be a rate-controlling step in the extraction of uranyl nitrate using TBP as the extractant. Experiments in which Amsco was used as the diluent⁽¹⁰⁾ on extraction into single drops have shown the organic and aqueous film transfer coefficients to be nearly equal. At least qualitatively, the concept of the rate of diffusion of TBP is in agreement with this fact.

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ABSTRACT

In connection with the study of aqueous-tributylphosphate (TBP) systems, the study of the interactions of various diluents with the TBP has been extended. The diluents used were mineral oil, Amsco 125-90W, dodecane, n-hexane, cyclohexane, benzene, n-octyl bromide, carbon tetrachloride, chloroform, and pentachloroethane. The solubility of TBP in water from solutions of these diluents and the solubility of water in the organic phase was determined. For the paraffin hydrocarbons as diluents the solubility of TBP in water was found to increase with increasing molal volume of the diluent. No evidence for the formation of a TBP-water complex of simple mole ratio was found.

The partial molal volume of TBP in all the diluents was constant up to a volume fraction of 0.75 and equal to the molal volume of TBP within ± 0.5 per cent.

No simple relationship could be found which related the viscosity to the concentration for TBP in the diluents dodecane, n-hexane, cyclohexane, and pentachloroethane whether the solutions were dry or water-saturated.

The self-diffusion coefficient of TBP was found to be 2.29×10^{-6} cm²/sec. For dodecane and pentachloroethane solutions the product $D\eta$ was found to be essentially constant.

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