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THERMODYNAMICS OF EXTRACTION OF NITRIC ACID BY TRI-n-BUTYL
PHOSPHATE--HYDROCARBON DILUENT SOLUTIONS

2. Densities, Molar Volumes, and Water Solubilities of TBP-Amsco 125-82-HNO₃-
H₂O Solutions

Wallace Davis, Jr.

ABSTRACT

Densities and water contents of nearly dry and of water-saturated TBP-Amsco 125-82 solutions were measured. From these the molar volumes of TBP and this diluent were calculated to be 273.6 and 246.4 ml, respectively, in the pure dry state. Within experimental accuracy, the molar volume of water was 18 ml in all solutions. Using this value for water, the molar volume of nitric acid in TBP-Amsco 125-82-HNO₃-H₂O solutions was calculated, from data previously presented (1), to be between 40.9 and 43.7 ml, the specific value depending on the TBP/diluent ratio. Solutions of TBP and the diluent are nearly ideal with respect to additivity of volumes, the maximum deviation from ideality being ~0.4%, or ~1 ml per mole of solution based on a diluent gram molecular weight of 185. The water content of TBP saturated with water at 25°C corresponds to a mole ratio $Y_{H_2O}^o / Y_{TBP}^o = 1.045 \pm 0.001$.

This paper is for review by Nuclear Science and Engineering.

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2. Densities, Molar Volumes, and Water Solubilities of TBP-Amsco 125-82-
 $\text{HNO}_3 - \text{H}_2\text{O}$ Solutions

by

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THERMODYNAMICS OF EXTRACTION OF NITRIC ACID BY TBP

2. Densities, Molar Volumes, and Water Solubilities

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ABSTRACT

Densities and water contents of nearly dry and of water-saturated TBP-Amsco 125-82 solutions were measured. From these the molar volumes of TBP and this diluent were calculated to be 273.6 and 246.4 ml, respectively, in the pure dry state. Within experimental accuracy, the molar volume of water was 18 ml in all solutions. Using this value for water, the molar volume of nitric acid in TBP-Amsco 125-82-HNO₃-H₂O solutions was calculated, from data previously presented (1), to be between 40.9 and 43.7 ml, the specific value depending on the TBP/diluent ratio. Solutions of TBP and the diluent are nearly ideal with respect to additivity of volumes, the maximum deviation from ideality being ~0.4%, or ~1 ml per mole of solution based on a diluent gram molecular weight of 185. The water content of TBP saturated with water at 25°C corresponds to a mole ratio $Y_{H_2O}^o / Y_{TBP}^o = 1.045 \pm 0.001$.

INTRODUCTION

The purpose of this report is to present data on the densities of TBP-Amsco 125-82-H₂O solutions and to summarize some of the thermodynamic properties subsequently calculated from these and previously reported densities (1) of similar solutions that also contained nitric acid.

Densities of the organic phase have frequently not been measured by people studying the equilibrium extraction of nitrates by TBP-hydrocarbon diluent solutions, although such data are needed for accurate calculations of thermodynamic equilibrium constants and for the eventual calculation of distribution coefficients under conditions not specifically studied experimentally. Tuck (2) measured volume changes of diluent-free TBP during the extraction of nitric acid and determined a molar volume of 41.5 ml for this acid. He also reported a change in the slope of the organic volume vs HNO₃ concentration at a point corresponding to a mole ratio $(\text{HNO}_3)_{\text{org}}/(\text{TBP}_s) = 1$. At higher ratios he reported a value of 55 ml as the molar volume of nitric acid. Tuck's interpretation of his data was based on the assumption that one mole of water is displaced from the TBP phase for each mole of nitric acid entering it, an assumption which was shown to be correct (1) only for $(\text{HNO}_3)_{\text{org}}/(\text{TBP}_s)$ ratios up to ~ 0.13 . At higher organic acidities the water content first remains constant at a $(\text{H}_2\text{O})_{\text{org}}/(\text{TBP}_s)$ value of 0.77 in the region $0.13 \leq (\text{HNO}_3)_{\text{org}}/(\text{TBP}_s) \leq 0.4$, and then decreases according to $-\Delta(\text{H}_2\text{O})_{\text{org}}/\Delta(\text{HNO}_3)_{\text{org}} \approx 0.5$ as the acidity is further increased to a value $(\text{HNO}_3)_{\text{org}}/(\text{TBP}_s) = 1$.

Data of the present report include densities of TBP-Amsco 125-82-H₂O solutions containing 5 to 100 vol % TBP in the diluent. Derived thermodynamic functions include the partial molar volumes of TBP, Amsco 125-82, HNO₃, and H₂O.

EXPERIMENTAL

Solutions of TBP in Amsco 125-82 were synthesized by weight using materials purified as described previously (1). Weights of each were corrected for water contents determined by the method described by Kelley et al. (3). The picnometric density at $\sim 25^\circ\text{C}$ and water content of each solution were determined, at least in duplicate, before and after vigorous contacting with water (Table 1). Duplicate densities with 10-ml pycnometers showed differences between 0.0000 and 0.0003 g/ml; water analyses were duplicated within a few per cent.

The two, or three, sets of primary data (Table 1) at each ratio $(\text{Dil})_{\text{org}}/(\text{TBP})_{\text{org}}$ were used to calculate the molal volume of the dry organic solution, V_{dry} , and the partial molar volume of water, $\bar{V}_{\text{H}_2\text{O}}$, by use of the equation

$$V = \frac{1}{\rho_{\text{org}}} \left(\frac{W_{\text{Dil}}}{W_{\text{TBP}}} + 1 \right) = V_{\text{dry}} + \bar{V}_{\text{H}_2\text{O}} \left[\frac{W_{\text{H}_2\text{O}}}{18.016 \rho_{\text{org}}} \left(\frac{W_{\text{Dil}}}{W_{\text{TBP}}} + 1 \right) \right] \quad (1)$$

where ρ_{org} is the density of the organic solution, g/ml or kg/liter; $W_{\text{H}_2\text{O}}$ is the water content, mg/ml; and $W_{\text{Dil}}/W_{\text{TBP}}$ is the weight ratio of diluent to TBP. This linear equation may be an oversimplification of the volume-concentration relation, but its use should not introduce significant errors in V_{dry} and $\bar{V}_{\text{H}_2\text{O}}$ since one of the two, or three, solutions at each $(\text{Dil})/(\text{TBP})$ ratio was nearly anhydrous; i.e., the degree of extrapolation to calculate V_{dry} is very small.

RESULTS

Partial Molar Volumes. Except for solutions containing only 5 or 10% TBP in the diluent, and therefore having the lowest dissolved water and density changes during the water saturation process, the molar volume of water (Table 1) is 18 ml, within experimental error. In analyzing the density-concentration data of TBP-Amsco 125-82-HNO₃-H₂O solutions, the molar volume of water was assumed to be identically 18 ml (Table 2).

Apparent molar volumes of TBP and Amsco 125-82 were calculated from the equations

$$\phi_{\text{TBP}} = \frac{V_{\text{dry}} - (\text{Dil})^m V_{\text{Dil}}^{\circ}}{3.75493} \quad (2)$$

and

$$\phi_{\text{Dil}} = \left(\frac{0.185}{\frac{W_{\text{Dil}}}{W_{\text{TBP}}}} \right) \left[\frac{1}{\rho} \left(1 + \frac{W_{\text{Dil}}}{W_{\text{TBP}}} \right) - \frac{1}{\rho_{\text{TBP}}^{\circ}} \right] \quad (3)$$

where ϕ_{TBP} and ϕ_{Dil} are the apparent molar volumes of TBP and diluent, respectively, $(\text{Dil})^m$ is the molality (moles diluent/kg TBP) of the diluent, based on an average gram molecular weight of Amsco 125-82 equal to 185, V_{Dil}° is the molar volume of dry diluent, ρ and $\rho_{\text{TBP}}^{\circ}$ are densities of dry solution and dry TBP, respectively.

Apparent molar volumes were plotted against the corresponding mole ratio, as for TBP in Fig. 1, and the curve through these data was used to obtain the quantities

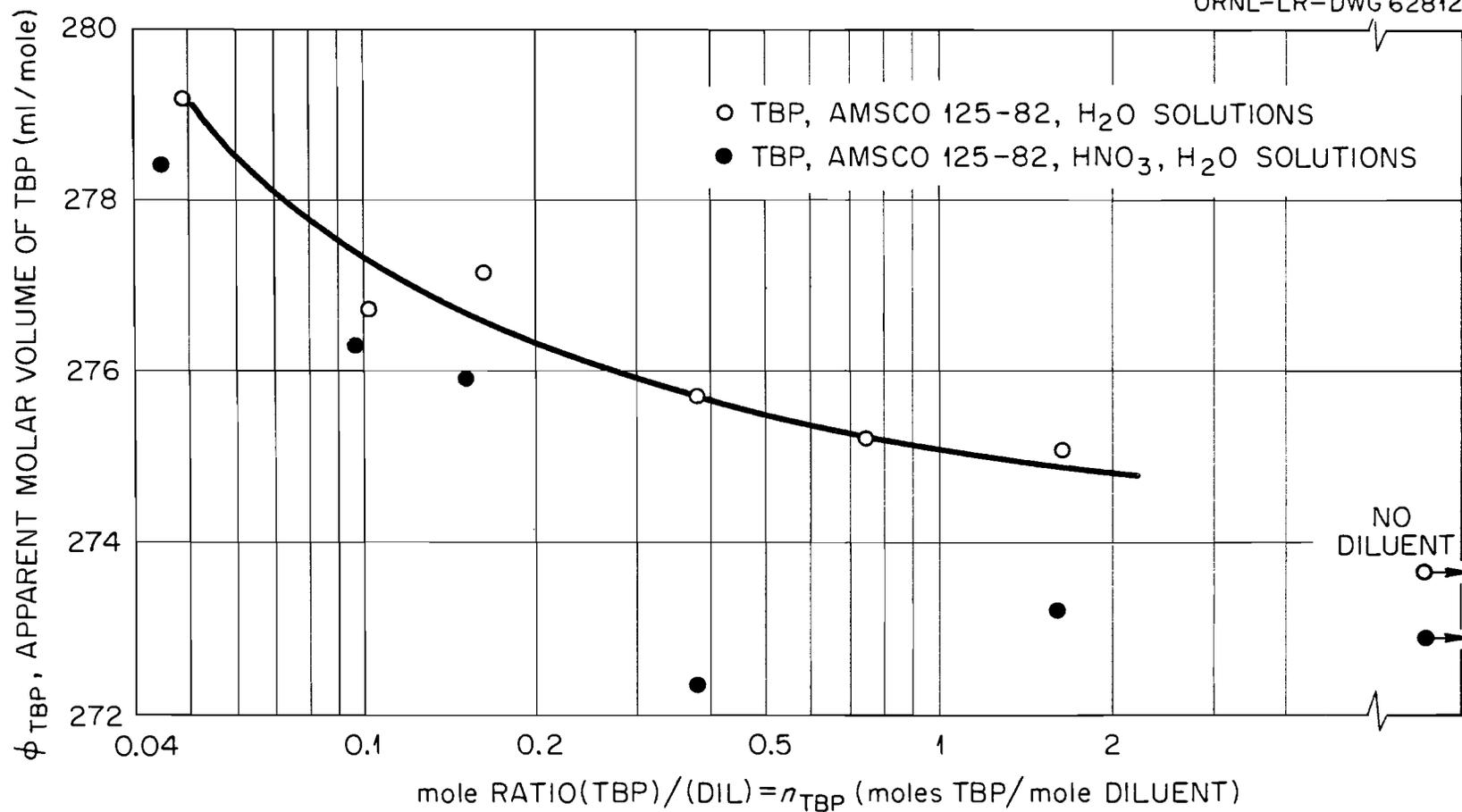


Fig.1. Variation of Apparent Molar Volume of TBP, with its Concentration in Amsco 125-82.

Table 1. Volume Parameters for TBP-Amsco 125-82-H₂O Solutions at 25°C^a

Nominal TBP Conc (vol %)	Weight Ratio, W _{Dil} /W _{TBP}	H ₂ O Conc, W _{H₂O} (mg/ml)	Density, ρ _{org} (g/ml)	Dry Molal Volume V _{dry} (l/kg TBP)	H ₂ O Part. Molar Vol, V̄ _{H₂O} (ml/mole)	Mole Ratio, ^d (Dil)/(TBP)	Partial Molar Volumes in Dry Solution ^d (ml/mole)	
							V̄ _{TBP}	V̄ _{Dil}
0		< 0.025	0.7507	---	---		---	246.4
5	14.19	0.083 0.35	0.76165 0.7617	19.948	23.	20.43	275.5	245.6
10	6.80	0.224 1.10	0.7727 0.77275	10.091	24.	7.786	274.9	246.0
15	4.325	0.32 1.81	0.7832 0.7836	6.800	17.	6.226	275.9	246.4
30	1.814	0.635 7.24	0.8155 0.8168	3.451	18.0	2.612	274.8	246.6
45	0.9291	1.10 14.91	0.8498 0.85245	2.2706	17.1	1.3375	274.5	247.0
65	0.4238	1.26 24.45	0.8916 0.89455	1.5972	17.6	0.6110	274.5	248.1
80	0.1970	1.79 34.90 37.01	0.9265 0.9302 0.9301	1.2917	18.1	0.2835	273.8	247.3
100	0.0000	0.22 1.8 64.372 ^b	0.97245 0.9725 0.97518 ^c	1.0275	18.0	0.0000	273.6	---

^aEach density and water value listed is the average of 2 or 3 determinations, except as noted. The highest water content for each TBP-diluent solution corresponds to saturation.

^bAverage of 25 values with standard deviation = 1.343 mg H₂O/ml.

^cAverage of 10 duplicate values with standard deviation = 0.00022 g/ml.

^dBased on gram molecular weight of Amsco 125-82 of 185.0.

$$\left[\frac{\partial \phi_{\text{TBP}}}{\partial \ln \left(\frac{m_{\text{TBP}}}{m_{\text{Dil}}} \right)} \right]_{m_{\text{Dil}}} \quad \text{and} \quad \left[\frac{\partial \phi_{\text{Dil}}}{\partial \ln \left(\frac{m_{\text{Dil}}}{m_{\text{TBP}}} \right)} \right]_{m_{\text{TBP}}}$$

for calculation of the partial molar volumes \bar{V}_{TBP} and \bar{V}_{Dil} of TBP and diluent (Table 1)

from the equations

$$\bar{V}_{\text{TBP}} = \phi_{\text{TBP}} + \left[\frac{\partial \phi_{\text{TBP}}}{\partial \ln \left(\frac{m_{\text{TBP}}}{m_{\text{Dil}}} \right)} \right]_{m_{\text{Dil}}} \quad (4)$$

$$\bar{V}_{\text{Dil}} = \phi_{\text{Dil}} + \left[\frac{\partial \phi_{\text{Dil}}}{\partial \ln \left(\frac{m_{\text{Dil}}}{m_{\text{TBP}}} \right)} \right]_{m_{\text{TBP}}} \quad (5)$$

Only the data of Table 1 were used in drawing the curve of Fig. 1; the apparent molar volumes calculated from the data of Table 2* are shown only for comparison. From these calculations the values of $\bar{V}_{\text{TBP}} = 273.6$ ml/mole for diluent-free, dry TBP and $\bar{V}_{\text{Dil}} = 246.4$ ml/mole for TBP-free, dry Amsco 125-82 were obtained.

* Table 2 gives apparent molar volumes lower than those calculated from Table 1, probably because the apparent molar volume of dry TBP is only 1.0248 liters, which is 2.7 ml lower than the corresponding value in Table 1.

Table 2. Volume Parameters for TBP--Amsco 125-82--H₂O--HNO₃ Solutions at 25°C

Nominal TBP Conc (vol %)	Weight Ratio, W_{Dil}/W_{TBP}	Dry Molal Volume V_{dry} (l/kg TBP)	HNO ₃ Part. Molar Vol, ^a \bar{V}_{HNO_3} (ml/mole)	Calc. Dry Density (g/ml)	Apparent Molar Volumes in Dry Solution (ml/mole)	
					ϕ_{TBP}	ϕ_{Dil}
0		---	---	---	---	(246.4)
5	15.541	21.739 $\sigma = 0.002$	43.73 1.06	0.7609	278.4	246.6
10	7.231	10.666 $\sigma = 0.001$	42.95 0.65	0.7717	276.3	246.7
15	4.612	7.177 $\sigma = 0.001$	42.59 0.75	0.7819	275.9	246.8
30	1.8050	3.426 $\sigma = 0.001$	40.93 0.85	0.8187	272.3	246.1
65	0.4353	1.6056 $\sigma = 0.0008$	42.83 0.46	0.8939	273.2	246.8
100	0.0000	1.0248 $\sigma = 0.0006$	42.46 0.41	0.9758	272.9	---

^aBased on a molar volume of H₂O equal to 18 ml.

The partial molar volumes of TBP and Amsco 125-82 do not vary much with composition, as would be expected for such solutions. If the ideal volume, V_i , is defined as

$$V_i = 273.6 Y_{\text{TBP}} + 246.4 Y_{\text{Dil}} \quad (6)$$

then the deviation of the solution from ideality is given by

$$V_{\text{obs}} - V_i = Y_{\text{TBP}} \left\{ \bar{V}_{\text{TBP}} - 273.6 \right\} + Y_{\text{Dil}} \left\{ \bar{V}_{\text{Dil}} - 246.4 \right\} \quad (7)$$

where

$$V_{\text{obs}} = Y_{\text{TBP}} \bar{V}_{\text{TBP}} + Y_{\text{Dil}} \bar{V}_{\text{Dil}} \quad (8)$$

The difference, $V_{\text{obs}} - V_i$, (Fig. 2) shows a maximum of ~ 1 ml out of ~ 250 ml, or 0.4% from ideality.

Solubility of Water in TBP-Hydrocarbon Diluent. As shown in a previous paper (1), an important variable in the extraction of nitric acid by TBP-Amsco 125-82 solutions, in addition to $(\text{HNO}_3)_{\text{org}}$ itself, is $Y_{\text{H}_2\text{O}}^{\circ} + Y_{\text{TBP}}^{\circ}$, the sum of the mole fractions of water and TBP in the acid-free TBP-diluent solution. Solubilities of water in the acid-free organic solutions are given in Table 1; these and the solubilities reported by Wagner and Farrand (4) who also used Amsco 125-82 as the diluent, by Healy and Brown (5) who used an odorless kerosene, and by Olander, Donadieu, and Benedict (6) who used n -hexane are summarized in Fig. 3. Lines in this figure are drawn through the data of this report and through the data of reference 6. In the region 20 to 80% TBP in the diluents Amsco 125-82 or odorless kerosene, the solubility, $Y_{\text{H}_2\text{O}}^{\circ}$, is very nearly a linear function of the

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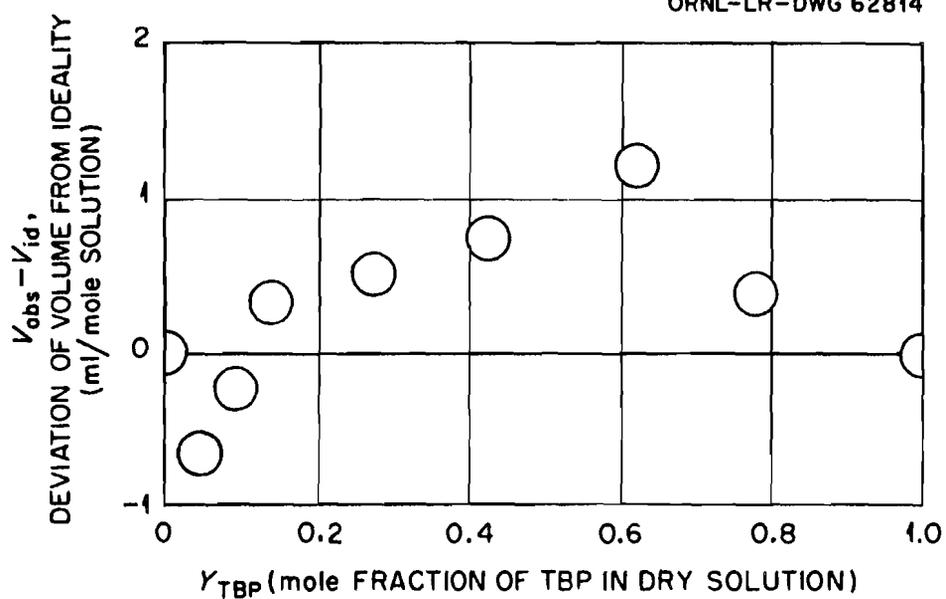


Fig. 2. Deviation of Volume of TBP-Amsco 125-82 Solutions from Volume Ideality. $V_{id} = 273.6 Y_{TBP} + 246.4 Y_{Dil}$.

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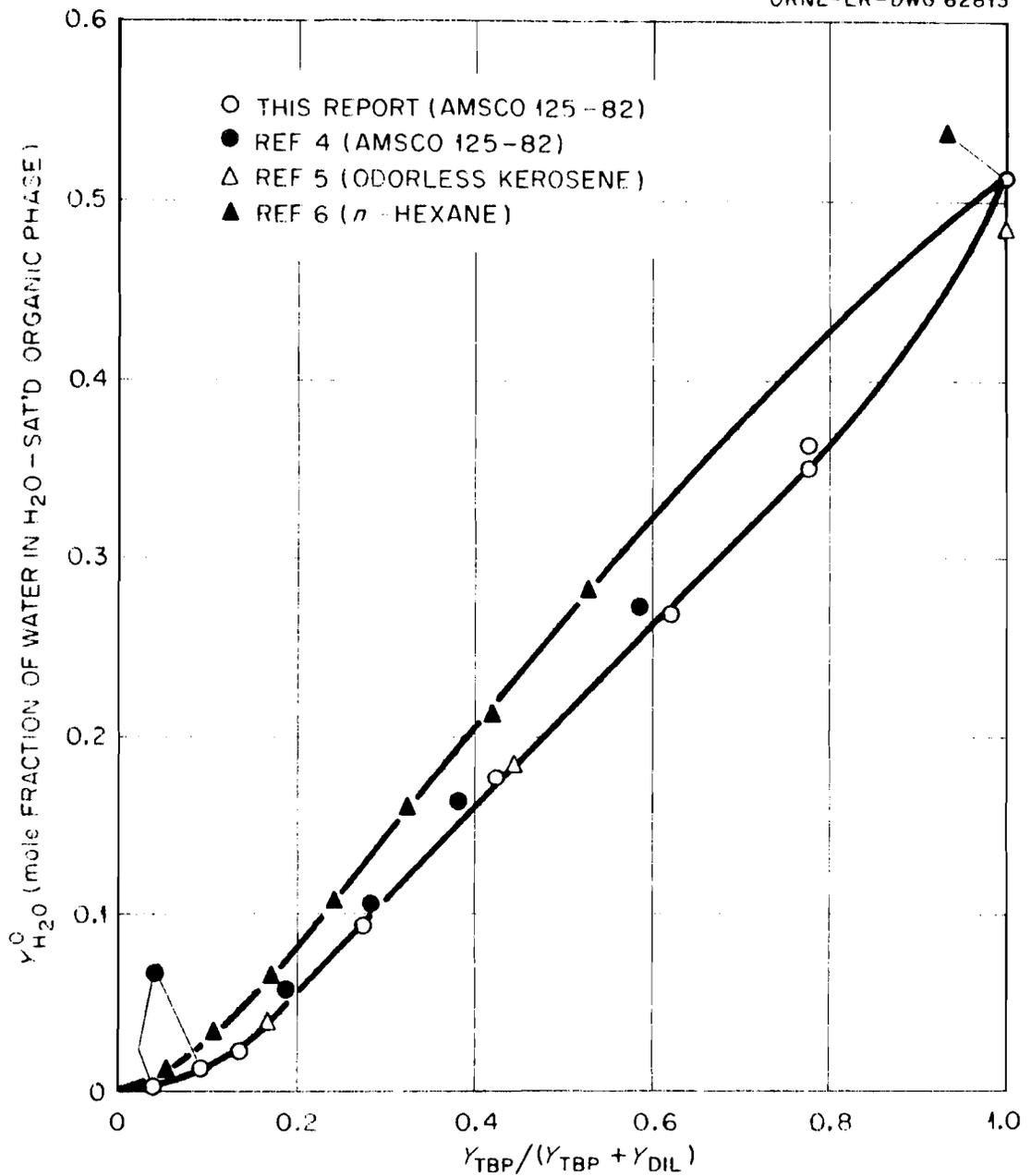


Fig.3. Variation of Solubility, $Y_{H_2O}^0$, of H_2O in TBP-Diluent Solutions with mole Fraction of TBP in Dry TBP-Diluent.

mole fraction of TBP in the dry, acid-free, TBP-diluent solution. A similar linearity applies with the diluent n-hexane in the region 20-70 mole % TBP.

Replicate values of the water content and density of diluent-free water-saturated TBP were obtained to help characterize the interaction between H₂O and TBP. From these analyses the mole ratio $Y_{\text{H}_2\text{O}}^{\circ}/Y_{\text{TBP}}^{\circ}$ is 1.045 and its standard deviation is 0.0012. Thus, the difference between the measured mole ratio and unity is statistically significant, which is equivalent to saying that the water content of the saturated solution is not due solely to the formation of a simple addition compound, if a compound is formed at all.

DISCUSSION

Solutions of TBP in Amsco 125-82 show very nearly ideal solution volume additivity. In addition, the molar volume of water is constant at 18 ml, within experimental error, and that of nitric acid, at concentrations up to ~5 M in the aqueous phase or ~3 molal in the organic phase, shows only a small change as the (Dil)/(TBP) concentration ratio changes. Using 185 as the gram molecular weight of Amsco 125-82, the molal volume of a solution containing TBP, Amsco 125-82, HNO₃, and H₂O is given at 25°C within ±0.5% by

$$V = 1.0275 + 1.3319 \left(\frac{W_{\text{Dil}}}{W_{\text{TBP}}} \right) + 0.0425 (\text{HNO}_3)_{\text{org}}^m + 0.018 (\text{H}_2\text{O})_{\text{org}}^m \quad \text{liters/kg TBP} \quad (9)$$

where $(\text{HNO}_3)_{\text{org}}^m$ and $(\text{H}_2\text{O})_{\text{org}}^m$ are molalities of nitric acid and water in the organic phase. By use of this equation, the solution volume, and therefore the true TBP concentration, can be calculated if the initial weight ratio $W_{\text{Dil}}/W_{\text{TBP}}$ and the quantities $(\text{HNO}_3)_{\text{org}}^m$ and $(\text{H}_2\text{O})_{\text{org}}^m$ are known. Densities need not be measured.

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BIBLIOGRAPHY

1. W. Davis, Jr., This Journal.
2. D. G. Tuck, Chem. Soc. 1958:2783.
3. M. T. Kelley, R. W. Stelzner, W. R. Laing, and D. J. Fisher, Analytical Chemistry, 31:220 (1959).
4. R. M. Wagner and R. Farrand, "Radiation Stability of Organic Liquids," Stanford Research Institute Semi-Annual Report No. 6 on Subcontract 1081 with the Chemical Technology Division of ORNL, Jan. 5, 1960.
5. T. V. Healy and P. E. Brown, U.K.A.E.A., C/R 1970, June 6, 1956.
6. D. R. Olander, L. Donadieu, and M. Benedict, A.I.Ch.E. J.7: 152 (1961).

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