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AN ISOPIESTIC INVESTIGATION OF DI(2-ETHYLHEXYL)-PHOSPHORIC ACID AND TRI-*n*-OCTYLPHOSPHINE OXIDE IN *n*-OCTANE

C. F. Baes, Jr.

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section C

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C. F. Baes, Jr.

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ABSTRACT

Isopiestic measurements are presented in which octane solutions of di(2-ethylhexyl)phosphoric acid (DPA) and tri-n-octylphosphine oxide (TPO) are compared with triphenylmethane (TPM)-octane as the reference solution. In the range 0-0.2 m the results show deviations up to 10 and 20% from ideal solution behavior of DPA dimer and TPO monomer, respectively. While partial trimerization of DPA (in qualitative agreement with previous iron(III) extraction results for DPA) and partial dimerization of TPO (which is not supported by molar polarization results) can account in part for the results, it is evident that nonspecific nonideal behavior of the solutes is also involved. Practical activity coefficients were estimated on two separate assumptions: (1) $\gamma_{TPM} \equiv 1$, giving log $\gamma_{(DPA)_2} = -0.5227\ m^{1/3}_{(DPA)_2} + 0.420\ m_{(DPA)_2}$ and log $\gamma_{TPO} = -1.168\ m_{TPO} + 0.149\ m^2_{TPO}$; and (2) log $\gamma_{(DPA)_2} \equiv -0.6432\ m^{1/3}_{(DPA)_2}$ (from iron(III) extraction results), giving $\gamma_{TPM} = -0.737\ m_{TPM}$ and log $\gamma_{TPO} = -1.886\ m_{TPO} + 0.245\ m^2_{TPO}$.

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1.0 INTRODUCTION

The isopiestic measurements reported here were undertaken in connection with recent solvent extraction studies of di(2-ethylhexyl)phosphoric acid (DPA)[1-4] and tri-n-octylphosphine oxide (TPO).[5,6] The extent to which solvent extraction behavior can be understood is often limited by one's knowledge of the chemistry of the organic solutions involved. It is therefore desirable that studies of solvent extraction behavior be supported by studies of the organic phase which verify the solute species present and, if possible, permit estimation of their activity coefficients. In this study the species of DPA and TPO present in octane solution were confirmed by isopiestic measurements, and their activity coefficients were estimated by two methods.

The isopiestic method, which has long been used to determine activity coefficients in aqueous solutions,[7] has found but limited application to organic solutions.[1,8] In the previously reported measurements on DPA-hexane solutions,[1] the accuracy (~2%) was much poorer than that attained in aqueous solutions (~0.1%) and solute molecular weights only could be estimated. In making the present measurements one purpose was to achieve sufficiently greater accuracy that the results would also permit the estimation of activity coefficients.

From previous studies[1,9-11] DPA is expected to form a stable dimer in octane solution. At 0.001 M no deviation from Beer's law was detectable in measurements[5] of the intensity of the absorption band in the infrared associated with the stretching of the H-bonded phosphoryl group of DPA in octane, and no band associated with the non-H-bonded phosphoryl group was found. It was concluded that no appreciable dissociation of the DPA dimer occurred at this low concentration. However, recent results[2] on extraction of iron(III) by DPA in octane suggest that DPA may undergo partial trimerization with increasing concentration in this solvent. Uranium(VI) extraction measurements[1] did not indicate a similar effect in hexane,* and the accompanying isopiestic measurements, though few and relatively inaccurate, did not show marked deviations from the expected dimer behavior. The present isopiestic measurements in octane provide a more direct comparison with the iron(III) extraction results.

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*A small deviation of the uranium(VI) extraction results from the expected second power dependence on DPA concentration was in the opposite direction, and it was tentatively suggested that this was caused by partial dissociation of the DPA dimer. In view of the evident stability of the dimer, this now seems unlikely.

The measurements on TPO were originally undertaken to check routine molecular weight measurements by freezing point in benzene, which were high for a series of purified samples.[12] The results are of interest because they confirm considerable positive deviation from Raoult's law even though association of TPO is not expected.

Acknowledgment. It is a pleasure to acknowledge the valuable technical assistance of W. E. Oxendine in this investigation.

2.0 RESULTS

The ratio of the TPM molality m_{TPM} to the DPA dimer molality $m_{(DPA)_2}$ at isopiestic equilibrium plotted against $m_{(DPA)_2}$ (Fig. 1) fell ~9% below unity in the range up to ~0.18 dimer molality and then rose sharply. The corresponding plot of the TPO results (Fig. 2) fell ~17% below unity and then rose sharply at about the same reference solute molality. Table 1 lists values of these ratios, given by the solid curves in the figures.

If these solutions contained only TPM monomer, TPO monomer, and DPA dimer species and all had unit activity coefficients, then all the observed isopiestic ratios would have been unity. The decrease of the ratios below unity are in the direction corresponding to association of DPA dimer and TPO monomer. It is difficult to decide, however, to what extent real association, leading to the formation of new chemical species, actually occurs in each case, as distinguished from less specific nonideal behavior of the solute. The sharp rise in the ratios begins at ~0.18 m TPM in both cases and is presumably the result of increasing nonideal behavior of the TPM-octane solutions as saturation (~0.27 m) is approached.

In the case of the DPA results, the abrupt drop in the isopiestic ratio in the low concentration range strongly suggests, in agreement with the iron(III) extraction results,[2] that association is occurring. The dashed curve represents the expected result assuming the trimerization reaction

$$3(DPA)_2 \rightleftharpoons 2(DPA)_3 \qquad (1)$$

with the quotient $Q_t = 1.2\ m^{-1}$ ($1.7\ M^{-1}$). However, it is evident that this can be only a partial explanation of the results at higher concentrations. Also, this indicated trimerization quotient is much lower than was estimated from the iron(III) extraction results (Q_t ~10 M^{-1}).

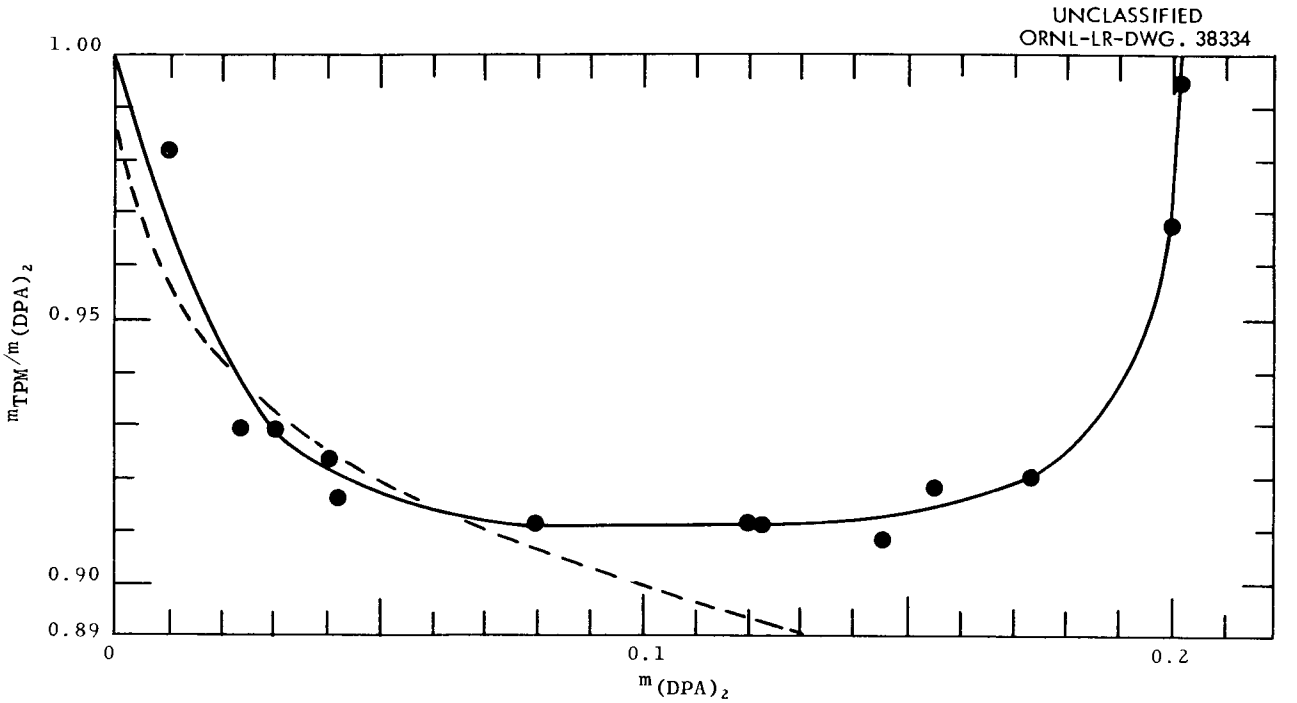

Fig. 1. Change in ratio of TPM molality to the DPA dimer molality in octane at isopiestic equilibrium with increasing DPA dimer molality. The dashed curve was calculated assuming partial trimerization of DPA (Q_t = 1.2 $\underline{m}^{-1}$) and ideal behavior of all solute species.

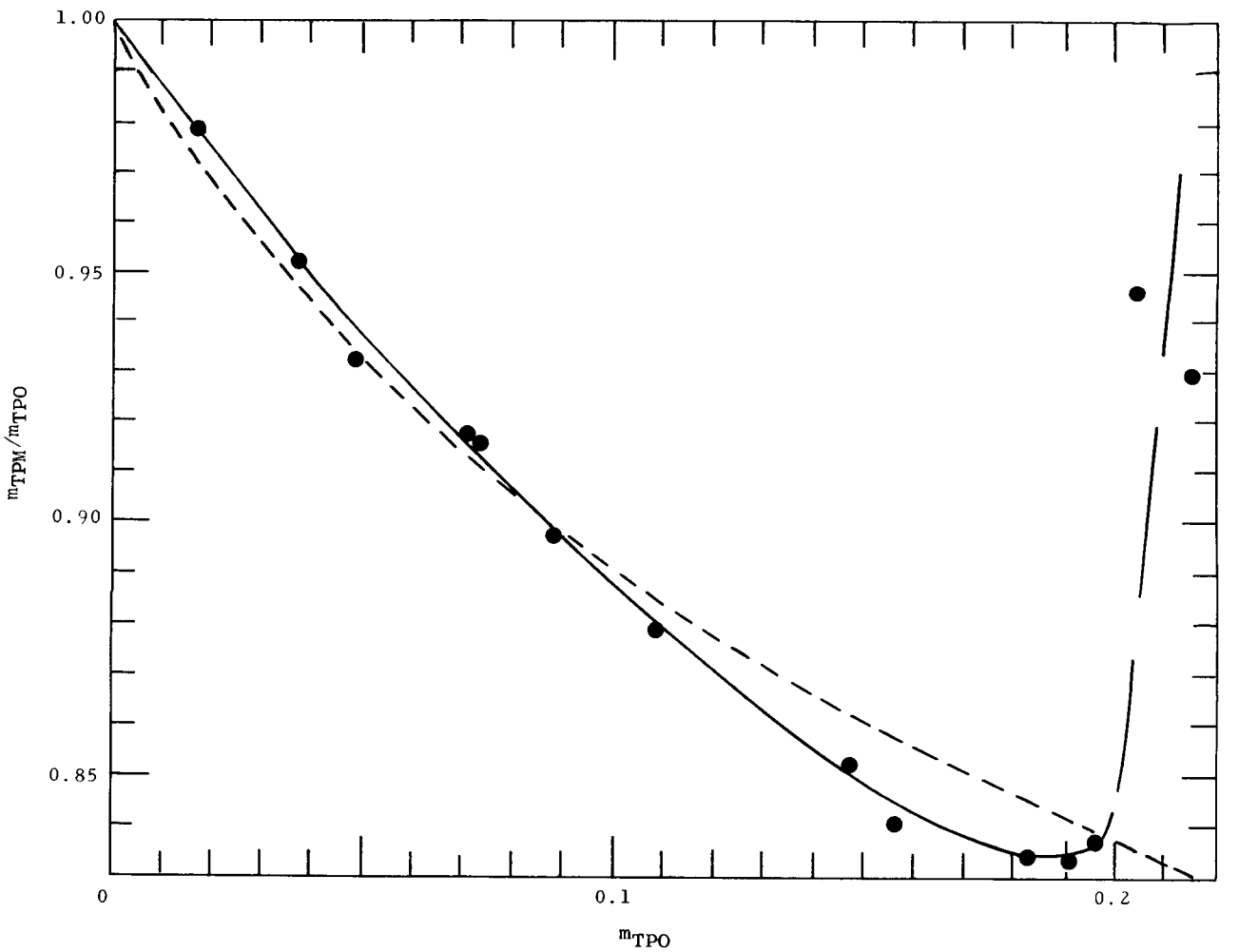

Fig. 2. Change in ratio of TPM molality to the TPO molality in octane at isopiestic equilibrium with increasing TPO molality. The dashed curve was calculated assuming partial dimerization, Q_d = 1.8 $\underline{m}^{-1}$, and ideal behavior of all solute species.

Table 1. Smoothed Molal Isopiestic Ratios[a]

Temp.: 25°C

$m_{(DPA)_2}$	$\frac{m_{TPM}}{m_{(DPA)_2}}$	m_{TPO}	$\frac{m_{TPM}}{m_{TPO}}$
0	(1.000)	0	(1.000)
0.02	0.945	0.02	0.974
0.04	0.921	0.04	0.949
0.06	0.914	0.06	0.927
0.08	0.911	0.08	0.906
0.10	0.910	0.10	0.888
0.12	0.911	0.12	0.871
0.14	0.913	0.14	0.856
		0.16	0.842
		0.18	0.834
		0.20	0.844

[a]These results may be converted to the molarity scale by the following relations based on density measurements:

$$M_{(DPA)_2} = 0.6986\ m_{(DPA)_2} - 0.3207\ m^2_{(DPA)_2} + 0.15\ m^3_{(DPA)_2}$$

$$M_{(TPO)} = 0.6986\ m_{(TPO)} - 0.2145\ m^2_{(TPO)} + 0.07\ m^3_{(TPO)}$$

$$M_{(TPM)} = 0.6986\ m_{(TPM)} - 0.1155\ m^2_{(TPM)} + 0.02\ m^3_{(TPM)}$$

In the case of TPO, the results confirm the pronounced deviations indicated by the freezing point measurements in benzene.[12] They also show a good extrapolation to the expected limiting ratio of unity, thus yielding a molecular weight in agreement with the calculated value. Again the results can be partially accounted for if association is assumed. The dashed curve is the expected result for partial dimerization ($Q_d = 1.8\ \underline{m}^{-1}$). Here such an interpretation must be regarded with some suspicion for two reasons. First, the deviation of the isopiestic ratio from unity is relatively small in the low concentration range and could well be the result of a nonspecific solution effect. Secondly, while dimerization might be expected to result from dipole-dipole interaction involving the phosphoryl group $\geq \overset{+}{P} \rightarrow \overset{-}{O}$, this was not supported by dielectric constant measurements,* which showed no appreciable change in the molar polarization of TPO with increasing concentration (Table 2). Absence of dipole-dipole association might well be predicted from the structure of TPO since the three long alkyl chains should screen the phosphoryl group rather effectively.

*These measurements were made with the collaboration of W. J. McDowell, using the equipment described by McDowell and Allen.[13]

Table 2. Molar Polarization of TPO in Octane

25°C (measured at 960 kc)

Conc. of TPO		Density,	Dielectric	Molar Polarization,[b]
Molarity	Mole Fraction	g/ml	Constant[a]	ml
0	0	0.6986	1.9465	
0.0100	0.001638	0.6994	1.9678	514
200	3286	0.7002	1.9878	499
300	4943	0.7010	2.0081	495
500	8289	0.7026	2.0497	493
700	0.01168	0.7042	2.0932	494
0.1001	1684	0.7066	2.1616	498
0.1499	2560	0.7105	2.2874	508
0.2000	3466	0.7145	2.4333	523

[a]These values were calculated from

$$\epsilon - \epsilon_a = (c - c_a)(\epsilon_s - \epsilon_a)/(c_s - c_a)$$

where c denotes capacitance and ϵ denotes dielectric constant; the subscripts a and s refer to dry air and cyclohexane, which was used as the standard; ϵ_a and ϵ_s were taken as 1.0006 and 2.0173, respectively.

[b]These values were calculated from

$$P_2 = \left(\frac{\epsilon - 1}{\epsilon + 2}\right)\left(\frac{x_1 M_1 + x_2 M_2}{d}\right)/x_2 + P_1$$

where P is the molar polarization, x the mole fraction, M the molecular weight, and d the density; the subscripts 1 and 2 refer to octane and TPO, respectively.

3.0 ESTIMATION OF ACTIVITY COEFFICIENTS

In view of the uncertainties of the above interpretations, it is more useful to express the observed nonideal behavior in terms of the activity coefficients $\gamma_{(DPA)_2}$, γ_{TPO}, and γ_{TPM}, which refer to infinite dilution standard states of DPA dimer and TPO and TPM monomer.

The relation between the isopiestic ratio m_B/m_A for two solutes A and B and their activity coefficients γ_A and γ_B is given by Robinson and Stokes[7] as

$$\ln \gamma_A = \ln \gamma_B + \ln (m_B/m_A) + \int_0^{m_B} \left(\frac{m_B}{m_A} - 1\right) d \ln \gamma_B m_B \quad (2)$$

Since the present measurements did not extend below 0.01 m, this was the lower limit of the integration. Also, an

equivalent form of this integral

$$\int \frac{\left(\frac{m_B}{m_A} - 1\right)}{\gamma_B m_B} \, d\gamma_B m_B$$

was found more convenient; it was evaluated by tabulation. Accordingly, the equations used in the present calculations were of the form

$$\ln (\gamma_A/c) = \ln \gamma_B + \ln\left(\frac{m_B}{m_A}\right) + \int_{m_B=0.01}^{m_B} \frac{\left(\frac{m_B}{m_A} - 1\right)}{\gamma_B m_B} \, d\gamma_B m_B \qquad (3)$$

in which c arises from the integration constant; i.e., ln c is the value of the integral between $\underline{m}_B = 0$ and $\underline{m}_B = 0.01$. In general, it will have a different value for each pair of solutes. It was determined by suitable graphical extrapolation of γ/c to $m = 0$.

If γ_{TPM} were known in octane, or if $\gamma_{(DPA)_2}$ or γ_{TPO} were known, the present results would yield by eq. 3 the activity coefficient of the other two solutes. Since no single set of γ values is known with certainty, however, two separate calculations of the results have been made based on different assumptions concerning the activity coefficient of one solute. In calculation I, γ_{TPM} was assumed to be unity throughout the range of measurements. From the ratios in Table 1, $\gamma_{(DPA)_2}$ and γ_{TPO} were determined by appropriate substitutions in eq. 3. In calculation II, the $\gamma_{(DPA)_2}$ values given by the iron(III) extraction results*[2] were assumed

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*The observed variation of the iron(III) extraction quotient

$$Q = \frac{[FeX_6H_3]_{org}[H^+]^3_{aq}}{[Fe^{+++}]_{aq}\, c^3_{(DPA)_2}}$$

with $c_{(DPA)_2}$, the DPA dimer molarity, is given by

$$Q^{1/3} = 152.4 - 0.3885 \sqrt{Q\, c_{(DPA)_2}}$$

(a relation of this form is predicted if partial trimerization of DPA is assumed). If the variation in Q is attributed to variation in the DPA dimer molar activity coefficient $y_{(DPA)_2}$, then the equilibrium constant $K = Q/y^3_{(DPA)_2} = (152.4)^3$. Substitution of $Q = (152.4)^3\, y_{(DPA)_2}$ into the above relation gives

$$y_{(DPA)_2} = 1 - 4.80\, y^{3/2}_{(DPA)_2}\, c^{1/2}_{(DPA)_2}$$

Activity coefficients from this relation, converted to the molality scale, are listed in Table 3.

Table 3. Estimated Activity Coefficients at 25°C

m	γ_{TPM},[a] Calc. II	$\gamma_{(DPA)_2}$ Calc. I[b]	$\gamma_{(DPA)_2}$ Calc. II[c]	γ_{TPO} Calc. I	γ_{TPO} Calc. II
0.02	0.967	0.740	0.672	0.950	0.919
0.04	0.934	0.689	0.601	0.903	0.848
0.06	0.903	0.661	0.560	0.861	0.786
0.08	0.873	0.643	0.529	0.824	0.733
0.10	0.844	0.630	0.503	0.790	0.684
0.12	0.816	0.620	0.482	0.761	0.645
0.14	0.788	0.613	0.464	0.734	0.608
0.16	0.762	0.608	0.450	0.709	0.575
0.18	0.737		0.436	0.691	0.548
0.20			0.423	0.685	0.530

[a]Calculation I was based on the assumption that $\gamma_{TPM} = 1$.

[b]These values are subject to a systematic uncertainty of 4% owing to uncertainty in the integration constant.

[c]Calculation II was based on these $\gamma_{(DPA)_2}$ values, obtained from iron(III) extraction measurements.[2]

correct for the present dry solutions. These values are listed in the fourth column of Table 3. γ_{TPM} was evaluated first, and these values were used to calculate γ_{TPO}.

By both calculations $\ln(\gamma_{TPO}/c)$ was found to be nearly a linear function of m_{TPO} and by calculation II $\ln(\gamma_{TPM}/c)$ was found to be a linear function of m_{TPM}. The integration constant was therefore determined in each case by direct extrapolation. However, a plot of $\ln(\gamma_{(DPA)_2}/c)$, by calculation I, vs. $\underline{m}_{(DPA)_2}$ showed enough curvature that it could not be extrapolated with confidence. Instead, since a relation analogous to that found from the iron extraction measurements (see footnote, p. 9) might be expected in this case, $\gamma_{(DPA)_2}/c$ was plotted vs. $(\gamma_{(DPA)_2}/c)^{3/2}\, m^{1/2}_{(DPA)_2}$ for extrapolation. It was a relatively long extrapolation, and the resulting c value had an estimated uncertainty of ±4%. Consequently, the $\gamma_{(DPA)_2}$ values from calculation I are subject to the same large, though systematic, uncertainty.

The results of calculations I and II are compared in Table 3. They are summarized within the precision of the calculations by the following empirical expressions:

	Calc. I	Calc. II
$\log \gamma_{TPM}$	$\equiv 0$ (assumed)	$= -0.737\ m_{TPM}$
$\log \gamma_{(DPA)_2}$	$= -0.5227\ m^{1/3}_{(DPA)_2} + 0.42\ m_{(DPA)_2}$	$= -0.6432\ m^{1/3}_{(DPA)_2}$ (assumed)
$\log \gamma_{TPO}$	$= -1.168\ m_{TPO} + 0.149\ m^2_{TPO}$	$= -1.886\ m_{TPO} + 0.245\ m^2_{TPO}$

While they are not in agreement, both sets of γ values reflect the nonideal behavior apparent from the observed isopiestic ratios, and for $\gamma_{(DPA)_2}$ and for γ_{TPO} the two sets of values are closer to each other than to unity.

Of the two separate assumptions made in these calculations, the assumption that $\gamma_{TPM} \equiv 1$ (calculation I) is probably the more extreme. Indeed, it is to be expected from what is known of solutions of nonelectrolytes that γ_{TPM} will decrease with increasing concentration. The magnitude of this decrease can be roughly estimated from a semiempirical treatment given by Hildebrand and Scott,[14] which expresses deviations from ideal behavior in terms of the molar volumes (V_1 and V_2) of the two components and their solubility parameters, δ_1 and δ_2, which are related to their heats of vaporization. The activity coefficient of the solute at low concentrations is given by*

$$\log \gamma_2 = \frac{M_1}{2.3 \times 1000}\left[-1+\left(\frac{V_2}{V_1}-1\right)^2 - \frac{2V_2^{\,2}}{V_1}\,\frac{(\delta_2-\delta_1)^2}{RT}\right]m_2 \qquad (4)$$

where M_1 is the molecular weight of the solvent. Introducing the following numerical values for component 1 (octane) and component 2 (TPM),

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*The equation given by Hildebrand and Scott (ref. 14, p. 131) is of the form

$$\ln a_2 = \ln \varphi_2 + \varphi_1\left(1 - \frac{V_2}{V_1}\right) + V_2\varphi_1^2(\delta_2-\delta_1)^2/RT$$

where a_2 is the activity of component 2 referred to the pure liquid (in this case, the hypothetical supercooled liquid TPM at 25°C) as the standard state. φ_1 and φ_2 are volume fractions. From this equation it can be shown (cf. ref. 7, pp. 243-245) that the molal activity coefficient γ_2 (referred to the infinite dilution standard state) at low concentrations of component 2 is given as

$$\ln \gamma_2 = -\frac{n_2}{n_1} + \frac{n_2}{n_1}\left(\frac{V_2}{V_1}-1\right)^2 - \frac{2n_2V_2^{\,2}}{n_1V_1}(\delta_2-\delta_1)^2/RT$$

$$M_1 = 114.22,\ V_1 = 164,\ \delta_1 = 7.55$$
$$V_2 = 237\ \text{ml},\ \delta_2 = 10.06$$

eq. 4 gives

$$\log \gamma_{TPM} = -0.40\ m_{TPM} \qquad (5)$$

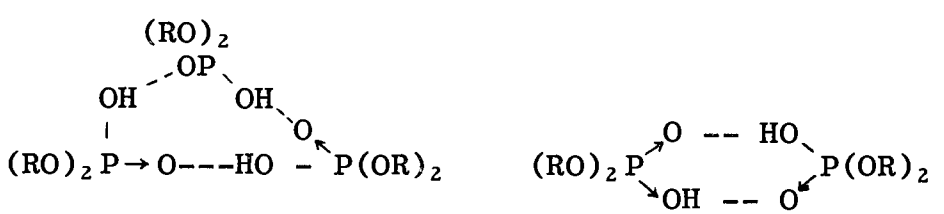
The molar volume of TPM was estimated from the density measurements of TPM-octane solutions. The solubility parameter for TPM could best be determined from its heat of vaporization. Since no reliable value has been found, δ_{TPM} was instead estimated by the following procedure: TPM is known[15] to behave ideally in dilute benzene solutions; accordingly, using the molar volume of benzene (89 ml) and its solubility parameter, 9.15,[13] δ_{TPM} was solved for by placing the right side of eq. 4 equal to zero.

Note that, while in principle eq. 5 is an independent evaluation of γ_{TPM}, it is too approximate to consider as another basis for estimating $\gamma_{(DPA)_2}$ and γ_{TPO}. The significance of this estimate is that it qualitatively supports the conclusions from analysis of the extraction data and lies between the results of calculations I and II.

The assumption on which calculation II is based, that $\gamma_{(DPA)_2}$ has the same value in dry solutions as was found in the water-saturated solutions of the iron(III) extraction measurements, is also open to some question. The solubility of water in DPA-octane solutions has been found to increase with the DPA concentration:

$$m_{H_2O} = 0.0034 + 0.030\ m_{(DPA)_2}$$

where $m_{(DPA)_2} = 0\text{-}0.08$. This suggests a weak interaction between DPA and water, which might well alter the value of $\gamma_{(DPA)_2}$. It is likely that the principal species present in solution are the dimer and the trimer. Of these, the trimer, owing to its more open structure,



might be expected to interact more strongly with water. If this is true, $\gamma_{(DPA)_2}$ should be lower for wet solutions than for dry solutions.

From these arguments, it seems likely that the correct γ_{TPM}, $\gamma_{(DPA)_2}$, and γ_{TPO} values lie somewhere between those

estimated by calculations I and II, and, in view of the non-ideal behavior expected for the reference solute, TPM (eq. 5), it is expected that they are nearer those given by calculation II.

4.0 APPARATUS AND PROCEDURE

The isopiestic apparatus, incorporating many of the features described by Scatchard, Hamer, and Wood,[16] has already been described.[1] It contains a mechanism, operated through a bellows, for covering and uncovering the sample cups while the apparatus is sealed.

Short-term temperature control of the oil thermostat (±0.002°C read on a resistance thermometer) has been better with a solenoid valve (actuated by the thermoregulator and relay) to control the flow of cooling water. Sufficient heating is produced by the bath stirrer.

It was observed in preliminary runs on octane solutions, using the outgassing procedure previously described,[1] that the time required for isopiestic equilibrium to be reached was generally longer than for hexane solutions and was extremely variable. It was concluded that the distillation rate was critically dependent on the partial pressure of air in the apparatus, the rate being greatly decreased by higher air pressures. Accordingly, the following, more thorough, outgassing procedure was adopted:

Before outgassing, the lower portion of the apparatus was immersed in a dry ice—ether bath. After 15 min of cooling, which was sufficient to freeze the sample solutions, the apparatus was outgassed by repeatedly opening it to an evacuated 1-liter bulb. Upon several such expansions, the partial pressure of air in the apparatus was a few microns (read on a McCleod gauge). The apparatus was then allowed to warm for 10 to 20 min, the sample cups were uncovered for a few minutes and then covered again, and the apparatus was cooled once more. The outgassing procedure was resumed until the indicated air pressure within the apparatus was 0.1 μ or less. The sample cups were then opened and the apparatus was placed in the thermostat. In runs at the lowest concentrations (0.01-0.05 $\underline{m}$), the apparatus was removed from the bath after 1 day, cooled once more, and opened to the vacuum system. It was found that the partial pressure of air had increased to several microns, presumably as the result of degassing of the sample solution. This gas was removed and the run resumed. In runs at higher concentrations, this second outgassing step was omitted. By this procedure, usually less than 1 ml of octane was removed from the apparatus.

Equilibration times of 10 days were sufficient for the lowest concentrations studied (0.01 m), decreasing to only 2 or 3 days for solutions more concentrated than 0.1 m.

In all the present measurements, anhydrous magnesium perchlorate was placed in the bottom of the apparatus. In a typical run, the same sample solution was placed in two cups and TPM reference solution was placed in the two remaining cups. The ratio of the initial solution concentrations was usually near the expected equilibrium ratio. At the end of a run duplicate sample concentrations usually agreed to within ±0.25%, the average for all the runs being ±0.14%.

Reagents. Procedures used at this laboratory for the preparation and purification of DPA[3,4,17] and TPO[6,12,18] have been described previously. The DPA used was 99.5% dioctyl phosphoric acid containing <0.1% monooctylphosphoric acid by potentiometric titration with standard sodium hydroxide. The remaining principal impurities were probably 2-ethylhexanol and the trioctyl phosphate ester. Their effect on the isopiestic results is expected to be no larger than the experimental uncertainty. The TPO was purified with special care, the final stage of purification involving repeated recrystallization from petroleum ether. The product contained <0.07% free and combined acid (as dioctylphosphinic and dioctylphosphinous acids). The TPM (Eastman Kodak White Label) was recrystallized from ethanol. n-Octane, the solvent, was Phillips Petroleum Co. Pure Grade (99 mole % minimum).

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