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Osmotic Coefficients of Triorganophosphorus Compounds in *n*-Octane and Benzene[†]

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Osmotic and activity coefficients are reported for a number of organophosphorus compounds dissolved at low concentrations in *n*-octane and in benzene. In both solvents, the most polar compound, tri-*n*-octylphosphine oxide, was the most nonideal, whereas the least polar compound, tri-*n*-octyl phosphate, was the most ideal. All the organophosphorus compounds were more ideal in benzene than in *n*-octane.

Introduction

Organophosphorus compounds, and in particular tributyl phosphate (TBP), have been widely used as extractants in the reprocessing of nuclear fuels (*1*). Thus we have been studying their adsorption at oil–water interfaces (*2*, *3*). To interpret our results, activity coefficients were needed. Previously we reported osmotic and activity coefficients of three organophosphates in *n*-octane (*4*) and in water (*5*). This allowed us to comment on the effect of changing the length and branching of the hydrocarbon chains. In this work, we report osmotic and activity coefficients of other organophosphorus compounds in *n*-octane and in benzene, to look at the effect of changing the nature of the phosphorus group and to compare the effect of an aliphatic solvent with an aromatic one.

Experimental Section

Osmotic coefficients were measured with a Corona/Wescan Model 232A vapor pressure osmometer. The general principle and operation of the instrument have been described previously (*4*, *6*). At each temperature the instrument was calibrated by using *n*-hexadecane in *n*-octane, and biphenyl in benzene (*4*, *5*). Osmotic coefficients were measured to ±0.005.

The *n*-octane and benzene were from Humphrey Chemical Co. (distilled in glass) and Phillips Petroleum Co. (pure grade), respectively. The vapor pressure osmometer standards, octadecane and biphenyl, were obtained from Aldrich Chemicals and Matheson, Coleman and Bell. The triorganophosphorus compounds were obtained from Alfa Products, Thiokol/Ventron Division.

Results and Discussion

Practical osmotic coefficients (ϕ) were calculated by using the equation

$$\phi = (\Delta V/m)/(\Delta V/m)_r \qquad (1)$$

where ΔV is the voltage difference required to maintain a given bridge current and m is the solute molality. The reference value of this ratio $(\Delta V/m)_r$ refers to the value of $\Delta V/m$ needed to maintain the same given bridge current for the two reference solutions, *n*-hexadecane in *n*-octane and biphenyl in benzene, and extrapolated to infinite dilution (*4*, *6*). Since the solutions are both close to ideal, plots of $\Delta V/m$ against m, used to extrapolate $\Delta V/m$ to zero molality, were linear with small slopes. The practical osmotic coefficients for the reference solutions at infinite dilution can thus be safely taken as 1.000.

The original osmotic coefficients are provided as supplementary material (see paragraph at the end of text regarding supplementary material). Osmotic coefficients were measured at 20, 30, 40, and 50 °C for tri-*n*-octyl phosphate (TOP) and tri-*n*-octylphosphine oxide (TOPO) in *n*-octane, and at 20, 30, and 40 °C for tri-isooctyl phosphite (TOPI) in *n*-octane. For this last system, runs at 50 °C were very irreproducible, perhaps because the vapor pressure of TOPI was excessive at this temperature. Osmotic coefficients were also measured at 30 °C for tributyl phosphate (TBP), TOP, TOPO, TOPI, tricresyl phosphate (TCP), and triphenyl phosphate (TPP) in benzene. Since many of these systems were close to ideal at 30 °C, the effect of temperature on the osmotic coefficients could not be measured with any accuracy.

Osmotic coefficients as a function of solute molality were described by a simple rational function using

$$\phi = (1 + A_1 m)/(1 + A_2 m) \qquad (2)$$

where A_1 and A_2 are fitting constants. A nonlinear least-squares fitting routine was used (*4*, *5*). The rational function gave smoother fits than did polynomials, at least for the rather scattered data obtained in these experiments. The constants resulting from the data fitting are shown in Table I, and the errors reported in that table are the standard deviations of the fit. In many cases, the two parameters are highly correlated. In some cases, where solutions were almost ideal, the program would not run, and A_2 was arbitrarily set to zero. As noted previously (*4*, *5*), the solute activity coefficient, γ_2, can be calculated from the constants A_1 and A_2 using

$$\ln \gamma_2 = \left(\frac{A_1 - A_2}{A_2}\right)\left[\ln (1 + A_2 m) + \frac{A_2 m}{1 + A_2 m}\right] \qquad (3a)$$

In the case of the linear fit, with A_2 set to zero, 3b is used.

$$\ln \gamma_2 = 2A_1 m \qquad (3b)$$

These solute activity coefficients have standard states such that unit activity coefficient is approached as the solute approaches infinite dilution in the solvent. They are thus analogous to activity coefficients used for electrolyte solutions and can only be related to those normally used for nonelectrolytes, unit activity for the pure component, if the vapor pressure of the pure solute is known (*4*).

Nonidealities can be conveniently presented in terms of total excess thermodynamic functions, where the total excess Gibbs energy, G^{ex} (*7*), is given by

$$G^{ex} = mRT(1 - \phi + \ln \gamma_2) \qquad (4)$$

where R and T have their usual significance. If the temperature dependence of the excess Gibbs energy is known, then the excess enthalpy is given by

$$H^{ex} = \frac{\delta(G^{ex}/T)}{\delta(1/T)} \qquad (5)$$

and the excess entropy is calculated in the usual way. Figure 1 shows total excess Gibbs energies for TOP in *n*-octane at 20,

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Table I. Constants of Eq 2 for Osmotic Coefficients of Organophosphorus Compounds in *n*-Octane and Benzene

system	T, °C	no. of points	A_1, kg·mol^{-1}	A_2, kg·mol^{-1}	10^3(rsds)
TOP/*n*-octane	20	11	6.705 ± 3.241	8.522 ± 3.591	1.270
	30	5	7.868 ± 5.110	11.50 ± 5.82	0.324
	40	9	−6.433 ± 0.710	−6.349 ± 0.730	0.126
	50	9	−0.310	0.0	
TOPO/*n*-octane	20	9	0.494 ± 0.606	3.452 ± 0.737	0.159
	30	19	1.569 ± 0.921	4.435 ± 1.146	3.353
	40	10	5.035 ± 1.973	8.040 ± 2.282	0.651
	50	7	2.682 ± 1.825	4.680 ± 2.003	0.103
TOPI/*n*-octane	20	9	−0.047	0.0	
	30	10	−0.455 ± 1.411	0.002 ± 1.488	0.263
	40	15	22.63 ± 18.18	23.46 ± 18.56	0.415
TBP/benzene	30	20	0.408	0.0	
TOP/benzene	30	12	0.534	0.0	
TOPO/benzene	30	13	21.47 ± 18.41	22.86 ± 19.01	0.756
TOPI/benzene	30	11	0.582	0.0	
TPP/benzene	30	10	−1.659 ± 7.579	−1.005 ± 7.850	0.644
TCP/benzene	30	10	77.84 ± 27.45	82.39 ± 28.59	0.188

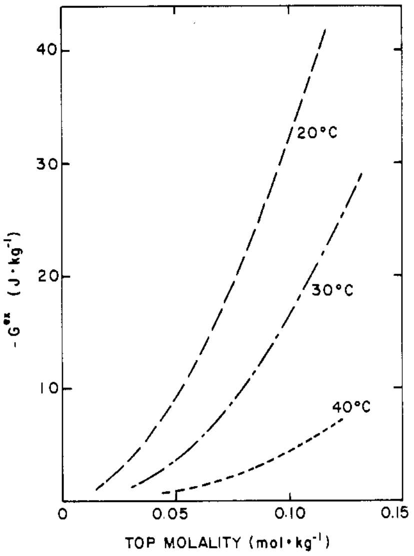

Figure 1. Total excess Gibbs energies for 0.1 mol·kg^{-1} TOP in *n*-octane as a function of TOP molality for 20 °C (– –), 30 °C (– – –), and 40 °C (—).

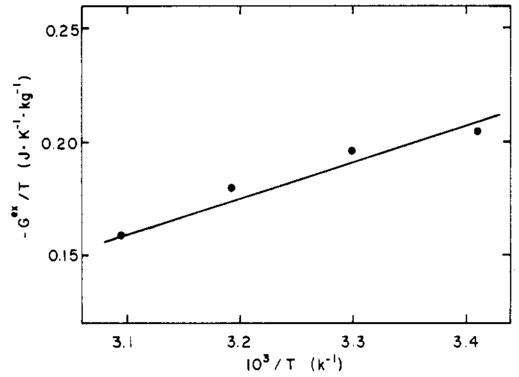

Figure 2. Total excess Gibbs energies divided by temperatures plotted against reciprocal temperatures for 0.1 mol·kg^{-1} TOPO in *n*-octane to determine total excess enthalpy.

30, and 40 °C, calculated from the constants listed in Table I. The system is clearly much more ideal at the higher temperatures. Figure 2 shows G^{ex}/T plotted against reciprocal temperature for 0.1 mol·kg^{-1} TOPO in *n*-octane. The slope of the line gives the total excess enthalpy. The total excess Gibbs energies at 30 °C at 0.1 mol·kg^{-1} and the total excess enthalpies, where determined, are listed in Table II.

Table II. Total Excess Gibbs Energies and Enthalpies at 30 °C and 0.1 mol•kg^{-1} Solute

system	G^{ex}, J·kg^{-1}	H^{ex}, J·kg^{-1}
TOP/*n*-octane	−20.0	−290
TOPO/*n*-octane	−58.2	−170
TOPI/*n*-octane	−11.8	160
TBP/*n*-octane[a]	−42.2	−100
TCP/*n*-octane[a]	−66.0	−300
TBP/benzene	10.3[b]	
TOP/benzene	13.5[b]	
TOPO/benzene	−19.5	
TOPI/benzene	14.4[b]	
TPP/benzene	−16.5	
TCP/benzene	−28.0	

[a] Reference *4*. [b] Linear fit.

From the data listed in Table II it is apparent that increasing the polarity of the solute increases nonideality. The TOPO is the most polar but, in TOP, the ether oxygens reduce the availability of electrons on the phosphoryl oxygen. Increasing solute chain length reduces nonidealities, as noted by comparing TOP results with those previously obtained for TBP (*4*). The effects of chain branching seem small, and finally, all solutes have more positive total excess Gibbs energies in benzene than they do in *n*-octane. The benzene partially screens out the polar interactions responsible for solute–solute attractions (*8*).

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Registry No. TBP, 126-73-8; TOPO, 78-50-2; TOPI, 25103-12-2; TOP, 1806-54-8; TCP, 1330-78-5; TPP, 115-86-6; benzene, 71-43-2; octane, 111-65-9.

Literature Cited

(1) Marcus, Y.; Kertes, A. S. *Ion Exchange and Solvent Extraction of Metal Complexes*; Wiley: New York, 1969; p 650.
(2) Sagert, N. H.; Lee, W.; Quinn, M. J. *Can. J. Chem.* **1979**, *57*, 1218.
(3) Sagert, N. H.; Lee, W. *Can. J. Chem.* **1980**, *58*, 2789.
(4) Sagert, N. H.; Lau, D. W. P. *Can. J. Chem.* **1982**, *60*, 2755.
(5) Sagert, N. H. *J. Chem. Eng. Data* **1984**, *29*, 423.
(6) Burge, D. E. *J. Appl. Polym. Sci.* **1979**, *24*, 293.
(7) Stokes, R. J. In *Activity Coefficients in Electrolyte Solutions*; Pytkowicz, R. M., Ed.; CRC Press: Boca Raton, FL, 1979; Vol. 1, pp 24–6.
(8) Apelblat, A. *J. Inorg. Nucl. Chem.* **1980**, *42*, 411.

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Supplementary Material Available: A list of all the original osmotic coefficients for all solutes in both solvents at all the temperatures used (5 pages). Ordering information is given on any current masthead page.