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Osmotic Coefficients of Trialkyl Phosphates in Water†

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Osmotic and activity coefficients are reported at several temperatures for triethyl phosphate (TEP) and tripropyl phosphate (TPP) at low concentrations in water. TEP forms solutions that do not depart from ideality as much as do those formed from TPP. At 15 °C the total excess Gibbs energies were −11 and −32 J·kg^{-1} at 0.05 mol·kg^{-1} for TEP and TPP, respectively. For TEP, the nonidealities resulted from a balance between entropic and enthalpic effects.

Introduction

Neutral organic phosphates are frequently used as extractants in the reprocessing of irradiated nuclear fuel (*1*). We are presently engaged in a program to study the adsorption of such extractants at oil/water interfaces (*2*, *3*) and, to interpret our adsorption results, activity coefficients of the solutes in both the oil and the water are required. This work reports osmotic and activity coefficients of two of the lower trialkyl phosphates, triethyl phosphate (TEP) and tripropyl phosphate (TPP), in water.

Experimental Section

Osmotic coefficients were measured at various temperatures by using a Corona/Wescan Model 232 A vapor pressure osmometer. The general principles and operation of this instrument have been described fully by Burge (*4*) and our procedures have been described previously (*5*).

At each measurement temperature the osmometer was calibrated against standard solutions of mannitol in water. The voltage difference between the two thermistors, ΔV, was divided by the mannitol molality, m, and $\Delta V/m$ was plotted against m. Since these solutions are close to ideal, straight lines were obtained with small slopes. The value of $\Delta V/m$, extrapolated to zero molality, was taken as the reference value, $(\Delta V/m)_r$.

Table I. Constants of Eq 2 for Osmotic Coefficients of TEP and TPP in Water

T, °C	no. of points	A_1, kg·mol^{-1}	A_2, kg·mol^{-1}	10^3(rsds)[a]
		TEP		
15	19	16.7 ± 5.2	19.1 ± 5.7	3.06
20	36	55.5 ± 13.9	62.4 ± 15.2	7.91
25	23	37.4 ± 7.5	43.8 ± 8.4	4.02
30	18	134.0 ● 39.4	154.1 ± 44.5	3.68
		TPP		
7.5	18	24.5 ± 8.6	30.9 ± 9.6	2.36
15	21	104.6 ± 29.9	124.8 ± 33.9	5.28

[a] Residual sum of deviations squared.

The sources and purification of TEP, TPP, and water have been described (*3*). The mannitol was ACS reagent grade, and it was dried at 110 °C and stored in a desiccator.

Results and Discussion

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 steady bridge current across the thermistors (*4*, *5*) and m is the solute molality. The reference values, $(\Delta V/m)_r$, were those obtained from the mannitol reference solutions extrapolated to infinite dilution, as noted above. This equation assumes that the practical osmotic coefficient, ϕ, for the reference solution at infinite dilution is 1.000.

The original osmotic coefficients are provided as supplementary material. (See paragraph at the end of text regarding supplementary material.) Osmotic coefficients for TEP were measured at 15, 20, 25, and 30 °C. However, for TPP they could only be measured at 7.5 and 15 °C. At higher temperatures, stable readings could not be obtained, probably because of the high volatility of the TPP. Since TPP is only sparingly soluble in water, even low concentrations give a high percentage of the equilibrium vapor pressure of the pure liquid over

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† Issued as AECL-8097.

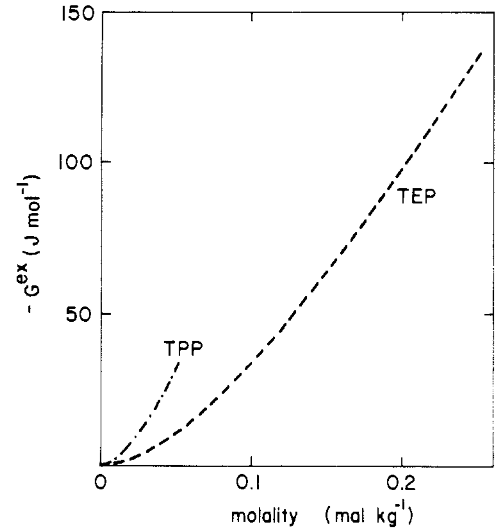

Figure 1. Total excess Gibbs energy of TEP (--) and TPP (-··-) in water. The temperature is 15 °C.

the solution. Although readings at the highest temperatures used were stable for 5 min, or more, it is possible that they were also affected by high solute volatility. The volatility of trimethyl phosphate made it impossible to measure osmotic coefficients with this technique.

The osmotic coefficients were fitted by a simple rational function using the equation

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

and employing a nonlinear least-squares fitting routine. For scattered data such as those obtained here, these gave smoother fits than the more conventional polynomials (*5*). The constants obtained from these fits are given in Table I and the errors reported are the standard deviations of the fit. If the Bjerrum expression is combined with eq 2, then solute activity coefficients, γ_2, can be calculated (*5*, *6*).

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

The activity coefficients have the standard state which approaches unit activity coefficient as the solute approaches infinite dilution in the solvent, rather than unit activity for the pure component, as is frequently used for nonelectrolytes.

The nonidealities can also be conveniently presented in terms of total excess thermodynamic functions. The total excess Gibbs energy, G^{ex} (*7*), is given by

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

The total excess enthalpies and entropies may then be calculated in the usual way from the temperature dependence of the total excess Gibbs energies. Figure 1 shows total excess Gibbs energies for TEP and TPP in water at 15 °C, as calculated from the fitted values of A_1 and A_2. The TPP shows much more nonideality in water than does TEP, as might be expected from the longer hydrocarbon chains. Figure 2 shows the total excess Gibbs energies for TEP divided by the absolute temperature plotted against the reciprocal of the absolute temperature. The slopes of these lines are the total excess enthalpies and correspond to 1.6, 2.3, and 3.0 kJ·mol^{-1} at 0.15, 0.20, and 0.25 mol·kg^{-1} TEP, respectively. Thus, nonidealities in the TEP/water system seem to be due to a balance between enthalpic and entropic effects.

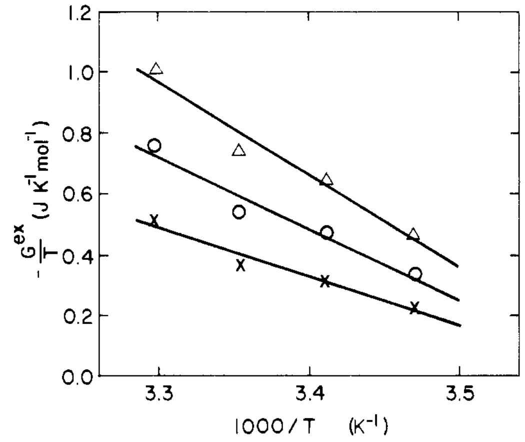

Figure 2. Determination of total excess enthalpies of TEP in water. The TEP molalities are 0.15 (X), 0.20 (O), and 0.25 (Δ) mol·kg^{-1}.

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Registry No. TEP, 78-40-0; TPP, 513-08-6.

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Supplementary Material Available: A list of all the original osmotic coefficients for both TEP and TPP as solutes and at all the temperatures used (4 pages). Ordering information is given on any current masthead page.