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THERMODYNAMIC AND SPECTROSCOPIC PROPERTIES OF PHOSPHORUS COMPOUNDS

Part 2. Excess volumes and excess dielectric properties of binary mixtures of trimethylphosphate with dichloromethane and 1,2-dichloroethane

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ABSTRACT

Excess molar volumes (V^E), excess dielectric permittivities (ϵ^E) and excess molar polarizations (P^E) were determined over the entire composition range for trimethylphosphate + dichloromethane and trimethylphosphate + 1,2-dichloroethane mixtures at 303.15 and 323.15 K. All three quantities are positive and almost the same for the two solvent systems over the whole composition range. The deviations from ideal behaviour are explained in terms of charge-transfer complex formation between electron donor and electron acceptor molecules.

INTRODUCTION

Phosphorus-containing compounds are ubiquitous and play a major role in biological systems. Thus the structure and physical and chemical properties of phosphorus compounds have been widely investigated by spectroscopic, thermodynamic, calorimetric and other methods, and by measuring colligative properties of the compounds and their distribution between immiscible solvents [1–5].

One important property of phosphorus compounds is their ability to form hydrogen-bonded complexes with certain proton donors in solution, and in particular, the electron-donor property of the phosphoryl oxygen atom is large [6,7].

In earlier work we have investigated the complex formation of phosphorus-containing compounds with various proton donors. The phosphorus compounds were triphenylphosphate, trimethylphosphate, triphenylphosphine oxide, triphenylphosphine sulphide and triphenylphosphine selenide [8–10]. These and other investigations showed that inductive effects of the substituents attached to the phosphorus play a major role in determining the complex formation ability.

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Charge-transfer complex formation with electron donors is another important interaction possibility for phosphorus compounds. In the present paper we report the values of thermodynamic excess quantities V^E, ϵ^E and P^E for two trimethylphosphate–haloalkane mixtures, trimethylphosphate being the only phosphorus compound we have studied that is liquid at room temperature.

EXPERIMENTAL

Trimethylphosphate from Aldrich (Belgium) was distilled several times, dried and stored over molecular sieves, type 4A. 1,2-Dichloroethane (puriss; Fluka) and dichloromethane (pro analysis; Merck) were dried and stored over molecular sieves, type 4A.

Densities were measured with a digital densitometer DMA 40 (Anton Paar K.G., Austria) with a reproducibility of ±0.0001 g cm^{-3}. The densitometer was calibrated with distilled water and air. The experimental values of the densities (ρ) were calculated from the equation

$$\rho = A(T^2 - B) \tag{1}$$

where A and B are calibration constants and T is the vibration period of the sample tube.

Dielectric permittivities were measured with a Dipolmeter DM 01 (Wissenschaftlich-Technischen Werksätten GmbH, Weinheim, BRD), in which the measuring cells used were MGP 1 and MGP 2. The dipolemeter was calibrated with acetone, 2-propanol, ethanol, 2-pyrrolidinone, methanol, dichloromethane and 1,2-dichloroethane. The calibration curve was a straight line when the dielectric permittivities of the solvents were presented as a function of the dipolarmetric reading(s).

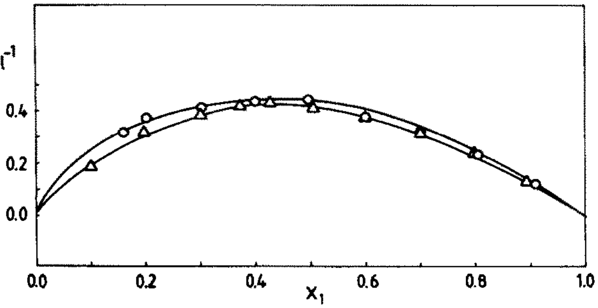

Fig. 1. Excess volumes of binary mixtures of trimethylphosphate + dichloromethane (○) and trimethylphosphate + 1,2-dichloroethane (△) at 303.15 K.

Refractive indices for solvents and phosphate solutions were measured with an Abbe refractometer.

The measuring conditions were held at a constant temperature within ±0.1 K with water circulating from a Lauda thermostat.

RESULTS AND DISCUSSION

The values of V^E, ϵ^E and P^E for trimethylphosphate + dichloromethane and trimethylphosphate + 1,2-dichloroethane mixtures are reported in Tables 1, 2 and 3, respectively. The values of excess molar volumes V^E in Table 1 were calculated by the equation

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_{12}} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \tag{2}$$

where x is mole fraction, M molar mass, ρ density and the subscripts 1, 2 and 12 refer to solvent, trimethylphosphate and the mixture, respectively.

TABLE 1

Molar excess volumes V^E for trimethylphosphate + dichloromethane and trimethylphosphate + 1,2-dichloroethane

Temperature (K)	x_1^a	V^E (cm^3 mol^{-1})	x_1^a	V^E (cm^3 mol^{-1})
Dichloromethane				
303.15	0.0000	0.0000	0.5959	0.3834
	0.1573	0.3087	0.6969	0.3152
	0.2011	0.3660	0.8017	0.2256
	0.3016	0.4096	0.9047	0.1213
	0.3969	0.4393	1.0000	0.0000
	0.4938	0.4428		
1,2-Dichloroethane				
303.15	0.0000	0.0000	0.5024	0.4061
	0.1025	0.1825	0.5980	0.3831
	0.1984	0.3127	0.6975	0.3106
	0.3014	0.3788	0.7978	0.2306
	0.3716	0.4143	0.8912	0.1312
	0.4265	0.4298	1.0000	0.0000
323.15	0.0000	0.0000	0.5024	0.4004
	0.1025	0.1762	0.5980	0.3769
	0.1984	0.2997	0.6975	0.3055
	0.3014	0.3707	0.7978	0.2174
	0.3716	0.4021	0.8912	0.1250
	0.4265	0.4376	1.0000	0.0000

[a] x_1 is mole fraction of trimethylphosphate.

TABLE 2

Excess dielectric permittivities ϵ^E for trimethylphosphate + dichloromethane and trimethylphosphate + 1,2-dichloroethane

Temperature (K)	x_1^a	ϵ^E	x_1^a	ϵ^E
Dichloromethane				
303.15	0.0000	0.0000	0.5959	2.1175
	0.1573	1.6445	0.6969	1.8814
	0.2011	2.0304	0.8017	1.2421
	0.3016	2.3643	0.9047	0.6570
	0.3969	2.4803	1.0000	0.0000
	0.4938	2.4352		
1,2-Dichloroethane				
303.15	0.0000	0.0000	0.5980	2.1314
	0.1025	1.1589	0.6975	1.7486
	0.1984	1.8987	0.7978	1.2661
	0.3014	2.3317	0.8912	0.7396
	0.3716	2.4477	1.0000	0.0000
	0.4265	2.4550		
	0.5024	2.3712		
323.15	0.0000	0.0000	0.5980	1.8965
	0.1025	0.8426	0.6975	1.5342
	0.1984	1.6542	0.7978	1.0893
	0.3014	2.0789	0.8912	0.5950
	0.3716	2.1967	1.0000	0.0000
	0.4265	2.1167		
	0.5024	2.1170		

[a] x_1 is mole fraction of trimethylphosphate.

The values of the excess dielectric permittivities ϵ^E in Table 2 were obtained from measured and calculated dielectric permittivities by eqns. (3) and (4),

$$\epsilon_{\text{calc}} = (\epsilon_2 - \epsilon_1)x_2 + \epsilon_1 \tag{3}$$

$$\epsilon^E = \epsilon_{\text{obs}} - \epsilon_{\text{calc}} \tag{4}$$

where ϵ_1 is the dielectric permittivity of solvent, ϵ_2 the dielectric permittivity of solute and x_2 the mole fraction of solute.

From measured dielectric permittivities, densities and refractive indices, the excess molar polarizations P^E in Table 3 were calculated by the eqns. (5) and (6)

$$P = \frac{(\epsilon - n_D^2)(2\epsilon + n_D^2)}{9\epsilon} V \tag{5}$$

$$P^E = P_{\text{obs}} - P_{\text{calc}} \tag{6}$$

TABLE 3

Excess molar polarizations P^E for trimethylphosphate + dichloromethane and trimethylphosphate + 1,2-dichloroethane

Temperature (K)	x_1^a	P^E ($cm^3\ mol^{-1}$)	x_1^a	P^E ($cm^3\ mol^{-1}$)
Dichloromethane				
303.15	0.0000	0.0000	0.5959	46.7140
	0.1573	27.8689	0.6969	43.6228
	0.2011	35.4467	0.8017	30.3767
	0.3016	43.9708	0.9047	16.8577
	0.3969	48.9224	1.0000	0.0000
	0.4938	50.8320		
1,2-Dichloroethane				
323.15	0.0000	0.0000	0.5980	45.4844
	0.1025	16.7125	0.6975	37.9782
	0.1984	34.0069	0.7978	27.8726
	0.3014	44.4922	0.8912	15.7039
	0.3716	48.3235	1.0000	0.0000
	0.5024	48.9090		
303.15	0.0000	0.0000	0.5024	53.6356
	0.1025	22.3374	0.5980	49.9626
	0.1984	38.1190	0.6975	42.4107
	0.3014	48.7882	0.7978	31.7755
	0.3716	52.6952	0.8912	19.1123
	0.4265	54.0048	1.0000	0.0000

[a] x_1 is mole fraction of trimethylphosphate.

where ϵ is the dielectric permittivity, n_D the refractive index and V the molar volume of the binary mixture.

The obtained V^E, ϵ^E and P^E values were fitted to the smoothing equation

$$y^E = x_1(1 - x_1) \sum_{k=0}^{n} A_k (1 - 2x_1)^k \tag{7}$$

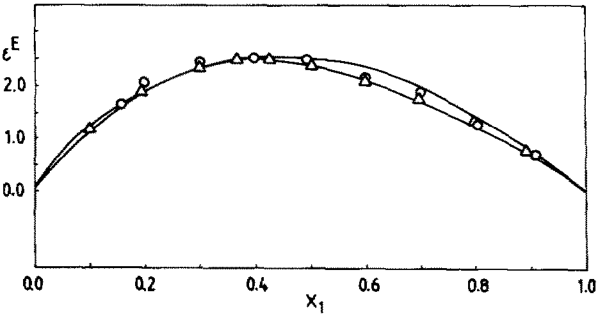

Fig. 2. Excess dielectric permittivities of binary mixtures of trimethylphosphate + dichloromethane (○) and trimethylphosphate + 1,2-dichloroethane (△) at 303.15 K.

TABLE 4

Values of least-squares parameters (A_k) and standard deviations (σ) of V^E for trimethylphosphate + dichloromethane and trimethylphosphate + 1,2-dichloroethane solution systems, fitting eqns. (7) and (8)

Compound	Temperature (K)	A_0 (cm^3 mol^{-1})	A_1 (cm^3 mol^{-1})	A_2 (cm^3 mol^{-1})	A_3 (cm^3 mol^{-1})	A_4 (cm^3 mol^{-1})	$\sigma(V^E)$ (cm^3 mol^{-1})
Dichloromethane	303.15	1.730	0.553	−0.125	0.350	0.959	0.007
1,2-Dichloroethane	303.15	1.657	0.444	0.035	−0.051	0.010	0.006
	323.15	1.653	0.443	−0.267	−0.059	0.320	0.009

TABLE 5

Values of least-squares parameters (A_k) and standard deviations (σ) of ϵ^E for trimethylphosphate + dichloromethane and trimethylphosphate + 1,2-dichloroethane solution systems, fitting eqns. (7) and (8)

Compound	Temperature (K)	A_0 (cm^3 mol^{-1})	A_1 (cm^3 mol^{-1})	A_2 (cm^3 mol^{-1})	A_3 (cm^3 mol^{-1})	A_4 (cm^3 mol^{-1})	$\sigma(\epsilon^E)$ (cm^3 mol^{-1})
Dichloromethane	303.15	9.571	3.438	2.931	0.107	−3.018	0.048
1,2-Dichloroethane	303.15	9.499	3.606	1.198	−0.677	−0.374	0.004
	323.15	8.351	3.513	2.589	−2.024	−5.868	0.033

TABLE 6

Values of least squares parameters (A_k) and standard deviations (σ) of P^E for trimethylphosphate + dichloromethane and trimethylphosphate + 1,2-dichloromethane solution systems, fitting eqns. (7) and (8)

Compound	Temperature (K)	A_0 (cm^3 mol^{-1})	A_1 (cm^3 mol^{-1})	A_2 (cm^3 mol^{-1})	A_3 (cm^3 mol^{-1})	A_4 (cm^3 mol^{-1})	$\sigma(P^E)$ (cm^3 mol^{-1})
Dichloromethane	303.15	200.517	14.537	37.507	−1.961	−57.067	1.011
1,2-Dichloroethane	303.15	195.683	47.191	22.381	−47.450	−93.621	0.393
	323.15	214.807	41.334	10.895	−18.543	−4.156	0.080

where y^E is V^E, ϵ^E or P^E, $k = 0, 1, \ldots, n$ and x_1 is the mole fraction of trimethylphosphate. Values for A_0, A_1, A_2, A_3 and A_4 evaluated at 303.15 K by the method of least squares are given in Tables 4, 5 and 6 along with the standard deviations, which are defined by eqn. (8)

$$\sigma(y^E) = \left[\sum\left(y^E_{\text{obs}} - y^E_{\text{calc}}\right)^2/(N - M)\right]^{1/2} \tag{8}$$

where N is the number of experimental points and M the number of parameters.

The results in Table 1 show the values of excess molar volumes (V^E) to deviate positively from the ideal values for both trimethylphosphate–dichloromethane and trimethylphosphate–1,2-dichloroethane mixtures. No special temperature dependences were observed, but the extremes appear at mole fractions of about 0.45–0.50 of trimethylphosphate. The deviations from ideal behaviour were slightly smaller at 323.15 K than at 303.15 K for trimethylphosphate–1,2-dichloroethane mixtures, however.

The behaviour of the excess dielectric permittivities (ϵ^E) (Fig. 2) and excess molar polarizations (P^E) (Fig. 3) was similar to that of the excess molar volumes for both trimethylphosphate–haloalkane mixtures. It is clear that trimethylphosphate is self-associated through dipole–dipole interactions, while both dichloromethane and 1,2-dichloroethane molecules are weak electron donors and able to form charge-transfer complexes with unlike molecules. The interactions between unlike molecules were weak in the present case, however, since the haloalkane molecules were able to disturb the dipole–dipole interactions between trimethylphosphate molecules only, in agreement with the positive V^E, ϵ^E and P^E values. It has been pointed out that ϵ^E is positive in systems in which molecular complexes, formed by the specific interactions between the unlike components of the mixture, increase the charge distributions in the molecules [11].

Positive excess molar volumes have also been obtained for other ester (methyl acetate and *n*-butyl acetate)–*n*-alkane systems [12]. The excess enthalpies of mixing are negative for tributylphosphate–chloroform mixtures, however, which demonstrates that there is hydrogen-bond formation between the H atom of the chloroform molecule and the oxygen atom of the phosphoryl group of the ester [13]. Tributylphosphate is one of the most powerful and widely used extractants for inorganic compounds from aqueous solutions. Chloroform and some alcohols are employed as diluents for this extractant. Thus it is of interest to study further the interaction properties of trimethylphosphate in various types of solvents.

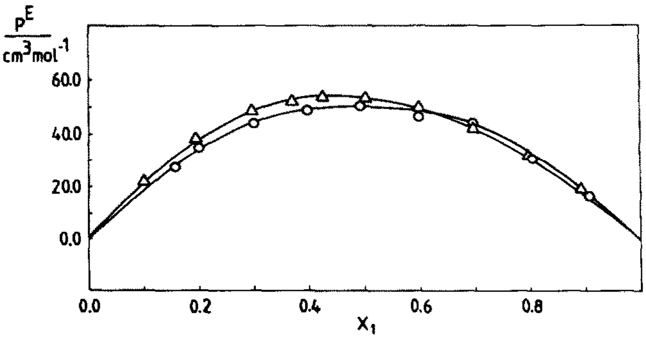

Fig. 3. Excess molar polarizations of binary mixture of trimethylphosphate + dichloromethane (○) and trimethylphosphate + 1,2-dichloroethane (△) at 303.15 K.

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