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The calorimetric investigation of phosphoric acid–*N*,*N*-dimethylformamide system

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Abstract

Solution and mixing enthalpies for the orthophosphoric acid (H_3PO_4)–*N*,*N*-dimethylformamide (DMF) system were measured over the whole concentration range at 25 °C. The standard value of solution enthalpy of phosphoric acid in DMF and the standard transference enthalpy of H_3PO_4 from water to DMF were calculated. The mixing enthalpy concentration dependence permitted making assumptions on complex formation in the system under investigation.

Keywords: Phosphoric acid; *N*,*N*-dimethylformamide; Solution enthalpy; Mixing enthalpy

1. Introduction

There is no doubt that the industrial and biological importance of phosphate systems caused an extensive investigation of thermodynamic properties of phosphoric acid solutions in different solvents. Orthophosphoric acid (H_3PO_4) in aqueous solutions may be considered as an acid of mean strength with respect to its first dissociation constant but weak with respect to the second and third dissociation constants. Its dissociation has been investigated using various techniques. The first dissociation constant was determined from electromotive force measurements [1–3] and from conductance data [4]. The degree of dissociation of H_3PO_4 in aqueous solutions was calculated over a wide concentration range from pH and vapour pressure measurements [5,6] and from Raman spectra [7]. The difference between these experimental results (especially at high acid concentrations) is probably linked to the differences in chemical assumptions made by the authors. In [5,6], the presence of phosphoric acid dimers is assumed. On the other hand, Preston and Adams [7] supposed that no dimers could be quantitatively determined in these solutions.

Different modifications of Pitzer's model have been applied for the description of the thermodynamics of this system [8–10]. The H^+, $H_2PO_4^-$, $H_5P_2O_8^-$ and H_3PO_4 species were taken into account in these models. In [11], the Raman spectra of aqueous phosphoric acid solutions have been investigated at concentrations of 0.3–9.7 mol dm^{-3}. To remove the discrepancy between the representations from spectra and other experimental data, a modified interpretation of the spectra was used for determination the concentrations of $H_2PO_4^-$, $H_5P_2O_8^-$ and H_3PO_4 species, deducing the corresponding degree of dissociation of the acid, as well as the speciation of the solutions as a function of the apparent concentration of phosphoric acid. As in [5], it was determined that the degree of dissociation has a minimum and then increases significantly for apparent phosphoric acid concentrations greater

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than 1 mol dm^{-3}. So for the aqueous phosphoric acid the use of these thermodynamic models permits good agreement with experimental data.

No works have been done on the representation of the thermodynamic equilibrium properties of phosphoric acid solutions in organic solvents. This work is devoted the investigation of thermodynamic properties of the phosphoric acid–*N*,*N*-dimethylformamide (DMF) system with calorimetric technique.

2. Experimental

The 100 wt.% phosphoric acid was prepared from 85 wt.% phosphoric acid (Russia, best quality). An excess of P_2O_5 reagent was dissolved in the 85 wt.% acid at 145 °C. The concentration of the resulting solution was determined by potentiometric titration with KOH and by the density of concentrated phosphoric acid solutions [12] and was estimated to be above 100 wt.% of H_3PO_4. Then the solution obtained was diluted with distilled water to form 100 wt.% phosphoric acid. All the solutions were held overnight at 100 °C to ensure equilibria distribution of the phosphate species. Because the freezing point of phosphoric acid is 42.35 °C, all experimental points for 100 wt.% concentration at temperatures 25 and 35 °C are regarded as metastable state points.

N,*N*-dimethylformamide (Russia, pure) was dried with CaO and molecular sieves and distilled. The content of water in DMF was 0.02 wt.%. The solutions of phosphoric acid in DMF were prepared by a gravimetric method.

The mixing and solution enthalpies were obtained with hermetic calorimeter [13]. A massive copper block inside a Dewar vessel is used as a thermostatic jacket. A resistance thermometer and heater are situated inside the block to control the temperature. The temperature in the thermostating jacket was kept out to within ±0.001 K. The experimental procedure has been reported earlier [14]. The accuracy of measurements of the heat effects was ±1.5%.

3. Results and discussion

The values of solution enthalpies of both phosphoric acid in DMF and DMF in phosphoric acid were measured. The experimental values obtained are presented in Tables 1 and 2.

One can observe (Fig. 1) the significant exothermic effect of H_3PO_4 dissolution in DMF. The values of heat effect increase sharply versus concentration up to 0.018 mole fraction (1 mol kg^{-1}) of phosphoric acid and then decrease slowly. Such behaviour is typical for weak electrolytes. To obtain the standard thermodynamic characteristic of a solution, we used the extrapolation equation that takes the process of ionic association into account:

$$\Delta_s H^m = \Delta_s H^\circ + \tfrac{1}{2}\nu\,\Delta_{dil} H_{DH} + (1-\alpha)\Delta_{ass} H^\circ, \quad (1)$$

Table 1
The integral solutions enthalpies of H_3PO_4–*N*,*N*-dimethylformamide system

m (mol kg^{-1})	$\Delta_s H^m$ (kJ mol^{-1})	m (mol kg^{-1})	$\Delta_s H^m$ (kJ mol^{-1})	m (mol kg^{-1})	$\Delta_s H^m$ (kJ mol^{-1})	m (mol kg^{-1})	$\Delta_s H^m$ (kJ mol^{-1})
0.0069	−23.83	0.05745	−34.08	0.1172	−34.06	0.6753	−40.26
0.007045	−0.78	0.06128	−31.81	0.1177	−37.83	1.421	−41.59
0.01623	−8.000	0.07284	−30.7	0.1190	−35.01	1.590	−41.54
0.01646	−22.03	0.07332	−40.03	0.1196	−43.18	2.503	−41.42
0.01681	−21.58	0.07433	−37.12	0.1324	−42.87	2.664	−41.37
0.01977	−29.14	0.083364	−32.84	0.1365	−35.2	2.831	−41.32
0.02222	−26.31	0.0877	−33.95	0.1456	−43.00	5.9599	−39.77
0.03333	−25.99	0.089	−40.82	0.1491	−35.92	6.036	−39.73
0.03406	−8.950	0.09408	−31.71	0.1621	−36.56	6.106	−39.69
0.03506	−0.6800	0.09487	−31.71	0.1792	−37.31	11.94	−35.61
0.03921	−30.74	0.09680	−34.33	0.1879	−36.48	12.27	−35.23
0.05488	−28.34	0.1013	−33.77	0.3019	−38.17	12.44	−35.12
0.05599	−45.43	0.1027	−35.60	0.4062	−39.23	13.71	−33.88
0.05705	−36.00	0.1038	−38.03	0.5423	−39.88		

m, molality of phosphoric acid in H_3PO_4–DMF solutions; $\Delta_s H^m$, solution enthalpies of H_3PO_4 in DMF.

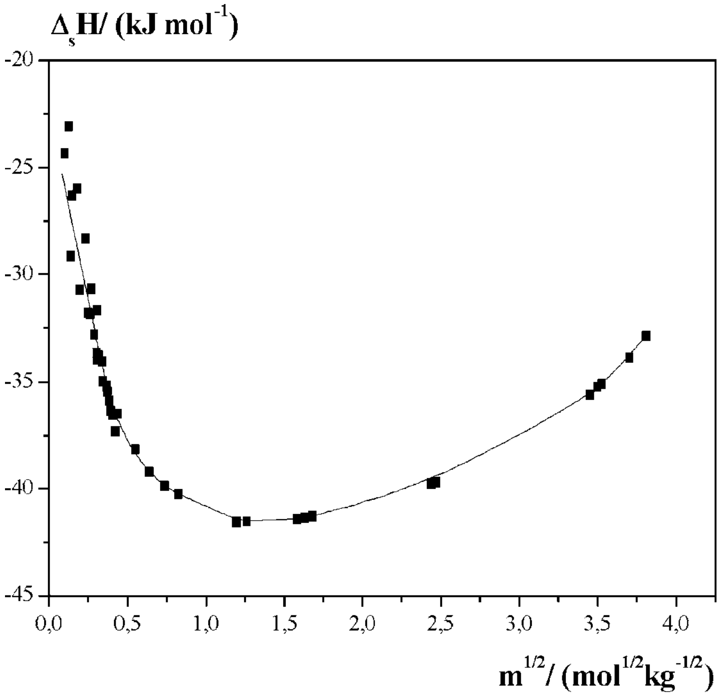

Fig. 1. Concentration dependence of solution enthalpies of phosphoric acid in DMF at 25 °C.

where $\Delta_{dil}H_{DH}$ is the contribution from the dilution of the completely dissociated part of the electrolyte which was calculated on the basis of the second approximation of the Debye–Hückel theory, α the degree of dissociation, and $\Delta_{ass}H^\circ$ the enthalpy change on the association of ions.

The standard solution enthalpy value was calculated for concentration range of 0–0.475 mole fraction (12.4 mol kg^{-1}) of H_3PO_4 with the assumption of phosphoric acid dissociation by first stage (this approach is defensible because even in aqueous solutions the second and third dissociation constants of phosphoric acid are small). So the extrapolation equation was:

$$\Delta_s H = \Delta_s H^\circ + \tfrac{1}{2}\alpha\nu|z_+z_-|A_H I^{1/2}\{(1+BaI^{1/2}) - \tfrac{1}{3}\sigma(BaI^{1/2})\} + bI + (1-\alpha)\Delta_{ass}H^\circ, \qquad (2)$$

where

$$A_H = -3RT^2A_\gamma\left\{\frac{1}{T} + \left(\frac{\partial(\ln\varepsilon)}{\partial T}\right)_P - \frac{1}{3}\left(\frac{\partial(\ln\rho)}{\partial T}\right)_P\right\},$$

$$A_\gamma = \left(\frac{2\pi N_A\rho}{1000}\right)^{1/2}\left(\frac{e^2}{\varepsilon kT}\right)^{3/2},$$

$$B = \left(\frac{2\rho e^2 N_A}{1000\varepsilon_0\varepsilon kT}\right)^{1/2},$$

$$\sigma(BaI^{1/2}) = \frac{3}{BaI^{1/2}}\{1 + BaI^{1/2} - (1+BaI^{1/2})^{-1} - 2\ln(BaI^{1/2})\},$$

Table 2
The solution enthalpies of DMF in 100 wt.% phosphoric acid

m (mol kg^{-1})	Δ_sH^m (J mol^{-1})
0.1703	57.66
0.2720	51.28
0.4221	47.69
0.5038	46.68
0.5901	46.14
0.7705	45.19
0.8899	44.87
0.9981	44.58
1.443	43.40
1.652	42.72

m, molality of DMF solutions in 100 wt.% H_3PO_4; Δ_sH^m, solution enthalpies of DMF in 100 wt.% H_3PO_4.

$$I = \frac{\alpha}{2}\sum z_i m,$$

$$\nu = \nu_+ + \nu_-,$$

where α is the dissociation degree of phosphoric acid, $K_{\text{ass}}^{(\text{m})} = (1-\alpha)/(\alpha^2 m \gamma_\pm^2)$ the association constant of phosphoric acid, $\gamma_\pm = \sqrt[\nu]{\gamma_+^{\nu_+}\gamma_-^{\nu_-}}$ the mean ionic activity coefficient, $\ln\gamma_\pm = -(\nu A_\gamma\,|z_+ z_-|\,\sqrt{I})/(1 + Ba\sqrt{I})$, $a = r_+ + r_-$ the distance of maximum approach of ions ($r(\text{H}^+) = 0.03\,\text{nm}$; $r(\text{H}_2\text{PO}_4{}^-) = 0.02\,\text{nm}$ [15]), ε the dielectric permittivity [16], ρ the density of pure solvent [16], e the electron charge (C), z_+ and z_- the cation and anion charges, N_A the Avogadro constant, k the Boltzmann constant, T the absolute temperature, ν the number of ions, ε_0 the constant in SI system, and I the ionic strength of solution.

For the system under investigation (Eq. (2)) has four fitting parameters: the standard enthalpies of solution ($\Delta_\text{s}H^\circ$), the standard enthalpies of association ($\Delta_\text{ass}H^\circ$), association constant (K_ass) and b (empirical coefficient, estimated to be $0.72 \pm 0.03\,\text{kg kJ mol}^{-1}$).

The $\Delta_\text{s}H^\circ_{\text{H}_3\text{PO}_4}$ value is calculated to be $-6.34 \pm 0.34\,\text{kJ mol}^{-1}$. The negative values of solution enthalpies are typical for electrolyte solutions in DMF [17].

Using the value of the standard solution enthalpy of H_3PO_4 in water ($\Delta_\text{s}H^\circ_{\text{H}_3\text{PO}_4}(\text{aq}) = -30.77\,\text{kJ mol}^{-1}$ [18]), the standard transference enthalpy of H_3PO_4 from water to DMF was calculated: $\Delta_\text{tr}H^\circ_{\text{H}_3\text{PO}_4}(\text{H}_2\text{O} \to S) = 43.45\,\text{kJ mol}^{-1}$.This value indicates that the interaction of phosphoric acid with water is more energy-favourable than with DMF. Probably it is due to the ability of water to form H-bonds with ions.

The value of standard association enthalpy calculated is $\Delta_\text{ass}H^\circ = -44.00\,\text{kJ mol}^{-1}$ that is typical for bond-formation process. In aqueous solution of H_3PO_4, $\Delta_\text{ass}H^\circ$ is equal to $7.9 \pm 0.4\,\text{kJ mol}^{-1}$ at association by first step [19]. Positive value of $\Delta_\text{ass}H^\circ$ in water results from significant contribution to this parameter from desolvation of ions in aqueous solution of H_3PO_4. These data confirm the fact that the ions of phosphoric acid are more solvated in water than in DMF.

The association constant was estimated to be of $K_\text{ass} = 270$. It has to be noticed that K_ass value being calculated from thermochemical data (from minimisa-

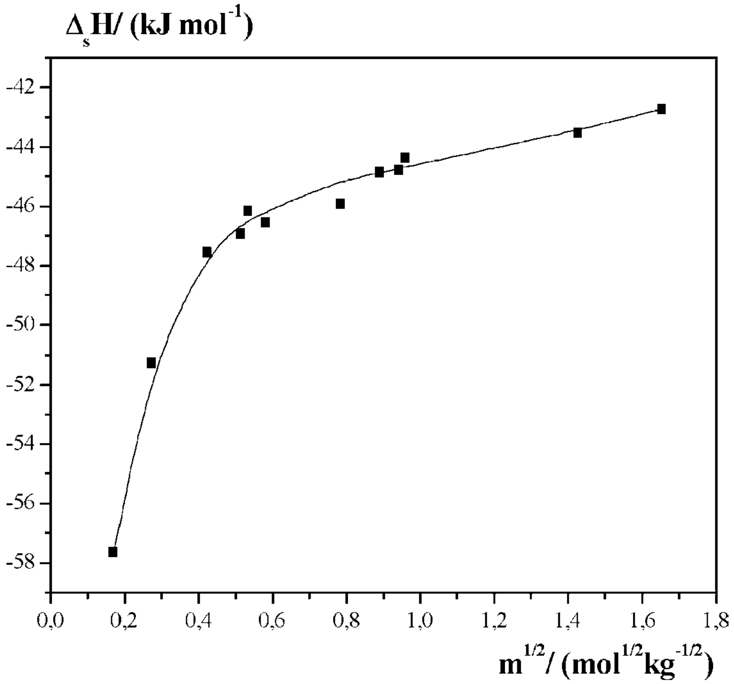

Fig. 2. Concentration dependence of solution enthalpies of DMF in phosphoric acid at 25 °C.

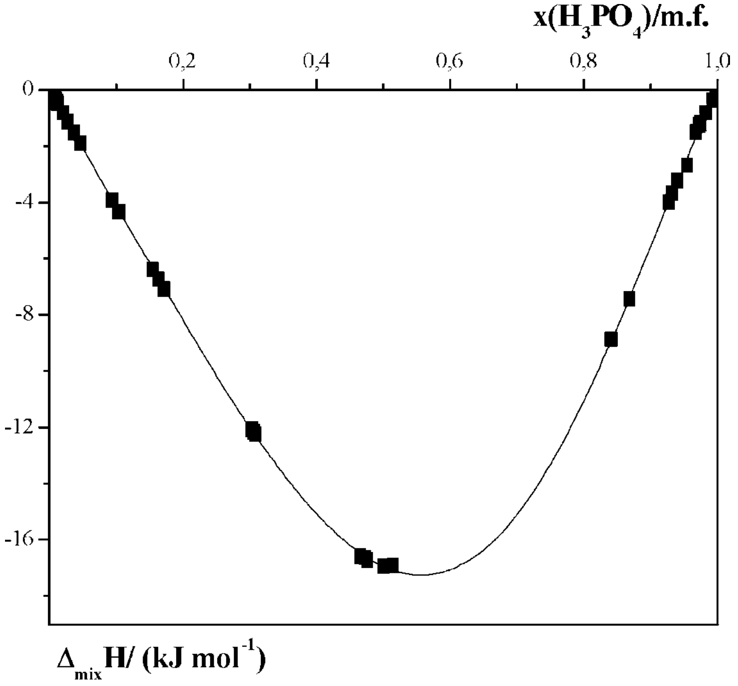

Fig. 3. Concentration dependence of mixing enthalpy of H_3PO_4–DMF system.

tion conditions) is a rough value. The uncertainty of K_{ass} value is about 25%. We intend to obtain a more accurate value of K_{ass} from conductivity data.

Dissolution of DMF in phosphoric acid just as H_3PO_4 in DMF proceeds with significant exo-effect (Table 2). The solution enthalpies of non-electrolytes in different solvents are slightly depended on concentration and these dependencies are linear. From Fig. 2 one can see the same dependence is observed at DMF concentrations above $0.5\,\mathrm{mol\,kg^{-1}}$. For more diluted solutions the $\Delta_s H$ values increase (the exothermic effects decrease) distinctly versus acid concentration.

The large values of mixing enthalpies of H_3PO_4 with DMF (Fig. 3) denote in these systems the strong intermolecular interactions. The data on excess mixing enthalpies of H_3PO_4 with DMF are satisfactorily described by Redlich–Kister equation over the concentration range investigated:

$$H^E = x_2(1-x_2)\sum_{i=0}^{n-1} n_i(1-2x_2)^i, \quad (3)$$

where x_2 is the mole fraction of phosphoric acid, n_i the fitting coefficients: $n_0 = -67.84 \pm 0.10$, $n_1 = 20.68 \pm 0.70$, $n_2 = 22.02 \pm 0.40$ and $n_3 = -16.71 \pm 1.20$.

The earlier investigations of physical–chemical properties of H_3PO_4–DMF systems have shown the presence of significant maximum on the concentration dependence of dynamic viscosity. The appearance of this maximum we connected with formation of the complexes with structure H_3PO_4/DMF = 2/1. This assumption explains the shift of extremum on the concentration dependence of mixing enthalpy of phosphoric acid with DMF to higher acid concentrations.

Acknowledgements

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