Thermochimica Acta, 217 (1993) 323–325
Elsevier Science Publishers B.V., Amsterdam

Note

The enthalpy of solution of tris(dimethylamino)phosphine oxide in water

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(Received 10 July 1992)

Tris(dimethylamino)phosphine oxide ($[(CH_3)_2N]_3PO$, also known as phosphoryl triamide or hexamethylphosphorotriamide (HMPT)) is a basic high-dielectric solvent with a long liquid range ($pK_a < 1.6$ at 25°C [1]; $\epsilon = 29.4$ [2]; m.p. = 7°C; b.p. = 231°C). Its physical constants [3–10], i.e. enthalpies of formation and vaporization, heat capacity, density, viscosity and dipole moment, have been determined. In particular, the thermodynamic excess functions in water mixtures, i.e. volume [5], heat capacity [5], enthalpy and entropy [11], have been interpreted in terms of a very strong water–HMPT interaction. Surprisingly, no enthalpies of solution in water at high dilution have been reported, the lowest concentration in the enthalpy of mixing study [11] referred to above being approximately 4.4 M.

This note reports the enthalpies of solution of HMPT in water at 298.15 K from 0.006 to 0.026 M, together with an extrapolated value at infinite dilution.

EXPERIMENTAL

Materials

HMPT (Aldrich) was purified by two distillations under reduced pressure in nitrogen, retaining the centre fraction (89°C, 3 mmHg) in each case, similar to the procedure of Jose et al. [12]. The purified material was protected from light [13], and stored as a solid at 4°C. It exhibited a single sharp feature at 23.98 ppm in its ^{31}P magnetic resonance spectrum using

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85% H_3PO_4 as external standard; the literature shift is 24 ppm [14]. HMPT is resistant to hydrolysis [15] and attempts to analyse a hydrolysate after digestion in 5 M HCl were unsuccessful owing to limited reaction.

Calorimeter

A purpose-built twin solution calorimeter was used and operated in the isoperibol mode at 298.15 K [16]. The calorimeter had been previously checked [17] by measuring the enthalpy of neutralization of tris-[(hydroxymethyl)amino]methane (THAM) in excess 0.1 M HCl. Two further determinations of this enthalpy were made: 29.80 kJ mol^{-1} ($n = 1955$) and 29.80 kJ mol^{-1} ($n = 1876$); n is the molar ratio of water to THAM. Prosen and Kilday [18] obtained -29.77 ± 0.03 kJ mol^{-1} ($n = 1345$) for this reaction.

RESULTS AND DISCUSSION

Six separate measurements of the enthalpy of solution in 100 cm^3 of deionized water were made and the results are collected in Table 1.

$$C_6H_{18}N_3PO(l) + nH_2O(l) = C_6H_{18}N_3PO\,nH_2O(sln) \qquad (1)$$

The results in Table 1 regress satisfactorily ($r^2 = 97\%$) yielding eqn. (2) where the uncertainty intervals are two standard deviations of the regression coefficients and c is the concentration.

$$-\Delta H_1/\mathrm{kJ\ mol^{-1}} = (50.03 \pm 0.04) - (13.7 \pm 2.2)c/\mathrm{M} \qquad (2)$$

At infinite dilution ($c = 0$), this expression indicates the enthalpy of solution is -50.03 ± 0.04 kJ mol^{-1}. This large value supports the suggestion of a strong HMPT–H_2O interaction. To view this result in perspective the value falls between the corresponding values for $H_3PO_4(l)$ (-26.8 kJ mol^{-1}) and $H_2SO_4(l)$ (-95.3 kJ mol^{-1}).

TABLE 1

Masses, concentrations of the final solutions, mole ratios and enthalpies of solution for HMPT in water at 298.15 K (reaction (1))

m [a] (g)	10^2c (M)	n [b]	$-\Delta H_1$ (kJ mol^{-1})
0.10705	0.597	9292	49.93
0.22525	1.257	4416	49.86
0.29783	1.662	3340	49.81
0.34491	1.925	2884	49.79
0.39764	2.219	2502	49.72
0.46560	2.766	2007	49.63

[a] Mass in vacuo; $\rho = 1.020$ g cm^{-3} [2]. [b] The mole ratio of water to HMPT (see reaction (1)).

ACKNOWLEDGEMENTS

The authors thank the British Council for financial support (to HAAM) and the Royal Society for a collaborative award with the High Temperature Institute, Moscow. Much of this work was completed during the course of an undergraduate research project by one of us (MNS).

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