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THERMODYNAMIC PROPERTIES OF LIQUID MIXTURES.
II. DIMETHYLFORMAMIDE–WATER

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ABSTRACT

The excess enthalpy of mixing of DMF–water was measured at 25°C in the 0–1 molar fraction range. The maximum of heat is developed for a 0.33 DMF molar fraction. The excess partial molar and other excess quantities were also calculated for the DMF–water system at 25°C. The results suggest a strong interaction between DMF and water.

INTRODUCTION

The physico-chemical properties of the dimethylformamide–water system have been fairly well established. However, there are few papers [1,2] about the enthalpies of mixing of this system. The maximum energy release at about 0.33 DMF molar fraction was first observed by Peters and Tappe [1], in an isothermic calorimeter, at 27°C. Using dilatometric and thermal methods, at 25 ± 0.01°C Geller [2] has verified a maximum compression in the 0.23–0.35 DMF molar fraction range and suggested the formation of a labile hydrate compound, DMF · n H_2O, where $n = 2$–4. Densities, viscosities and surface tension measurements at 25°C, as well as freezing point determination, indicated the formation of an addition compound, DMF · 2 H_2O, which melts at −50°C and may occur at room temperature in an appreciable concentration [3].

EXPERIMENTAL

Dimethylformamide ("Merck" high purity grade) with 0.1% water was further purified as described previously [4]. Distilled water was demineralized in a Permution model 1800 demineralizer. The calorimetric measurements were carried out in an adiabatic calorimeter built in this laboratory [5]. The addition of the components (DMF and water) was made with piston burettes (Metrohm models E-274-5 and E-274-20) with an accuracy of 5×10^{-6} and 2×10^{-5} l, respectively. The system was prethermostated with an ultrathermostat type UTZN-69/CZSP-D3-96 with a precision of 0.05°C. The experimental procedure has been described elsewhere [6]. Each experiment was repeated at least three times and only the average values are reported, with a probable error of 0.5%.

RESULTS

The thermodynamic quantities obtained for the system DMF–H_2O are listed in Table 1. The experimental results for $\overline{H}^E$ were correlated with eqn. (1) within ± 0.02 kJ mole^{-1}.

$$\overline{H}^E = X_1 X_2 \left[-6.95 + 5.38(2X_2 - 1) - 2.475(2X_2 - 1)^2 \right] kJ \tag{1}$$

where X is the molar fraction and the indexes 1 and 2 represent water and DMF, respectively.

Reasonable agreement was observed between the enthalpies of mixing measured in this work ($\overline{H}_2^E = -14.77$ kJ mole^{-1} at $X_2 = 0$ and $\overline{H}_2^E = -4.01$ kJ mole^{-1} at $X_2 = 1$) and those measured by Geller [2] ($\overline{H}_2^E = -15.21$ kJ mole^{-1} at $X_2 = 0$ and $\overline{H}_2^E = -3.63$ kJ mole^{-1} at $X_2 = 1$ at 25°C) and by Peters and Tappe [1] ($\overline{H}_2^E = -14.84$ kJ mole^{-1} at $X_2 = 0$ and $\overline{H}_2^E = -3.28$ kJ mole^{-1} at $X_2 = 1$ at 27°C). The maximum heat developed (-2.03 kJ mole^{-1}) is also in close agreement with that measured by Peters and Tappe [1] at 27°C (-2.19 kJ mole^{-1}).

The free energy of mixing and the excess free energy per mole of solution were obtained from the activity coefficient (γ) [7] using the equations

$$\Delta G^{\text{mix}} = RT(X_1 \ln a_1 + X_2 \ln a_2) \tag{2}$$

$$G^E = RT(X_1 \ln \gamma_1 + X_2 \ln \gamma_2) \tag{3}$$

where the indexes 1 and 2 are water and DMF, respectively. The temperature–entropy product was obtained from

$$\Delta G^{\text{mix}} = \Delta H^{\text{mix}}_{\text{calcd.}} - T\Delta S^{\text{mix}} \tag{4}$$

Figure 1 shows ΔH^{mix} or H^E, ΔG^{mix} and $T\Delta S^{\text{mix}}$ per mole of solution as a function of the DMF molar fractions at 25 ± 0.05°C. The excess partial molar enthalpies, $\overline{H}_1^E$ and $\overline{H}_2^E$, were calculated by differentiation of eqn. (1) and the excess partial molar entropies, $\overline{S}_1^E$ and $\overline{S}_2^E$, were obtained from the equation

$$\overline{S}_i^E = \frac{\overline{H}_i^E}{T} - R \ln \gamma_i \tag{5}$$

TABLE 1

Thermodynamic quantities for the DMF–water system at 25 ± 0.05°C

X_2	$-\Delta H^{\mathrm{mix}}_{\mathrm{exp}}$ (kJ mole^{-1})	$-\Delta G^{\mathrm{mix}}$ (kJ mole^{-1})	$T\Delta S^{\mathrm{mix}}$ (kJ mole^{-1})	$-\overline{H}^{\mathrm{E}}_2$ (kJ)	$-\overline{H}^{\mathrm{E}}_1$ (kJ)	$-G^{\mathrm{E}}$ (kJ mole^{-1})	$-\overline{S}^{\mathrm{E}}_2$ (J K^{-1})	$-\overline{S}^{\mathrm{E}}_1$ (J K^{-1})
0.000		0.00	0.00	14.77	0.00	0.00	46.0	0.0
0.030	0.44	0.37	−0.04	12.76	0.03	0.03	39.1	0.1
0.067	0.80	0.69	−0.15	10.56	0.14	0.08	31.6	0.5
0.104	1.23	0.94	−0.25	8.67	0.32	0.12	25.4	1.1
0.158	1.54	1.25	−0.31	6.37	0.66	0.18	18.2	2.1
0.206	1.70	1.47	−0.32	4.74	1.02	0.20	13.2	3.3
0.237	1.85	1.58	−0.30	3.87	1.27	0.23	10.6	4.0
0.256	1.89	1.64	−0.29	3.40	1.42	0.24	9.3	4.4
0.277	1.94	1.71	−0.25	2.93	1.59	0.25	8.0	4.9
0.333	2.03	1.84	−0.16	1.91	2.04	0.27	5.2	6.1
0.376	1.98	1.91	−0.06	1.34	2.35	0.27	3.7	6.9
0.443	1.85	1.97	0.10	0.71	2.78	0.26	2.0	8.1
0.510	1.68	1.95	0.25	0.34	3.12	0.23	1.1	8.9
0.572	1.56	1.91	0.40	0.16	3.33	0.22	0.5	9.5
0.653	1.36	1.76	0.51	0.05	3.49	0.15	0.3	10.0
0.722	1.05	1.60	0.60	0.03	3.54	0.14	0.1	10.2
0.813	0.72	1.27	0.58	0.03	3.55	0.08	0.1	10.5
0.926	0.25	0.69	0.41	0.01	3.69	0.02	~ 0.0	11.1
1.000		0.00	0.00	0.00	4.01	0.00	~ 0.0	11.5

DISCUSSION

The enthalpies of mixing of the DMF–water system are negative over the entire concentration range. The enthalpy value decreases with the addition of DMF in water until -2.03 kJ mole^{-1} (minimum) at $X_2 = 0.33$, and then it increases to zero at $X_2 = 1.0$ (Fig. 1). This behaviour shows a strong interaction between DMF and water. Viscosity measurements [3,8–10] for DMF aqueous solutions have shown a maximum for a system with $X_2 = 0.33$ and it seems to indicate the formation of the DMF · 2 H_2O complex [3].

The occurrence of a maximum in the η vs. X curves for other amide aqueous solutions [11] has also been interpreted as an indication of complex formation. Measurements of surface tension, density [3] and heat of evaporation of 1 mole of the solution [12] have shown an irregular behaviour at about $X_2 = 0.3$. Furthermore, for X_2 (l) < 0.333 the DMF osmotic pressure increases sharply and linearly as X_2 (l) decreases [12]. Assarsson and Eirich [13] suggested that the existence of a minimum in the ΔH^{mix} curves, and the changes in the heat capacities vs. composition curves for a series of amines in water are also strong evidence of complex formation.

The $(\partial V^{\mathrm{E}}/\partial P)_T$ and $\ln \eta^{\mathrm{E}}$ vs. X_2 curves also show a maximum at about $X_2 = 0.33$ [8] for the DMF–water system. Dielectric constant measurements [14] for this system provide further evidence of DMF · 2 H_2O complex formation.

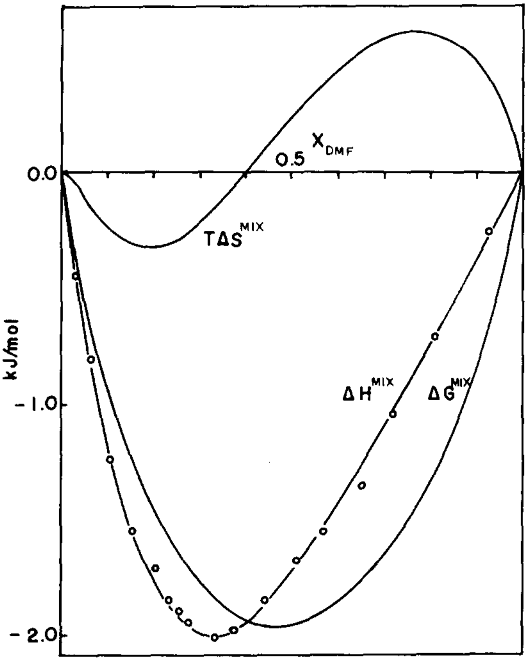

Fig. 1. Enthalpy, free energy and entropy of mixing for DMF–water as a function of DMF molar fraction at 25 ± 0.05°C. ○, Experimental; ——, calculated from eqn. (1).

All these facts seem to indicate that the minimum in the $\bar{H}^E$ vs. X_2 curve (Fig. 1) is due to the formation of the DMF · 2 H_2O complex. However, ultrasonic velocity and absorption studies of DMF–water solutions [15,16} showed that the molar association of water–DMF at 3 : 1 is the most probable [16]. Measurements of dielectric properties [17] and fusion diagrams [18] for this system also indicate DMF · 3 H_2O complex formation. On the other hand, spin-lattice relaxation time T_1 measurements [19] for protons in the systems water–DMF, water–DMF-d_7 and D_2O–DMF seem to indicate the formation of a complex with nearly 2 : 1 water–DMF up to about $X_2 = 0.05$ and 1 : 2 water–DMF up to $X_2 > 0.95$, and both water clusters and associates occur in the intermediate region simultaneously, but it is difficult to make any kind of quantitative deduction for the middle concentration regions. Raman spectroscopy of DMF aqueous solutions shows the formation of $C{=}O \ldots H_2O$ bonds at the expense of water–water hydrogen bonds [20]. This indicates that DMF acts as a water-structure breaker [21].

Although there are some ambiguities in the various theories about the structure of water, it is accepted that the rise in temperature leads to the breaking of hydrogen bonds, resulting in an increase in the fraction of unbonded or smaller cluster molecules of water [22].

Spectroscopic studies of mixtures of a non-electrolyte and water can be interpreted as: (i) the two types of OH oscillators differing in their interaction energies with the oxygen acceptor are in equilibrium [23]; (ii) the non-electrolyte is associated with the water "free" OH which is in equilibrium with a water molecule having one lone-pair of electrons not participating in the hydrogen bond and bulk water [24].

In considering the water structure [22], spectroscopic studies [23,24] and the results of MacDonald et al. [25], the exothermic enthalpies of mixing for the DMF · H_2O system can be interpreted as resulting from:

(i) the polar and strongly basic carbonyl group associating with water molecules;

(ii) the repulsive interaction between the hydrophobic groups (CH_3) and water causing the cluster distribution to shift in the direction of larger or, possibly, longer lived clusters.

This second factor causes an energy release. As has been pointed out by Petersen [26], hydrogen bonds between water and carbonyl oxygen are stronger than those between water molecules, and then the former also must give an exothermic contribution.

Although the negative values for the excess quantities are indicative of strong interactions between DMF and water, formation of the complexes is not clearly established from these thermodynamic data.

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