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THERMODYNAMIC PROPERTIES OF LIQUID MIXTURES. III. ACETONE–WATER

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ABSTRACT

The excess enthalpy of mixing of acetone–water was measured at 25°C in the 0–1 molar fraction range. The minimum and the maximum in the $\bar{H}^E$ (X_2) curve occurred at $X_2 = 0.18$ and $X_2 = 0.85$, respectively. The excess partial molar and other excess quantities were also calculated for the acetone–water system at 25°C. The results are interpreted in view of the influence of acetone on the structure of water.

INTRODUCTION

There are some calorimetric studies about the acetone–water mixture [1–5], but the excess enthalpies or other thermodynamic properties, related with the structure of the environment, are little discussed. The results of Khurma and Fenby [5] and Coomber and Wormald [4] for the excess enthalpies are in disagreement over a relatively large range of concentrations. The $\bar{H}^E$ vs. X_2 curves have a minimum at $X_2 \simeq 0.20$ and a maximum at $X_2 \simeq 0.85$.

In this work, the excess molar enthalpies of acetone–water mixtures at 298.15 K in the 0–1 molar fraction range of acetone, and other thermodynamic quantities of this system, are reported.

EXPERIMENTAL

The acetone was purified in a similar way to that described by Assumpção and Morita [7]. After treatment with $H_2SO_4 + KMnO_4$ and distillation, the acetone was dried with anhydrous CaO, filtered and distilled on a 1.5 m long vigreaux column and stored on molecular sieves of 3 Å. Gas chromatography did not reveal any impurity above 10 ppm in the solvent, and the water content (< 0.2% m/V) was determined by the Karl–Fischer method. Distilled water was demineralized in a Permution demineralizer, model 1800.

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The calorimetric measurements were carried out in a calorimeter built in this laboratory [8]. The experimental procedure has been described elsewhere [9]. 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 acetone–water system are listed in Table 1 and shown in Fig. 1. The experimental results for $\bar{H}^{\mathrm{E}}$ were correlated with eqn. (1) within ± 0.02 kJ mole^{-1}

$$\bar{H}^{\mathrm{E}}(X_2) = X_2(1 - X_2)\left[-0.34 - 3.60(1 - 2X_2) - 2.37(1 - 2X_2)^2 - 3.28(1 - 2X_2)^3\right] \text{ kJ} \tag{1}$$

where X_2 is the molar fraction of acetone.

The $\bar{H}^{\mathrm{E}}$ values obtained in this work for the acetone–water system are in agreement, within a range of ± 5 J, with the results of Coomber and Wormald [4] for $X_2 > 0.30$, and Khurma and Fenby [5] for $X_2 < 0.20$ and $X_2 > 0.85$, but differ by about 50 J with those of Khurma and Fenby [5] for X_2 between 0.25 and 0.85, and are about 0.1 kJ more negative than the results of Coomber and Wormald [4] at the minimum ($X_2 \simeq 0.2$).

The $\Delta\bar{G}^{\mathrm{mix}}$ values were obtained using the equation

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

where a_1 and a_2, X_1 and X_2 are the activities and molar fractions of water

Table 1

Thermodynamic quantities for the acetone–water system at 25.00 ± 0.05°C

X_2	$\Delta H^{\mathrm{mix}}_{\mathrm{exptl.}}$ (kJ mole^{-1})	ΔG^{mix} (kJ mole^{-1})	$T\Delta S^{\mathrm{mix}}$ (kJ mole^{-1})	$\bar{H}_2^{\mathrm{E}}$ (kJ)	$\bar{H}_1^{\mathrm{E}}$ (kJ)	$\bar{G}^{\mathrm{E}}$ (kJ)	$\bar{S}_2^{\mathrm{E}}$ (J K^{-1})	$\bar{S}_1^{\mathrm{E}}$ (J K^{-1})
0.000		0.00	0.00	−9.69	0.00	0.00	−46.2	0.0
0.030	−0.24	−0.15	−0.10	−7.19	−0.04	0.12	−37.2	−1.3
0.101	−0.62	−0.26	−0.32	−2.94	−0.31	0.57	−21.2	−1.8
0.146	−0.67	−0.30	−0.36	−1.29	−0.55	0.73	−14.5	−3.0
0.196	−0.61	−0.32	−0.34	−0.10	−0.80	0.91	−9.3	−4.2
0.307	−0.44	−0.35	−0.13	0.96	−1.12	1.17	−3.5	−6.3
0.405	−0.30	−0.35	0.08	1.00	−1.14	1.33	−1.3	−8.0
0.504	−0.13	−0.38	0.30	0.80	−0.98	1.32	−0.1	−8.8
0.604	0.10	−0.38	0.46	0.63	−0.76	1.26	0.3	−10.0
0.709	0.25	−0.44	0.65	0.49	−0.47	1.07	0.5	−11.0
0.803	0.28	−0.45	0.72	0.34	−0.02	0.81	0.7	−11.3
0.902	0.22	−0.38	0.63	0.14	1.26	0.44	0.5	−9.2
0.973	0.11	−0.18	0.28	0.02	3.21	0.12	0.1	−4.3
1.000		0.00	0.00	0.00	4.27	0.00	0.0	−1.4

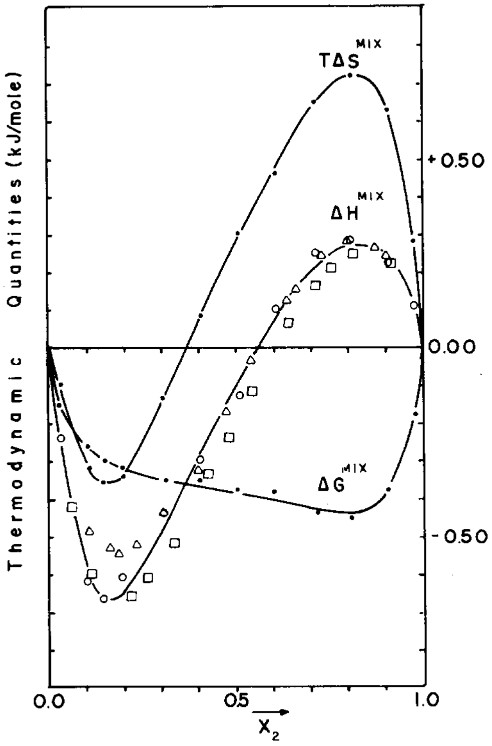

Fig. 1. Enthalpy, free energy and entropy of mixing for the acetone–water system as a function of the acetone molar fraction at 25.00±0.05°C. ——— ΔH^{mix} calculated from eqn. (1). ○, This work; △, ref. 4; □, ref. 5.

and acetone, respectively. The activities of the components in the mixture were obtained from the literature [10], using the method of Othmer and Gilmont [11].

The excess free energy was obtained from the equation

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

and the activity coefficients γ_i were obtained from the relation $\gamma_i = a_i / X_i$. This method has some restrictions in the limits of the composition, when $X_2 \to 0$ for γ_2 and when $X_2 \to 1$ for γ_1, but they are surpassed by plotting the $\ln \gamma_i$ vs. $(1 - x_i)^2$ curve, which although not strictly linear, always shows a finite slope [12] when $X_i \to 0$.

The excess partial molar enthalpies for the two components were taken from the derivatives of the $\overline{H}^{\mathrm{E}}(X_2)$ polynomial expression, and the partial molar entropies were taken from the equation

$$\overline{S}_i^{\mathrm{E}} = \frac{\overline{H}_i^{\mathrm{E}}}{T} - R \ln \gamma_i \tag{4}$$

The partial molar enthalpy at an infinite dilution ($\overline{H}_2^0$) obtained in this work for acetone is in agreement over a 2% range with other data [3,5] and with the direct measurements of Duer and Bertrand [6].

DISCUSSION

The enthalpies of mixing for the acetone–water system are negative for X_2 between 0 and 0.55 and positive for $X_2 > 0.55$. The minimum and maximum in the $\bar{H}^E(X_2)$ curve occurred at $X_2 = 0.18$ and $X_2 = 0.85$, showing stronger and weaker interactions in the system, respectively, compared with the pure state.

The strongly negative value for the partial molar enthalpy at infinite dilution for acetone ($\bar{H}_2^0 = -9.69$ kJ mole^{-1}) suggests the existence of stronger interactions between the acetone and water molecules than those between the acetone–acetone molecules, and also that the water is more structured with the addition of small quantities of acetone. The negative values for the molar enthalpy of the mixture for this system in the water-rich region can be interpreted on the basis of intermolecular interactions. The carbonyl group in the structure of acetone is able to form hydrogen bonds with water, as suggested by IR studies [13,14], semi-empirical molecular orbital calculations [15], and the distribution coefficients between ketones in water [16]. The repulsive interaction between the hydrophobic groups (CH_3) and water can cause the cluster distribution to shift in the direction of large or, possibly, longer-lived clusters [17].

The $\bar{H}_1^0$ value of +4.27 kJ mole^{-1} indicates the existence of weaker interactions between the water–acetone molecules than those between water–water, probably because these bonds are broken and so less intensive interactions are established when small portions of water are added to acetone.

The excess partial molar entropy values ($\bar{S}_i^E$), at finite dilution, indicate that the addition of small quantities of acetone in water causes an ordering, and thus a structuring in the system, compared to the configuration of the ideal mixture, because $\bar{S}_2^E$ is negative (-46 J mole^{-1} degree^{-1}) for $X_2 \rightarrow 0$; otherwise, the addition of small portions of water to acetone causes the system to behave more like the ideal system, because $\bar{S}_i^E$ is close to zero for $X_2 \rightarrow 1$.

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