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Densities and Excess and Partial Molar Volumes of Aqueous Pyrrolidine at 25 and 50 °C and Aqueous Morpholine at 25 and 60 °C

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The densities of aqueous pyrrolidine at (25 and 50) °C and of aqueous morpholine at (25 and 60) °C were determined over the entire composition range. The excess molar volumes of these mixtures and the partial molar volumes of the components were calculated.

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1. Introduction

The preferential solvation of many aqueous mixtures of organic solvents has been investigated[1] by means of the Kirkwood−Buff integrals. For their determination, several quantities are required, among them the excess molar Gibbs energies of mixing and the partial molar volumes of the components. As a part of the examination of additional systems, it was found that partial molar volumes, obtainable from the densities, have not been reported for aqueous pyrrolidine mixtures at any temperature. Those for aqueous morpholine have not been published for elevated temperatures (until this work was completed), at which excess molar Gibbs energies of mixing are available.[2] It was therefore necessary to undertake the determination of these data.

The molar volumes of the mixtures, V, are calculated from the densities d obtained at the mole fractions x_S of the organic components (S for the organic solvent, W for water) as

$$V = [x_S M_S + (1 - x_S) M_W]/d \qquad (1)$$

where M is the molar mass and d is the density of the designated component. The excess molar volumes, V^E, are then

$$V^E = V - [x_S(M_S/d_S) + (1 - x_S)\,(M_W/d_W)] \qquad (2)$$

The partial molar volumes are

$$v_W = V - x_S\, dV/dx_S = V_W + V^E - x_S\, dV^E/dx_S \qquad (3)$$

$$v_S = V + x_W\, dV/dx_S = V_S + V^E + x_W\, dV^E/dx_S \qquad (4)$$

for water and the organic component, respectively.

2. Experimental Section

The densities of the aqueous mixtures of pyrrolidine and morpholine were measured with an Archimedes sinker density balance. A Mettler electronic balance (capacity 51 g) for weighing under the balance pan was equipped with a thin gold chain supporting a sealed glass sinker weighted with lead shot. The volume of the sinker (ca. 1.82 cm^3), up to the top of the second link of the chain, to which it was always immersed, was determined as a function of the temperature by means of its weight-loss when immersed in water, the density of which was taken from the literature.[3] A high-temperature Julabo MD immersion circulator was used with a jacketed glass vessel permitting circulation of silicone oil in the jacket encircling a cylindrical measuring space for the liquid mixtures and a tube for the digital thermometer temperature probe. Temperatures were steady within ±0.05 °C and accurate to ±0.2 °C. The entire assembly was placed in a well ventilated fume hood, in view of the relative volatility and mild toxicity of the organic components, with a glass tube surrounding the gold chain to prevent oscillations. Weights were read to ±0.01 mg but were accurate to ±0.1 mg on repeated readings.

The pyrrolidine and morpholine were obtained from Aldrich, both specified as 99+ mass% pure, and were used without further purification. Gas-chromatography−mass-spectrometry did not detect any substantial impurities except possibly water. The content of the latter was determined by Karl Fischer titration. The materials used were taken to be 99.5 mol % of the organic solvent + 0.5 mol % water. The water used was triple distilled deionized water. Mixtures were prepared by successive dilutions from both sides on a mass basis.

3. Results

The mass loss ΔW of the sinker in water was determined at several temperatures from (20 to 60) °C as

$$[\Delta W/d(t)]/\mathrm{cm}^3 = (-1.8252 \pm 0.0003) + (1.07 \pm 0.07) \times 10^{-4}(t/°\mathrm{C}) \qquad (5)$$

where $d(t)$ is the density of water[3] at the relevant temperature t. The standard deviation of the determination from two runs was 0.00031 cm^3, i.e., 0.017%.

3.1. Density of Aqueous Pyrrolidine. The density of aqueous pyrrolidine was determined at 25 and 50 °C in two independent runs. The values found for neat pyrrolidine (i.e., 99+ mass%) were (0.8546 ± 0.0016) g cm^{-3} at 25 °C (0.85380 g cm^{-3})[4] and (0.8337 ± 0.0009) g cm^{-3} at 50 °C. The densities of the aqueous mixtures are shown in Table 1.

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Table 1. Densities of Aqueous Pyrrolidine Mixtures

run # 1			run # 2		
	d/g cm^{-3}			d/g cm^{-3}	
$x_{\text{pyrrolidine}}$	at 25 °C	at 50 °C	$x_{\text{pyrrolidine}}$	at 25 °C	at 50 °C
0.000	0.99705[a]	0.98804[a]	0.000	0.99705[a]	0.98804[a]
0.099	0.9760	0.9600	0.100	0.9739	0.9636
0.204	0.9528	0.9372	0.199	0.9566	0.9415
0.297	0.9347	0.9212	0.299	0.9388	0.9245
0.396	0.9258	0.9040	0.399	0.9254	0.9074
0.497	0.9121	0.8911	0.498	0.9115	0.8912
0.589	0.9011	0.8835	0.596	0.9002	0.8799
0.675	0.8938	0.8713	0.697	0.8934	0.8685
0.796	0.8771	0.8586	0.786	0.8799	0.8583
0.888	0.8656	0.8456	0.882	0.8653	0.8435
0.995	0.8529	0.8346	0.995	0.8562	0.8328

[a] Calibration value.

The excess molar volumes were calculated for the two temperatures from eq 2 and were fitted at 25 °C by

$$V^{E}/\text{cm}^{3}\ \text{mol}^{-1} = x_{S}(1 - x_{S})[-6.587 - 0.526(1 - 2x_{S}) + 1.271(1 - 2x_{S})^{2}] \quad (6a)$$

and at 50 °C by

$$V^{E}/\text{cm}^{3}\ \text{mol}^{-1} = x_{S}(1 - x_{S})[-6.811 - 0.539(1 - 2x_{S}) + 0.604(1 - 2x_{S})^{2}] \quad (6b)$$

The partial molar volumes of water and morpholine were calculated from eqs 3 and 4. The average results of V^{E} and v_{W} and v_{S} at smoothed mole fractions of pyrrolidine are shown in Table 2.

3.2. Density of Aqueous Morpholine. The density of aqueous morpholine was determined at (25 and 60) °C in two independent runs. The values found for neat morpholine (i.e., 99+ mass%) were (0.9960 ± 0.0005) g cm^{-3} at 25 °C (0.99545[5] and 0.99517[6] g cm^{-3}) and (0.9659 ± 0.0014) g cm^{-3} at 60 °C (0.96822[6] g cm^{-3}). The densities of the aqueous mixtures are shown in Table 3.

The excess molar volumes were calculated for the two temperatures from eq 2 and conformed at 25 °C to

$$V^{E}/\text{cm}^{3}\ \text{mol}^{-1} = x_{S}(1 - x_{S})[-6.537 - 1.597(1 - 2x_{S}) + 2.097(1 - 2x_{S})^{2}] \quad (7a)$$

and at 60 °C to

$$V^{E}/\text{cm}^{3}\ \text{mol}^{-1} = x_{S}(1 - x_{S})[-6.702 - 2.348(1 - 2x_{S}) + 0.780(1 - 2x_{S})^{2}] \quad (7b)$$

The partial molar volumes of water and morpholine were calculated from eqs 3 and 4. The average results of V^{E} and v_{W} and v_{S} at smoothed mole fractions of morpholine are shown in Table 4.

4. Discussion

The ±0.1 mg probable error in the mass values used to calculate the density data led to a ±0.07 cm^{3} mol^{-1} probable error in the excess molar volumes of the mixtures, V^{E}, and to a ±1 cm^{3} mol^{-1} probable error in the partial molar volumes, v_{W} and v_{S}. These uncertainties are adequate for the purpose of these determinations, as described in the Introduction.

Table 2. Smoothed Values of the Excess Molar Volume and of the Partial Molar Volumes of the Components of Aqueous Pyrrolidine Mixtures

	cm^{3} mol^{-1}					
	25 °C			50 °C		
$x_{\text{pyrrolidine}}$	V^{E}	v_{W}	v_{S}	V^{E}	v_{W}	v_{S}
0.0	0	18.07	77.9	0	18.2	78.8
0.1	−0.52	18.0	78.3	−0.60	18.2	79.9
0.2	−0.97	17.9	79.0	−1.07	18.0	81.0
0.3	−1.32	17.6	79.9	−1.41	17.6	82.0
0.4	−1.53	17.1	80.8	−1.61	17.1	83.0
0.5	−1.59	16.4	81.7	−1.67	16.5	83.8
0.6	−1.50	15.5	82.4	−1.58	15.7	84.4
0.7	−1.25	14.6	82.9	−1.34	14. 8	84.9
0.8	−0.88	13.8	83.2	−0.97	13.8	85.2
0.9	−0.41	13.1	83.3	−0.48	12. 8	85.4
1.0	0	12.8	83.4	0	11.8	85.5

Table 3. Densities of Aqueous Morpholine Mixtures

run # 1			run # 2		
	d/g cm^{-3}			d/g cm^{-3}	
$x_{\text{morpholine}}$	at 25 °C	at 60 °C	$x_{\text{morpholine}}$	at 25 °C	at 60 °C
0.000	0.99705[a]	0.98320[a]	0.000	0.99705[a]	0.98320[a]
0.100	1.0106	1.0012	0.100	1.0232	1.0054
0.199	1.0259	1.0105	0.199	1.0315	1.0062
0.298	1.0309	1.0106	0.299	1.0296	1.0068
0.398	1.0284	1.0061	0.398	1.0298	1.0051
0.497	1.0234	1.0006	0.498	1.0255	0.9966
0.597	1.0194	0.9990	0.591	1.0168	0.9903
0.696	1.0135	0.9896	0.692	1.0135	0.9826
0.796	1.0039	0.9764	0.793	1.0057	0.9760
0.895	0.9974	0.9689	0.897	0.9992	0.9693
0.995	0.9960	0.9673	0.995	0.9949	0.9644

[a] Calibration value.

Table 4. Smoothed Values of the Excess Molar Volume and the Partial Molar Volumes of the Components of Aqueous Morpholine Mixtures

	cm^{3} mol^{-1}					
	25 °C			60 °C		
$x_{\text{morpholine}}$	V^{E}	v_{W}	v_{S}	V^{E}	v_{W}	v_{S}
0.0	0	18.07	80.4	0	18.41	82.0
0.1	−0.59	18.0	80.9	−0.75	18.3	84.1
0.2	−1.09	17.9	82.0	−1.28	18.0	86.0
0.3	−1.44	17. 5	83.1	−1.61	17.5	87.5
0.4	−1.63	16.8	84.3	−1.75	16.8	88.7
0.5	−1.64	16.0	85.3	−1.70	16.1	89.5
0.6	−1.48	15.2	86.0	−1.52	15.4	90.1
0.7	−1.18	14.4	86.4	−1.21	14.8	90.5
0.8	−0.78	13.9	86.6	−0.83	14.33	90.6
0.9	−0.35	14.0	86.6	−0.42	14.2	90.7
1.0	0	15.1	86.5	0	14.5	90.7

The densities determined for the neat solvents at 25 °C agree, within the error limits, with those reported in the literature. No data for neat pyrrolidine at $t > 30$ °C nor for aqueous pyrrolidine mixtures at any temperature were found. However, approximate values of the molar volume of neat pyrrolidine were given by Wu et al.[7] at (40 and 60) °C: (84.7 and 86.6) cm^{3} mol^{-1}, to be compared with 85. 5 obtained by us at 50 °C (Table 2).

Approximate values (two digits) of the molar volumes of neat morpholine at (75.2 to 120.2) °C were given by Wu et al.[2] These can be extrapolated linearly to 60 °C to yield $v_{S}^{*} = 90.6$ cm^{3} mol^{-1}, to be compared with 90.7 obtained by us (Table 4).

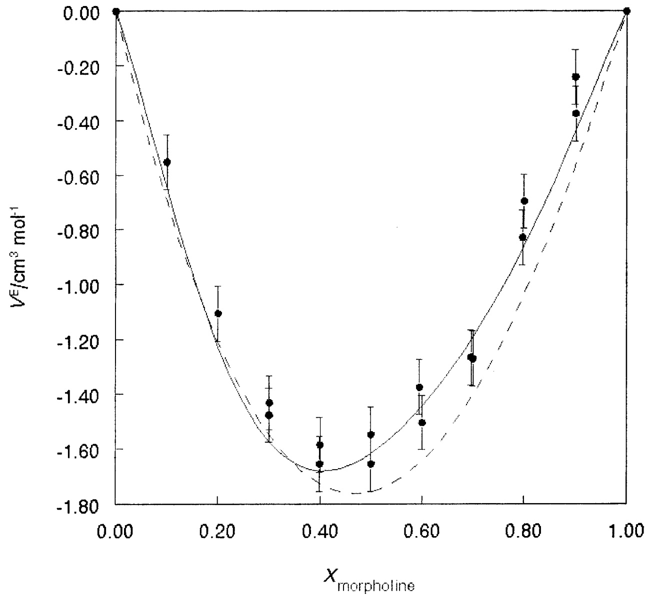

Figure 1. Excess molar volumes of aqueous morpholine from the present work (at 25 °C, circles and error bars), from Maham et al.[6] (continuous line), and from Ernst et al.[9] (at 25.2 °C, dashed curve).

For aqueous morpholine, there are the data of Tremaine et al.[8] for dilute solutions at (20 to 55) °C, of Ernst et al.[9] over the entire composition range at (20.0, 25.2, 29.35, and 34.35) °C and the very recent data by Maham et al.[6] at (25, 30, 40, 60, and 70) °C for comparison. The partial molar volumes of morpholine at infinite dilution, v_S^∞, reported by Tremaine et al.[8] are (81.36, 82.23, 83.66, and 84.25) $cm^3\ mol^{-1}$ at (10, 25, 40, and 55) °C with an uncertainty given as $\pm 1\ cm^3\ mol^{-1}$, compared with our values of (80.38 and 82.50) $cm^3\ mol^{-1}$ at (25 and 60) °C, respectively, with a similar expected uncertainty. Agreement is good within the combined estimated uncertainties, as it is with the value of $v_S^\infty = (80.95 \pm 0.21)\ cm^3\ mol^{-1}$ for morpholine at 25.2 °C reported by Ernst et al.[9] The values given by Maham et al.[6] are somewhat higher: (82.7 and 85.5) $cm^3\ mol^{-1}$ at (25 and 60) °C, respectively.

Maham et al.[6] and Ernst et al.[9] reported the coefficients of the Redlich−Kister expression for the excess molar volume:

$$V^E = x_W x_S[a_0 + a_1(1 - 2x_S) + a_2(1 - 2x_S)^2 + ...] \quad (8)$$

The $V^E(x_S)$ curves calculated from these coefficients at (25.0[6] and 25.2[9]) °C are compared with our data at 25 °C according to eq 7a in Figure 1. The agreement is good within the probable errors. It should be pointed out, however, that the temperature trend of V^E reported by Maham et al.,[6] although small, is in the opposite direction to what is found here (also for pyrrolidine) and what was reported by Ernst et al.[9] at the lower temperatures. The expected errors of the Maham et al.[6] V^E values was not reported, and it is impossible to judge whether the trend reported by them is real or not.

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