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Note

EXCESS THERMODYNAMIC PROPERTIES FOR MIXTURES OF WATER AND *N,N*-DIMETHYLFORMAMIDE AT 303.15 K

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Thermodynamics of mixtures of amides and water have been the subject of many studies [1–3] due to the importance of amides. Aqueous solutions of amides can serve as model compounds for the investigation of peptide properties and in the studies relating to solubility of drugs [4]. Among the amides, *N,N*-dimethylformamide is of particular interest due to the lack of hydrogen bonding in the pure solvent. This significant property of *N,N*-dimethylformamide has enabled us to systematically examine the influence of solvent structure on the thermodynamic properties of hydrophobic solutes in mixtures of *N,N*-dimethylformamide and water [5,6]. In view of the importance of the binary system, water + *N,N*-dimethylformamide, we report on the excess volume, V^E, excess isentropic compressibility, k_s^E, excess isothermal compressibilities k_T^E and excess thermal expansivities, α^E, over the entire range of composition determined at 303.15 K.

EXPERIMENTAL

Excess volumes were measured using the batch dilatometer technique described earlier [7] and the values were accurate to ±0.003 $cm^3\ mol^{-1}$. Isentropic compressibilities were determined indirectly using sound velocity and density data. Sound velocities were measured with a single crystal interferometer at a fixed frequency of 1 MHz and were accurate to ±0.1%. Density values for the pure components were measured with a bicapillary pyknometer and, in the case of mixtures, the data were obtained from measured excess volumes using the relation

$$\rho = \frac{x_1 M_1 + x_2 M_2}{x_1 V_1 + x_2 V_2 + V^E} \tag{1}$$

Density data obtained from both the methods were accurate to $\pm 5 \times 10^{-5}$ g cm^{-3}.

AnalaR grade *N,N*-dimethylformamide (BDH) was further purified by the method described earlier [8]. Deionized water was double distilled just

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before use. The purity of the samples was ascertained by comparing the values of density and boiling point data with the literature [9].

RESULTS AND DISCUSSION

Excess volumes are given in Table 1 and the data also represented as a function of mole fraction in Fig. 1. Isentropic compressibilities, k_s, are calculated using the relation

$$k_s = \frac{1}{U^2 \rho} \tag{2}$$

The values of sound velocity, U, density, ρ, and isentropic compressibility for the pure components and mixtures are given in Table 2. Thermal expansivities, $\alpha = (1/V)[dV/dT]_p$, are calculated from the slopes of the molar volume versus temperature plots. For binary mixtures molar volumes are computed using excess volume data reported in the literature [2] and for pure components molar volumes are obtained from the measurements of density.

Isothermal compressibilities, k_T, are evaluated using the following equation:

$$k_T = k_s + \frac{TV\alpha^2}{C_p} \tag{3}$$

Heat capacity (C_p) values at the required mole fraction are taken from the data reported in the literature [3]. The values of k_T, α, C_p and V for the pure components and mixtures are included in Table 2.

TABLE 1

Mole fraction, x_1, and volume fraction, ϕ_1, of water. Excess volumes, V^E (cm^3 mol^{-1}), excess thermal expansivities, α^E (K^{-1}), excess isentropic compressibilities, k_s^E (TPa^{-1}), and excess isothermal compressibilities k_T^E (TPa^{-1}) for water (1) + N,N-dimethylformamide at 303.15 K

x_1	ϕ_1	V^E	$\alpha^E \times 10^3$	k_s^E	k_T^E
0.0997	0.0251	−0.411	0.024	−21	−22
0.2451	0.0702	−0.842	0.063	−46	−49
0.3487	0.1107	−1.015	0.079	−63	−70
0.4358	0.1523	−1.081	0.075	−78	−92
0.5499	0.2212	−1.065	0.050	−98	−127
0.6364	0.2893	−0.992	0.011	−115	−153
0.7394	0.3975	−0.821	−0.041	−124	−170
0.9048	0.6885	−0.355	−0.081	−86	−121

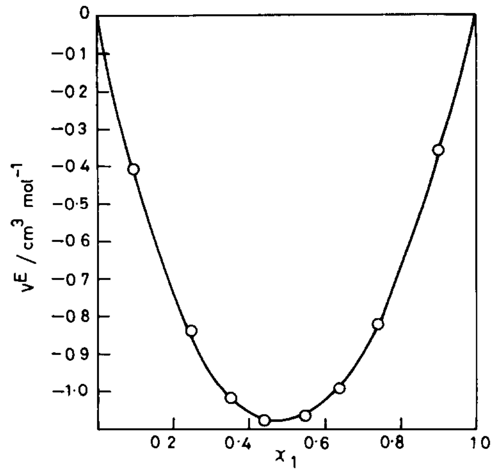


Fig. 1. Mole fraction versus excess volume for water (1) + N,N-dimethylformamide at 303.15 K.

Excess isentropic compressibility, excess isothermal compressibility and excess thermal expansivity are computed using the general equation represented as

$$X^E = X_{mix} - (\phi_1 X_1 + \phi_2 X_2) \tag{4}$$

Where ϕ_1 and ϕ_2 are volume fractions of the components water and N,N-dimethylformamide. The values of k_s^E, k_T^E and α^E are given in Table 1 and the data also presented graphically in Figs. 2 and 3.

TABLE 2

Mole fraction of water, x_1, density, ρ (g cm^{-3}), sound velocity, U (m s^{-1}), molar volume, V (cm^3 mol^{-1}), thermal expansivity, α (K^{-1}), heat capacity, C_p (J K^{-1} mol^{-1}), isentropic compressibility, k_s (TPa^{-1}), and isothermal compressibility k_T (TPa^{-1}) for water (1) + N,N-dimethylformamide at 303.15 K

x_1	ρ	U	V	$\alpha \times 10^3$	C_p	k_s	k_T
0.0000	0.93967	1445	77.788	0.945	150.8	510	650
0.0997	0.94649	1471	71.425	0.953	144.6	488	624
0.2451	0.95638	1511	62.314	0.963	135.2	458	587
0.3487	0.96305	1538	55.956	0.953	130.2	439	557
0.4358	0.96845	1564	50.690	0.922	124.4	422	527
0.5499	0.97519	1609	43.896	0.853	117.5	396	478
0.6364	0.98037	1649	38.804	0.770	111.2	375	438
0.7394	0.98606	1683	32.826	0.648	102.9	358	399
0.9048	0.99318	1639	23.418	0.420	87.6	375	389
1.0000	0.99585	1512	18.090	0.302	75.3	439	446

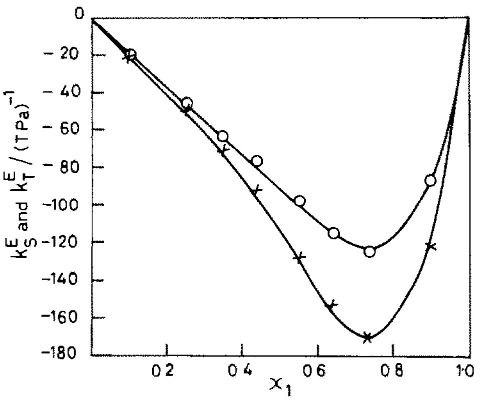


Fig. 2. Mole fraction versus excess isothermal compressibility (○), and excess isentropic compressibility (×), for water (1)+ *N,N*-dimethylformamide at 303.15 K.

The variation of excess thermodynamic properties with mole fraction has been represented by an empirical equation of the form

$$X^E = x_1 x_2 \Sigma a_i (x_1 - x_2)^i \tag{5}$$

The values of the parameters a_i are obtained by the method of least squares and are given in Table 3 along with the standard deviation $\sigma(X^E)$.

The data presented in Table 1 and in the figures reveal that the values of V^E, k_S^E and k_T^E are negative over the entire range of composition. Excess thermal expansivity changes sign from positive to negative with an increase in the mole fraction of water. The observed negative values may be attributed to the formation of hydrogen bonds between unlike molecules. Further, the data also reveal that the strength of the hydrogen bond between

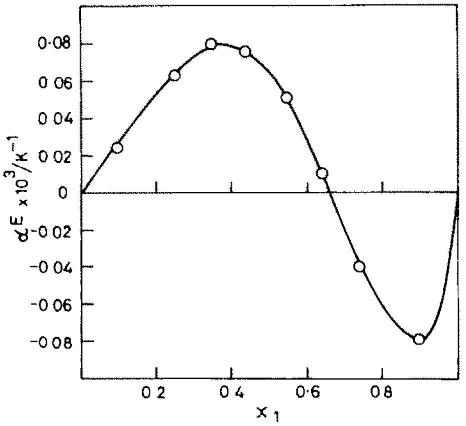


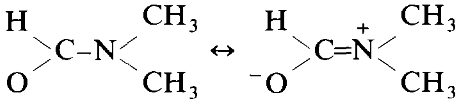
Fig. 3. Mole fraction versus excess thermal expansivity for water (1) + *N,N*-dimethylformamide at 303.15 K.

TABLE 3

Least squares parameters and standard deviation for water (1) + N,N-dimethylformamide at 303.15 K

X^E	a_0	a_1	a_2	$\sigma(X^E)$
V^E (cm^3 mol^{-1})	-4.3578	0.2347	0.2346	0.005
$\alpha^E \times 10^3$ (K^{-1})	0.2693	-0.6696	-0.9193	0.007
k_s^E (TPa^{-1})	-360.54	-439.13	-386.12	2.1
k_T^E (TPa^{-1})	-445.11	-677.91	-575.13	2.3

unlike molecules is stronger than the hydrogen bond between water molecules. This is in accordance with the points made by Petersen [10] that the hydrogen bond between a carbonyl oxygen and water is stronger than between water molecules. In the case of N,N-dimethylformamide this effect has been further enhanced due to the existence of the following resonance forms:



Further, the figures show that the values of k_s^E and k_T^E are skewed towards a higher mole fraction of water and α^E is more negative in the water-rich region. This observation may suggest that the extent of complex formation between unlike molecules is greater in this mole fraction region.

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