Excess volumes and ultrasonic velocities of some amide + water systems at 298.15 K

Amalendu Pal*, Yoginder P Singh & Wazir Singh

Department of Chemistry, Kurukshetra University, Kurukshetra 132119, India

Excess volumes (V^E) and isentropic compressibilities (K_S) have been determined at 298.15 K for the systems water + N-methylformamide, + N,N-dimethylformamide, + N-methyl-2-pyrrolidinone and + N,N-dimethylacetamide. Excess volumes have been measured directly by means of a successive-dilution dilatometer and isentropic compressibilities have been computed from experimentally determined densities and velocities of sound. The speed of sound u has been obtained at 4 MHz in the whole composition range at 298.15 K, using sing-around technique. Excess volumes and deviation in isentropic compressibility are all negative over the whole composition range. The values of both V^E and ΔK_s have been discussed in terms of intermolecular interactions between the mixing component of the binary mixture.

The composition dependence of thermodynamic properties of binary liquid mixtures has proved to be a useful tool in helping to understand the nature and extent of the patterns of molecular aggregation resulting from intermolecular interactions between the components.

In the present program, our intention is to explore the sensitivity of the composition dependence of the ultrasonic velocity, plus the isentropic compressibility, and the excess molar volume to variation of amides in order to seek evidence of the existence of amide aggregates and to explore the effects, upon the character of self aggregation, of their interaction with water. We have made measurements of ultrasonic velocities and excess volumes for the binary liquid mixtures of water with N-methylformamide, N,N-dimethylformamide, N-methyl-2-pyrrolidinone and N,N-dimethylacetamide at 298.15 K across the entire mole fraction range, and the results obtained have been interpreted in this paper.

Materials and Methods

N-Methylformamide (NMF) from Fluka purum (99 mole per cent or greater) and N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA) and N-methyl-2-pyrrolidinone (NM2P) were of SDS spectroscopic grade reagents with purities greater than 99 mole per cent and were used as such. Densities for pure substances were measured at 298.15 K as described previously[1].

The measurements of density at (298.15 ± 0.01) K have an estimated reproducibility of 3×10^{-4} gcm^{-3}. The density of water at 298.15 K were taken from the literature[2].

Binary mixtures were prepared by mass, with a precision of ± 0.05 mg, from thoroughly degassed freshly deionized and freshly distilled water. Samples of the mixtures were degassed through vacuum pump just prior to measurements so as to avoid air bubbles. Corrections were made for buoyancy. The accuracy of the mole fraction was $\pm 1 \times 10^{-4}$.

Excess volumes, which are accurate to ± 0.003 cm^{3}mol^{-1}, were measured with a continuous-dilution dilatometer similar to that described by Dickinson, Hunt and Mclure[3] over the entire mole fraction range at 298.15 K. The dilatometer was clamped vertically into the water-bath. The temperature of the water-bath was kept constant to within ± 0.01 K at the fixed temperatures. Readings of the reference marks and those of liquid levels filling the dilatometer in each capillary were measured with a Cathetometer having precision of ± 0.001 cm. Each run was covered just over half of the mole fraction range so as to give an overlap between two runs. For testing the dilatometer, measurements were made on [x CH$_2$OHCH$_2$OH + (1 − x)H$_2$O] at 298.15 K. The value of V^E were correlated by:

$$V_m^E/(cm^3 mol^{-1}) = x(1-x)[-1.3338 + 0.6324$$

$$(2x-1)-0.2292(2x-1)^2$$
$$-0.3050(2x-1)^3$$
$$+0.4807(2x-1)^4]$$

with a standard deviation of ± 0.0015 cm^3 mol^{-1}; V_m^E at $x=0.5$ is -0.336 cm^{3}mol^{-1} compared with -0.338 cm^{3}mol^{-1} reported by Douhéret and Pal[4].

Ultrasonic velocities in both the pure liquids and the binary mixtures were measured at 4 MHz using a NUSONIC (Mapco. Model 6080 Concentration analyser) velocimeter based on the sing around technique with a single transducer cell. The original glass sample jar supplied with the instrument was replaced by a specially designed low-volume cell (fabricated by the Glass Technology Unit, NPL, New Delhi) in which the first component of about 100 cm^3 was required to cover transducer portion of the transducer assembly. The second component was introduced into the cell from glass syringe by mass. The cell was immersed in a water-bath controlled at (298.15 ± 0.01)K. The ultrasonic velocities, u, in units of ms^{-1}, at a given temperature t in degrees Celsius, are obtained from the average round-trip period of the ultrasonic wave in the fixed path length between the piezoelectric transducer and reflector. The period is expressed as a frequency, f in Hertz, and relation (1) is used to calculate u

$$u = \frac{\text{fl}(1 + \alpha t)}{7 - \text{fb}} \qquad \ldots (1)$$

where l and b are the sonic path length in meters and electronic time delay constants in microseconds, respectively, and α is the coefficient of thermal expansion of the transducer metal. The velocimeter was calibrated at 298.15 K by making measurements of the speed of sound of water and aqueous sodium chloride solutions. The results obtained are in very good agreement (within 0.1 unit) with the literature values[5,6]. In order to minimize errors, calibration were performed prior to every series of measurements. The precision in the ultrasonic velocity was found to be better than ± 0.15 ms^{-1}.

Results and Discussion

The experimental excess volumes for four binary mixtures as a function. of compositions at 298.15 K are graphically represented in Fig. 1. The results for all the mixtures were fitted to an empirical equation of the form

$$V^E (\text{cm}^3\text{mol}^{-1}) = x(1-x) \sum_{i=0}^{5} a_i(2x-1)^i \qquad \ldots (2)$$

where x is the mole fraction of amide. The values of the coefficients a_i obtained by the least squares procedure with all points weighted equally are included in Table 1 along with the standard deviation. $\sigma(V^E)$ were obtained by Eq. 3

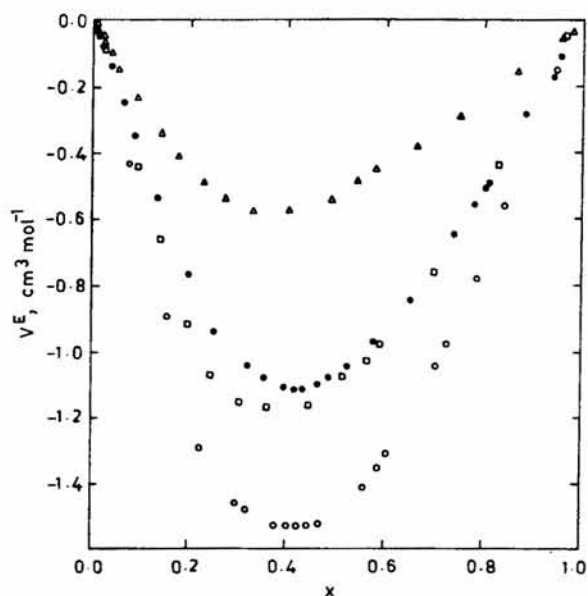$$\sigma(V^E) = [\Sigma(V^E_{expt} - V^E_{cal})^2/(n-p)]^{1/2} \qquad \ldots (3)$$

Fig. 1 – Excess Volume versus mole fraction of amide at 298.15 K for mixtures of water with (O) DMA, (□) NM2P, (●) DMF and (△) NMF.

Table 1 – Values of the parameters of Eq. (2) and standard deviation of the fit $\sigma(V^E)$ at 298.15 K

System	a_0	a_1	a_2	a_3	a_4	a_5	$\sigma(V^E)$ cm^{3}mol^{-1}
N,N-Dimethylacetamide + Water	-5.9883	1.9369	-0.8771	2.1640	3.7791	-4.1355	0.0295
N-Methyl-2-pyrrolidinone + Water	-4.4078	2.2594	-1.7684	-0.5487	4.3376	-0.3806	0.0153
N,N-Dimethylformamide + Water	-4.2900	1.7757	0.4462	-0.9775	0.7965	-0.5600	0.0082
N-Methylformamide + Water	-2.1284	1.4442	-0.0214	-0.9215	$-$	$-$	0.0074

where n is the total number of data points and p is number of coefficient considered.

The excess volumes at 298.15 K for the NM2P-water system obtained in this laboratory and those reported by Uosaki *et al.*[10] from density values obtained using pyknometer are very similar over the whole mole-fraction range.

Davis data[9] for the NMF, DMF-water systems employing Sodev vibrating-tube densimeter exhibit a pleasing level of internal consistency over the entire composition range at 298.15 K with the results from this laboratory in terms of the excess molar volumes. For DMA-water, our experimental values of V^E at 298.15 K are lower than those of Gamaa[11] at mole fractions $x > 0.4$, but agree with our V^E values at lower mole fraction range.

Excess volume versus composition plots in Fig. 1 show that V^E is negative over the entire range of composition in the four mixtures. In all mixtures, the minimum occurs around $x = 0.4$. The minimum of the secondary amide is roughly half that of the tertiary. One notes, however, that the minima for NMA-water[14] and 2-pyrrolidinone-water[9] at 298.15 K are roughly -1.10 and -0.52 cm^3 mole^{-1}, respectively. These large negative values of V^E arise due to increased interactions between water and amide or very large difference in the molar volume of pure components. The observed V^E values may be explained qualitatively by postulating the two opposing sets of contributions: (a) expansion due to dipole-dipole interactions of the amide by the water or the water by the amide and size differences; (b) contraction due to hydrogen bonding between water and amide or self-association of the components. The actual value would be the balance between two opposing effects. The experimental results suggest that the latter effect is more prominent than the former. In the case of DMA, NM2P and DMF, the minima are an indication of strong associations through multiple hydrogen bonding between the polar group of the amides and water, but their pure liquids are presumed to be highly structured. The secondary amides, i.e. NMF have relatively high melting points, boiling points, viscosity[8] and also the Kirkwood's correlation factor, g (ref. 15), which are attributable to the existence of strong intermolecular hydrogen bonding. On dilution with water, there occurs merely an interchange of hydrogen bonding between NMF and water. The hydrogen bond strength in these mixtures is in the order DMA > NM2P > DMF > NMF. The steric hindrance of the two methyl groups of DMF[16] makes DMF weaker than DMA in hydrogen bonding

ability. In the case of NM2P, the pyrrolidone ring affords better packing in the liquid state as is evidenced by its larger density and sound velocity compared with the other solvents.

Ultrasonic velocities (u) measured for the four mixtures are plotted against the mole fraction x of amide in Fig. 2. It can be seen from Fig. 2 that there is a maximum in ultrasonic velocity in the water-rich region and its magnitude decreases from tertiary to secondary amide. The isentropic compressibilities were calculated from the relation

$$K_s = (\rho u^2)^{-1} \qquad \ldots (4)$$

where ρ is the density. The values of K_s are accurate to ± 0.3 TPa^{-1}. The deviation in isentropic compressibilities of mixture (ΔK_s) from the ideal value, assumed to be additive with respect to volume fraction, is estimated using Eq. (5)

$$\Delta K_s = K_s - \Sigma K_{s,i}^0 \phi_i \qquad \ldots (5)$$

and

$$\phi_i = \frac{x_i v_i^0}{\Sigma x_i v_i^0} \qquad \ldots (6)$$

where x_i and ϕ_i are the mole fraction and volume fraction of i in the mixture stated in terms of the unmixed components, respectively $K_{s,i}^0$ and v_i^0 are
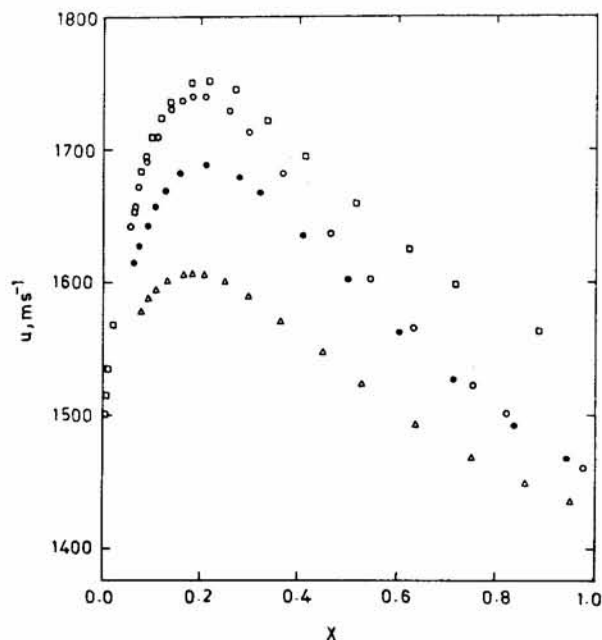

Fig. 2 – Ultrasonic velocity versus mole fraction of amide at 298.15 K for mixtures of water with (O) DMA, (□) NM2P, (●) DMF and (△) NMF.

Table 2 – Densities ρ, ultrasonic velocities u, and isentropic compressibilities K_{s}^{0} of pure components at 298.15 K

Component	ρ, g cm^{-3}		u (ms^{-1})	K_{s}^{0} (TPa^{-1})
	This work	literature		
Water	—	0.997048[2]	1496.687[5]	448.0
N,N-Dimethylacetamide	0.9365	0.9366[7], 0.9350[8]	1455.4	504.1
N-Methyl-2-pyrrolidinone	1.0279	1.02759[9], 1.02821[10] 1.0286[8], 1.0279[12]	1544.5	407.8
N,N-Dimethylformamide	0.9436	0.94383[9], 0.94376[13]	1456.7	499.4
N-Methylformamide	0.9990	0.99889[9], 0.9988[7]	1430.7	489.0

Table 3 – Values of the parameters of Eq. (7) and standard deviation of the fit $\sigma(\Delta K_s)$ at 298.15 K

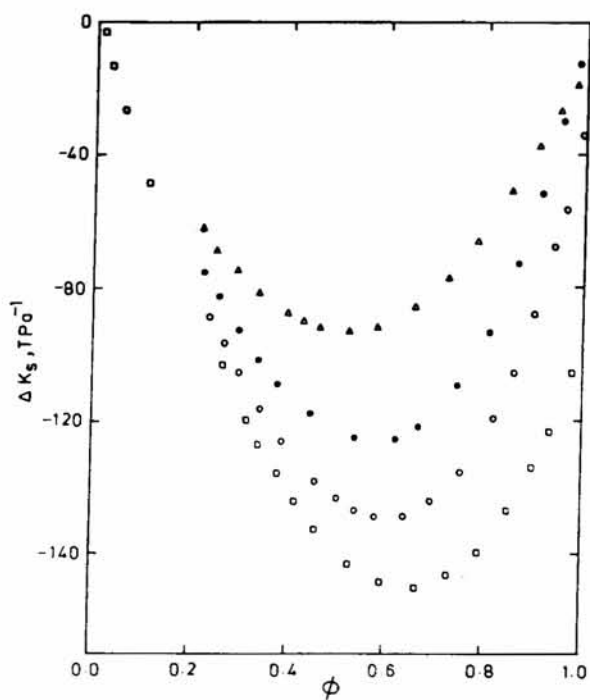| System	b_0	b_1	b_2	b_3	b_4	b_5	$\sigma(\Delta K_s)$ TPa^{-1}
N,N-Dimethylacetamide + Water	− 582.885	− 217.423	148.972	14.973	− 948.632	—	8.95
N-Methyl-2-pyrrolidinone + Water	− 657.074	− 426.360	179.501	1250.341	− 1341.448	− 2589.802	13.93
N,N-Dimethylformamide + Water	− 493.069	− 163.532	− 83.315	158.747	97.343	− 346.904	1.12
N-Methylformamide + Water	− 372.881	− 72.291	− 53.606	461.514	226.445	− 1026.120	3.28

Fig. 3 – Deviation in isentropic compressibility versus volume fraction of amide at 298.15 K for mixtures of water with (O) DMA, (□) NM2P, (●) DMF and (△) NMF.

the isentropic compressibility and molar volume for pure component i. The values of ρ, u and $K_{s,i}^{0}$ for pure components used for these calculations are listed in Table 2. Molar volumes of the components and densities of the mixtures were calcu-

lated from the densities of the pure components and the excess volumes. The dependence of ΔK_s on volume fraction is expressed by an empirical equation of the type (7).

$$\Delta K_s (\text{TPa}^{-1}) = \phi(1-\phi) \sum_{i=0}^{5} b_i (2\phi - 1)^i \qquad \dots (7)$$

Values of the coefficients b_i calculated by the method of least-squares with all points weighted equally and standard deviation $\sigma(\Delta K_s)$ are given in Table 3.

Figure 3 shows the variations of ΔK_s with volume fraction of amide. The values of ΔK_s become increasingly negative for all the four mixtures with the trend NM2P > DMA > DMF > NMF over the whole range of compositions. Negative values of ΔK_s mean that the mixture is less compressible than the corresponding ideal mixtures suggesting the predominant hydrogen bond interaction between water and amide. As the amide is added to water, thereby causing a breakdown of the less dense hydrogen bonded structures of water, and a denser packing of the molecules through hydrogen bond results in an increase in the ultrasonic velocity and a decrease in the compressibility of these solutions. This process continues for all the mixtures over the concentration range $0.21 < x < 0.12$ at which water cavities are filled up by interstitial solvation, as well as formation of hydrophobic amide aggregates, or as a

consequence of both. However, further studies are needed to confirm this.

Acknowledgement

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