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Excess compressibility and excess dielectric constant for a morpholine–*n*-butyl alcohol liquid mixture

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Abstract. The variation in excess compressibility β^E and excess dielectric constant ϵ'^E as a function of mole fraction x at room temperature have been determined for a liquid mixture of morpholine (as the solute) with *n*-butyl alcohol (as the solvent). The excess compressibility was found to be negative for this liquid mixture and is explained in terms of solute–solvent interactions. The excess dielectric constant was found to be abnormally positive for this liquid mixture at a mole fraction of around 0.25 and is explained in terms of the alignment of dipoles.

1. Introduction

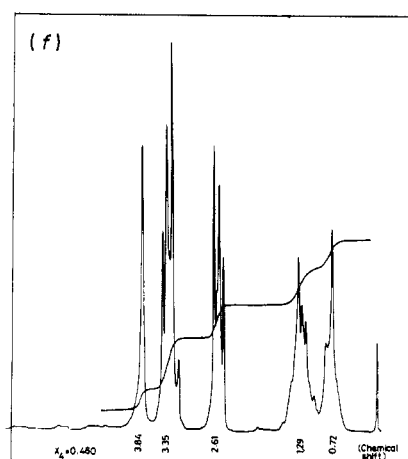
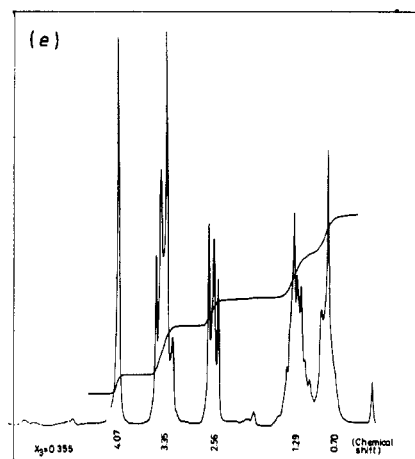
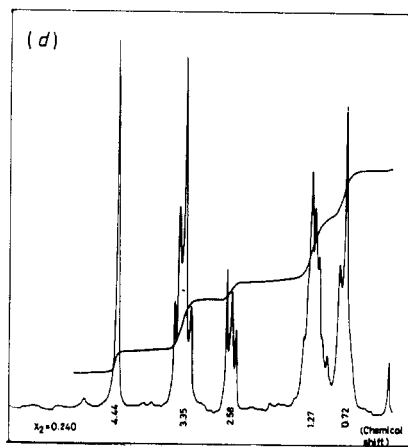
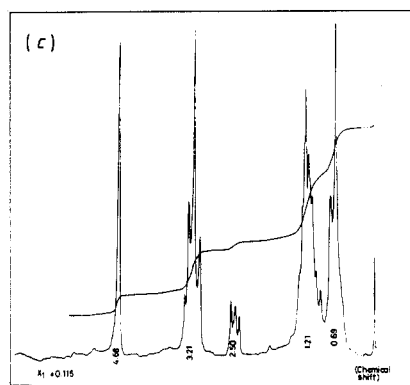
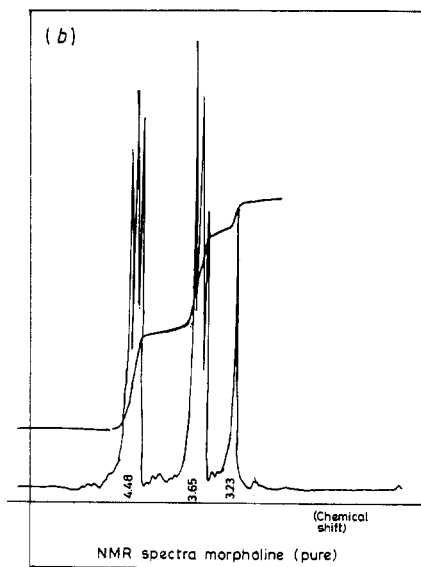
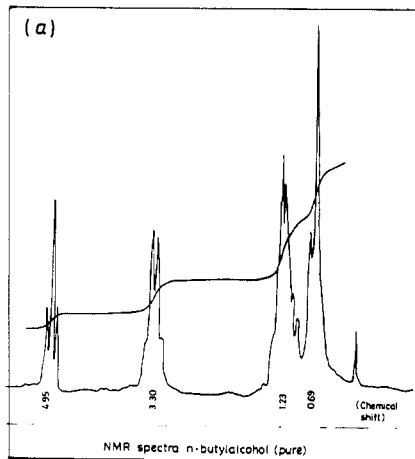
The propagation characteristics of ultrasonic waves in liquids and liquid mixtures are widely used to study the intermolecular interactions [1, 2]. Departures from linearity of a physical property when studied as a function of concentration (in the case of liquid mixtures), i.e. the excess parameters such as excess molar volume, excess compressibility, excess heat capacity, excess Grüneisen parameter and excess dielectric constant, provide better insight into the molecular process [3–7].

Similar studies on excess dielectric constant [8, 9] in liquid mixtures throw light on the nature of interactions between the molecular components and alignment of dipoles, etc. Franks and Ives [10] have given a detailed review on excess parameters for an alcohol–water mixture and alcohol with other organic liquids and have suggested reasons for the deviations of the physical properties from the ideal values.

This paper presents studies carried out on excess dielectric constant in an organic liquid mixture of morpholine (as the solute) with *n*-butyl alcohol, an isomer of butyl alcohol as the solvent at room temperature. *n*-butyl alcohol is a hydrogen-bonded liquid because of the O–H group in the alcohol, and hydrogen bonding may take place with other organic liquids.

2. Purification of the liquids

Both the experimental liquids, namely morpholine and *n*-butyl alcohol, which were supplied by E Merck, were distilled twice and kept in a desiccator before use. The density of the liquid was measured correct to the third decimal place, using a specific



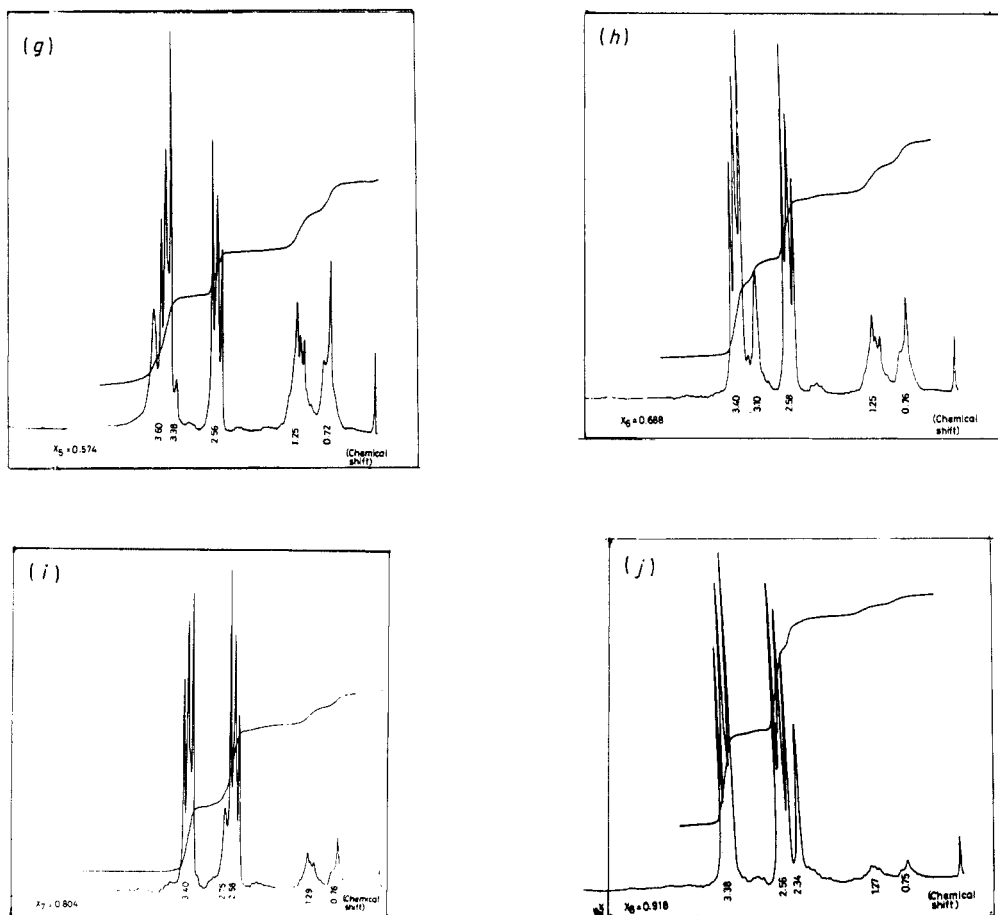


Figure 1. NMR spectra of (a) pure *n*-butyl alcohol, (b) pure morpholine and (c)–(j) with various mole fractions x ((c) 0.015; (d) 0.24; (e) 0.355; (f) 0.46; (g) 0.574; (h) 0.688; (i) 0.804; (j) 0.918) at 30 °C.

gravity bottle and an analytical balance. The values of the densities and boiling points of the liquids that we determined agree well with the values given in the literature.

3. Excess compressibility studies from ultrasonic measurements

Morpholine was mixed into the *n*-butyl alcohol in various mole fractions x ranging from 0 to 1. The ultrasonic velocities were measured for the pure liquids and the liquid mixtures (at the different mole fractions prepared) using a single-crystal variable-path ultrasonic interferometer supplied by M/s Mittal Enterprises, New Delhi. The densities of the liquids were measured using a specific gravity bottle, as mentioned earlier.

The adiabatic compressibility β_S of a liquid is determined from the ultrasonic velocity and density measurements using the well-known relation

$$\beta_S = 1/\rho u^2 \quad (1)$$

where ρ is the density of the liquid and u is the ultrasonic velocity in the liquid.

The excess compressibility β_S^E , i.e. the deviation from the ideal value, is given by

$$\beta_S^E = \beta_{S(\text{exptl})} - \beta_{S(\text{ideal})} \quad (2)$$

$$\beta_{S(\text{ideal})} = \beta_{S1}x + \beta_{S2}(1-x) \quad (3)$$

where $\beta_{S(\text{exptl})}$ is the experimentally determined compressibility value of the liquid mixture, β_{S1} is the adiabatic compressibility of the solute, β_{S2} is the adiabatic compressibility of the solvent and x is the mole fraction of the solute in the solvent.

3.1. Results and discussion

The molecular formula for *n*-butyl alcohol is $C_4H_{10}O$ and has a chain like structure. Morpholine has a chair configuration [11]. From NMR spectra, it has been observed that the hydrogen bonding of *n*-butyl alcohol takes place through both the 'oxygen' atom and the 'N-H' group of morpholine. As an illustration, the NMR spectra for pure morpholine, for pure *n*-butyl alcohol and for liquid mixtures with various mole fractions are shown in figure 1. It is seen from figure 2 that β_S^E is negative at all mole fractions, with a maximum value at a mole fraction of around 0.5.

The force A-A interaction (between the molecules of alcohol) is strong because *n*-butyl alcohol has a chain-like structure. In *n*-butyl alcohol the intermolecular forces of attraction are strong owing to hydrogen bonding and comparable with the interaction of morpholine molecules. Initially, i.e. for small mole fractions of morpholine, a smaller

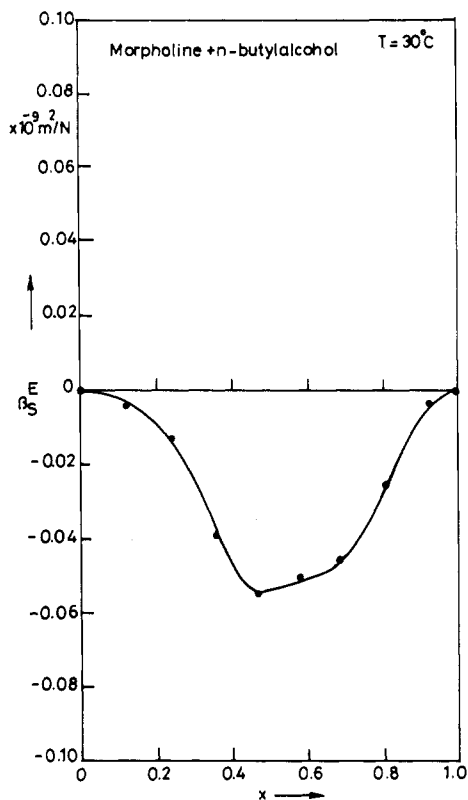


Figure 2. Variation in the excess compressibility β_S^E (using equation (2)) of morpholine-*n*-butyl alcohol with mole fraction x at 30 °C.

degree of hydrogen bonding of the alcohol takes place with morpholine and so the force of the A-B interaction is not very much greater than the forces of the A-A or B-B interactions (the molecules of morpholine). Hence a smaller negative deviation in compressibility results at a lower concentration of morpholine (figure 2). As the concentration of morpholine increases, the interaction of the alcohol with the morpholine increases with increasing x . This is possibly due to the availability of a large number of morpholine molecules. Hence the A-B interaction predominates (H bonding with morpholine is strong) over the A-A and B-B interactions, resulting in a larger negative deviation in the excess compressibility. NMR spectra (figure 1) also show that the individual identities of the N-H of the morpholine and the O-H of *n*-butyl alcohol are lost and both of them collapse to one resonance value as the concentration of morpholine in the alcohol increases. Beyond a mole fraction of 0.5 or 0.6, morpholine molecules are predominant; this was also reflected in the NMR spectra. At higher mole fractions of morpholine, the A-B interaction is weaker than the B-B interaction and hence there is a smaller negative deviation in β_3^E -values.

The experiment was also carried out at temperatures of 40 and 50 °C; there was not much change in the values of β_3^E and the trends remain the same.

4. Excess dielectric constant studies

As in the case of the compressibility studies, here also morpholine was mixed into *n*-butyl alcohol at different mole fractions x ranging from 0 to 1. The dielectric constant of a liquid is determined from capacitance measurements. We used a GR 1620A capacitance bridge which works on the null detector method. A two-terminal gang condenser of capacitance about 25 pF (C_0) with leads was used in the present work. There was no electrode polarisation as the dissipation factor was negligible. The system has a certain lead capacitance C_L due to its leads and edge effects. The value of the capacitance of the gang condenser in air is given by

$$C_{\text{air}} = C_0 + C_L. \quad (4)$$

The condenser is kept in a double-walled glass cell and filled with a liquid of known dielectric constant $\varepsilon'_{\text{std}}$ (benzene was used); again the capacitance of the system is measured as

$$C_{\text{std}} = \varepsilon'_{\text{std}} C_0 + C_L. \quad (5)$$

By solving equations (4) and (5), C_0 and C_L are obtained. The dielectric constant ε' of any liquid is determined by measuring the capacitance of the system C_{liq} (the condenser immersed in the liquid) which is given by

$$C_{\text{liq}} = \varepsilon'_{\text{liq}} C_0 + C_L. \quad (6)$$

As all the quantities except $\varepsilon'_{\text{liq}}$ in equation (6) are known, the dielectric constant $\varepsilon'_{\text{liq}}$ of the liquid can be determined. The dielectric constant ε' was determined for some standard organic liquids such as chlorobenzene, cyclohexanone, cyclohexane and carbon tetrachloride, and the values obtained agreed well with the values in the literature. The experiment was extended to our system at 100 kHz.

On the assumption that the dielectric constant obeys the additive law [12], the excess

dielectric constant ϵ'^E is given by

$$\epsilon'^E = \epsilon'_{\text{exptl}} - \epsilon'_{\text{ideal}} \quad (7)$$

$$\epsilon'_{\text{(ideal)}} = \epsilon'_1 x + \epsilon'_2 (1 - x) \quad (8)$$

where ϵ'_{exptl} is the actual experimentally determined value of the dielectric constant of the liquid mixture, ϵ'_1 is the dielectric constant of the solute (morpholine), ϵ'_2 is the dielectric constant of the solvent (alcohol) and x is the mole fraction of the solute in the solvent.

4.1. Results and discussion

The variation in the excess dielectric constant ϵ'^E (using equation (7)) for various mole fractions x (0 to 1) for the liquid mixture of morpholine and *n*-butyl alcohol at 30 °C is shown in figure 3. The variation in ϵ'^E is positive and is as high as +24.0 at a mole fraction of around 0.25 and ϵ'^E drops to zero at a mole fraction of around 0.5.

The dipole moment μ was calculated theoretically for the pure liquids and the liquid mixtures, as described briefly below [13].

One starts with an estimated geometry as input and minimises the energy by geometrical optimisation. The algorithm finds the closest minimum on the potential energy surface.

Calculations done with the present program provide the heat of formation of

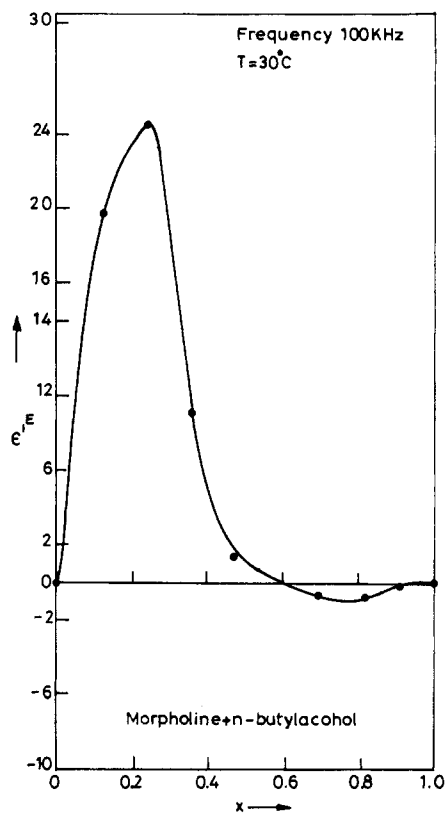


Figure 3. Variation in the excess dielectric constant ϵ'^E (using equation (7)) of morpholine-*n*-butyl alcohol with mole fraction x at 30 °C (frequency, 100 kHz).

molecules, the optimised geometry, the contributions to the energy in terms of the various components mentioned initially, dipole moments, etc. This version of the program has been parametrised to handle hydrogen bonding to 'oxygen' and 'nitrogen' atoms.

In general, the square of the dipole moment μ^2 is proportional to the dielectric constant ϵ' at low frequencies [14]. So, on the assumption that the dipole moment of a liquid mixture obeys the additive law [15], then for a non-interacting or ideal system

$$\mu_{\text{non-int}}^2 = x\mu_1^2 + (1-x)\mu_2^2 \quad (9)$$

where μ_1 is the dipole moment of the solute (morpholine) and μ_2 is the dipole moment of the solvent (*n*-butyl alcohol).

For interacting systems, i.e. interaction through hydrogen bonding,

$$\mu_{\text{int}}^2 = \sum_{i=1}^5 x_i \mu_i^2 \quad (10)$$

where μ_3 is the average dipole moment of the 1:1 H-bonded complex, μ_4 is the average dipole moment of the 1:2 H-bonded complex and μ_5 is the dipole moment of the 1:3 H-bonded complex. x_i are the mole fractions obtained by setting up and solving kinetic equations for the formation of the various hydrogen-bonded complexes mentioned above, with the three initial ratios of morpholine to alcohol being 1:1, 1:2 and 1:3.

The final theoretically calculated values of μ_{int}^2 for the three ratios (1:1, 1:2 and 1:3) are presented in table 1.

Denoting μ_{int}^2 as μ_{mix}^2 , and $\mu_{\text{non-int}}^2$ as μ_{calc}^2 , the values of μ_{mix}^2 and μ_{calc}^2 are presented in table 1. The values of $\Delta\mu^2 = \mu_{\text{mix}}^2 - \mu_{\text{calc}}^2$ are also presented in table 1 for the three molar ratios. It is seen from table 1 that $\mu_{\text{mix}}^2 > \mu_{\text{calc}}^2$ at all the molar ratios and is a maximum at the 1:3 molar ratio. Probably at this molar ratio, i.e. a mole fraction of 0.25, the degree of alignment of dipoles in the liquid mixture is a maximum. It is seen from figure 3 that at a mole fraction of around 0.25, ϵ'^E has a maximum positive value. The experimental value of the dielectric constant of the liquid mixture at a mole fraction of around 0.25 is much greater than (about twice) the dielectric constant of the constituent species, namely *n*-butyl alcohol and morpholine.

As an auxiliary test, the excess dielectric constant for a liquid mixture of non-polar dioxane and *n*-butyl alcohol was determined. It was found that ϵ'^E was slightly negative at all the mole fractions. Even by the molecular mechanics approach, it was found that $\mu_{\text{mix}}^2 - \mu_{\text{calc}}^2$ was negligible for the molar ratios of both 1:1 and 1:2. The molecular formula of dioxane is $C_4H_8O_2$. The dipole moment of dioxane is zero, because it has an 'oxygen' atom at both ends of the structure and there is symmetry in the system. On adding *n*-butyl alcohol to dioxane, i.e. attaching *n*-butyl alcohol molecules to both the 'oxygen' atoms of dioxane, hydrogen bonding takes place through both the 'oxygen' atoms. Still

Table 1. Calculated values of μ_{mix}^2 and μ_{calc}^2 for different molar ratios for hydrogen-bonded complexes (morpholine and *n*-butyl alcohol).

Sample	Molar ratio	μ_{mix}^2	μ_{calc}^2	$\mu_{\text{mix}}^2 - \mu_{\text{calc}}^2 = \Delta\mu^2$
1	1:1	12.39	2.758	9.632
2	1:2	23.23	2.879	20.350
3	1:3	35.40	2.89	32.51

the symmetry of the system is not disturbed much, and the theoretically obtained value of the dipole moment of the 1:2 complex was found to be close to zero. However, when one 'oxygen' atom of dioxane is replaced by an 'N-H' group, which is the structure of morpholine, interesting results have been obtained, namely large positive values of ϵ'^E as seen above.

5. Conclusions

If one compares and analyses the results of the excess compressibility and the excess dielectric constant of a morpholine-*n*-butyl alcohol liquid mixture, some sort of correlation exists between these two. In the case of the morpholine-*n*-butyl alcohol liquid mixture, the excess compressibility is negative, showing that there is a strong solute-solvent interaction. This was also supported by NMR experiments. For this same liquid mixture the large dielectric constant obtained implies a high degree of alignment of dipoles.

Acknowledgments

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