Physico-chemical behaviour of binary liquid mixtures : n-butyl alcohol in cyclohexane

S SUBBA RAO and R GOPALAKRISHNAN
Department of Physics, Sri Venkateswara University College of Engineering,
Tirupati 517 502

Abstract. Magnetic susceptibilities, ultrasonic velocities, refractive indices and dielectric constants of the mixtures, n-butyl alcohol in cyclohexane were determined as a function of concentration. Deviations from the normal behaviour were observed which may be attributed to the deassociation of hydrogen bonds and interstitial occupation of non-polar solvent molecules.

Keywords. Magnetic susceptibility; ultrasonic velocity; dielectric constant; refractive index; n-butyl alcohol; cyclohexane; liquid mixtures.

1. Introduction

It has been shown that mixtures of associated liquids show large variations in the properties like magnetic (Gopalakrishnan 1970), ultrasonic (Rao and Rao 1962), dielectric and refractive indices. In order to understand the nature of the deviations the behaviour of n-butyl alcohol in an inert solvent (cyclohexane) has been studied. An attempt has been made to discuss the behaviour of these mixtures on the basis of structure breaking and interstitial occupation of non-polar molecules.

2. Experimental

The magnetic susceptibilities were determined using an improved Gouy method. Effect of magnetic impurities were eliminated by standard methods from the measurements made at different field strengths in the range 3,000 to 11,000 Gauss. The reproducibility in current settings is facilitated by a sensitive galvanometer connected across a small resistor placed in series with an ammeter in the electromagnet circuit. The susceptibilities were determined to an accuracy better than one per cent.

The ultrasonic velocities were determined using a single crystal interferometer working at a fixed frequency of 2 MHz to an accuracy of $\pm 0.01\%$.

The dielectric constants were measured using a universal dielectrometer working at a frequency of 2 MHz to an accuracy of ± 0.1 to 0.3%. The refractive index

was measured using an Abbe refractometer to an accuracy of $\pm\, 0\cdot0001$. Densities were determined using a double stem pyknometer. The uncertainty in determining density was 12 in 10^5. The solutions were prepared by mixing the accurately weighed quantities of pure liquids. In our discussion, alcohol is designated as the component B and the solvent cyclohexane as A.

3. Results and discussion

The measured susceptibility of the mixture under study showed considerable deviations from the values obtained on the basis of the law of additivity. The excess susceptibility χ^E defined as the difference between the experimental value and the additive value is calculated. It is represented as a function of mole fraction C_B of the second component in figure 1. The mole fraction of the solvent is C_A.

The peculiar behaviour of the mixture can be explained following the general ideas of Rowlinson (1957). When small quantities of cyclohexane are added to the alcohol, the intermolecular weak hydrogen bonds between the alcohol molecules are gradually broken resulting in an increase in the value of χ. As the concentration of cyclohexane increases, the deassociation of alcohol polymer molecules become more pronounced. This situation corresponds to the maximum positive deviation in figure 1 at about $0\cdot8$ mole fraction of C_B. On further addition of cyclohexane, the solvent molecules begin to find places in the interstices of alcohol clusters in addition to a small degree of breaking of bonds. This is in the concentration range $0\cdot3$ to $0\cdot7$. In the concentration range of alcohol below $0\cdot3$ mole fraction, the graph shows a negative deviation which may be ascribed to predominant effect of interstitial placement of the diluent molecules as has been explained by Gopalakrishnan (1964, 1971) in some alcohol mixtures.

The ultrasonic behaviour of the system shown in figure 2 has already been studied by Seshadri *et al* (1974). The velocity vs mole fraction curve shows the
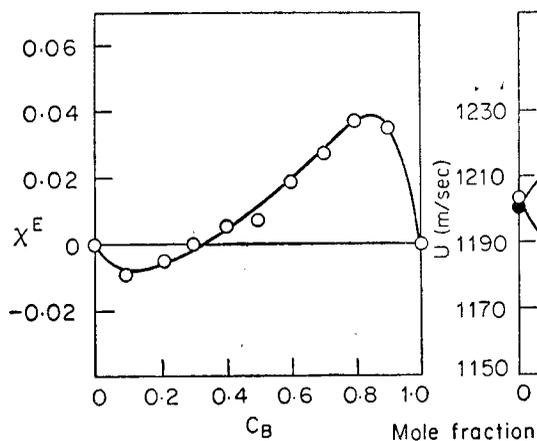

Figure 1   Figure 2

Figure 1. Variation of excess susceptibility with mole fraction of the mixtures, cyclohexane + *n*-butyl alcohol.
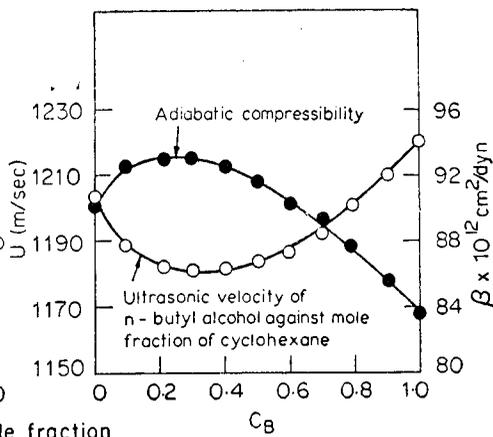
Figure 2. Variation of ultrasonic velocity and adiabatic compressibility of the mixtures, cyclohexane + *n*-butyl alcohol.
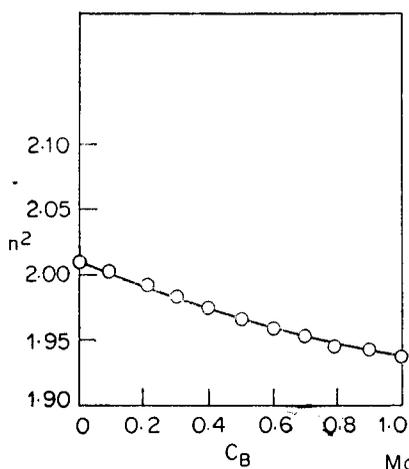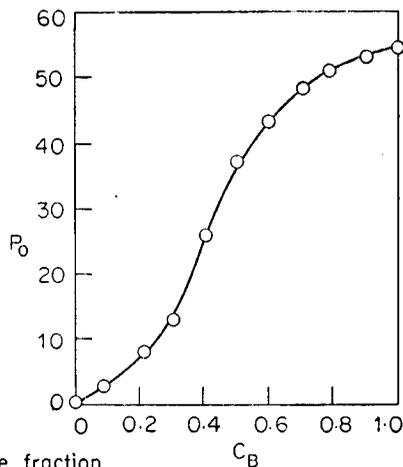
Figure 3

Figure 4

Figure 3. Variation of the square of the refractive index against mole fraction of the mixtures, cyclohexane + n-butyl alcohol.

Figure 4. Variation of orientation polarisation against mole fraction of the mixtures, cyclohexane + n-butyl alcohol.

same trend as that noticed by Seshadri *et al* (1974). The behaviour at high concentrations of cyclohexane may be due to the interstitial occupation of the cyclohexane molecules rather than the readjustment of molar volume appropriate to that of solvent as is evident from the magnetic behavour discussed above.

In the present study n^2 vs C_B plot shown in figure 3 does not show a change in slope or any positive deviation, thereby indicates the absence of any new complex formation (Arshid *et al* 1956; Liler and Kosanovic 1957).

The molar polarisation of the mixture P_{AB} and the orientation polarisation P_0 were calculated from the experimentally determined dielectric constant (ϵ) and the density (d) following the method of Smyth (1955). The plot P_0 vs C_B shown in figure 4 is also in accord with the conclusions given above, namely, progressive dilution of alcohol brings about a sharp fall in the value of P_0 and a gradual fall thereafter indicating the interstitial placement of the diluent molecules.

References

Arshid F M, Giles C H and Jain S K 1956 *J. Chem. Soc.* 559
Gopalakrishnan R 1964 *Physica* **30** 2019
Gopalakrishnan R 1970 *Bull. Chem. Soc. Jpn.* **43** 1607
Gopalakrishnan R 1971 *J. Prakt. Chem.* **313** 778
Liler M and Kosanovic Dj 1957 *Symposium on hydrogen bonding* (London : Pergamon Press) p. 529
Rowlinson J S 1957 *Symposium on hydrogen bonding* (London : Pergamon Press) p. 423
Seshadri K, Prabhakara Rao N and Reddy K C 1974 *Z. Phys. Chem.* (*NF*) **89** 108
Seshagiri Rao M G and Ramachandra Rao B 1962 *J. Sci. Ind. Res.* **B21** 331
Smyth C P 1955 *Dielectric behaviour and structure* (New York, Toranto, London : McGraw-Hill) p. 18