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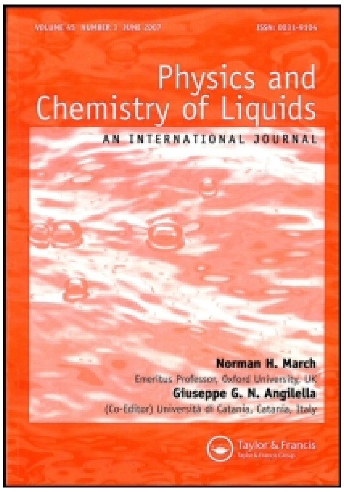

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ULTRASONIC STUDY OF BINARY SOLUTIONS OF METHANOL, ETHANOL AND PHENOL IN SULPHOLANE

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The velocity (v) of ultrasonic waves of 3 MHz frequency and density (ρ) have been measured in various binary solutions of methanol, ethanol and phenol in sulpholane at 313.15 K and used to calculate several acoustical parameters. The interaction with sulpholane has been found to be in the order of MeOH > EtOH > PhOH. In spite of the greater electron density on phenoxide ion, the ion-solvent interaction is least in phenol-sulpholane solutions; presumably due to intensive delocalization of electrons on the phenoxide ion.

KEY WORDS: Ultrasonic velocity, density, thermodynamic parameters, ion-solvent interaction.

INTRODUCTION

In continuation of our previous ultrasonic study of ion-solvent interaction in sulpholane[1-3], the work has now been extended to the binary solutions of this solvent in hydrogen bonded and protic solvents such as methanol, ethanol and phenol at 313.15 K. Determination of the velocity of the propagated ultrasonic wave leads to the calculation of several very useful parameters, employed in ascertaining in solutions the degree of molecular association, dissociation, complex formation etc. The survey of literature reveals that almost all the alcohols have been undertaken as one or two components in different binary and ternary systems[4]. However, such a study in sulpholane seems to be completely missing. The selection of alcohols as one component is due to their polar nature and hydrogen bonding interaction. Molecules of methanol and ethanol are small enough as compared to relatively larger and resonance-stabilized phenoxide ion. Another of our ideas for choosing phenol, was to examine the interaction between an aromatic and non-aromatic (sulpholane) cyclic molecules.

EXPERIMENTAL

Sulpholane (Fluka, puriss) was purified by method reported elsewhere[1]. Methanol (Sarabhai) and ethanol (Sarabhai) were purified by fractional distillation. Phenol (Anal AR) was purified by standard method[5]. All solvents and their solutions were kept under vacuum for about an hour before experiment in order to remove traces of dissolved air. The velocity (v) of ultrasonic wave of 3 MHz frequency at 313.15 K was measured by Ultrasonic Interferometer (accuracy 0.03%). The desired temperature was maintained by circulating thermostatically controlled water through the outer jacket of measurement cell from a 'Toshniwal Constant Temperature Bath' (accuracy $\pm 0.01°$). To reduce the heat loss due to dissipation, the water circulatory system was further augmented with a 'Tullu' water pump. The density (ρ) of all solutions at 313.15 K was measured with the help of a precalibrated dilatometer. With the help of measured v and ρ, adiabatic compressibility (β), specific acoustic impedance (Z), intermolecular free length (L_f), molar volume (V), molar sound velocity (R), molar compressibility (W), available volume (V_a), relative association (R_A), degree of molecular interaction (α), excess adiabatic compressibility (β^E) and excess intermolecular free length (L_f^E) have been calculated using known equations[1,6,7].

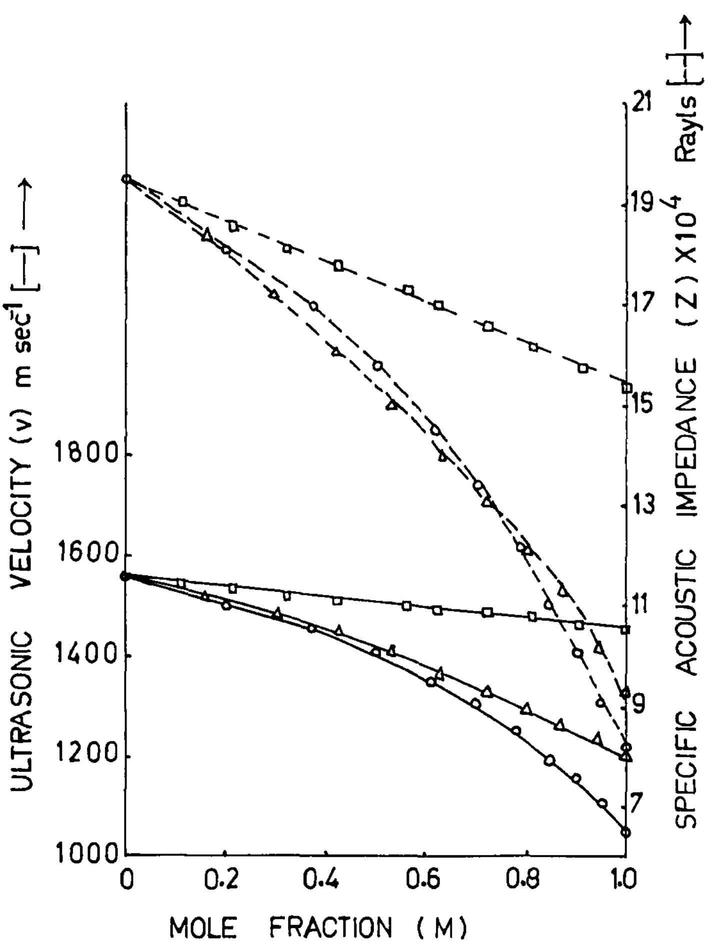

Figure 1 Ultrasonic velocity and specific acoustic impedance versus mole fraction graph for MeOH–sulpholane [○○] EtOH–sulpholane [△△] and PhOH–sulpholane [□□] solutions at 313.15 K.

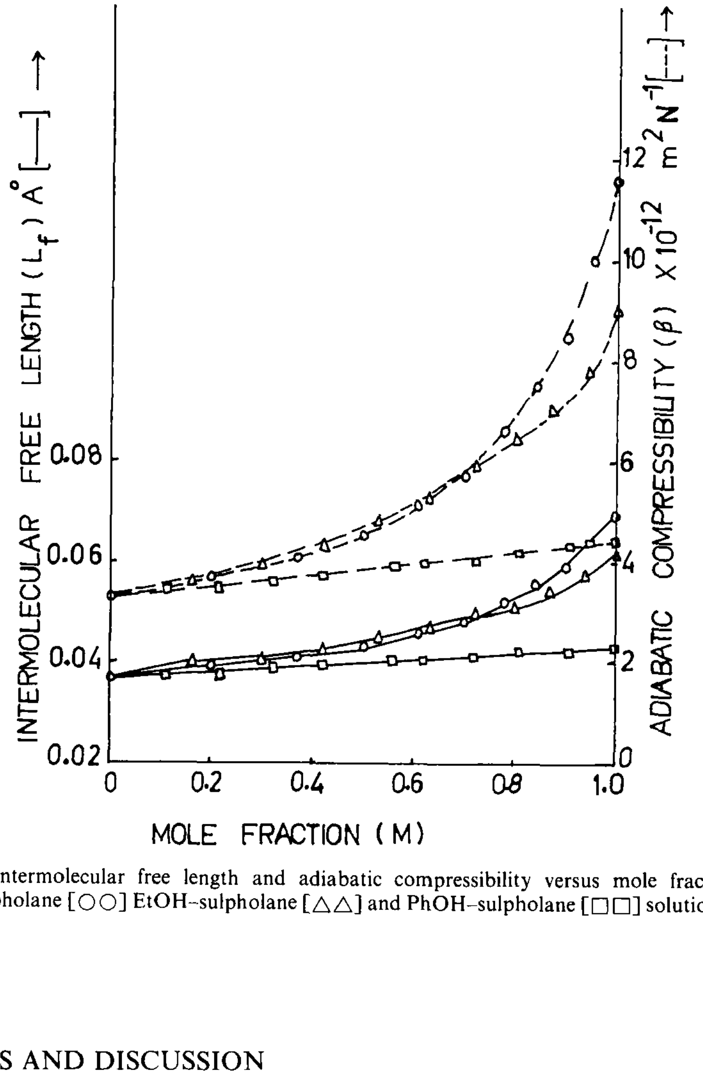

Figure 2 Intermolecular free length and adiabatic compressibility versus mole fraction graph for MeOH–sulpholane [○○] EtOH–sulpholane [△△] and PhOH–sulpholane [□□] solutions at 313.13 K.

RESULTS AND DISCUSSION

The variation of ultrasonic velocity (v) and other derived thermodynamic parameters, including excess functions, have been plotted against the mole fraction of methanol, ethanol and phenol each in Figures 1–6.

The v and Z decrease with the increase in mole fraction of methanol, ethanol and phenol (Figure 1) while the β and L_f show a gradual increase in curves as the concentration of solutes increases (Figure 2). However, W decreases with the increase in solute mole fractions (Figure 3). The variation in these parameters is almost negligible in phenol-sulpholane solution while the magnitude of increase in β and L_f and decrease in v, Z and W is larger in ethanol-sulpholane and still more in methanol-sulpholane solutions. The linearity in the curves of β, v and W in phenol-

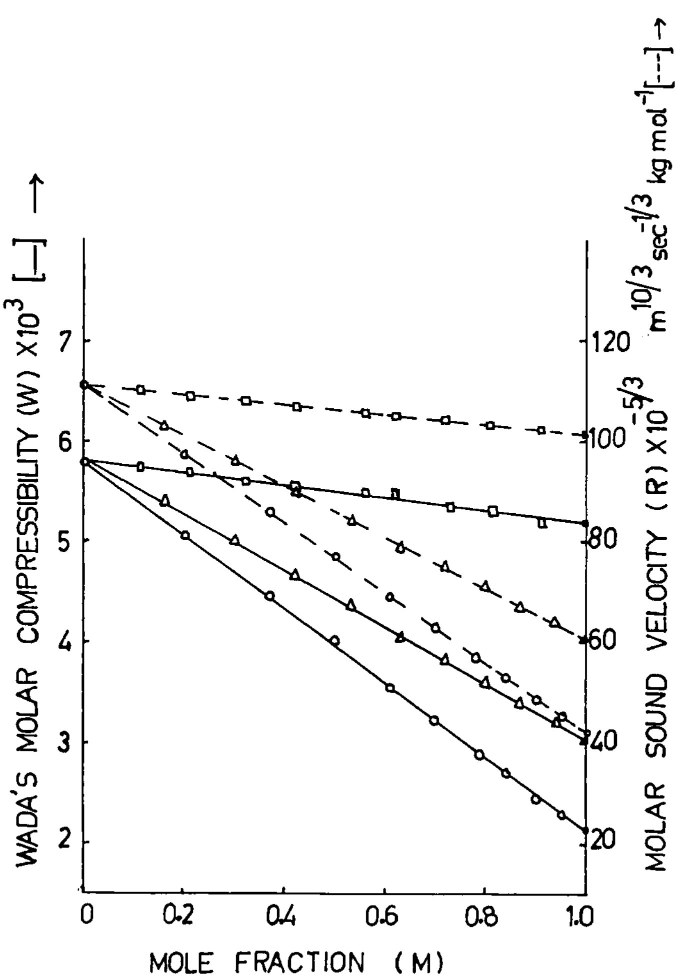

Figure 3 Wada's molar compressibility and molar sound velocity versus mole fraction graph for MeOH-sulpholane [○○] EtOH-sulpholane [△△] and PhOH-sulpholane [□□] solutions at 313.15 K.

sulpholane shows the absence of any complex formation[8], as is also indicated by the increase in R[9] (Figure 3).

The excess functions of adiabatic compressibility (β^E) and intermolecular free length (L_f^E) show a negative deviation which is maximum in methanol-sulpholane followed by ethanol-sulpholane and least in phenol-sulpholane solutions (Figure 4). These deviations seem to be entirely due to the molecular association caused by weak bonds. The same is also evident by the degree of molecular interaction vs. mole fraction curves (Figure 5) which shows a peak at 0.6 mole fraction in methanol-sulpholane and ethanol-sulpholane solutions while the phenol-sulpholane solution shows a slight decrease. It may be due to the difference in size of solute molecules[4]. The methanol, being smallest in size is more capable of forming weak bonds with sulpholane while

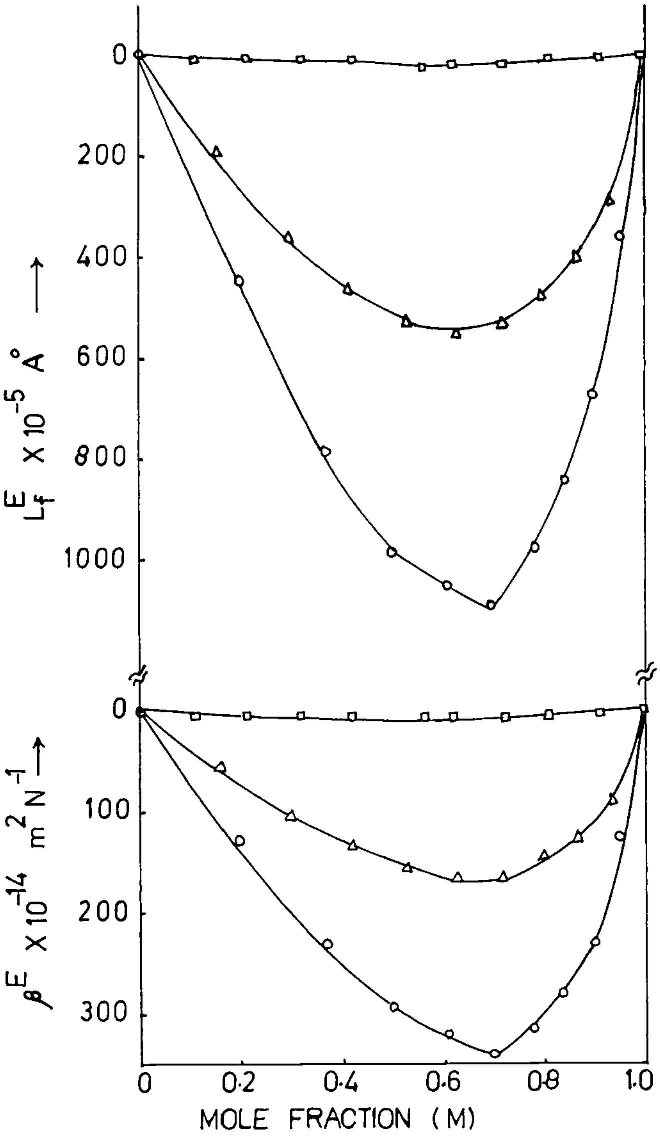

Figure 4 Excess adiabatic compressibility (β^E) and excess intermolecular free length (L_f^E) versus mole fraction graph for MeOH-sulpholane [○○] EtOH-sulpholane [△△] and PhOH-sulpholane [□□] solutions at 313.15 K.

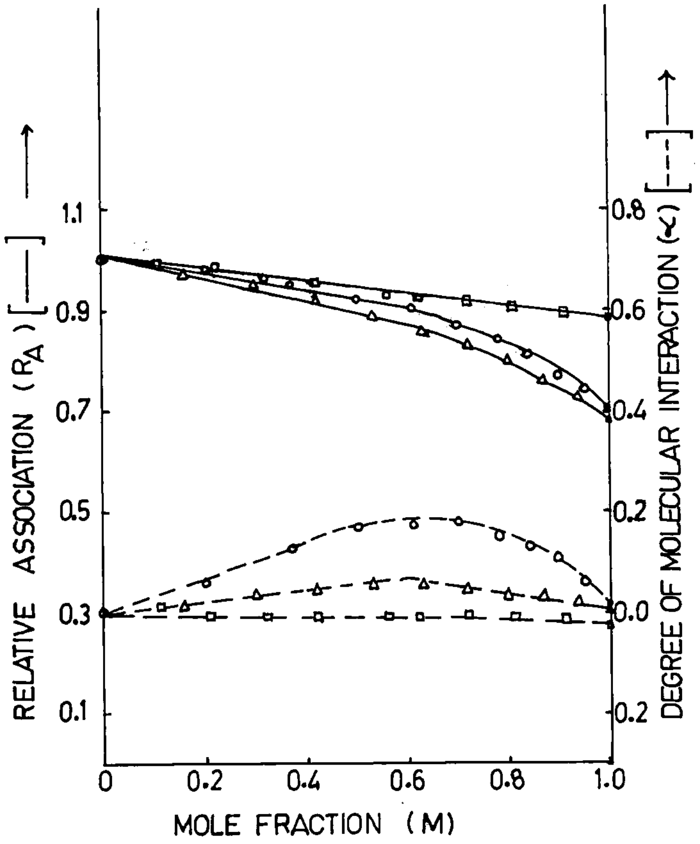

Figure 5 Relative association and degree of molecular interaction versus mole fraction graph for MeOH-sulpholane [○○] EtOH-sulpholane [△△] and PhOH-sulpholane [□□] solutions at 313.15 K.

the probability of these bonds is quite less in phenol because of steric hinderance. The R_A, however, decreases with the increase in solute concentrations (Figure 5).

As expected, the V decreases with the increase in solute concentrations (Figure 6). This decrease increases with the decrease in molecular weight of solutes i.e. in the order $CH_3OH > C_2H_5OH > C_6H_5OH$. The V_a increases with the increase in solute concentrations (Figure 6) and is found to be maximum in ethanol-sulpholane followed by methanol-sulpholane and least in phenol-sulpholane solutions, suggesting that the increasing concentration of smaller molecule exerts strong hydrophobic repulsion compared to the large size molecules.

To conclude, we may say that the interaction between sulpholane and phenol molecules is far less compared to between smaller molecules of methanol and ethanol perhaps due to the larger size and high delocalization of electron of phenol molecules leading to very poor selection of the site of interaction by the solvent molecules.

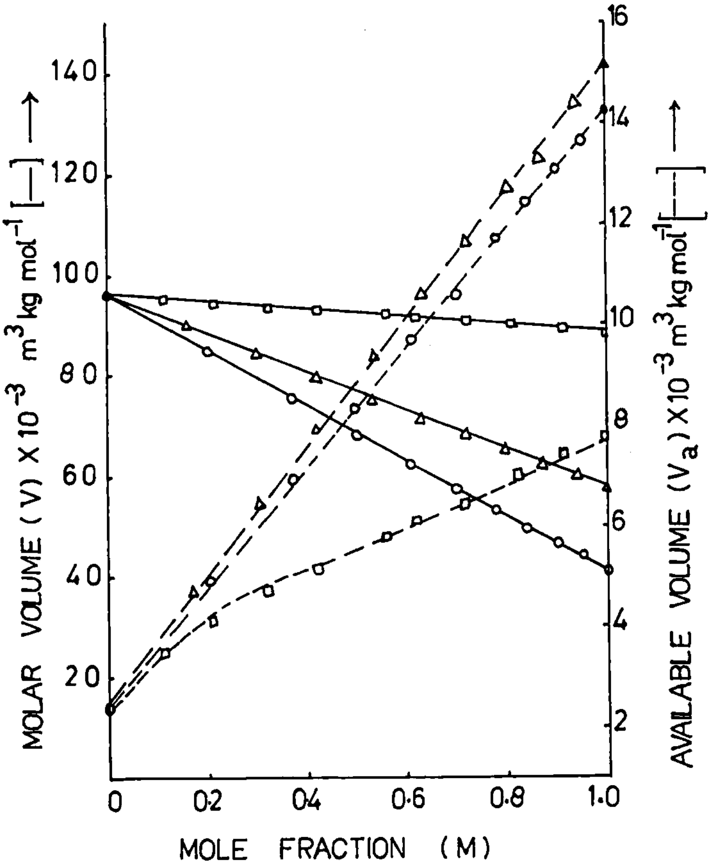

Figure 6 Molar volume and available volume versus mole fraction graph for MeOH–sulpholane [○○] EtOH–sulpholane [△△] and PhOH–sulpholane [□□] solutions at 313.15 K.

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