

PHYSICO-CHEMICAL STUDIES OF SOLVENT-SOLVENT AND ION-SOLVENT INTERACTIONS IN BINARY AND TERNARY MIXTURES

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Thermodynamic and physicochemical studies of binary and ternary liquid mixtures are of considerable theoretical and technological importance as they provide a wide range of solvents of varying composition and properties. Such studies are of particular significance owing to the practical applications of mixed solvents in various analytical techniques, e.g., chromatography and liquid-liquid extraction. Mixed solvents, with varying dielectric constants, are increasingly being used for the study of the kinetics of various reactions in these solvents. Therefore, we must know the role played by the medium (i.e. solvent) for studying such reactions. For instance, the presence of solvent can speedup or slowdown a reaction by a factor of ~ 1020 , a change of one solvent to another or addition a co-solvent can bring about a million-fold change in the reaction rate. Reactions that, in protic solvents, proceed slowly even at high temperatures to give low yields, are found, in an aprotic solvent to proceed rapidly, often at room temperature, to give high yields. Therefore, a deeper knowledge of the solution structure and intermolecular and ion-solvent, in case of electrolyte-solvent system, interactions between components of the binary and ternary mixtures will be important in providing a better understanding of many chemical, technological and biological processes in these mixed solvent media.

In view of the practical applications of the mixed solvents, densities, ρ and ultrasonic speeds, u in pure acetonitrile (ACN), formamide (FA), N,N-dimethylformamide (DMF), N,N-dimethyl-acetamide (DMA), 1-pentanol, tetrahydrofuran (THF), n-heptane, n-octane n-decane, 1-heptanol, 1-octanol, benzene, and those in the binary mixtures: ACN + FA, ACN + DMF, ACN + DMA, 1-pentanol + FA, 1-pentanol + DMF, 1-pentanol + DMA, THF + n-heptane, THF + n-octane, THF + n-decane, benzene + 1-pentanol, benzene + 1-heptanol, and benzene + 1-octanol were measured over the entire composition range at 35 °C. Using experimental values of ρ and u , a number of parameters such as isentropic compressibility, k_s , intermolecular free length, L_f , relative association, RA, acoustic impedance, Z, molecular association, MA, molar sound speed, R_m , isothermal compressibility, β_T , thermal expansion coefficient, α , deviations in

isentropic compressibility, D_{ks} and ultrasonic speed, D_u , excess free length, L_{fE} , excess volume, V_E , excess acoustic impedance, Z_E , apparent molar volume, $V_{f,2}$ of amides (FA, DMF and DMA) in 1-pentanol; apparent molar isentropic compressibility, $K_{f,2}$, apparent molar volume, $V_{f,2}$, partial molar compressibility, $^{\circ}K_{of,2}$, and partial molar volume, $^{\circ}V_{of,2}$ of n-alkanes (n-heptane, n-octane and n-decane) in THF were calculated. The variation of these parameters with composition of the mixtures are found to be very sensitive to the intermolecular interactions in these mixtures. Hence, they were critically examined in order to have a deeper knowledge of the interactions between the component molecules in the above binaries. Moreover, the ultrasonic behaviour of the binary liquid mixtures under study were theoretically examined by calculating the theoretical values of ultrasonic speed in these mixtures using free length theory (FLT), collision factor theory (CFT), Nomoto relation (NOM) and Van Dael-Vangeel (VDV) ideal mixing relation. The relative merits of these theories and relations in reproducing the experimental values of ultrasonic speed were discussed.

All the curves of the functions, Y_E (L_{fE} , D_{ks} , D_u , V_E and Z_E) against mole fraction, x were smoothed by the method of least-squares using a polynomial equation

$$Y_E = \sum_{i=1}^5 A_i (1 - 2x)^{i-1}$$

where A_i are the coefficients of the polynomial equation

Finally, the densities, ρ and viscosities, η of 0.01, 0.05, 0.10, 0.15 and 0.20 molar (M) magnesium sulphate ($MgSO_4$) in 20, 40 and 60 % (v/v) FA + ethylene glycol mixed solvents were measured at 25 °C. The experiment values of ρ and η were used to calculate the values of apparent molar volume, v_f , partial molar volume, $^{\circ}v_f$ at infinite dilution of solute, A and B-coefficients of Jones-Dole equation $\eta_r = \eta/\eta_0 = 1 + AC^{1/2} + BC$

where $\eta_r = (\eta/\eta_0)$ is the relative viscosity. Also, the free energies of activation of viscous flow, $\Delta m_1^{\circ*}$ and $\Delta m_2^{\circ*}$ per mole of the solvent and solute, respectively, were calculated. The behaviours of these parameters suggest strong ion-solvent interaction in these systems and that $MgSO_4$ acts as structure-maker in FA + ethylene glycol mixed solvents.