Thermophysical and Sonochemical Behaviours of Some Organic Liquid Mixtures

Scholar Bhajanlal Supervisor

Prof. Anwar Ali Department of chemistry Jamia Millia Islamia New Delhi-25

Densities r , and viscosities h , have been measured for pure N,N dimethylacetamide (DMA), 1-hexanol, 1-heptanol and for their eighteen binary mixtures, with DMA as common component, covering the entire composition range at 298.15, 303.15, 308.15, 313.15 and 318.15 K. Using the experimental values of r and h , the excess molar volume, V^E , deviations in viscosity, D h , excess rheochore, $[R^E]$, excess partial molar volume, ` $V_{2^\circ}^E$, of alkanols in DMA at infinite dilution and excess free energy of activation of viscous flow, D G^{*E} (or G^{*E}), enthalpy D H^{*}, and entropy D S^{*}, of activation of viscous flow have been calculated. The variation of these parameters with composition suggests that the interaction DMA-alkanol < DMA- DMA or alkanol-alkanol interactions. Densities, viscosities, ultrasonic speeds and refractive indices of benzene, n-butanol, iso-butanol, sec-butanol and tert-butanol and their binary mixtures, with benzene as common component, were measured at 303.15 K over the whole composition range. The dependence of u on composition of the mixture was checked by using the polynomial equation

 $\ln u(x_1) = \text{ å } \ln u_i x_1^{i}(1)$

i = 0

From the measured values of u and r , the isentropic compressibility, k_s , intermolecular free length, L_f , relative association, R_A , acoustic impedance, Z, molar sound speed, R_m , deviations in isentropic compressibility, D k_s , excess intermolecular free length, L_f^E , deviations in ultrasonic speed, D u, excess acoustic impedance, Z^E , apparent molar compressibilities, Kf _{,1} and Kf _{,2}, and partial molar compressibilities, ` K° f _{,1} and ` K° f _{,2} of benzene in alcohols and alcohols in benzene, respectively, at infinite dilution have been calculated. The variation of these parameters with composition indicates the presence of weak interactions between the component molecules and this interaction decrease in order: n-butanol > iso-butanol > sec-butanol > tert-butanol. The effect of branching in alcohols on the interaction between unlike molecules were examined.

Densities r and viscosities h pure of DMA, benzyl alcohol (BA), and their binary mixture were measured at 298.15, 303.15, 308.15, 313.15, and 318.15 K; densities, ultrasonic

speeds, viscosities and refractive indices of pure benzene, benzyl alcohol (BA), benzonitrile (BN), benzoyl chloride (BC), chlorobenzene (CB), and their thirty six binary mixtures, with benzene as common component, measured at 303.15 K over the entire composition range. The values of r , u, h , and n of these binary mixtures were used to evaluate V^E, D u D k_s, Z^E, D h , G^{*E}, ` V_{1}° , ` $V_{2,}^{\circ}$, K° f _{,2}, D H^{*} and D S^{*}. The presence of specific interactions, viz., H-bonding, dipole-dipole interaction between DMA and BA molecules have been suggested. In case of binary mixtures of benzene with BA, BN, BC, and CB, an increased cohesion (molecular order) in the solutions is noticed and that interaction (A-B) > (A-A) or (B-B). Densities, ultrasonic speeds, viscosities, and refractive indices of binary mixtures of anisole with benzyl chloride, (BC), nitrobenzene (NB), and chlorobenzene, (CB), including those of pure liquids, have been measured at 303.15 K. The values of D k_s, V^E, D u, D h , G^{*E}, [R^E], D n, Kf _{,2}, and Vf _{,2}, of BC, CB and NB in anisole at infinite dilution were calculated. The variations of these properties with composition suggest that the strength of interaction in these mixtures follow the order: BC > NB > CB.

Theoretical values of viscosities, ultrasonic speeds and refractive index of binary mixtures were predicted using the corresponding values of pure components. Theoretical values of viscosity of the binary mixtures were evaluated using Grunberg-Nissan, Hind, McLaughlin–Ubbelohde, Katti–Chaudhari and Herric–Brewer relations. Theoretical values of ultrasonic speed in binary mixtures were calculated using, Collision factor theory (CFT), Free length theory (FLT), Nomoto (NOM), Van Dael–Vangeel (VDV), Auerbach (ABR), Junjie (JUN) relations. Theoretical values of refractive index in binary mixtures were calculated using, Lorentz–Lorenz (L–L), Gladstone–Dale (G–D), Arago–Biot (A–B), Heller (H), Eykman (Eyk) and Oster's (Os) relations.