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Title of Thesis: '**Experimental and Theoretical Studies of Molecular Interactions in Non-Aqueous Binary Mixtures of Industrially Important Organic Solvents**'

# ABSTRACT

The research work incorporates collection of a new set of experimental data on various physicochemical properties such as density, speed of sound, viscosity and refractive index for the binary liquid systems comprising of liquid polymers (polyethylene glycols), diethylene glycol, 1-butanol, 2-butanol, 1,4-butanediol, dimethylsulphoxide and acetonitrile as one of the components at different temperatures and compositions. Subsequently, various thermodynamic functions for the individual properties from the measured data on pure and binary mixtures were evaluated. The composition dependence of the thermodynamic properties as a function of temperature, size, shape and the nature of components was also investigated. Hence, the work highlights how the knowledge of the composition and temperature dependences of the thermodynamic, optical, transport and acoustical properties of multi-component liquid mixtures provide substantial information on the molecular influence on the intensity of the intermolecular interactions among component molecules. The work also involves testing some existing theories of solutions with the experimentally derived properties for the binary liquid systems at different temperatures and compositions.

The densities and refractive indices for DMSO + PEG200/PEG300/PEG400 binary mixtures have been measured over whole composition range at four different temperatures. From the experimental data, the values of $V_{\mathrm{m}}^{\mathrm{E}}$, $n_{\mathrm{D}}^{\mathrm{E}}$, $\overline{V}_{m,1}^{\circ E,\infty}$, $\overline{V}_{m,2}^{\circ E,\infty}$, $\overline{V}_{\phi,1}^{\circ E,\infty}$ and $\overline{V}_{\phi,2}^{\circ E,\infty}$ have been calculated. The results indicate the presence of specific interactions between DMSO and PEG molecules. The negative deviations in $V_{\mathrm{m}}^{\mathrm{E}}$ and $n_{\mathrm{D}}^{\mathrm{E}}$ values follow the order: PEG200 < PEG300 < PEG400. It is observed that $V_{\mathrm{m}}^{\mathrm{E}}$ and $n_{\mathrm{D}}^{\mathrm{E}}$ values depend upon the chain length of PEG molecules. The refractive index data are well correlated by various mixing rules.

The densities for (AN + PEG200 or PEG300 or PEG400) binary mixtures have been measured and the values of $V_{\mathrm{m}}^{\mathrm{E}}$, $\overline{V}_{m,1}$, $\overline{V}_{m,1}^{\circ\infty}$, $\overline{V}_{m,1}^{\circ E,\infty}$, $\overline{V}_{m,2}$, $\overline{V}_{m,2}^{\circ\infty}$, and $\overline{V}_{m,2}^{\circ E,\infty}$ were

calculated. The $V_{\mathrm{m}}^{\mathrm{E}}$ values were found negative for all the mixtures and at each temperature studied, indicating the presence of specific and non-specific interactions between AN and PEG molecules. Moreover, the existence of specific interactions due to the directional bonds and non-specific interaction due to the structural differences between the components with the predominance of the latter, is also supported by the trends observed for the values of $\Delta_{\phi}n$ and $\Delta\kappa_s$. The extent of deviations in all the excess values determined, show that the interactions in these mixtures follow the order: PEG400 > PEG300 > PEG200.

The densities and ultrasonic velocities had been measured for the binary mixtures of DEG with 1-butanol, 2-butanol and 1,4-butanediol and calculated the excess molar volumes and deviations of isentropic compressibility. The values of $V_m^E$ and $\Delta\kappa_s$ show similar trends with temperature over the entire composition range. It is concluded from the values of $V_m^E$ and $\Delta\kappa_s$ that the interactions between DEG + 2-butanol are strong than those between DEG + 1-butanol in the case of 2-butanediol than 1-butanol and quite unfavourable for 1,4-butanediol. It has also been inferred from the results that it is the hydrogen bonds (both intra – and intermolecular) and those involved in hetero association are responsible for the observed values. Moreover, this fact is corroborated by the values of various volumetric parameters for all the three binary systems.

The viscosities and refractive indices for the binary mixtures of DEG + 1-butanol, + 2-butanol and + 1,4-butanediol have been measured over the entire composition range and at four different temperatures. The values of $\Delta\eta$, $\Delta_{\phi}n_D$ and $\Delta R_m$ have been calculated from the measured values. The results indicate that the strength of intermolecular interactions in these mixtures follow the order: 2-butanol > 1-butanol > 1,4-butanediol. These conclusions further reinforce the earlier conclusions drawn from the trends in $V_m^E$ and $\Delta\kappa_s$. Moreover, the trends obtained for ΔG*, enthalpies, $\Delta H^*$ and entropies, $\Delta S^*$ values over the entire composition range for the investigated binary mixtures are in agreement with the conclusion drawn above. The refractive index data are well correlated by various mixing rules.

The densities and ultrasonic speeds for DMF + MA, or EA, or BA binary mixtures have been measured and the values of $V_{\mathrm{m}}^{\mathrm{E}}$, $\overline{V}_{\mathrm{m},1}$, $\overline{V}_{\mathrm{m},2}$, $\overline{V}_{\mathrm{m},1}^{\circ\infty}$, $\overline{V}_{\mathrm{m},2}^{\circ\infty}$, $V_{\mathrm{m},1}^{\circ\mathrm{E},\infty}$ and $\overline{V}_{\mathrm{m},2}^{\circ\mathrm{E},\infty}$ were calculated. The $V_{\mathrm{m}}^{\mathrm{E}}$ values were found negative for all the mixtures. The magnitudes of $V_{\mathrm{m}}^{\mathrm{E}}$, $\overline{V}_{\mathrm{m},1}^{\circ\mathrm{E},\infty}$ and $\overline{V}_{\mathrm{m},2}^{\circ\mathrm{E},\infty}$ values show that order of the interactions between DMF and acrylate molecules in these mixtures follows the sequence: MA > EA > BA, i.e., interaction decrease with increase in size of alkyl group in acrylate molecules.