PHYSICO-CHEMICAL AND THERMODYNAMIC INVESTIGATIONS OF SOME BINARY LIQUID MIXTURES

A Thesis submitted
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DOCTOR OF PHILOSOPHY

by
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CERTIFICATE

This is to certify that the thesis entitled 'PHYSICO-CHEMICAL AND THERMODYNAMIC INVESTIGATIONS OF SOME BINARY LIQUID MIXTURES' being submitted by Mr. Yarramareddy Pitcha Rao to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bona fide research work carried out by him. Mr. Pitcha Rao has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis which, to my knowledge, has reached the requisite standard.

The results contained in this dissertation have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

The excess thermodynamic properties and transport properties are known to be extremely useful for elucidating the nature and strength of molecular interactions that are prevalent in liquid mixtures and for testing the current theories of solutions because of their sensitivity to the difference in magnitude of intermolecular forces and geometry of the component molecules. Various physicochemical and thermodynamic investigations on the binary liquid mixtures containing one polar component and the other non-polar or slightly polar component are described in this thesis. We have studied excess volumes, V^E, deviations of isentropic compressibilities, K_s, and excess visocisities, η^E, for eighteen binary mixtures of diethylamine (DEA), triethylamine (TEA) and tetrahydrofuran (THF) with benzene, toluene, ethylbenzene, o-, m-, and p-xylenes. We have also measured excess enthalpies of mixing, H^E, for some representative amine solutions to understand the energetics of the interactions. The nature and the degree of the interactions in the binary mixtures have been deduced from V^E, H^E, K_s and η^E results.

The thesis is divided into seven chapters.

Chapter I of the thesis describes briefly the current theories of liquid mixtures. This is followed by a brief discussion on the scope of present investigations.

Chapter II deals with the methods of purification of solvents and the details of experimental procedures employed for the determination of V^E, H^E, K_s and η^E. The experimental procedures contain

the details of measurement of densities with pycnometer and the oscillating tube digital density meter, enthalpies using LKB microcalorimeter, sound velocities with ultrasonic interferometer and viscosities with the Ubbelohde viscometer.

Chapter III embodies the results of V^E of the eighteen binary liquid mixtures under investigation at 293.15 and 313.15 K. In order to derive a possible correlation between the strength of interactions with the change in size, shape and nature of the alkyl substituent in hydrocarbons, we have also studied the volumetric behaviour of TEA and THF in various other aromatic and aliphatic (straight chain, branched chain and cyclic) hydrocarbons at 313.15 K.

The results have been analysed in the light of like N-H...N, like $\pi-\pi$, unlike N-H... π and unlike n- π interactions in DEA solutions; like $\pi-\pi$ and unlike n- π interactions in TEA solutions and in terms of possible charge-transfer type interaction between lone pair electrons on the oxygen atom of THF and π-electron system of aromatic hydrocarbon. In solutions containing aliphatic hydrocarbons, the data have been discussed in terms of dispersion forces. The V^E data of THF with benzene, toluene, ethylbenzene, o-, m-, and p-xylenes are analysed in the light of Prigogine's average potential model coupled with Balescu's theory.

Chapter IV contains the H^E of some selected binary liquid mixtures containing DEA and TEA at 313.15 K. The results have

been discussed in the light of various like and unlike interactions as mentioned above.

In Chapter V, the results of deviations of isentropic compressibilities, K_s, for the eighteen binary mixtures under consideration over the entire composition range are given at 293.15 K. The results of K_s are used to study the departure from ideal behaviour and to determine the strength of interactions between the component molecules as K_s values are sensitive to change in free volume.

Chapter VI describes the η^E results for the binary mixtures under investigation at 293.15, 303.15 and 313.15 K. η^E and the molar Gibbs free energy for activation of flow, G^{*E}, obtained from experimental viscosity data have been used to study the strength of interaction between component molecules. The viscosity data have been fitted into a single parameter empirical equation and it was found that the viscosities of binary liquid mixtures can be calculated from the knowledge of the viscosities of pure components with reasonable accuracy.

The summary of the thesis is given in Chapter VII.

C O N T E N T S