

'PHYSICO-CHEMICAL AND THERMODYNAMIC INVESTIGATIONS OF SOME BINARY LIQUID MIXTURES OF FURFURAL''

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by
NAOREM HOMENDRA




to the
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INDIAN INSTITUTE OF TECHNOLOGY, DELHI
NEW DELHI-110016
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CERTIFICATE

This is to certify that the thesis entitled, "PHYSICO-CHEMICAL AND THERMODYNAMIC INVESTIGATIONS OF SOME BINARY LIQUID MIXTURES OF FURFURAL", being submitted by Mr. Naorem Homendra to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. Naorem 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.

IIT, Delhi
July, 25, 1989


(Sushil K. Suri)
Assistant Professor
Department of Chemistry

A C K N O W L E D G E M E N T

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ABSTRACT

The thermodynamic excess properties and transport properties are known to be extremely useful for elucidating the nature and strength of molecular interactions that are present in liquid mixtures. These are also useful for testing the theories of solution because of their sensitivity to the difference in magnitude of intermolecular forces and geometry of the component molecules. While most of the theories are able to explain the solution behaviour of liquid mixtures composed of non-polar spherical molecules, none of these can explain satisfactorily the solution behaviour of mixtures of polar molecules of different size and shape because of the presence of specific interactions between the unlike molecules.

The thermodynamic excess functions namely : excess enthalpy, H^E , excess volume, V^E , excess isentropic compressibility, K^E , and excess viscosity, η^E of mixing for the binary mixtures of furfural with six aromatic hydrocarbons viz. benzene, toluene, ethylbenzene, o-, m-, and p-xylenes ; six aliphatic alcohols viz. methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol; and three aliphatic ketones viz. acetone, 2-butanone, and 2-pentanone have been determined at 308.15 K over the whole composition range and reported. In order to establish the

effect of introduction of a functional group in the furan ring on the overall volumetric behaviour, V^E for the binary mixtures of furan and furfuryl alcohol with the same set of aromatic hydrocarbons has also been studied. The binary mixtures of tetrahydrofuran, furan, furfural, and furfuryl alcohol with chlorobenzene and bromobenzene were studied to understand the effect of nature of the substituent group in the aromatic ring on the overall volumetric behaviour of the furan derivatives.

The H^E values for all the furfural binary mixtures with aromatic hydrocarbons and aliphatic alcohols are found to be positive over the whole range of composition. The H^E results have been analyzed in the light of the Flory theory and the Flory interaction parameter X_{12} for the binary mixtures have been computed.

The V^E results for the furfural binary mixtures under consideration revealed that V^E values, unlike H^E , are very sensitive to any change in the geometry of the component molecules. It was also observed that the volumetric behaviour of binary mixtures containing a substituted furan is mostly determined by the substituent group. For furan mixtures, like $\pi-\pi$ interactions are more predominant. The introduction of π -clouds into tetrahydrofuran ring was found to decrease the unlike and increase the like interactions in the mixtures. The Flory interaction

parameter $X_{12} (H^E)$ is unable to predict even the sign of V^E for the binary mixtures containing furfural and this has been attributed to the presence of fairly strong unlike interactions in the mixtures. The V^E for the mixtures have also been analyzed in the light of the Prigogine's average potential model coupled with Balescu's theory. It was observed that the parameter Θ was very sensitive to the composition and hence could not be used as an adjustable parameter.

The K^E values for all the furfural binary mixtures studied are found to be negative over the whole composition range and its magnitude increases with the strength of the unlike interactions in the mixtures.

The η^E for all the binary mixtures of furfural under consideration are negative over the entire composition range except for the mixtures containing acetone and 2-butanone for which it was found to be positive. The results have been discussed in terms of molecular interactions. The viscosity data for the binary mixtures have been fitted to a single parameter equation of the type proposed by our school earlier. The results indicate that the viscosity of the binary mixtures studied can be evaluated from the knowledge of the viscosities of the pure components within the experimental uncertainty.

The optimum conditions for the maximum extraction yield of furfural from rice husk using three common commercial grade acids viz. sulfuric acid, hydrochloric acid, and acetic acid under different experimental conditions at atmospheric pressure have been estimated and reported in Appendix to the thesis.

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