Ultrasonic study of binary mixture of DIBK (di-isobutylketone) with polar liquids

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Ultrasonic velocity (C) and density (p) of binary mixture of di-isobutylketone (DIBK) with bromobenzene, chlorobenzene and toluene have been measured at temperature 303.16 K and frequency 2 MHz. The data of C and p have been used to calculate isentropic compressibility (β), acoustic impedance (Z) and inter-molecular free length (L₀) and also excess of these quantities to study the molecular interactions.

[Keywords: Ultrasonic velocity, Isentropic compressibility, Acoustic impedance]

Solvent extraction is an analytical technique used for extraction and purification of actinides and lanthanides in the nuclear energy industry. The common extractants tri-n-butyl phosphate (TBP), methyl isobutyl ketone (MIBK), acetylacetone (HAA), di-isobutylketone (DIBK) etc., are used in mixtures with polar and non-polar diluents to give greater dispersal and more rapid phase disengagement. However, HAA and DIBK have been employed as both chelating agents and solvents in extraction technology. The liquid-liquid extraction of uranium (VI) with HAA in different diluents from acidic pH media has been investigated by various workers.

The ultrasonic velocity in liquid mixtures can be helpful in assessing the degree of interaction between molecules. Various acoustic parameters such as isentropic compressibility, inter-molecular free length and acoustic impedance and molar compressibility can be obtained from the knowledge of the ultrasonic velocity and density of liquid. Such properties provide information about molecular environments and the nature of the interaction involved in the extraction process. It is, therefore, important to know the nature of the molecular interaction of DIBK with its diluents, as this might provide insight into the mechanism of solvent extraction. In the present study, inter-molecular free length, isentropic compressibility and specific acoustic impedance in binary mixtures of DIBK with bromobenzene, chlorobenzene and toluene to analyse their concentration dependence in the binary mixtures have been evaluated.

Experimental details — In the present investigation, the chemicals used are of analytical grade (E. Merck) purified by standard procedure and redistilled before use. Density was determined with a pycnometer of 25 cm³ capacity, calibrated at 303.16K with de-ionized, doubly distilled water. At a fixed temperature, the density was determined with an error of one in 10⁶. Ultrasonic velocity was measured by a single crystal variable path interferometer operating at a frequency of 2 MHz. Circulating water from thermostatically regulated bath around the sample holder with double wall, maintains the temperature of the liquid constant with a precision of ±0.1 °C. Binary mixtures of DIBK were prepared with bromobenzene, chlorobenzene and toluene with varying mole fraction of DIBK and measurements were made on three mixtures of 303.16 K.

Results and discussion — The data of C and p were used to calculate β, L₀ and Z. Excess values of isentropic compressibility βε and excess acoustic impedance Zε were computed with accuracy up to the third decimal digit. Some of the relevant data are displayed graphically, in Figs 1 to 3.
It is observed that, the value of \( L \), increases steadily in all three systems. The rate of variation of \( L \) is rapid, in low concentration region of DIBK and is the maximum for DIBK+bromobenzene mixture. This difference in trend, obviously, depends on the value of \( L \) in the components in the pure state and no significance need be attributed to it concerning the nature of interaction. According to Subba Rao et al.\(^{15}\) the nature of variation of \( L \) depends upon the relative size of components. For unequal sizes, it is non-linear. Furthermore, if the molecular size of the diluent is small, the deviation is negative. This is similar in system of the authors and the deviation is maximum for bromobenzene, where molecular size is relatively smaller.

In spite of these observations, it is worthwhile to review the results on the basis of the findings of dielectric investigations of the authors. Earlier, in this study\(^{14,15}\), it was observed that, the linear correlation factor \( g \) for DIBK was 1.56, indicating predominance of \( \alpha \)-multimers with parallel dipolar orientation. DIBK is an equilibrium mixture of two tautomers\(^{10}\) the keto and enol forms and there is a possibility of self-association, in the same liquid, in both forms. A woodpile arrangement in both tautomeric forms of DIBK\(^{5,10}\) does result in parallel alignment and hence, \( \alpha \)-multimers predominate in pure liquid, whereas anti-parallel alignment leads to \( \beta \)-multimers in pure liquids. In enol form, there is internal hydrogen bonding between \( \text{H}^\circ \) and \( \text{O}^\circ \) in the monomeric species. Addition of another polar liquid tends to rupture this bond and bi-functional groups are free to form intra-molecular hydrogen bonding which leads to creation of micro heterogeneous clusters of unlike molecules.

As the trend of variation in \( L \), \( \beta \) and \( Z \) indicates, the variation in bromobenzene is relatively non-linear. In the bromobenzene deficient region, it drops at almost the same rate as in the other polar liquid.
media, while the rate of fall slows down in bromobenzene-rich region, and even shows slight increase in trend, as DIBK concentration tends to zero. Of the three polar solvents used here, the chlorobenzene is more reactive because, the chlorine atom is bonded with SP\(^3\) hybridised carbon atom and consequently can be removed easily. So, the rate of reaction with chlorobenzene is faster. Due to hyper-conjugative effect in case of toluene, the methyl group has electron-pushing tendency to the benzene ring, leaving partially charged carbonium (C\(^+\)) ion. This is likely to result in unfavourable interaction with more active group of C=O DIBK. On the other hand, bromobenzene is less reactive because of its double bond character between carbon and bromine atom. This slow reaction in case of bromobenzene may also be attributed to its being heavier. Thus, the molecular interaction is likely to be more affected, resulting in a greater degree of variation in the ultrasonic parameter observed here.

Excess parameters are regarded as more suitable for evaluating the degree of interaction. The result shows that, \( \beta^5 \) is negative in bromobenzene, chlorobenzene and positive in toluene. The maximum value occurs at around equimolar concentration range. The value of \( \beta^6 \) is greater in magnitude, in case of bromobenzene, than other two polar liquids.

According to Fort & Moore\(^7\), an increasingly negative \( \beta^6 \) indicates greater interaction between components. The higher degree of interaction in DIBK is probably due to the presence of C=0 groups. The value of \( Z^5 \) is appreciably positive, for bromobenzene, chlorobenzene and negative, for toluene. Prakash et al.\(^8\) in their study of \( Z^5 \) reported that, more than one type of interaction may be present in any given system. Dispersion forces make a positive contribution to the excess values, while dipole-dipole interaction should make negative contributions. The magnitude of \( Z^5 \) being positive maximum in bromobenzene system agree with the result from \( \beta^6 \).

**Conclusion** — From the experimental findings it appears that the interactions of DIBK in toluene, chlorobenzene and bromobenzene media follow an increasing order. Furthermore, the interaction is relatively stronger in DIBK+bromobenzene system. This corroborates our findings reported earlier that bromobenzene is probably a more effective diluent in the presence of the nuclear extractant DIBK.

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**References**