ULTRASONIC ABSORPTION STUDIES IN SOME BINARY LIQUID MIXTURES

ULTRASONIC absorption in binary liquid mixtures, in which the two components form strong hydrogen bonds, is found to be strongly temperature dependent and manyfold greater than that of either of two pure components. A peak in ultrasonic absorption and velocity, at intermediate concentrations is observed for such systems. Typical of such systems are the aqueous solutions of non-electrolytes. Intermolecular relaxation process due to molecular association in such systems was suggested[1-3] as the cause for the peak absorption. A frequency independent sound absorption maximum was observed at intermediate concentrations for some non-aqueous solutions of non-electrolytes by Murthy and Rao[4], Raju[5] and Nana Rao *et al*[6].

Absorption studies in aqueous solutions of non-electrolytes have been extensive but relatively little work is done on the non-aqueous solutions of non-electrolytes, where a frequency independent absorption maximum is observed at the intermediate concentrations. With a view to study the excess absorption in solutions of this kind, two binary mixtures, β-Picoline-O-Chlorophenol and γ-Picoline-O-Chlorophenol, have been chosen for the present investigation. These systems exhibit finite heat of mixing and marked peaks in shear viscosity at the intermediate concentrations.

The ultrasonic velocity and absorption for both the systems have been measured over the entire composition range and at three temperatures 15°, 20° and 25° C. Absorption is measured in the frequency range of 3–21 MHz and velocity at 3 MHz only, as no significant dispersion could be observed. The velocity and absorption measurements are correct to $\pm 0{\cdot}5\%$ and $\pm 8\%$ respectively. Chemicals (BDH Analar grade) are distilled before use. The temperature is controlled to $\pm 0{\cdot}1°$ C with the ultrathermostat type NBE. Density is measured with a Pyknometer to an accuracy of $\pm 0{\cdot}1\%$ and the shear viscosity is determined by the use of an Ostwald Viscometer.

The following facts are observed from the studies on the two systems:

(i) For both the systems, a maximum in absorption at an intermediate concentration is observed. The absorption decreases with increasing temperature and is independent of frequency for the range studied (3–21 MHz).

(ii) The Sound velocity and the shear viscosity have a Peak value at an intermediate concentration.

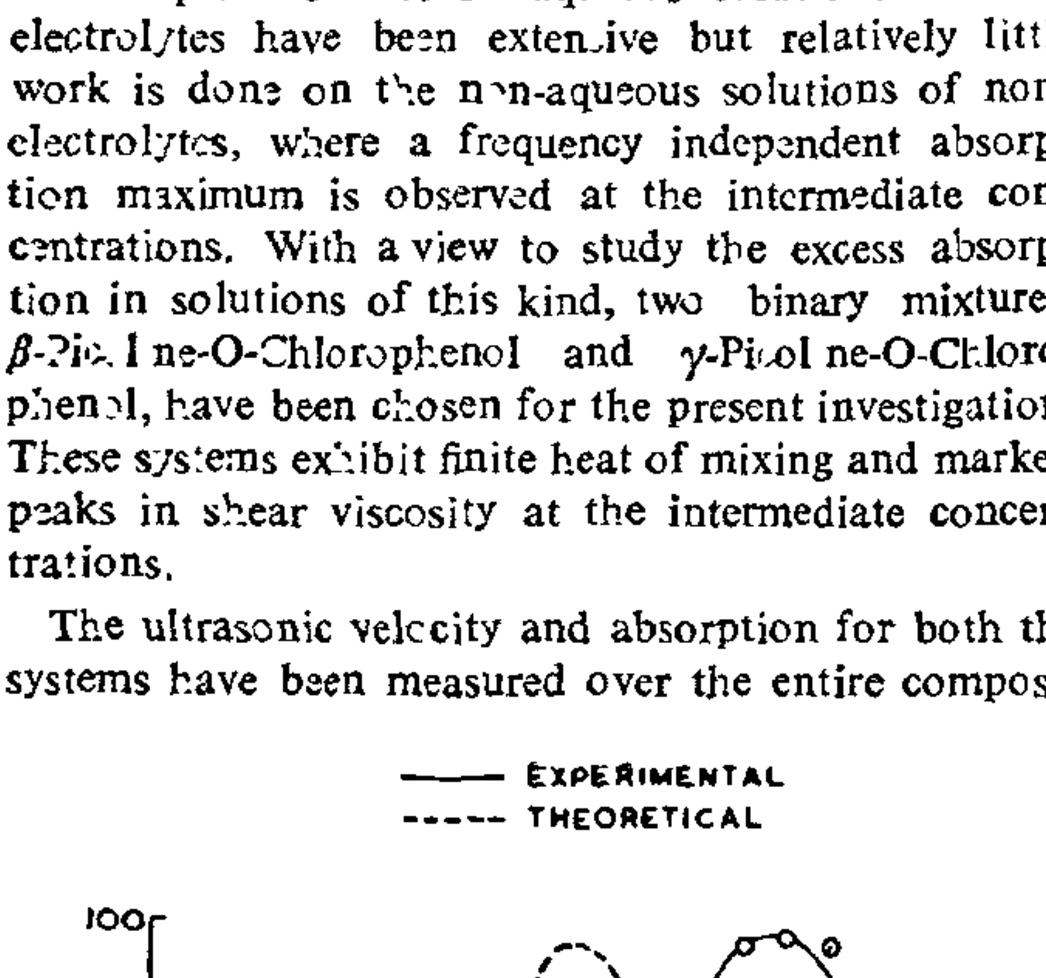

FIG. 1. Comparison of theoretical and experimental Excess Absorption values for some temperatures in β-Picolline-O-Chlorophenol System.

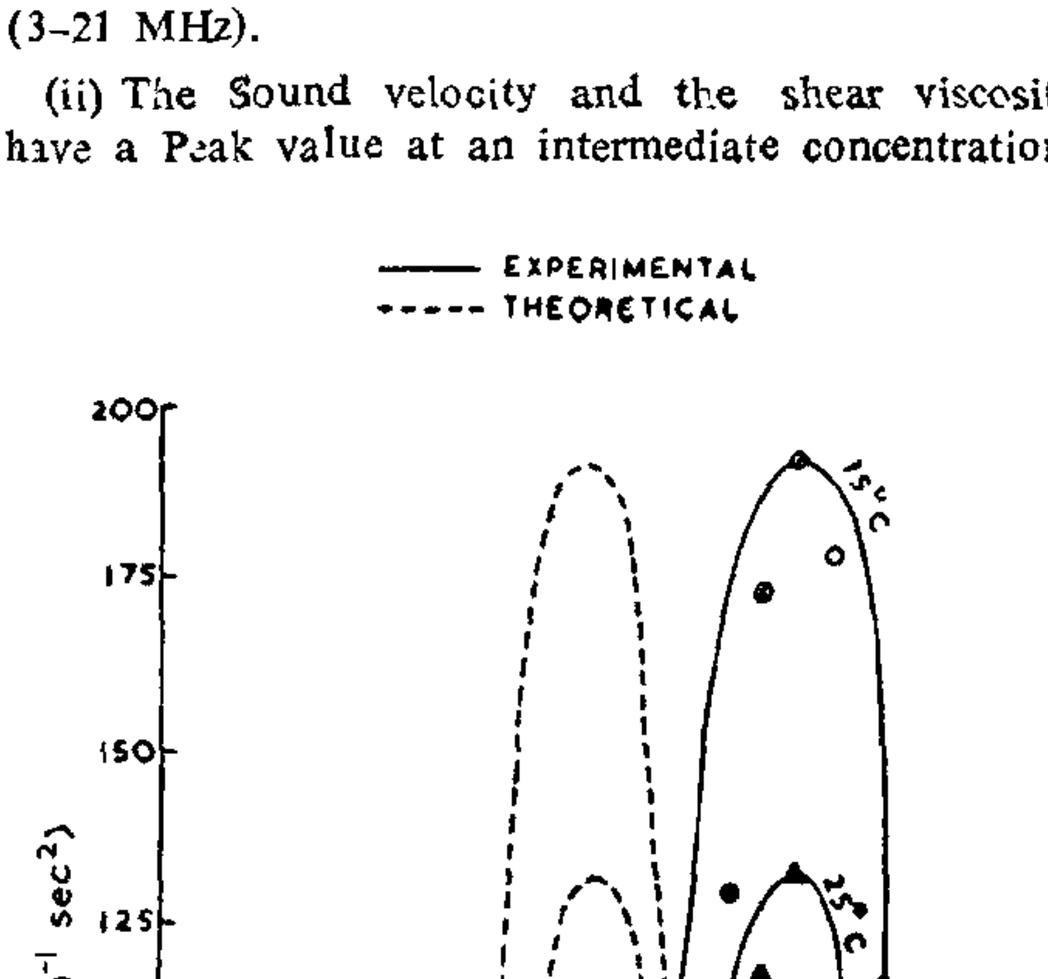

FIG. 2. Comparison of theoretical and experimental Excess Absorption values for some temperatures in γ-Picoline-O-Chlorophenol System.

(iii) There is a finite heat of mixing of the two components which rises to a maximum at an intermediate concentration. This is accompanied with a contraction in volume which reaches a maximum at an intermediate concentration.

These observations indicate a complex formation in these systems. Storey[1] qualitatively explained, the excess in sound absorption in the aqueous solutions of ethyl alcohol, by assuming that association of different molecules are present in the solutions and that the equilibrium among them is altered by temperature changes associated with sound wave. The absorption parameter a/f^2 in such a system would reach a maximum when the proportions of the constitutents are more favourable for a complex formation. In the two systems studied here, the intermolecular association complex can be formed by way of hydrogen bonding between protons of O-Chlorophenol and lone pair electrons of the Picoline molecules.

A comparison of the experimental results of this study with the theoretical values obtained by the use of Barfield and Schneider model[2] is shown in Figs. 1 and 2. It can be seen that, though the calculated curves satisfactorily reproduce the shape of the measured absorption curves, the Peaks are shifted to lower concentration of O-Chlorophenol. The lack of perfect agreement between the theoretical and experimental absorption curves might be due to the inadequacy of the simple two-state model assumed by Barfield and Schneider, which does not take into account the difference in the number of protons and donor atoms available for hydrogen bonding between the two liquids forming hydrogen bonding complex. The theoretical model for complex formation as suggested by Andreae *et al.*[3], could not be tested for the present study, because of the lack of absorption data at high frequencies extending into the relaxation region.

Ultrasonic Research Laboratories,
Physics Department,
Andhra University,
Waltair-530 003, *October* 3, 1979.

VIJAY KUMAR KAUL.
M. G. SESHAGIRI RAO.

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ROTATIONAL ANALYSIS OF 0, 0 BAND OF B–X SYSTEM OF CuBr MOLECULE

THE spectrum of CuBr molecule has been investigated by several workers[1–3]. It consists of four band systems *viz.*, A–X, B–X, C–X and D–X extending in the region 5000–3700 Å. Out of these four band systems only C–X system has been studied at a high dispersion and rotational constants have been reported. The C system has been assigned on electronic transition $^1\Sigma^+ - {}^1\Sigma^+$. The present note deals with the rotational analysis of B–X system of the molecule.

The spectrum of CuBr molecule was excited in a high frequency discharge (10–15 MHz) having an output of 125 W. Specpure sample of copper bromide was kept in a conventional type of quartz discharge tube and the blue colour of discharge was maintained by intermittant external heating. The 0, 0 band of the system was photographed in the sixth order of a 2 meter plane grating spectrograph at a reciprocal dispersion of 0·6 Å/mm. Spectrum was recorded on WU3 plates. Measurements were made on an Abbe Comparator against iron arc standards.

Out of all the bands photographed only the 0, 0 band was free from overlapping and could be utilized for carrying out the rotational analysis. Rotational isotope effect for ^{79}Br and ^{81}Br was clearly observed at high J values. Three branchs, *viz.*, P, Q, R for each isotope of Bromine could be picked up. The J numbering of rotational lines and their analysis has been carried out by the method suggested by Yougner and Winans[4]. The analysis revealed a Λ-type doubling in the upper state $^1\pi$. Λ-type doubling constant q has been calculated by the method of combination defect. The doubling of rotational lines in some branches of 0, 0 band has been attributed to the isotope effect of Bromine. The appearance of structure observed in the band (a part of photometric record given in Fig. 1) shows five to six components, indicating overlapping of different branches. This overlapping persists even upto high J values. Presence of two isotopes thus provides a useful check on the present analysis, *i.e.*, observed $B_v'/B_v = \rho^2$ (0·9929) agrees with calculated value $\rho^2 = 0{\cdot}9889$. The results are given in Table I.

TABLE I

State	B_v cm^{-1}	$D_v \times 10^6$ cm^{-1}	q cm^{-1}	r_e Å
$B\,^1\pi$	$B_0 = 0{\cdot}0992$	6·57	$1{\cdot}8 \times 10^{-4}$	2·093
$X\,^1\Sigma$	$B_0 = 0{\cdot}1058$	6·25	..	..