

Study of Electronegativity and Inductive Effect in Polar-Non Polar Liquid Mixtures

K. VIJAYALAKSHMI* and V. LALITHA†

Department of Physics, Bishop Heber College, Tiruchirappalli-620 017, India

Tel: (91)9994647287; E-mail: viji71naveen@yahoo.com

Infrared spectra of several hydrogen bonded liquids in the pure state and their mixtures are recorded using Perkin Elmer 577 IR spectrophotometer. The alcohols from methanol upto hexanol and dioxane are taken for study. The neat spectra of the mixtures of various proportions are recorded at 25 °C. Variation of absorbance A of various modes of vibrations of the mixtures with respect to concentration and wave number are used for the study of interaction between the pure liquids.

Key Words: Molecular interaction, Hydrogen bonding, Electronegativity, Inductive effect.

INTRODUCTION

The study of molecular interaction between the liquid mixtures through spectroscopic technique provides valuable information regarding the nature and strength of various inter molecular interactions, formation of hydrogen bonding, *etc.*¹. The present work deals with the infrared spectroscopic study of several hydrogen bonded liquids in the pure state and their binary mixtures particularly of OH bands. The effects of electronegativity and induction on the liquid mixtures have been analyzed.

EXPERIMENTAL

When infrared spectra of liquids and their mixtures are run on the pure state without using any solvent medium as a reference beam, we get neat spectra². Binary mixtures of *n*-alcohols from methanol upto hexanol and dioxane were mixed exactly in different proportions namely 20, 40 and 50 % *etc.* by volume. Neat infrared spectra of pure liquids and their mixtures were recorded at 25 °C using Perkin Elmer 577 IR spectrophotometer at optimum speed. The scan duration for each spectrum was 5 min. The wave number region is 4000-200 cm^{-1} . Variation of absorbance A of various modes of vibration of the mixtures with respect to concentration and wave number are calculated using the reported formula³.

†Department of Physics, Seetha Lakshmi Ramasamy College, Tiruchirappalli-620 002, India.

$$A_{\text{band}} = \log (\% T_1 / \% T_2)$$

The shift of A with respect to wave number is used for the study of interaction between the liquids.

RESULTS AND DISCUSSION

Usually bands belonging to free –OH groups are narrow and sharp. But in associated liquids the –OH bands are broad and are found at much lower wave numbers. In the case of pure alcohols due to hydroxyl group broad absorption band is observed in the region of 3700-3100 cm^{-1} . The infrared spectra show that the width of the –OH bands of methanol is broadest among the six indicating that the association decreases from methanol to higher alcohols in the pure state. Moreover as the order of alcohols increases, the number of –CH₂– groups increases and hence the chain length increases⁴. The bond between the carbon atom are non polar. The highly electronegative oxygen attached to the end carbon atom of the chain creates inductive effect and propagates through the carbon chain. As a result of large inductive effect of the alkyl group, the polar character, of the –OH group is reduced and hence their capacity to enter into hydrogen bonding is also reduced⁵.

Infrared spectra of alcohol-dioxane mixtures: The absorbance (A) and wave number of –OH stretching vibrations of alcohol-dioxane mixtures with respect to concentration of dioxane are represented graphically (Figs. 1 and 2). In pure methanol due to bonded hydroxyl groups, a broad band is observed in the region of 3660-3100 cm^{-1} with a peak value at 3300 cm^{-1} . The intensity of the band is 0.459. For pure dioxane, a small peak is observed at 3470 cm^{-1} which may be due to C–O–H stretching vibrations. When methanol and dioxane are mixed, these two bands overlap and a broad band is observed in the region of 3700-3040 cm^{-1} having a peak maximum at 3340 cm^{-1} with an absorbance (A) value of 0.4411 and the absorbance is found to decrease due to the addition of dioxane upto a concentration of 30 % of dioxane by volume and increase thereafter become maximum at equimolar (50:50) concentration and again decreases due to further addition of dioxane.

The peak is found to shift towards higher wave number upto 40 % of dioxane. The band shift towards higher wave number side when dioxane is added indicates the possibility for the breaking of association in methanol molecules. But at equimolar concentration, the curve shows minimum. The frequency shift is about 60 cm^{-1} towards lower wave number side. The absorbance is found to be a maximum (1.813). This frequency shift towards lower wave number may be due to the interaction of methanol and dioxane through hydrogen bonding. The attractive force between the –OH group of methanol and CO group of dioxane may be sufficient to form a

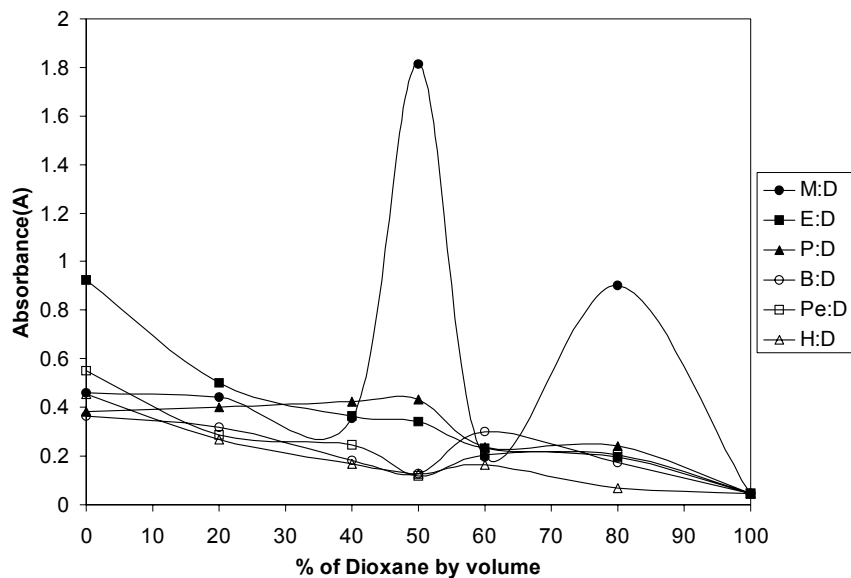


Fig. 1. Absorbance of $-OH$ stretching vibrations of alcohol-dioxane systems

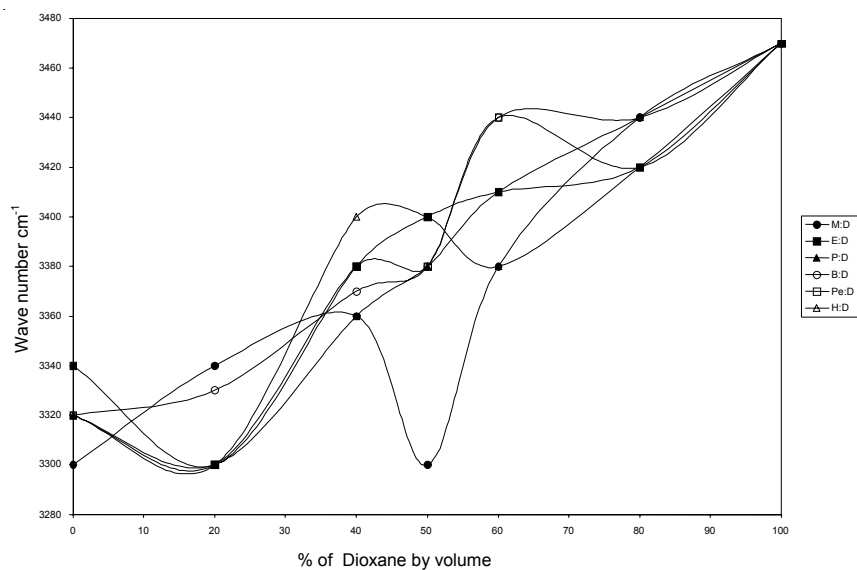


Fig. 2. Wave number of $-OH$ stretching vibrations of alcohol-dioxane systems

hydrogen bond between the two groups⁶. This intermolecular hydrogen bond is formed due to the absorption of maximum energy from the incident infrared radiation. At higher dioxane contents, since only small number of methanol molecules are present possibility for interaction is less.

But in all the other alcohol-dioxane systems, there is a shift in peak towards lower wave number side initially at 20 % of dioxane, which may be due to a weak interaction between polar and non-polar components⁷. But with further addition of dioxane the frequency of the band shifts towards higher wave number side indicating only the depolymerization of alcohol molecules.

Interaction strength between dioxane and alcohols from methanol to hexanol: While moving from methanol to hexanol the extent of hydrogen bonding decreases due to electronegativity and inductive effect⁸. These characteristics are reflected also in their mixtures with dioxane. From the infrared graph, the bonding effect between methanol and dioxane is the most predominantly one at 50 % of dioxane. The –OH peaks become broader and are shifted towards lower wave number side.

The depolymerization of alcohol is more than the intermolecular association between ethanol and dioxane. The –OH stretching bands become sharper and are shifted towards higher wave number side. Due to electronegativity and inductive effects ethanol, propanol, butanol, pentanol and hexanol molecules are not capable of forming hydrogen bond with dioxane molecules. However the absorbance values suggest a slight electrostatic attraction between the alcohol and dioxane mixtures. Intermolecular hydrogen bonding is possible and most predominant in methanol-dioxane mixtures due to large number of O–H groups and lesser number of –CH₂– groups.

REFERENCES

1. K.K. Baral and R.K. Mandal, *J. Pure Appl. Ultrasonics*, **20**, 39 (1998).
2. N. Jaggi and R.M.P. Jaiswal, *Indian J. Pure Appl. Phys.*, **39**, 122 (2001).
3. K. Vijayalakshmi, *J. Acoust. Soc. (India)*, **29**, 136 (2001).
4. M.V. Kaulgud and K.J. Patil, *Acoustica*, **28**, 130 (1973).
5. J.H.V. Maas, *Basic Infrared Spectroscopy*, Heyden and Sons Ltd., London, p. 94 (1972).
6. J. Nath and A.P. Dixit, *J. Chem. Thermodyn.*, **54**, 282 (1984).
7. J.B. Thakare, D.T. Dongre and Deogaonkar, *J. Acoust. Soc. (India)*, **28**, 365 (2000).
8. M.M. Szczeswiak, Z. Latajka and H. Ratajczak, *Chem. Phys. Lett.*, **72**, 115 (1980).