Research Paper

Volume : 3 | Issue : 4 | April 2014 • ISSN No 2277 - 8179

Kerr Constant Measurement of Water-Acetone System and Molecular Structure in Solution

Science

KEYWORDS : Water-acetone solution; Molar Kerr constant; Electro-optical polarizability; Pulsed electric field technique.

R. K. KHANNA Viveknanda Global University, VIT campus, Jagatpura, Jaipur, Rajasthan

GEETA GARG 62, Luniya Colony, Mitranagar, Ratidang, Ajmer , Rajasthan, India

ABSTRACT

Water-Acetone is very interesting but complex system. The Kerr constant for acetone-water mixture was measured at the wavelength of 632.8 nm using a pulsed electric field technique. A deviation from the pure additivity of the Kerr constant was observed for the mixture. This non-additive behaviour is discussed in terms of the refractive index, dielectric constant and density results of the solution.

A Kerr effect result of this binary liquid system reveals the possibility of dihydroxy structure in aqueous acetone. Anomalous behaviour of refractive index in this system also indicates the formation of complex structure.

1. Introduction

Most isotropic liquids become birefringent when subjected to a strong electric field and phenomenon is known as Kerr effect (Kerr, 1875). The origin of such effect is the preferred orientation of the molecules of the fluid in a permanent electric field. Such orientation makes the medium of which these molecules are part, optically anisotropic. This effect is molecular in origin and is primarily due to interactions of applied field with the permanent dipoles and/or the anisotropy of polarizability of the molecules. The induced birefringence is a quadratic function of field strength i.e.

$$n_p - n_s = \lambda B E^2$$

Where n_p and n_s are the refractive indices for radiation with electric vector parallel and perpendicular to the applied electric field E (in volts/meter), λ is the wavelength in meter of light used. B (in mV^{-2}) is known as Kerr constant.

The study of the electro-optical Kerr effect in variety of materials allow one to obtain deeper knowledge of the electrical and optical polarizability of the molecules, giving some time very important information about their molecular configuration (Le Fever,1972). We know that value of Kerr constant of liquid system depends on the number of macroscopic parameters like dielectric constant, density, dipole moment, shape and size of molecule etc. Apart from that its magnitude also depends upon various types of molecular interactions in solutions (Yoshioks & Watanabe, 1969), between solute- solute and solute- solvent. Kerr constant measurements have been used successfully to explore molecular structure parameters (Harrison & Jennings, 1993, Philip & Rao, 1991, Khanna et al., 1978). However it is very difficult to account for the variation of Kerr constant of liquid system with any one of these parameters, as relationship between these parameters and the chemical structures of the molecules is not unique in nature (Neto et al., 1991) and some time varies with system to system.

Some of the fast optical shutters and electro-optical modulators employ Kerr effect. Apart from molecular studies, much work in the field of Kerr effect is still under progress in order to find new materials for such type of electro-optical applications (Qasymeh et al., 2008). Efforts has been devoted to study the behaviour of B for the case of binary mixtures of non-polar as well polar liquids (Patz & Ratzsch, 1979, Piazza et al., 1986). These measurements have been successfully used to explore molecular structure and inter-molecular interactions (Hyun et al., 2002, Rajagopal & Rao, 1994, Lavrenko et al., 2006).

Acetone is a very useful polar solvent and will dissolve a great number of organic molecules. Acetone is miscible with water in all proportion and as the percentage of acetone in the acetone-water mixture increases, it increases the solubility of non-water soluble molecule in this new solution (Rong & Prieve, 2007). Water continues to engage the attention of scientists today as it remains incompletely understood in spite of intense study over many years. This is primarily because water is anomalous in many of its physical and chemical properties. Some of water's unique properties are literally essential for life, while others have profound effects on the size and shape of living organisms. The strength and high directionality (anisotropy) of the intermolecular interaction in water lead to highly peculiar thermodynamic and structural properties (Rick & Berne, 1996). The nature of the intermolecular interactions allied to water's low molecular weight and small moments of inertia, allow for a complex pattern of intermolecular force fluctuations in both length and time scales, promoting a dynamical behaviour that is unique to water. Because of all these reasons, water-acetone system is subjected to variety of studies (Mclain & Soper, 2007, Teixeira & Longeville, 2006, Venables & Schmuttenmaer, 2000, Shukla, 1973, Toryanik & Taranenko, 1991) and work is under taken in this study employing electro-optical Kerr effect technique.

2. Experimental arrangement and technique

Measurements of the Kerr effect on the conductive liquids system were carried out by using pulsed electric field of short duration and high intensity. A schematic diagram of the experimental arrangement is given in Fig. 1. The optical system was formed by 2 mW He-Ne laser operating at 632.8 nm and polarizer and analyzer (Glen Thompson prisms). Sample liquid under study and reference liquid for comparative measurement is kept in specially designed Kerr cells consisting of two parallel stainless steel electrodes. The beam successively passes through two Kerr cells, one filled with the liquid under study and the other with reference liquid. These cells must be kept in optical alignment with their electrodes parallel. The polarizer and analyzer are crossed and set so that the plane of polarization of the light makes an angle 45^0 with the direction of electric field in the cells. The light transmitted by the analyzer prism (during the application of the field) is measured by the photomultiplier tube. A detailed description of the electric pulse generator, Kerr cell design and detection optical system can be found elsewhere (Khanna et al., 1978, Khanna & Sharma, 1988, Ellis & Llewellyn, 1977)

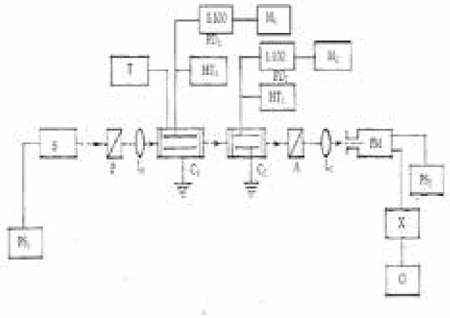

Fig 1: Essential Set Up for the Kerr Effect Measurement
PS_1- Light source supply, S- Light Source, P- Polarizer, L_1-

Convex lens, C_1- Kerr cell, C_2- Cell filled with CS $_2$, A- Analyzer, L_2- Convex lens, PM- Photo-multiplier Tube, PS_2-Photo-multiplier tube power supply, X- Virtual earth amplifier, O- Oscilloscope, HT_1 & HT_2- High voltage power supply, PD- Potential divider, M_1 & M_2 - Voltage Measuring unit, T- Thermostat

The Kerr constant B of the samples under study can be measured by determining the relative retardation (δ) of the parallel and perpendicular components of the electric vector of the linearly polarised light passing through the fluid, perpendicular to the applied electric field. The magnitude of the relative retardation δ (in radians) can be related to Kerr constant (B) as

$$\delta = 2\pi B l E^2$$

Where L (in meter) is the optical path length along the sample under study i.e. length of electrodes of the cell and E is the electric field strength. The measurement of δ was done using optical signal strength for the case of crosses polarizer and analyser employing photomultiplier tube. The slope of the straight line obtained by plotting ' δ ' as a function of square of electric field gave us the value of Kerr constant (B) for each sample. .

Different experimental procedures and techniques were adopted by various workers to measure Kerr constant of different type of systems (Philip & Rao, 1991, Prezhdo et al., 2005, Orttung & Mayers, 1963) In the present study, for the determination of Kerr constant, comparative technique employing two cells is used (Khashchina et al., 1975). In this technique first cell is filled with liquid under study and second cell is filled with standard liquid. Such measurement lead to the ratio of Kerr constant provided the length, plate separation and electric field across the plate of each cell containing standard liquid and sample under study are known. Carbon disulphide (B = 3.24x 10^{-14} mV^{-2}) is used as reference liquid. This method reduces the errors in the measurements due to stray birefringent present in the cells or system as a whole due to stress and related reasons as well as any of the background effects that are superimposed on the output of PM-tube.

The electro-optical Kerr constant, density, dielectric constant and refractive index of water-acetone system were measured over the whole concentration range from pure acetone to pure water. All these measurements were done at 25^0 C. In this study we used the water which was distilled and deionised. Conductivity of the entire water samples employed for measurement was of the order of 10^{-4} S m^{-1}. Acetone was obtained from BDH Ltd and was of AR grade. Fresh samples were used with further purification. Refractive index was measured with the help of Abbes Refrectometer and dielectric constant of the samples was measured using LCR Bridge and specially designed cell, at 10 KHz.

3. Results and discussion

The variation of refractive index, density, dielectric constant and Kerr constant, with respect to mole fraction of water for water–acetone system are shown in Fig. 2 to 5 respectively.

Variation of refractive index of this system as a function of water mole fraction in acetone is shown in Fig. 2. The refractive index of the mixture increases first up to 0.30 mole fraction of water in acetone and then it got saturated up to 0.67 mole fraction with the addition of water in acetone. Finally value of refractive index rapidly decreases and reaches the value of pure water (1.332). This anomalous behaviour for this system is also reflected in Kerr constant measured results. This unexpected variation in this system indicates some unusual interaction between their components. Formation of some type of structure because of bonds is expected in this solution at different concentrations reflected in the Fig.2. The IR and UV spectral studies of the carbonyl group of acetone in binary mixture with water (Gorbunov & Neberukhin, 1974) indicate two types of spectrally different complexes formation and it was found that at low acetone concentration the acetone molecules form hydrogen bonds with the water. At this acetone concentration each acetone molecule enters into two hydrogen bonds. It is expressed that the stabilization of water by a polar non-electrolyte by their entry into defects of the structure at globule boundaries.

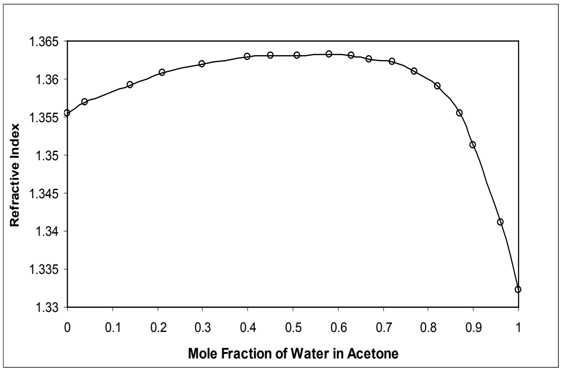

Fig. 2: Plot of Refractive Index of Water-Acetone System against Mole Fraction of Water in Acetone

Variation of density as a function of water mole fraction in acetone is shown in Fig. 3. The density of the mixture increases almost linearly with the mole fraction of water in acetone. Results plotted in Fig.3 indicate that the value of density for pure acetone is 0.785 x 10^{-3} $Kg\text{-}m^{-3}$ and that of pure water is 0.997 x 10^{-3} $Kg\text{-}m^{-3}$.

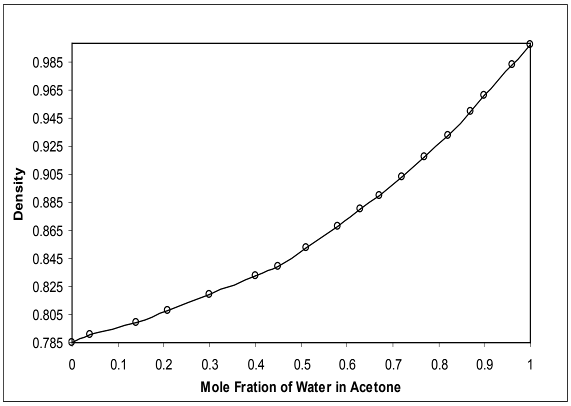

Fig. 3: Plot of Density of Water-Acetone System against Mole Fraction of Water in Acetone

Fig. 4 shows the variation of dielectric constant of this system as a function of water mole fraction in acetone at 25^0 C. Presented dielectric results are at 10 KHz. The dielectric constant of the mixture increases monotonically with the mole fraction of water in acetone from its value from 20 (for acetone) to 78.06 (for pure water).

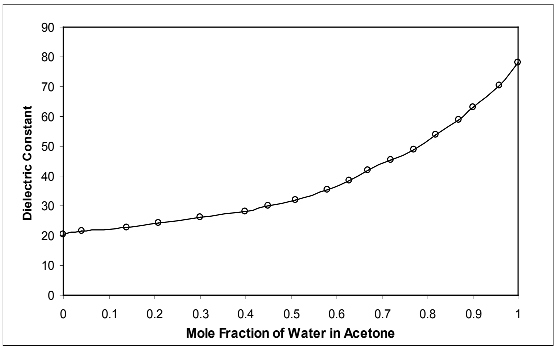

Fig. 4: Plot of Dielectric Constant of Water-Acetone System against Mole Fraction of Water in Acetone

It is shown that at low frequency region of dielectric relaxation in water is connected with redistribution of the positions of protons in the processes of formation and breakup of proton excitons (exciprotons). Acetone has practically no intermolecular hydrogen bonds at temperature above 20^o C. Low frequency dielectric relaxation in caused by thermal reorientation of polar molecules, the distribution of mutual orientation of the molecules being chaotic. Thus the underlying mechanism of dielectric relaxation in water-acetone should change with increasing acetone concentration. On the basis of relaxation time dielectric properties, molecular structure of acetone solution in water are predicted (Shakhparonov & Akhadov, 1965).

Measured values of Kerr constant of solutions of different mole fraction of water in acetone are plotted and presented in Fig. 5. Results are interesting and do not follow a trend as observed in dielectric and density plots. A deviation from the pure additivity of the Kerr constant in the mixture of two liquids was observed. One should expect a strict additivity of the Kerr constant only for the systems where both the mixing liquids have approximately the same value of their refractive index (n), dielectric constant (ϵ) and molar volume (V) (the ratio between the molar weight and the density of the liquids). For acetone and water values of refractive index and dielectric constant are quite different which explain the observed non-additive behaviour of Kerr constant of solution under study. Neto and Villaverde (Neto & Villaverde, 1996) in their study on water-acetone solution observed a strong positive deviation from the straight additivity. Their observations are different then present study. These results can be attributed not only to high ratio between the molar volume of the two liquids (V_A / V_W = 4.08) but also to the large difference between their dielectric constant (ϵ = 57.8). The Kerr constant of the mixtures are in good agreement with the dependence of the parameters n, ϵ and V i.e. the observed behaviour for B approaches that expected from the mean field theory of Patz and Ratzsch (1979). In the Fig.5, observed anomaly in the form of small peaks may be caused by the reaction between the components and formation of some structures in solution.

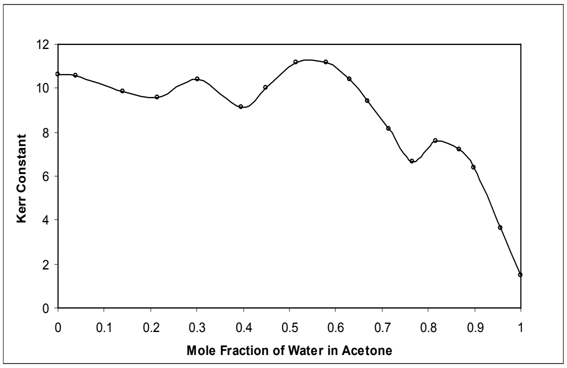

Fig. 5: Plot of Kerr Constant of Water-Acetone System against Mole Fraction of Water in Acetone

Careful inspection of results shown in Fig.5, for water-acetone system indicate that the Kerr constant of the acetone- water mixture as solute molar fractions in very dilute region (0.05 mole fraction of water) and at 0.3 mole fraction shows a deviation from smooth variation (higher values). Otherwise the value of Kerr constant decreases continuously as a function of mole fraction of water with broad inflexion point centred about 0.5 mole fraction. Many aldehydes and ketones are known to be partly hydrated in aqueous solutions according to equation (Bell & Medougall, 1960).

$$> C = O + H_2O = > C\ (OH)_2$$

Inflexion point at 0.5 mole fraction of water, indicates the possibility that a dihydroxy structure $(CH_3)_2$ C $(OH)_2$ is favoured in aqueous acetone. This observation is in agreement with nonlinear dielectric measurements (Bradley et al., 1975) but contribution to the Piekara factor was too small to establish it with certainty. The present study revels that no strong interaction occurs between acetone and water as is observed in water-dioxane system (Khanna et al., 1978). Formation of the hemihydrates is favoured in the case of dioxane, which involves only one oxygen atom per molecules.

There are conflicting views on aqueous acetone solutions. Most researchers consider acetone as a non-electrolyte capable of forming quasi-elathrate structure in water, since there are solid elathrates $(CH_2)_2CO_2 17H_2O$ (Toryanik & Taranenko, 1987). Acetone dissolved in water strengthens the structure. The question is up to what concentration this occurs i.e. what concentration gives the maximum stabilisation. It is also not clear whether the system is homogeneous or heterogeneous at sufficiently high acetone concentration. Some researcher considers that microsegregation occurs at medium concentration (Yank et al., 2010). But there are at present no convincing experimental evidences for this.

Stabilisation in water–nonelectrolyte system means structuring i.e. strengthening in the hydrogen bond network. Small amounts of acetone in water strengthen the network (Bourne et al., 1978). It is reported on the basis of spectroscopy studies that there is a loss of tetrahedral water structure on mixing, yet water molecules have a strong tendency to aggregate, especially in the acetone.

4. Conclusions

Water-acetone system is very complex binary mixture and appears to be sensitive of concentration of component liquids. In this system different complexes were detected by different researchers. At very low concentrations of acetone in water, the acetone molecules form hydrogen bonds with water and affect the clusters structures in water. Present study of Kerr effect of acetone- water system reveals the possibility of a dihydroxy structure in aqueous acetone. Observed anomalous behaviour of refractive index in this system also favoured the formation of complex structures in solution. A result of present study indicates non-additive nature of Kerr constant and refractive index of its constituent components. Modified theory need to be developed for the proper understanding of such short of reactive binary mixtures.

Acknowledgement

One of the authors RKK thanks the VGU management for encouraging this research work. Author GG thanks the Principal of Government College, Ajmer for providing facilities for doing this work.

REFERENCE

1. Bell R. P. and MeDougall A. O., (1960), Trans.Faraday.Soc. 56, 1281. | 2. Bourne J. R., Davey R. J. and McCulloch J., (1978) Chem. Engg. Sci., 33 199. | 3. Bradley P. A., Jones G. P., Kolodziej H. A. and Davies M., (1975) J. Chem. Soc. Faraday Trans., 11 1200. | 4. Ellis J. O. and Llewellyn J. P., (1977) J. Phys. E.: Sci. Instrum., 10 1249. | 5. Gorbunov B. Z. and Naberukhin Yu. I., (1974) J. Stru. Chem., 5 5. | 6. Harrison N. J. and Jennings B. R., (1993) J. App. Phys, 73 8076. | 7. Hyun B. R., Dzyuba S. V. and Bartsch R. A. and Quitevis E. L., (2002) J. Phys. Chem. A, 103 7579. | 8. Kerr J., (1875) Phil. Mag., 50 337. | 9. Khanna R. K. and Sharma P. K. (1988) Czech. J. Phys., 38B 346. | 10. Khanna R. K., Dempsey E. and Jones G. P., (1978) Chem. Phys. Lett., 53 542. | 11. Khanna R. K., Dempsey E. and Jones G. Parry, (1978)J. Phys. E: Sci. Instrum., 11 1210. | 12. Khanna R. K., Dempsey E. and Jones G.P., (1978) Opt. Commun., 27 88. | 13. Khashchina M. V., Raff V. S. and Zamkov V. A., (1975) Instr. Exp. Tech.,18 200. | 14. Lavrenko P. N., Kolomiets I. P., Andreeva L. N., Belyaeva E. V., Gribanav A. V., Kalnin K. K. and Makarova N. N., (2006) Poly. Sci. Series A, 48 547. | 15. Le Fever C.G. and Le Fever R.J.W., (1972) Physical Methods of Chemistry, Wiley-International, NewYork | 16. McLain S. E. and Soper A. K., (2007) J. Chem. Phys, 127 2504. | 17. Neto J. M. and Villaverde A. B., (1996) J. Phys.: Condens. Matter 8 2791. | 18. Neto J. M., Munin E. and Villaverde A. B., (1991) Meas. Sci. Technol., 2 1026. | 19. Orttung W. H. and Mayers J. A., (1963) J. Phys. Chem., 67 1905. | 20. Patz R. and Ratzsch M. T., (1979) Z. Phys. Chem. 260 788. | 21. Patz R. and Ratzsch M. T., (1979) Z. Phys. Chem., 260 769. | 22. Philip J. and Rao T. A. Prasada, (1991) J. Mol. Liqs., 48 85. | 23. Philip J. and Rao T.A. Prasada, (1991) J. Mol. Liq., 50 207. | 24. Piazza R., Degiorgio V. and Bellini T., (1986) J. Opt. Soc. Am. B, 3 1642. | 25. Prezhdo O. V., Switek L., Zubkova V. V. and Prezhdo V. V., (2005) Acta Physica Polonica-A, 108 429. | 26. Qasymeh M., Cada M. and Ponomarenko S. A., (2008) IEEE- J. Quantum. Electronics, 44 740. | 27. Rajagopal K. and Rao T. A. Prasada, (1994) J. Mol. Liq., 62 147. | 28. Rick S. W. and Berne B. J., (1996) J. Am. Chem. Phys., 118 672. | 29. Rong F. and Prieve D. C., | (2007) Am. Chem. Soc., 23 8048. | 30. Shakhparonov M. I. and Akhadov Ya. Yu., (1965) J. Struc. Chem. 6 15. | 31. Shukla S. K., (1973) Chromatographia, 6 463. | 32. Teixeira J. and Longeville S., (2006) J. Phys, Con. Matts., 18 82353. | 33. Toryanik A. I. and Taranenko V. N., (1987) J. Struc. Chem., 28 714. | 34. Toryanik A. I. and Taranenko V. N., (1991) J. Stru.Chem., 32 675. | 35. Venables D. S. and Schmuttenmaer C. A., (2000) J. Chem. Phys., 113 11222. | 36. Yang F., Wang X., Yang M., Krishtal A. and Senet P., (2010) Phy. Chem. Chem. Phy., 12 9239. | 37. Yoshioks K. and Watanabe H., (1969) Physical Principles and Techniques of Protein Chemistry, Academic Press Inc., NewYork. |