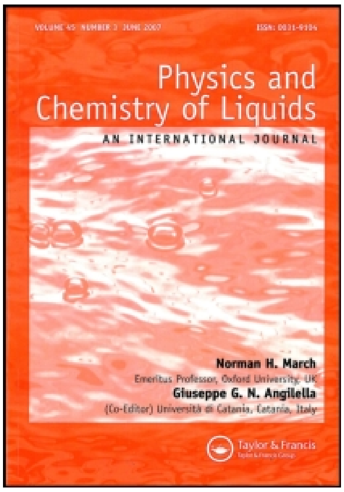

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Relaxational and Associative Aspects of X...HO Bond Complexes

Aashees Awasthi[a]; Madhu Rastogi[a]; J. P. Shukla[a]
[a] Department of Physics, Lucknow University, Lucknow, UP, India

To cite this Article Awasthi, Aashees , Rastogi, Madhu and Shukla, J. P.(2003) 'Relaxational and Associative Aspects of X...HO Bond Complexes', Physics and Chemistry of Liquids, 41: 4, 337 — 345
To link to this Article: DOI: 10.1080/0031910031000105268
URL: http://dx.doi.org/10.1080/0031910031000105268

Physics and Chemistry of Liquids
Vol. 41, No. 4, August 2003, pp. 337–345

Taylor & Francis
Taylor & Francis Group

RELAXATIONAL AND ASSOCIATIVE ASPECTS OF X···HO BOND COMPLEXES

AASHEES AWASTHI, MADHU RASTOGI and J.P. SHUKLA*

Department of Physics, Lucknow University,
Lucknow-226 007, UP, India

(Received 7 January 2003)

Relaxational and associative aspects of X···HO bond complexes in ternary liquid mixtures of aromatic halogen compounds, namely, chlorobenzene and bromobenzene with ethanol in benzene have been studied at 10 GHz frequency and a temperature range of 30–60°C using dielectric relaxation data. Due to the observed high values of distribution parameter, the relaxation mechanism has been further resolved in terms of two separate relaxation times. The dipole moment, association equilibrium constant and thermodynamic parameters associated with the complexes have also been determined. All the results indicate the occurrence of weak molecular interaction in both the systems. This is in agreement with the ultrasonic results on these systems, reported earlier by Kannappan and Palani.

Keywords: Ternary liquid mixtures; Relaxation time; Association equilibrium constant

INTRODUCTION

Ultrasonic studies of polar molecules in non-polar solvent have been extensively used to study the molecular structures including the molecular interactions in liquid mixtures [1–4].

The investigation of dielectric relaxation phenomena has provided an important approach to explore the structural behaviour of complex organic polar molecules in different non-polar solvents. Dielectric relaxation studies in the microwave region provide meaningful information about self association, solute–solute and solute–solvent type of molecular association among polar molecules [5–13]. Tucker and Walker [5] studied the complexes of pyrrole and indole with 1,4-diazobicyclo (2,2,2) octane (D.B.O.) in cyclohexane through the dielectric method and resolved the data in terms of two relaxation times. The studies [5,6] of Tucker and Walker suggest that the simultaneous determination of relaxation time, dipole moment and distribution parameter provide an elegant and most effective method to examine the complex formation. The relaxation time and thermodynamic parameters have been determined using the measured dielectric data. Recently, dielectric absorption studies on some polymers,

---

*Corresponding author. E-mail: aasheesawasthi@rediffmail.com

ISSN 0031-9104 print: ISSN 1029-0451 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/0031910031000105268

namely, poly(methyl acrylate) (PMA) and poly(isobutyl methyacrylate) (PiBMA) in dilute solution were reported by our group [7]. Vyas and Vashisth [8] have reported the dielectric absorption of some fluoro, chloro, bromo substituted anilines and their mixtures in benzene. Basak *et al.* [9] have studied the dielectric relaxation of some disubstituted benzene and aniline derivatives under static and high frequency electric fields and suggested a convenient method for simultaneous determination of relaxation time and dipole moment.

Dielectric studies of flexible molecules have been of interest to the scientists. Many workers [10,11] have investigated the dielectric relaxation of non-rigid molecules. The relaxational and associative studies of molecular behaviour in ternary liquid mixtures from the dielectric relaxation measurements at microwave frequencies are limited, specially of aromatic halogen compounds with ethanol, hence it was considered that the present studies may provide useful information regarding the molecular interactions and the formation of complexes in the mixtures of chlorobenzene–ethanol and bromobenzene–ethanol in benzene. The permittivity data have been analysed by the single frequency method of Gopalakrishna [14] and also by Higasi [15] and Higasi *et al.* [16] methods. The distribution parameter along with relaxation times associated with different processes, dipole moment, association equilibrium constant and thermodynamic parameters have been evaluated for these ternary systems using dielectric data at 10 GHz frequency and at five different temperatures, 30, 40, 50, 55 and 60°C. The results obtained strongly support the presence of weak molecular interaction in these ternary liquid mixtures.

EXPERIMENTAL DETAILS

The dielectric constant (ε') and dielectric loss (ε'') have been measured at the microwave frequency of 10 GHz (X-band) and in the temperature range of 30–60°C using short circuited wave guide method reported by Roberts and von Hippel [17] and later modified by Dakin and Works [18]. The static constants (ε_o) at different temperatures were measured at 300 kHz by using HP impedance/gain phase analyser (HP 4194 A). The refractive indices (n_D) of the solutions were measured by Abbe's refractometer, which in turn determined the optical permittivity ($\varepsilon_\infty = n_D^2$). The temperature was maintained constant by circulating water from a thermostatically controlled water bath with an accuracy of ±0.1°C. The density of solvent and various mixtures have been evaluated using a sensitive pycnometer with an accuracy of 0.5 $\mathrm{kg/m^3}$.

The chemicals used were of AR grade procured from BDH. All the chemicals were purified by standard procedures discussed by Perrin and Armarego [19] before use.

THEORY

Evaluation of Relaxation Times, Distribution Parameter and Dipole Moment

The Gopalakrishna method [14], for evaluation of the single relaxation time of polar molecule in the dilute solution of non-polar solvent, is a single frequency concentration variation method. The equation for the relaxation time (τ_{GK}) is given by

$$\tau_{\mathrm{GK}} = \frac{\lambda}{2\pi c}\frac{dY}{dX}$$

where, λ is the free space wavelength, c is the velocity of light and dY/dX is the slope of the straight line plot drawn between X and Y given by

$$X = \frac{\varepsilon'^2 + \varepsilon''^2 + \varepsilon' - 2}{(\varepsilon' + 2)^2 + \varepsilon''^2}$$

$$Y = \frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2}$$

If the molecule is of flexible nature i.e. has more than one relaxation time, the dielectric dispersion may be resolved into two relaxation parameters using single frequency concentration variation method of Higasi *et al.* [16] as

$$\tau_{(1)} = \frac{1}{\omega}\cdot\frac{a''}{(a' - a_\infty)}$$

$$\tau_{(2)} = \frac{1}{\omega}\cdot\frac{a_o - a'}{a''}$$

where, $\tau_{(1)}$ corresponds to the group relaxation and $\tau_{(2)}$ to the molecular relaxation and a_o, a', a'' and a_∞ are the slopes.

The average relaxation time (τ_o) may be calculated as

$$\tau_o = \sqrt{\tau_{(1)}\tau_{(2)}}$$

Higasi [15] also gave expression to obtain the most probable relaxation time (τ_{OH}) and the distribution parameter (α) as

$$\tau_{(\mathrm{OH})} = \frac{1}{\omega}\left(\frac{A^2 + B^2}{C^2}\right)^{1/(2(1-\alpha))}$$

$$1 - \alpha = \frac{2}{\pi}\tan^{-1}\frac{A}{B}$$

where, A, B and C are the constants, defined as

$$A = a''(a_o - a_\infty)$$

$$B = (a_o - a')(a' - a_\infty) - a''^2$$

$$C = (a' - a_\infty)^2 + a''^2$$

The dipole moment (μ) of the complexed species have been calculated by Koga *et al.* method [20] using equation

$$\mu \approx \frac{27kTM_2V_1}{4\pi N}\cdot\frac{(a_o - a_\infty)}{(\varepsilon_1' + 2)^2},$$

where, d_1 is the density of the solvent, M_2 is the molecular weight of the solute and ε'_1 is the dielectric constant of pure solvent.

Evaluation of Equilibrium Constant

In the case of complexes, Singh and Saxena [21] have suggested a method for evaluating the association equilibrium constant (K) indicating the strength of complex formation.

The weight factor of the ith component of a system of n components may be given as

$$C_i = \frac{f_i \mu_i^2}{\sum_{i=1}^{n} \mu_i^2}$$

where, f_i and μ_i are the mole fraction and dipole moment of the ith component. In the case of ternary system, C_3 (weight factor of the 1 : 1 complexed species) in equilibrium positions would be given by

$$C_3 = \frac{f_3 \mu_3^2}{f_1 \mu_1^2 + f_2 \mu_2^2 + f_3 \mu_3^2}$$

where, subscripts 1,2 and 3 refer to solute 1, solute 2 and 1 : 1 complex, respectively. If a and b are the initial mole fractions of the interacting solutes 1 and 2, respectively, then $f_1 = (a - f_3)$ and $f_2 = (b - f_3)$. On substituting these values of f_1 and f_2 in above equation, we get

$$C_3 = \frac{f_3 \mu_3^2}{f_3(\mu_3^2 - \mu_1^2 - \mu_2^2) + a\mu_1^2 + b\mu_2^2}$$

On rearranging for f_3, we get

$$f_3 = \frac{(a\mu_1^2 + b\mu_2^2)C_3}{\mu_3^2(1 - C_3) + C_3(\mu_1^2 + \mu_2^2)}$$

The association equilibrium constant can be evaluated by taking the usual assumption that each species behave ideally in the solution, hence

$$K = \frac{f_3}{(a - f_3)(b - f_3)}$$

where, a, b, μ_1 and μ_2 are known and if C_3 and μ_3 could be obtained, f_3 can be evaluated and hence the equilibrium constant from the above equation.

Evaluation of Thermodynamic Parameters for Association Process

The associative behaviour of complexes may also be examined in terms of thermodynamic parameters for association process evaluated using the association equilibrium constant (K) given in the following text.

The standard free energy change (ΔG^o), the standard enthalpy change (ΔH^o) and the standard entropy change (ΔS^o) in the ternary mixture may be calculated using the association equilibrium constant [22] such that

$$\Delta G^o = -2.303\,RT\log K$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$2.303\log K = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

From the above equation, if ΔH^o and ΔS^o are constants and independent of temperature, then $\log K$ would be a linear function of $1/T$. The parameter ΔH^o may thus be determined from the slope of the straight line drawn between log K *versus* $1/T$. The ΔS^o may also be determined knowing the parameters ΔG^o and ΔH^o.

RESULTS

The slopes a_o, a', a'' and a_∞ calculated for both chlorobenzene–ethanol and bromobenzene–ethanol systems in the temperature range 30–60°C, have been listed in Table I. The distribution parameter (α) and relaxation times evaluated using Higasi method [15] and Higasi *et al.* method [16] along with dipole moment (μ) evaluated by Koga *et al.* method [20] for both the system have been reported in Table II. Association equilibrium constant (K) at different mole fractions (f_3) values of adducts have been given in Table III. Relaxation times using Gopalakrishna method [14] and enthalpies of activation of individual interacting components and their 1 : 1 mixtures in dilute solutions of benzene have been given in Table IV. Association equilibrium constants for nearly equal mole fractions (solute concentrations 3 : 1) of both chlorobenzene and ethanol and bromobenzene and ethanol along with thermodynamic parameters for the association process such as the standard enthalpy change (ΔH^o), the standard free energy change (ΔG^o) and the standard entropy change (ΔS^o) calculated using association equilibrium constant [22], have been listed in Table V.

TABLE I Values of slopes of dielectric constants (ε_o,ε',ε'' and ε_∞) against weight fractions at different temperatures

Substance	*Temp* (°C)	a_o	a'	a''	a_∞
Chlorobenzene + ethanol	30	2.08	1.72	0.41	0.24
	40	1.97	1.63	0.39	0.20
	50	1.94	1.61	0.38	0.19
	55	1.88	1.57	0.37	0.17
	60	1.85	1.55	0.36	0.15
Bromobenzene + ethanol	30	2.36	1.96	0.68	0.28
	40	2.20	1.86	0.58	0.26
	50	2.11	1.83	0.49	0.23
	55	2.04	1.79	0.44	0.21
	60	1.95	1.74	0.39	0.20

TABLE II Relaxation time (τ) and distribution parameter (α) using Higasi and Higasi *et al.* methods along with dipole moment (μ) values

Substance	*Temp.* (°C)	α	$\tau_{(1)}$ (psec)	$\tau_{(2)}$ (psec)	$\tau_{(o)}$ (psec)	$\tau_{(OH)}$ (psec)	μ (Debye)
Chlorobenzene + ethanol	30	0.27	4.4	13.8	7.8	3.7	1.69
	40	0.29	4.3	13.9	7.7	3.6	1.70
	50	0.29	4.2	13.7	7.6	3.5	1.74
	55	0.29	4.1	13.5	7.5	3.4	1.74
	60	0.28	4.0	13.1	7.3	3.3	1.76
Bromobenzene + ethanol	30	0.10	6.5	9.4	7.8	6.4	2.04
	40	0.12	5.8	9.4	7.4	5.6	2.02
	50	0.14	4.9	9.1	6.7	4.5	2.03
	55	0.15	4.4	8.8	6.3	4.0	2.03
	60	0.16	4.0	8.5	5.9	3.5	2.02
Ethanol							1.69
Chlorobenzene							1.69
Bromobenzene							1.70

TABLE III Association equilibrium constants (L/mol) at different mole fractions of adducts at 30°C

Substance	*Solute concentration* (wt.fraction)	*a*	*b*	f_3	*K*
Chlorobenzene + ethanol	1 : 1	0.036	0.089	0.012	6.494
	2 : 1	0.070	0.086	0.021	6.593
	3 : 1	0.102	0.083	0.030	7.862
	4 : 1	0.132	0.080	0.039	10.228
	5 : 1	0.159	0.078	0.049	15.361
Bromobenzene + ethanol	1 : 1	0.027	0.091	0.008	5.073
	2 : 1	0.052	0.088	0.014	4.979
	3 : 1	0.075	0.085	0.020	5.594
	4 : 1	0.098	0.083	0.026	6.335
	5 : 1	0.119	0.081	0.034	8.511

TABLE IV Relaxation times using Gopalakrishna method and enthalpies of activation for various systems in dilute solutions of benzene

Substance	*Ethanol*		*Chlorobenzene*		*Bromobenzene*		*Chlorobenzene +ethanol (1:1)*		*Bromobenzene +ethanol (1:1)*	
Temp. (°C)	τ_{GK} (psec)	ΔH_ε (kJ/mol)	τ_{GK} (psec)	ΔH_ε (kJ/mol)	τ_{GK} (psec)	ΔH_ε (kJ/mol)	τ_{GK} (psec)	ΔH_ε (kJ/mol)	τ_{GK} (psec)	ΔH_ε (kJ/mol)
30	7.3	3.4	2.9	3.9	6.3	4.4	7.4	7.2	6.5	6.0
40	6.1		2.4		5.2		5.8		5.6	
50	5.6		2.0		4.6		4.5		4.3	
55	5.1		1.8		3.8		3.6		3.5	
60	4.1		1.5		3.2		2.8		2.4	

DISCUSSION

It is seen from Table II that the distribution parameter (α) has sufficiently high values (0.27–0.29) for chlorobenzene–ethanol and (0.10–0.16) for bromobenzene–ethanol systems, which suggests the flexible nature of X···HO bonding, where X is a halogen group [21,23,24]. It has been suggested by many workers [21,23,24] that if a system

TABLE V Association equilibrium constant (*K*) (solute concentration 3 : 1) and thermodynamic parameters obtained using *K* values.

Substance	*Temp.* (°C)	*K* (L/mol)	ΔH^o (kJ/mol)	ΔG^o (kJ/mol)	ΔS^o (J/mol – K)
Chlorobenzene + ethanol	30	7.76	1.66	– 5.16	22.51
	40	7.65		– 5.29	22.21
	50	7.26		– 5.32	21.61
	55	7.21		– 5.39	21.49
	60	7.02		– 5.39	21.17
Bromobenzene + ethanol	30	5.50	0.67	– 4.29	16.37
	40	5.64		– 4.50	16.52
	50	5.50		– 4.58	16.25
	55	5.50		– 4.65	16.22
	60	5.59		– 4.76	16.31

has a high value of α, then the relaxation mechanism may be resolved into two separate processes, i.e., the group relaxation ($\tau_{(1)}$) and the molecular relaxation ($\tau_{(2)}$) processes, where, $\tau_{(1)}$ corresponds to the rotation of one of the interacting solute molecules and $\tau_{(2)}$ corresponds to the rotation of the complex molecule as a whole. The observed $\tau_{(1)}$ was in the range (4.0–4.4 psec) for chlorobenzene–ethanol system and (4.0–6.5 psec) for bromobenzene–ethanol system. The larger values of $\tau_{(1)}$ for bromobenzene–ethanol system are perhaps due to the bulkier bromobenzene molecule taking part in the rotational process. This is in agreement with the earlier studies of Singh and Vij [25] on substituted benzaldehydes and Chauhan *et al.* [26] on phenol and cresols.

The observed range of $\tau_{(2)}$ was (13.1–13.9 psec) for chlorobenzene–ethanol system and (8.5–9.4 psec) for bromobenzene–ethanol system. The $\tau_{(2)}$ values for chlorobenzene–ethanol system are much higher than bromobenzene–ethanol system. This could be reasonable because chlorine atom has greater electronegativity than bromine atom thus chlorine atom could interact with hydrogen atoms of more than one ethanol molecules resulting into a bulkier complexed species which give rise to the higher $\tau_{(2)}$ values for chlorobenzene–ethanol system than bromobenzene–ethanol system. The $\tau_{(1)}$ and $\tau_{(2)}$ values are sufficiently different from each other. According to Higasi a wide separation in $\tau_{(1)}$ and $\tau_{(2)}$ indicates the existence of more than one relaxation process in the system which shows the flexible nature of the solute molecules under the microwave field [23,26,27]. The $\tau_{(1)}$, $\tau_{(2)}$, τ_o and τ_{OH} were found to decrease regularly with increasing temperature. This indicates the flexibility of molecules under study [23].

The dipole moment calculated by the method of Koga *et al.* [20] was found to be (1.69–1.76 D) for chlorobenzene–ethanol system and (2.02–2.04 D) for bromobenzene–ethanol system over the entire temperature range of 30–60°C (Table II). Dipole moment of chlorobenzene–ethanol system was found to be lower than that of bromobenzene–ethanol system. This is due to the combined effect of atomic size and electronegativity of the chlorine and bromine atoms. Due to smaller atomic size and higher electronegativity, chlorine atom could interact with the hydrogen atom of ethanol molecule with greater strength which give rise to the chlorobenzene and ethanol molecules close to each other. This may probably be the reason for lower values of dipole moment for chlorobenzene–ethanol system than bromobenzene–ethanol system. Dipole moment of the complexed species was found to be equal or slightly higher than that of each interacting component and the effect of temperature variation on dipole moment was negligible which is probably due to the presence of very weak associative interaction between the interacting components in the solution.

Further, it is seen from Table III that the association equilibrium constant (K) for chlorobenzene–ethanol system has been found to be greater than bromobenzene–ethanol system. As the proportion of chlorobenzene and bromobenzene is increased in solution the association equilibrium constant increases, but increment is found to be greater in chlorobenzene–ethanol system than in bromobenzene–ethanol system. This may be due to the greater electronegativity of chlorine atom which causes interaction more easily with the hydrogen atom of ethanol molecule. In order to investigate the effect of temperature variation on association equilibrium constant, mixtures of nearly equal mole fractions of chlorobenzene and ethanol and bromobenzene and ethanol were taken (3 parts of chlorobenzene and bromobenzene and 1 part of ethanol). Association equilibrium constant for chlorobenzene–ethanol system decreases regularly with increasing temperature from 30 to 60°C (Table V). The most probable explanation for this variation is that an increase in temperature results in an increase in kinetic energy of the molecules and the number of molecules of the complex which possess sufficient kinetic energy to break the bond holding the two molecules together will increase. But in bromobenzene–ethanol system, association equilibrium constant is found to be almost constant throughout the temperature range (30–60°C) which may probably would be due to the presence of much weaker complexation in the system [22].

Kannappan and Palani [2] have studied the molecular interaction in the ternary liquid mixtures of chlorobenzene, bromobenzene and acetophenone with ethanol in benzene using ultrasonic velocity measurements. They have reported a weak molecular interaction due to dipolar action and dispersion forces between the components of the mixture, on the basis of excess parameters and molecular interaction parameter. The molecular interaction parameter has been found to exhibit maxima at 0.1153 for chlorobenzene–ethanol system, at 0.1433 for bromobenzene–ethanol system and at 0.2529 for acetophenone–ethanol system for varying concentrations of the components. The high positive values of molecular interaction parameter in the solutions has been attributed to the existence of a weak dipolar interaction between the molecules of the system [4]. Moreover, the molecular interaction parameter suggest the degree of molecular interaction in the respective systems, in .the order, chlorobenzene–ethanol system > bromobenzene–ethanol system > acetophenone–ethanol system.

Further, in order to explore the weak molecular interactions in these ternary systems as reported above, relaxation times (τ_{GK}) using Gopalakrishna method and enthalpies of activation (ΔH_ε) of individual interacting components and their 1 : 1 mixtures in dilute solutions of benzene were also measured (Table IV). The enthalpy of activation was found to be 7.2 kJ/mol for chlorobenzene–ethanol system and 6.0 kJ/mol for bromobenzene–ethanol system. The observed values of enthalpies of activation for both the systems were found to be higher than that for each interacting components. This indicates the occurrence of molecular interaction between the interacting components [28]. The lower value of enthalpy of activation for bromobenzene–ethanol system than chlorobenzene–ethanol system suggests the weaker molecular interaction in bromobenzene–ethanol system than chlorobenzene–ethanol system.

In order to study the complexation behaviour along with reaction mechanism further, the thermodynamic parameters were also evaluated by using association equilibrium constant for both the chlorobenzene–ethanol and the bromobenzene–ethanol systems (Table V). The sign and magnitude of ΔG^o indicates whether the reaction goes strongly towards the products (large negative value), towards the reactants (large positive value) or equal concentration of reactants and products ($\Delta G^o = 0$). The ΔG^o values for both the systems undertaken here have been found to be negative which indicates that the reaction goes towards the product. The positive values of ΔH^o suggests that the reaction is endothermic. The ΔS^o for both the systems were found to be positive and comparatively low, which suggests a less ordered behaviour for the products than the reactants. Thus, the observed values of thermodynamic parameters indicate that these reaction processes are of the forward and endothermic type [22].

CONCLUSION

It may be concluded that the dielectric investigation gives valuable information about the dynamics of molecules at the molecular level and provides insight into the nature of the molecular interaction between chlorobenzene and ethanol and bromobenzene and ethanol arising from the bonding between the halogen atom of chlorobenzene and bromobenzene molecules and the hydrogen atom of ethanol molecule. The values of distribution parameter, relaxation times, dipole moment, association equilibrium constant and thermodynamic parameters and their variations with concentration and temperature, strongly support the presence of weak molecular interaction in these ternary liquid mixtures.

References

[1] A. Awasthi, M. Rastogi, M. Gupta and J.P. Shukla (1999). *J. Mol. Liq.*, **80**(1), 77.
[2] A.N. Kannappan and R. Palani (1996). *Indian J. Phys.*, **70B**(1), 59.
[3] A. Awasthi and J.P. Shukla (2003). *Ultrasonics* (in press).
[4] P.R. Palaniappan, A.N. Kannappan and M. Kamalakannan (1988). *Z. Phys. Chemie Leipzig*, **269**, 779.
[5] S.W. Tucker and S. Walker (1966). *Trans. Faraday Soc.*, **62**, 2690.
[6] S.W. Tucker and S. Walker (1970). *J. Chem. Phys.*, **52**, 2545.
[7] A. Awasthi, M. Rastogi, M. Gupta and J.P. Shukla (2000). *Indian J. Pure & Appl. Phys.*, **38**, 319.
[8] A.D. Vyas and V.M. Vashisth (1988). *J. Mol. Liq.*, **38**, 11.
[9] R.C. Basak, S.K. Sit, N. Nandi and S. Acharyya (1996). *Indian J. Phys.*, **70B**(1), 37.
[10] C.P. Smyth (1967). *Adv. Mol. Relaxation & Interaction Processess*, **1**, 1.
[11] K. Chitoku and K. Hagasi (1971). *Bull. Chem. Soc. Japan*, **44**, 992.
[12] P.J. Singh and K.S. Sharma (1996). *Pramana*, **46**, 259.
[13] M. Jorg, A. Ghoneim, G. Turky and M. Stockhauson (1995). *Phys. Chem. Liq.*, **29**, 263.
[14] K.V. Gopalakrishna (1957). *Trans. Faraday Soc.*, **53**, 767.
[15] K. Higasi (1966). *Bull. Chem. Soc. Japan*, **39**, 2157.
[16] K. Higasi, Y. Koga and M. Nakamura (1971). *Bull. Chem. Soc. Japan*, **44**, 988.
[17] S. Roberts and A. von Hippel (1946). *J. Appl. Phys.*, **17**(7), 610.
[18] T.W. Dakin and C. Works (1947). *J. Appl. Phys.*, **18**, 789.
[19] D.D. Perrin and W.L.F. Armarego (1998). *Purification and Lab Chem*, 3rd Edn. Pergamon Press Oxford.
[20] Y. Koga, M. Takahashi and K. Higasi (1973). *Bull. Chem. Soc. Japan*, **46**, 3359.
[21] A. Singh and M.C. Saxena (1983). *J. Mol. Liq.*, **25**, 81.
[22] A. Singh, R. Mishra, J.P. Shukla and M.C. Saxena (1983). *J. Mol. Liq.*, **26**, 29.
[23] S.K. Saxena, C.L. Gupta, M.N. Sharma and M.C. Saxena (1980). *Acta Phys. et Chem.*, **26**, 141.
[24] S.K. Saxena and M.C. Saxena (1981). *Indian J. Pure & Appl. Phys.*, **19**, 550.
[25] B. Singh and J.K. Vij (1975). *Bull. Chem. Soc. Japan*, **489**, 2551.
[26] M. Chauhan, M. Gupta, S.K. Saxena and J.P. Shukla (1982). *Pramana* **18**, 339.
[27] J.M. Gandhi and G.L. Sharma (1988). *J. Mol. Liq.*, **38**, 23.
[28] M. Gupta, M. Chauhan, S.K. Saxena and J.P. Shukla (1982). *Adv. Mol. Relaxation & Interaction Processes,* **23**, 203.