



MICROWAVE DIELECTRIC RELAXATION STUDIES OF TERNARY LIQUID MIXTURES OF DIOCTYL PHTHALATE AND DIETHYL PHTHALATE WITH ISOBUTANOL

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ABSTRACT The molecular structure and molecular forces in liquids and solution in particular have been investigated by dielectric relaxation studies. The nature and strength of the molecular interactions have been established as the main cause for the chemical behavior of compounds. The dielectric behavior of dioctyl phthalate and diethyl phthalate with isobutanol has been studied at microwave frequency 9.36 GHz at different temperatures 303K, 313K and 323K. Different dielectric quantities like dielectric constant (ϵ'), dielectric loss (ϵ''), static dielectric constant (ϵ_0) and dielectric constant at optical frequency (ϵ_∞) have been determined. The relaxation time (τ) has been calculated by both Higasi's method and Cole-Cole method. The complex system investigated shows the maximum relaxation time values at temperatures by both Higasi's method and Cole-Cole method.

KEYWORDS : Cole-Cole method, dielectric constant, dielectric loss, Higasi's method, diethyl phthalate, isobutanol

1. Introduction:

The dielectric relaxation behavior of mixtures of polar molecules under varying conditions of complexation, temperature and environmental factors has evoked considerable interest. Based on the results, models of relaxation process in liquid mixtures have been formulated. So many researchers [1-6] studied the association of two polar molecules due to hydrogen bonding from the dielectric measurements at microwave frequencies. Purcell and Smyth [7] were the first to detect solute-solvent interactions through measurements of relaxation time. The dielectric relaxation studies of ternary mixtures of polar solvents in dilute solutions of non-polar liquids provide valuable information about solute-solute and solute-solvent interactions.

In order to provide experimental data on ternary mixture, dioctyl phthalate, and diethyl phthalate with isobutanol in benzene at various concentrations were studied at microwave region at different temperatures (303K, 313K and 323K). The study is expected to provide better understanding of the nature of molecular orientation processes.

2. Experimental details:

Dioctyl phthalate and diethyl phthalate with isobutanol in benzene were used. The molar ratio of the ternary mixture of dioctyl phthalate + isobutanol and diethyl phthalate + isobutanol in benzene are 1:9, 2:8, 3:7, 4:6, 5:5, and 6:4. The measurement of dielectric constant at an angular frequency (ϵ') and dielectric loss (ϵ'') was carried out in the X band microwave frequency at 9.36 GHz. The static dielectric constant (ϵ_0) was measured by heterodyne beat method at three different temperatures (303K, 313K and 323K) using a dipole meter operated at 220 volts. The refractive index was measured by Abbe's refractometer. The errors in the measurements of density and refractive index are ± 0.002 g/cc and 0.002 respectively. The temperature of all these measurements was maintained at 303K, 313K and 323K using a water circulating thermostat. The density was measured with a 20ml. specific gravity bottle.

3. Theory:

Conformational changes occurred when two or more liquids are mixed together, which can be studied by relaxation mechanisms.

3.1. Higasi method:

This method provides multiple relaxation times, one for overall rotation and another for group rotation. Higasi assumed a linear variation of ϵ_0 , ϵ' , ϵ'' and ϵ_∞ with weight fraction w_2 of the solute and hence once can write

$$\begin{aligned}\epsilon_0 &= \epsilon_{01} + a_0 w_2 \\ \epsilon' &= \epsilon'_1 + a' w_2 \\ \epsilon'' &= a'' w_2 \\ \epsilon_\infty &= \epsilon_{\infty 1} + a_\infty w_2\end{aligned}\quad (1)$$

where a_0 , a' , a'' and a_∞ are constants known as the Higasi's parameters.

Higasi et al. [8] derived a relation connecting τ_0 and α .

$$\tau_0 = \frac{1}{\omega} \left(\frac{A^2 + B^2}{C^2} \right)^{\frac{1}{(1-\alpha)}} \quad (2)$$

$$(1-\alpha) = \frac{2}{\pi} \tan^{-1} \left(\frac{A}{B} \right) \quad (3)$$

Where τ_0 is the most probable relaxation time, α is the distribution parameter, ω is the angular frequency and

$$\begin{aligned}A &= a'' (a_0 - a_\infty) \\ B &= (a_0 - a') (a' - a_\infty) - a''^2 \\ C &= (a' - a_\infty)^2 + a''^2\end{aligned}$$

The Debye equation in terms of a_0 , a' , a'' and a_∞ yields two independent equations [9]

$$\tau_1 = \frac{a''}{\omega (a' - a_\infty)} \quad (4)$$

$$\tau_2 = \frac{(a_0 - a')}{\omega a''} \quad (5)$$

τ_1 is the molecular relaxation time of the complex as a whole and τ_2 indicates the relaxation time of the base molecule of amines.

$\sqrt{\tau_1 \tau_2} = \tau$ may be the mean relaxation time and will be calculated.

3.2 Cole-Cole method:

The measured values of permittivity and dielectric loss at microwave frequency, static permittivity and permittivity at optical frequency were fitted in a complex plane plot with a depressed circular arc. The angle made by the diameter drawn through the centre from the ϵ_∞ point and the X-axis is given by $(\alpha \pi/2)$. From the Cole-Cole plot, the relaxation time τ can be found out using the following equation [5]

$$(\omega \tau)^{1-\alpha} = \left(\frac{v}{u} \right) \quad (6)$$

Where α is the distribution parameter, ω is the angular frequency, v is the distance between ϵ_0 and the experimental point on the Cole-Cole plot and u is the distance between ϵ_∞ and that point on the Cole-Cole plot.

Eyring relations are used to compute the activation free energy from

$$\tau = \left(\frac{h}{kT}\right) \exp\left(\frac{\Delta F_{\tau}}{RT}\right) \quad (7)$$

$$\eta = \left(\frac{N h}{V}\right) \exp\left(\frac{\Delta F_{\eta}}{RT}\right) \quad (8)$$

where N, k, h, R, V and T are Avagadro's number, Boltzmann's constant, Planck's constant, gas constant, molar volume and temperature respectively. ΔF_{τ} refers to the activation free energy due to the relaxation mechanism and ΔF_{η} stands for activation energy due to viscosity.

4. Results and discussion:

For both systems, it is found that,

- i) The value of ϵ' decreases with the increase of concentration.
- ii) The value of ϵ'' increases with the increase of concentration.
- iii) The average relaxation time τ increases with concentration.
- iv) The difference between the values of $\tau(1)$ and $\tau(2)$ is appreciable.
- v) The values of τ are lower than $\tau(2)$.

Khameshara et al.[10] found that for some monoalcohols, the values of τ are lower than the values of the relaxation time for overall rotation of the molecules $\tau(2)$. It was explained as due to the fact that the former method gives the average value of relaxation time whereas the latter gives the relaxation time for overall orientation only. The difference between the two relaxation times is explained as due to the existence of intra molecular relaxation process in addition to the overall molecular relaxation process. Our results show that $\tau < \tau(2)$. This may be due to the presence of intra molecular relaxation process in the systems studied [11].

For both systems, it is found that,

- vi) The relaxation times for the mixture are found to lie in between the values of the two individual components [12-19]. This shows that there is no strong interaction among the partners.

Our results show that ' τ ' values obtained by Cole-Cole plot are lower than the values obtained by Higasi method [20-25]. This may be attributed due to the non-rigid behavior of the solute molecules. Similar results were reported in the literature.

Gandhi et al.[26] have mentioned different mixing rules such as simple mixing rule given as

$$\tau_m = \sum_{i=1}^N X_i \tau_i \quad (9)$$

and reciprocal mixing rule given as

$$\frac{1}{\tau_m} = \sum_{i=1}^N \frac{X_i}{\tau_i} \quad (10)$$

and another mixing rule depending on the shape, size, viscosity, etc., given as

$$\frac{1}{\tau_m} = \sum_{i=1}^N \frac{A_i}{\tau_i} \quad (11)$$

Where A_i is a constant.

The computed values by three different methods are not well compared themselves. Moreover compared with the experimental value of τ , the deviations occur and the second method seems to have a better agreement. But none of the method is found to be successful for the entire systems.

For both systems, it is found that,

- vii) The values of $\tau(2)$ are greater than $\tau(1)$. The very large difference in $\tau(1)$ and $\tau(2)$ values indicate that the distribution due to the two mechanisms is wide enough to show
- viii) The distribution parameter (α) is large [27-29] indicating the solute-solvent interactions.
- ix) The values of $\tau(1)$ decrease on dilution. The decrease of $\tau(1)$ with dilution is assigned to the decrease in the sizes of the n-mers due to the intervention caused by the solvent [30,31]. The coupling between the dipoles is also decreased by the solvent enabling the dipoles to rotate more freely.

For dioctyl phthalate+ isobutanol system, it is found that,

- x) The values of $\tau(2)$ increase on dilution. The increase of $\tau(2)$ with dilution is assigned to the increase in the sizes of the n-mers due to the intervention caused by the solvent [30, 31]. The coupling between the dipoles is also increased by the solvent disabling the dipoles to rotate more freely. For diethyl phthalate+ isobutanol system, it is found that,
- xi) The values of $\tau(2)$ decrease on dilution. The decrease of $\tau(2)$ with dilution is assigned to the decrease in the sizes of the n-mers due to the intervention caused by the solvent [30, 31]. The coupling between the dipoles is also decreased by the solvent enabling the dipoles to rotate more freely.

Davidson [32] showed that the relaxation process for any system can be resolved into the intermolecular relaxation time $\tau(1)$ and the intramolecular relaxation time $\tau(2)$ components only if the ratio of the two relaxation times ($\tau(1)/\tau(2)$) is greater than 6.

In our present investigation no such resolution is found to occur due to the increased overlap of two nearly equal regions. The different sizes of the relaxing units give rise to a changed environment, but not a distinguishable change in the multimeric unit responsible for different relaxation times. Our results are consistent with the interpretation that there is a progressive change in the n-mer and not any abrupt change on dilution. The decrease of $\tau(1)$ and $\tau(2)$ with dilution is assigned to the reduction in the sizes of the n-mers due to the intervention caused by the solvent. The coupling between the dipoles is also reduced by the solvent enabling the dipoles to rotate more freely.

- xii) The values of ΔF_{τ} are less than ΔF_{η} .

The free energy of activation of dipole orientation ΔF_{τ} is less than the corresponding value of the viscous force ΔF_{η} which is expected because viscous flow involves translational as well as rotational motion of the molecule, whereas dielectric relaxation process involves only rotational motion. Similar conclusion was arrived at by Purohit et al.[33].

Gandhi et al.[26] have reported a lower value of ΔF_{η} for the mixture of two polar liquids than the corresponding values for their pure components. It was ascribed due to the interaction of dissimilar molecules resulting in the lowering of activated state. Our results show that ΔF_{η} value lies between the corresponding values of pure components. This indicates that the interaction between the dissimilar molecules may not lower the activated states. The individual characteristics of the liquids are retained in the mixture.

- xiii) The values of ΔF_{τ} and ΔF_{η} decrease on dilution.

This may be due to the increase in the size of the molecules. Larger size of the molecules requires greater energy to lift a molecule over the potential energy barrier. Increase in the value of ΔF_{τ} decreases the probability of a jump from one orientation into another resulting in the increase in the value of the relaxation time.

- xiv) The values of $\Delta\mu$ are found to be negative.

The excess dipole moment is a qualitative index for the presence of hydrogen bond in the ternary systems. The dipole moment of the mixture is obtained using Eq.(7.49). The excess dipole moment is obtained using Debecker and Huyskens[34] equation

$$\Delta\vec{\mu} = \vec{\mu}_{ab} - \vec{\mu}_a - \vec{\mu}_b \quad (12)$$

The dipole moment of the components is determined by Halverstadt and Kumler method. The presence of a hydrogen bond between the hydrogen of the phthalates with the oxygen of the alcohols in these systems is indicated by the excess dipole moment values. Such a hydrogen bond between acetone + acetonitrile system was reported by Shobanadri et al. [35] and between cresol + acetonitrile / acrylonitrile systems was reported by Subramanian et al.[36]. The excess dipole moment may be attributed to the proton-transfer in this bond.

the equations given below [6].

Table.1 Variation of $\epsilon_0, \epsilon_\infty, \epsilon', \epsilon''$, and relaxation time by Higasi and Cole-Cole methods with w_2 for Benzene + Dioctyl phthalate+ Isobutanol system

Temp K	w_2	ϵ_0	ϵ_∞	ϵ'	ϵ''	Relaxation Time (ps)			
						Higasi et al. method			Cole-Cole method
						τ_1	τ_2	T	
303	0.011	3.653	2.179	2.676	0.110	4.197	151.022	25.175	19.54
	0.022	3.673	2.177	2.672	0.174	6.656	97.906	25.528	21.08
	0.033	3.705	2.176	2.670	0.237	9.083	74.400	25.996	22.58
	0.044	3.717	2.171	2.631	0.345	14.369	53.529	27.734	25.77
	0.056	3.739	2.168	2.605	0.403	17.754	47.898	29.162	27.72
0.067	3.773	2.165	2.578	0.524	24.612	38.753	30.883	29.84	
313	0.011	3.770	2.178	2.699	0.123	4.441	148.127	25.649	19.85
	0.022	3.792	2.175	2.685	0.186	6.874	101.392	26.399	21.60
	0.033	3.816	2.173	2.675	0.244	9.191	79.434	27.020	23.22
	0.044	3.832	2.171	2.648	0.355	14.105	56.781	28.301	26.22
	0.056	3.877	2.166	2.613	0.411	17.635	52.300	30.370	28.85
0.067	3.903	2.161	2.589	0.532	23.986	42.028	31.750	30.85	
323	0.011	3.839	2.174	2.694	0.134	4.825	145.276	26.475	20.35
	0.022	3.856	2.171	2.694	0.207	7.435	95.390	26.632	22.11
	0.033	3.880	2.168	2.681	0.259	9.494	78.616	27.319	23.64
	0.044	3.893	2.164	2.653	0.367	14.169	57.390	28.516	26.52
	0.056	3.913	2.163	2.618	0.467	19.517	47.129	30.328	29.31
0.067	3.956	2.159	2.586	0.563	25.241	41.404	32.328	31.55	

Table.2 Variation of $\epsilon_0, \epsilon_\infty, \epsilon', \epsilon''$, and relaxation time by Higasi and Cole-Cole methods with w_2 for Benzene + Diethyl phthalate + Isobutanol system

Temp K	w_2	ϵ_0	ϵ_∞	ϵ'	ϵ''	Relaxation Time (ps)			
						Higasi et al. method			Cole-Cole method
						τ_1	τ_2	T	
303	0.011	4.135	2.200	3.166	0.727	13.498	22.677	17.496	17.03
	0.022	4.124	2.198	3.089	0.749	15.161	23.493	18.872	18.40
	0.033	4.276	2.195	3.074	0.780	16.036	26.196	20.496	20.05
	0.044	4.284	2.194	3.049	0.786	16.634	26.717	21.081	20.64
	0.056	4.312	2.190	3.020	0.799	17.439	27.511	21.903	21.46
0.067	4.376	2.187	3.015	0.800	17.488	28.934	22.494	22.07	
313	0.011	4.250	2.200	3.211	0.708	12.527	24.957	17.682	17.25
	0.022	4.323	2.197	3.110	0.735	14.486	28.105	20.177	19.74
	0.033	4.345	2.194	3.094	0.746	14.922	28.545	20.638	20.21
	0.044	4.398	2.191	3.091	0.787	15.756	28.252	21.098	20.69
	0.056	4.467	2.188	3.077	0.792	16.070	29.839	21.898	21.50
0.067	4.522	2.185	3.051	0.810	16.900	30.884	22.846	22.47	
323	0.011	4.393	2.174	3.216	0.541	9.266	37.006	18.518	18.01
	0.022	4.395	2.179	3.101	0.597	11.637	36.860	20.711	20.11
	0.033	4.552	2.176	3.096	0.627	12.229	39.502	21.979	21.32
	0.044	4.544	2.174	3.081	0.783	15.507	31.767	22.195	21.83
	0.056	4.585	2.167	3.034	0.724	15.032	36.464	23.412	22.96
0.067	4.677	2.160	3.012	0.612	12.957	46.272	24.486	23.58	

Table.3 Variation of $\Delta F\eta, \Delta F\tau$ and excess dipole moment with w_2 for Benzene + Dioctyl phthalate+ Isobutanol system

Temp K	w_2	$\Delta F\eta$ (kJ / mol)	$\Delta F\tau$ (kJ / mol)	$\Delta\mu$ Debye
303	0.011	12.39	12.75	-3.228
	0.022	15.37	12.78	-3.726
	0.033	15.98	12.83	-3.941
	0.044	16.72	12.99	-4.072
	0.056	17.29	13.12	-4.159
	0.067	17.82	13.26	-4.220
313	0.011	13.29	13.05	-3.142
	0.022	15.10	13.12	-3.664
	0.033	16.18	13.18	-3.893
	0.044	16.93	13.30	-4.031
	0.056	17.55	13.48	-4.116
	0.067	18.03	13.59	-4.183
323	0.011	13.47	13.38	-3.084
	0.022	15.32	13.40	-3.625
	0.033	16.39	13.46	-3.861
	0.044	17.16	13.57	-4.004
	0.056	17.79	13.73	-4.099
	0.067	18.29	13.90	-4.163

Table.4 Variation of $\Delta F\eta$, $\Delta F\tau$ and excess dipole moment with w_2 for Benzene + Diethyl phthalate + Isobutanol system				
Temp K	w_2	$\Delta F\eta$ (kJ / mol)	$\Delta F\tau$ (kJ / mol)	$\Delta\mu$ Debye
303	0.011	12.39	11.83	-2.967
	0.022	15.37	12.02	-3.554
	0.033	15.98	12.23	-3.766
	0.044	16.72	12.30	-3.923
	0.056	17.29	12.40	-4.026
	0.067	17.82	12.46	-4.093
313	0.011	13.29	12.09	-2.890
	0.022	15.10	12.43	-3.469
	0.033	16.18	12.49	-3.735
	0.044	16.93	12.55	-3.885
	0.056	17.55	12.64	-3.983
	0.067	18.03	12.75	-4.057
323	0.011	13.47	12.45	-2.786
	0.022	15.32	12.74	-3.424
	0.033	16.39	12.90	-3.660
	0.044	17.16	12.92	-3.836
	0.056	17.79	13.06	-3.944
	0.067	18.29	13.18	-4.014

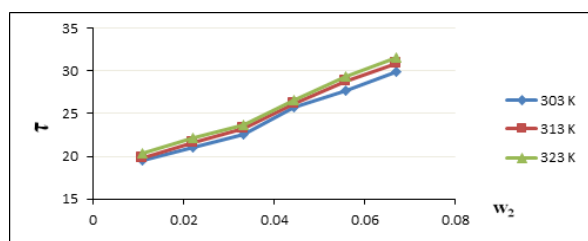


Fig.1 Variation of τ with w_2 for Benzene + Diethyl phthalate + Isobutanol system

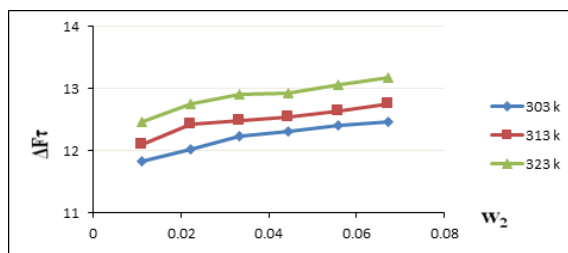


Fig.5 Variation of $\Delta F\tau$ with w_2 for Benzene + Diethyl phthalate + Isobutanol system

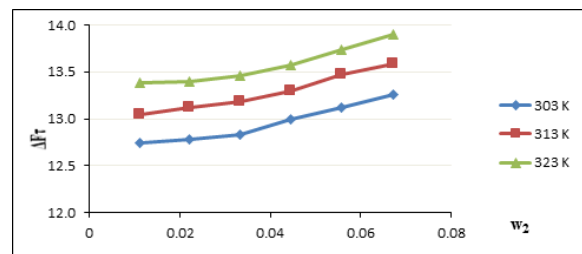


Fig.2 Variation of $\Delta F\tau$ with w_2 for Benzene + Diethyl phthalate + Isobutanol system

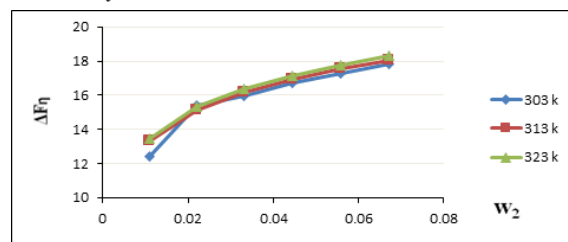


Fig.6 Variation of $\Delta F\eta$ with w_2 for Benzene + Diethyl phthalate + Isobutanol system

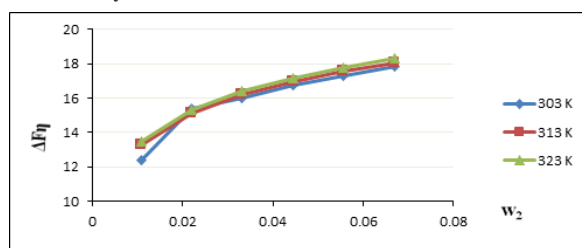


Fig.3 Variation of $\Delta F\eta$ with w_2 for Benzene + Diethyl phthalate + Isobutanol system

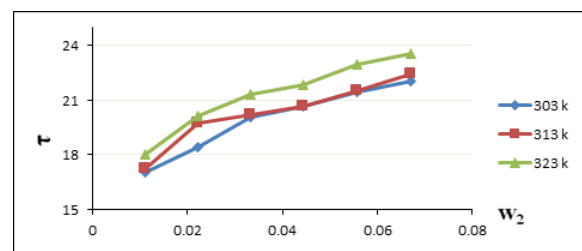


Fig.4 Variation of τ with w_2 for Benzene + Diethyl phthalate + Isobutanol system

5. References:

- Kumar,R., Rangra, V.S., Sharma,D.R., Thakur, N. and Negi, N.S., Z. Naturforsch. 61 a, 197(2006).
- Sharma,V., Thakur,N., Sharma, D.R., Rangra,V.S. and Negi, N.S., Z.Phys.Chem., 229, 325(2006).
- Mushtaq Ahmed Khan, A. and Subramanian, M., Dielectric Relaxation Studies of Ternary Mixture of Dimethyl Phthalate and Heptanol in Benzene, Z. Naturforsch, June (2015)932-784.
- Mushtaq Ahmed Khan, A. and Subramanian, M., "Dielectric Relaxation Studies of Ternary Liquid Mixtures of Dimethyl Phthalate with Triethylamine in the Microwave Region", International Journal of Innovative Research in Science, Engineering and Technology, Vol. 3, Issue 9, September 2014.
- Higasi, K., "Dielectric Relaxation and Molecular Structure II, Notes on Analysing Dielectric data on Dilute Solution", Bulletin of the Chemical Society of Japan, Vol. 39, pp.2157,1966.
- Thenappan,T. and Sankar, U., "Study of correlation factors and dipolar excess free energies of esters in benzene," Journal of Molecular Liquids, Vol. 126, No. 1-3, pp. 23-28, 2006.
- Purcell,W.P. and Smyth,C.P., "Dielectric Properties and Molecular Behavior", Journal of American Chemical Society, Vol. 86, pp.152, 1963.
- Higasi, K. A., Koga, Y. and Nakamura, M., "Dielectric relaxation and molecular structure Application of the single frequency method to systems with two Debye dispersions," Bulletin of the Chemical Society of Japan, Vol. 44, pp.988, 1971.
- Khameshara, S.M. and Sisodia, M.L., Adv. Mol. Relaxation Processes., 15 (1979) 213.
- Sengwa R.J., Ind. J. Pure and Appl. Phys., 41 (2003) 295-300.
- Rana, V.A., and Vyas, A.D., Ind. J. Pure and Appl. Phys., 39(5) (2001), 316-320.
- Garg, S.K., Klip, H. and Smyth, C.P., J. Chem. Phys., 45 (1966) 2799.
- Gupta,K.K., Bansal,A.K., Sing,P.J., and Sharma K.S., Ind. J. Pure and Appl. Phys., 42 (2004) 849-853.
- Kamble,S., Sudake, Y.S., and Mehrotra,S.C., J. Koren. Chem. Soc., 55(3) (2011) 373.
- Rana, V.A., and Vyas, A.D., Ind. J. Pure and Appl. Phys., 39(5) (2001), 316-320.
- Memmaniwari, B., and Kadam, P., Chem. Sci. Trans., 3(3) (2014) 839.
- Kumar,R., Rangra, V.S., Sharma, D.R., Thakur, N., and Negi, N.S., Z. Naturforsch., 61a (2006) 197.
- Sharma,V., Thakur,N., Sharma, D.R., Rangra,V.S., Negi, N.S., Z. Phys. Chem., 220 (2006) 325.
- Kumar, S., Sharma, D.R., Thakur,N., Negi, N.S., Rangra,V.S., Z. Phys. Chem., 219 (2005) 1649.
- Kumar,R. and Rangra, V.S., Z. Phys. Chem., 219 (2005) 169.

20. A.D. Vyas and V.A. Rana, *Ind. J. Pure and Appl. Phys.*, 40 (2002) 69.
21. S.L. Abd-El-Messieh, *J. Mol. Liq.*, 95 (2002) 167.
22. Kumar, R. and Thakur, N., *Z. Naturforsch.*, 63a (2008) 230-236.
23. Khameshara, S.M., Kavidia, M.S., Lodha, M.S., Mathur, D.C. and Vaidya, V.K., *J. Mol. Liquids*, 26 (1983) 77-84.
24. Kalaivani, T., Kumar, S., and Krishnan, S., *Ind. J. Pure and Appl. Phys.*, 43 (2005) 542-544.
25. Kalaivani, T., Krishnan, S., *Ind. J. Pure and Appl. Phys.*, 47 (2009) 383-385.
26. Gandhi, J.M. and Gopal Lal Sharma, *J. Mol. Liquids*, 38 (1988) 23-25.
27. Tanwar, A., Gupta, K.K., Singh, P.J., and Vijay, Y.K., *Ind. J. Pure and Appl. Phys.*, 44 (2006) 548.
28. Sandeepkumar Sharma, D.R., Thakur, N., Negi, N.S. and Rangra, V.S., *Ind. J. Pure and Appl. Phys.*, 44 (2006) 264-268.
29. Kumar, S., Periyasamy, P., and Jeevanandham, P., *Int. J. ChemTech. Research*, 3 (2011) 369-375.
30. Kalaivani, T., Kumar, S., and Krishnan, S., *Ind. J. Chem.*, 43A(2004)291-293.
31. Thenappan, T., "Studies on the fluid structure and molecular interactions of monoalcohols and monolayers of fatty alcohols", Ph.D. Thesis, Alagappa University, 1994.
32. Davidson, D.W., *Can. J. Chem.*, 39 (1961) 57.
33. Purohit, H.D. and Sengwa, R.J., *J. Mol. Liq.*, 40 (1989) 237
34. Debecker, G. and Huyskens, P., *J. Chem. Phys.*, 68 (1971) 268.
35. Madhurima, V., Sathyan, N., Murthy, V.K.R. and Sobhanadri, J., *Ind. J. Pure and Appl. Phys.*, 36 (1998) 144-148.
36. Subramanian, M., and Thenappan, T., *Philo. Mag. Lett.*, 88 (2008) 889-895