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6. DIELECTRIC STUDIES OF THE BINARY SYSTEM OF ALKYL *p* - HYDROXY BENZOATES AND ISOPROPANOL IN BENZENE SOLUTION AT ROOM TEMPERATURE

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Abstract:

Plunger and cavity methods in microwave frequency region, LCR bridge for static dielectric constant and Abbe's refractometer for measurement of high frequency dielectric constant were used in order to calculate relaxations times. For dipole moments Higasi method is used in the dielectric study of the various concentrations of the binary system of alkyl *p*-hydroxy benzoates (where alkyl carbon number n=2, 3, 4 and 6) and Isopropanol and benzene as solvent.There is an increase in the relaxation time as the concentration of the benzoate is increased in solute system in different concentrations of non-polar solvent benzene and there is a decrease in the dipole moment as the concentration of the benzoate is increased in solute system in non-polar solvent benzene and they are attributed to the formation of hydrogen bond between the solute systems.

Keywords: Plunger and Cavity techniques, Higasi method, dipole moment, relaxation time.

Introduction:

Study of liquid mixtures have gained importance[1-3] because it provides one way of bringing together the molecules of different compounds and allow them to interact with one another. The physical forces responsible for such interactions cannot be studied when such molecules are isolated. Molecular mixtures bring about changes in thermodynamic properties like entropy, free energy and heat of mixing. Changes in physical properties like density, molar volume, viscosity, surface tension, refractive index, dielectric constant and speed of acoustic waves are manifestations of intermolecular interactions in liquid mixtures. Dielectric investigations of solutions containing varying amounts of interacting molecules help to detect the formation and composition of complexes in them. The nature of complex formation in binary mixtures is still far from clear. The Present trend is of liquid mixtures leading to formation of hydrogen bonding in the system due to solute-solvent interactions. Hydrogen bonding is a complex in the liquid state because of the uncertainty in identifying the particular bonds and the number of molecules involved. One of the physical parameters used for conformational analysis of any resultant structure is the net dipole moment besides relaxation time, thermodynamic parameters such as enthalpy

and entropy values[4-6]. With this in view, the present investigation is aimed at studying the dielectric behaviour of binary mixtures of alkyl *p*-hydroxy benzoates *(where n=2, 3, 4 and 6)* and Isopropanol in benzene which may provide useful information about the formation of complex in the mixture.

Experimental:

Alkyl *p*-hydroxy benzoates *(where n=2, 3, 4 and 6)* are used in various fields viz. food preservatives, cosmetic preservatives[7-9] and has biological importance. Alkyl *p*-hydroxy benzoates *(where n=2, 3, 4 and 6)* which were of extra pure quality with 99.5% purity were supplied by M/s Frinton Laboratories Inc, USA. Both Isopropanol and Benzene were supplied by Qualigens. Both of them were ExcelaR grade and were double distilled before use.

Benzene is used as solvent, the binary system of Alkyl *p*-hydroxy benzoates *(where n=2, 3, 4 and 6)* and Isopropanol is used as solute in the preparation of solution. Alkyl *p*-hydroxy benzoates *(where n=2, 3, 4 and 6)* are dissolved in Isopropanol in various concentrations. All the weights are measured using a single pan electronic balance Dhona make, model 100 DS with an accuracy of 0.01 mg.

Each concentration of solute is diluted with benzene in volume fractions of 90% benzene and 10% solute, 80% benzene and 20% solute, 70% benzene and 30% solute, and 60% benzene and 40% solute.

The dielectric studies are carried out by using LCR bridge (static dielectric constant), the microwave bench adopting plunger and cavity[3,10-14] methods (in X-band) and Abbe's refractometer for refractive index (high frequency) at room temperature.

Results and discussion:

In order to calculate the relaxation times, the plunger or cavity readings at microwave frequency region, LCR for static dielectric constant and Abbe's refractometer for measurement of high frequency dielectric constant using the refractive index were used. All these data were used to fit in an Argand diagram to calculate the relaxation times. The representative dielectric data at microwave frequency for one concentration (0.01% of PHB in isopropanol taken as solute and benzene as solvent for concentration of 90% benzene and 10% solute) is given in Table 2. and typical graph for the same concentration is given in Fig. 1. We have observed a distribution of relaxation times as witnessed from Cole-Cole arc plot instead of Debye arc plot. Although Cole-Cole[15] equations which signify the distribution of relaxation times, eventually a macroscopic relaxation time (predominant relaxation time) and dipole moments were measured and the data is given in Tables 1&3(for the systems EHB and 6HB respectively).

Calculation of relaxation time

The dielectric data (0.02% of 6HB) in isopropanol taken as solute and benzene as solvent for concentration of 70% benzene and 30% solute) is represented in complex plane (ε' Vs ε'') resulting Cole-Cole plot and is shown in Fig. 2.

The parameters obtained from Cole-Cole arcs such as distribution parameter 'h' and the corresponding angle $\theta = \pi\alpha/2$, u, v parameters and the relaxation times are calculated from these Cole-Cole plots.

Calculation of Dipole moment

The dipole moments are calculated from Higasi method [16].

$$\mu^2 = \frac{27\ kTM_2}{4\pi N d_1} \cdot \frac{(a_0 - a_\alpha)}{(\varepsilon_1 + 2)^2}$$

where M_2 is molecular weight of solute, ε_1 is the dielectric constant of benzene, N is the Avogadro's number, d_1 is density of solvent, ε_0 and ε_∞ are respectively the slopes of a_0 and a_∞ with respect to the concentration.

The data required for calculating dipole moment is given along with the dipole moment for the above concentration in Table 4.

The values of a_0 and a_∞ are found from the graphs of ε_0 (static permittivity) and ε_∞ Vs concentration respectively which are shown in Fig. 3 and 4 respectively for 0.02 mole fraction of HHB in isopropanol.

It is evident from the data given in the Tables 1 & 3, the dielectric constant increases with the increase of frequency. The microwave data show that these compounds are polar in nature and correspondingly the dielectric constant is a complex quantity. The relaxation time is found to increase in magnitude for a given concentration of Alkyl *p*-hydroxy benzoates *(where n=2, 3, 4 and 6)* in isopropyl alcohol with the increase of dilution in benzene which shows that the molecules are free to rotate as benzene concentration decreases. The dipole moment values decrease with increase of Alkyl *p*-hydroxy benzoates *(where n=2, 3, 4 and 6)* in Isopropyl alcohol which is probably due to the hydrogen bonding in the system.

Table 1: Comprehensive data on dielectric constant, relaxation time, dipole moment for various concentrations of (EHB + Isopropanol(ISP)) in Benzene

% of EHB in isopropanol	Volume fraction of solvent + solute	ε_{static}	$\varepsilon_{microwave}$ plunger method	$\varepsilon_{microwave}$ cavity method	n^2 (Optical frequency)	Relaxation Time τ (pico sec)	Dipole moment μ (Debye)
0.02%	90+10	2.91	2.89-j0.24	2.91-j0.22	2.22	5.6	3.66
	80+20	3.64	3.02-j0.37	3.04-j0.36	2.19	8.9	
	70+30	4.07	3.52-j0.69	3.49-j0.71	2.13	9.5	
	60+40	---	3.06-j0.48	3.04-j0.49	2.1		
0.03%	90+10	2.92	2.75-j0.33	2.74-j0.35	2.19	8.5	3.69
	80+20	3.30	2.94-j0.43	2.96-j0.45	2.17	10.3	
	70+30	4.15	3.48-j0.94	3.52-j0.96	2.14	11.4	
	60+40	---	4.15-j0.29	4.18-j0.26	2.11		
0.04%	90+10	2.92	2.75-j0.22	2.78-j0.21	2.21	5.5	3.55
	80+20	3.36	3.01-j0.52	3.05-j0.50	2.18	10	
	70+30	4.07	3.08-j0.70	3.11-j0.68	2.15	19	
	60+40	---	3.34-j0.84	3.36-j0.82	2.11		
0.05%	90+10	2.83	2.75-j0.21	2.74-j0.23	2.20	5.7	2.93
	80+20	3.36	2.88-j0.27	2.89-j0.26	2.17	8.7	
	70+30	3.61	3.16-j0.62	3.14-j0.64	2.14	11.4	
	60+40	---	3.04-j0.76	3.06-j0.74	2.11		

Table 2: Microwave bench (X-band) readings obtained by moving plunger in 0.01

Distance (mm)	Voltage (mV)	Distance (mm)	Voltage (mV)	Distance (mm)	Voltage (mV)	Distance (mm)	Voltage (mV)
0	15.2	26	15.4	52	13.4	78	13.7
1	14.2	27	15.5	53	14.2	79	13.8
2	12.5	28	14.9	54	14.6	80	13.9
3	10.6	29	14.1	55	14.6	81	14
4	9.9	30	13.1	56	14.4	82	14.2
5	12	31	12.1	57	13.9	83	14.2
6	15	32	11.9	58	13.3	84	14.1
7	15.9	33	13.1	59	12.8	85	14
8	16	34	14.4	60	12.8	86	13.9
9	15.6	35	15.1	61	13.3	87	13.8
10	14.7	36	15.3	62	13.9	88	13.8
11	13.5	37	14.9	63	14.5	89	13.9
12	11.8	38	14.3	64	14.5	90	14
13	10.8	39	13.5	65	14.4	91	14.1
14	11.8	40	12.5	66	14.1	92	13.9
15	14	41	12.2	67	13.9	93	13.9
16	15.3	42	12.7	68	13.5	94	13.9
17	15.7	43	13.7	69	13.4	95	13.9
18	15.5	44	14.6	70	13.8		
19	14.8	45	14.9	71	14.3		
20	13.8	46	14.7	72	14.4		
21	12.5	47	14.3	73	14.4		
22	11.6	48	13.7	74	14.3		
23	11.8	49	12.9	75	14.2		
24	13.5	50	12.5	76	14		
25	14.9	51	12.7	77	13.5		

% of Propyl *p*-Hydroxy Benzoate (PHB) in Isopropanol taken as solute and benzene as solvent for concentration of 90% benzene and 10 % solute

***** Distance means length of liquid column in dielectric cell with respect to mica film as

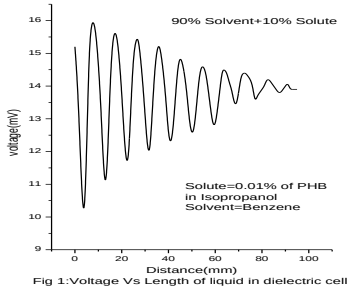

Fig 1:Voltage Vs Length of liquid in dielectric cell

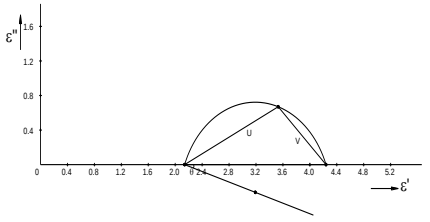

Fig 2: Cole – Cole plot for Solute=0.03% of 6HB in ISP Solvent = Benzene, 70% Solvent 30% Solute

Table 3: Comprehensive data on dielectric constant, relaxation time, dipole moment for various Concentration of (6HB + Isopropanol(ISP)) in Benzene.

% of 6HB in Isopropanol	Volume fraction of solvent + solute	ε_{static}	$\varepsilon_{microwave\ Plunger}$	$\varepsilon_{microwave\ Cavity}$	n^2 (Optical frequency)	Relaxation Time τ (pico sec)	Dipole moment μ (Debye)
0.02%	90+10	3.03	2.78-j0.39	2.81-j0.37	2.23	11.23	4.42
	80+20	3.73	3.53-j0.51	3.52-j0.52	2.19	4.41	
	70+30	4.43	3.91-j0.75	3.90-j0.78	2.15	6.68	
	60+40	5.24	4.40-j0.86	4.39-j0.87	2.12	6.83	
0.03%	90+10	3.40	3.21-j0.46	3.22-j0.47	2.22	6.54	3.55
	80+20	3.81	3.44-j0.51	3.46-j0.50	2.18	7.21	
	70+30	4.24	3.53-j0.67	3.53-j0.66	2.14	8.96	
	60+40	4.77	4.41-j0.86	4.43-j0.84	2.12	5.95	
0.04%	90+10	3.37	3.21-j0.34	3.19-j0.36	2.23	5.57	4.14
	80+20	4.05	3.62-j1.11	3.64-j0.98	2.19	11.12	
	70+30	4.77	4.40-j0.86	4.41-j0.85	2.15	5.95	
	60+40	5.26	4.98-j0.98	4.96-j0.99	2.10	5.15	
0.05%	90+10	3.39	3.19-j0.58	3.17-j0.60	2.24	9.40	4.17
	80+20	4.11	3.44-j0.51	3.44-j0.50	2.18	7.75	
	70+30	4.96	4.41-j0.86	4.42-j0.85	2.15	6.09	
	60+40	5.33	4.99-j0.98	5.11-j0.94	2.10	5.26	

Table 4 : Values of parameters for dipole moment in 0.02% of 6HB in isopropanol

Weight of solute (W_1)	Weight of solvent (W_2)	Weight fraction of solute (W_1/ (W_1+ W_2))	ε_{static}	n^2 (Optical frequency)	a_o	a_α	Dipole moment (μ) Debye
4.232	39.46	0.0968	3.03	2.23			
8.468	39.08	0.1944	3	2.19	7.499	-0.373	4.42
12.696	30.69	0.2926	3.73	2.15			
16.928	26.31	0.3915	3	2.12			
			4.43				
			3				
			5.24				

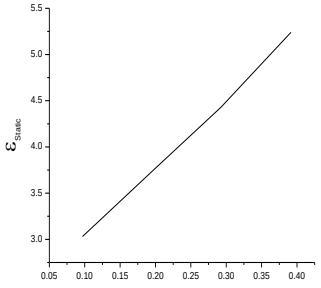

Fig-3 ε_{Static} Vs weight fraction of solute (0.02MF of 6HB in Isopropanol)

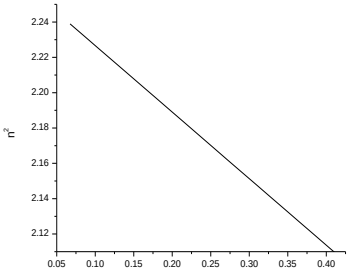

Fig-4 n^2 Vs weight fraction of solute (0.02MF of 6HB in Isopropanol)

Conclusions:

1. The low frequency static dielectric constant and microwave frequency dielectric constant increased with increase in the concentration of the solute binary system (benzoates and alcohols) in non-polar solvent benzene at room temperature.
2. The optical refractive index value decreased with increase in the concentration of the solute binary system (benzoates and alcohols) in non-polar solvent benzene at room temperature.
3. There is an increase in the relaxation time as the concentration of the benzoates is increased in solute system in different concentrations of non-polar solvent benzene and it is due to the formation of hydrogen bond between the solute systems.
4. There is a decrease in the dipole moment as the concentration of the benzoates is increased in solute system in non-polar solvent benzene and it is due to the formation of hydrogen bond between the solute systems.

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REFERENCES:

1. P Debye, "Polar Molecules", The Chemical Catalog Co., New York,1929
2. C P Symth, "Dielectric Behaviour and Structure", Mc Graw-Hill Book Co., New York 1955.
3. Nora E Hill, W E Vaughan, A H Price and M Davies, "Dielectric properties and molecular behaviour", Nostrland Reinhold Company, London, 1968.
4. V Madhurima, Ph.D. thesis IIT Madras Chennai, 1998.
5. M Chitra, Ph.D. thesis IIT Madras Chennai, 2002.
6. S N Viogradov, "Hydrogen bonding" Litton Educational Company, 1971
7. E Marengo, M C Gennaro, and V Gianotti, *J.Chromaographic sci.*, **39,** 339 (2001).
8. K.L Pedersen, S N Pedersen, L B Christiansen, B Korsgaard, and P Bjerregaard,*Basic & Clinical pharmacology & Toxicology*, **86**, 31 (2000).
9. Emanuel Barker, Katherine G Sloman, and Arthur K Foltz, *Food*, **39**, 5 (1967)
10. K V Gopalakrishna, *Trans. Faraday Soc.*, **53**, 767 (1957).
11. A V Ramana Rao, Ch Harinath, M Venkateswarlu, S Sreehari Sastry and V R K Murthy, National seminar on Ferrionics, CVR College of Engineering, Hyderabad, June 29-30, 2006
12. M Chitra, R Dhamodharan, V Madhurima, B Subramanyam, and V R K Murthy , Proceedings of 1999 IEEE 13th international conference on Dielectric liquids, Nara, Japan 20-25, July 1999
13.C. N.Works, T.W. Dakin and F.W.Boggs, *Trans. Am. Inst. Electri. Engineers*, **63**, 1092 (1944)
14. B.S.Bellubbi, Ph.D. Thesis, IIT, Madras 1993.
15. K S Cole and R H Cole, *J. Chem. Phys*, **9**, 341 (1941).
16. K A Higasi, Y Koga and M Nakamura, *Bull. Chem . Soc .Jpn*, **44**, 988 (1971).