Computational And Dielectric Studies On Binary Mixtures Of Propan-2-Ol With N-Alkyl P -Hydroxy Benzoates

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Abstract

The dielectric studies on the polar binary mixtures propan-2-ol with n-alkyl p-hydroxy benzoates (n=7 and 9) have been carried out at various mole and volume fractions. LF impedance analyzer, Microwave bench and Abbe's refractometer are used respectively in radio, microwave (X-Band) and high frequency regions to determine the dielectric data. The experimental data is used to calculate the dielectric constant, dielectric loss, relaxation time, dipolemoment and excess dipolemoment. Hamiltonian quantum mechanical calculations are performed for both pure and equimolar binary systems with optimized converged geometry procedure using PC Spartan modeling software. Dipole moments of the pure and binary mixtures are calculated experimentally from the dielectric data using Higasi's method and compared with the theoretical results. Conformational analysis of the formation of hydrogen bond between propan-2-ol and n-alkyl p-hydroxy benzoates is supported by the FT-IR spectra.

1. Introduction

The aim of the dielectric relaxation study is to understand intermolecular and intramolecular interactions in a molecular system. Extensive studies have been done to understand these interactions on different types of binary polar mixtures. Many workers have reported dielectric relaxation studies of polar molecules and their binary mixtures in dilute solutions of nonpolar solvents [1-3] as well as in pure state [4-8]. Hydrogen bonding in liquid systems has been intensively studied for long and it is still subject to a lively scientific debate, because of its outstanding role in chemistry and biology. Much attention has been also directed towards the physicochemical properties of alcohols not only due to their widespread use as solvents but also because of their fascinating features [9, 10]. As molecules with −OH groups form associative liquid due to hydrogen bonding, the effect of the presence of molecules with other functional groups on these molecules is very important to understand the behavior of hydrogen bonding. Alkyl p - hydroxy benzoates are non-associated in solution, good hydrogen bonding acceptors and important industrial chemicals that are widely used in food and cosmetic preservatives. For the present study propan-2-ol is selected as an associative compound and Heptyl p- hydroxy benzoate, Nonyl p-hydroxy benzoate are selected as non associative compounds.

Dielectric dispersion studies like dipole moment and the relaxation behavior phenomena of polar liquids such as alcohols, benzoates and their binary mixtures were carried out to determine the nature of interaction existing between the molecules due to hydrogen bonding. Dipole moments are determined for the polar solute system diluted in non-polar solvent benzene to minimize the dipole-dipole interaction. The dielectric behavior of some hydrogen bonded polar liquid mixtures was studied by Vishwam *et, al.* [11]. The non associative compounds Heptyl p-hydroxy benzoate and nonyl p-hydroxy benzoate of the present study are useful for hydrogen bonding formation with liquid crystals [12] which eventually affect the dipole moment and relaxation time. The relaxation time studies have been carried out in the binary mixtures of propan-2-ol with methyl and ethyl benzoates [13].

The objective of the present work is to report the influence of non associative molecule on the associative

molecule in liquid state by studying the dielectric behaviour of the binary mixtures − propan-2-ol with n-alkyl *p*-hydroxy benzoates (n=7 and 9) (solute system) in non-polar solvent medium (benzene) with different concentration. The average relaxation times are calculated from the respective Cole-Cole plots [14]. Dipole moment values are calculated using the Higasi's method [15] and compared with the theoretical Hamiltonian quantum mechanical calculations. Minimum energy structures of the polar systems propan-2-ol, n- alkyl *p*-hydroxy benzoates and their equimolar binary system are determined with optimized converged geometry optimization procedure using PC Spartan modeling software [16]. Conformational analysis of the formation of hydrogen bond between the mixture systems is carried out from FT-IR spectra in 400-4000 cm^{-1} region.

2. Experimental

Propan-2-ol (IPA) and benzene are Qualigen chemicals of Analar grade and double distilled before use. Heptyl *p*-hydroxy benzoate (7HB) and Nonyl *p*-hydroxy benzoate (9HB) are purchased from M/s Frinton Laboratories, USA. In the preparation of solution the binary mixtures − propan-2-ol + Heptyl *p*-hydroxy benzoate (system 1) or propan-2-ol + Nonyl *p*-hydroxy benzoate (system 2) is used as solute and benzene is used as solvent. First n- alkyl *p*-hydroxy benzoates are dissolved in propan-2-ol at various mole fractions (MF) i.e., 0.01%, 0.02%, 0.03%, 0.04% and then each concentration of solute is diluted with solvent in different volume fractions (10%, 20%, 30% and 40%) of the solution . The mass measurements are performed on a digital electronic balance (Mettler Toledo AB 135, Switzerland) with an uncertainty of ± 0.00001 g.

The permittivity values at spot frequencies 1 kHz (ε_{static}), 10 kHz, 100 kHz, 1 MHz and 10 MHz for the above systems are measured using HP-LF impedance analyzer (Model No: 4192 A). The real (ε') and imaginary (ε'') parts of the complex dielectric permittivity ($\varepsilon^* = \varepsilon' - j\varepsilon''$) are determined in X-Band (8.60 GHz) using microwave bench with plunger technique [17]. The high frequency dielectric permittivity ($\varepsilon_\infty = n^2$) is obtained from the refractometer measurements using M/s ASCO make Abbe's refractometer with sodium D light as source. The average uncertainties in the measurement of ε_{static} ,

ε_∞, ε' and ε'' are ± 0.002, ± 0.0002, ± 0.01 and ± 0.03 respectively. The FT-IR-spectra of pure and equimolar binary mixture systems are recorded in 400-4000 cm^{-1} region on Perkin-Elmer (spectrum bX) series.

3. Theory

The dielectric data obtained i.e., ε_{static} , $\varepsilon^* = \varepsilon' - j\varepsilon''$, ε_∞ and the data from LF-impedance analyzer is used to fit in an Argand diagram to calculate the relaxation time (τ). The distribution of relaxation time is witnessed from Cole-Cole arc plot. In Cole-Cole method, the semicircle corresponding to one relaxation time is generally replaced by the arc of a circle in which the center lies below the actual axis. The diameter of this circle cuts the axis of abscissas at the point corresponding to the value of ε_∞ and forms an angle $\theta \left(\dfrac{\pi\alpha}{2} \right)$ with the axis of abscissa. By plotting through the experimental points, determined for various frequencies, an arc is obtained whose center lies below the ε' axis. It is possible to find the value of relaxation time by the equation,

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

where α (distribution parameter), u and v values are determined from their respective Cole-Cole plots. A typical Cole-Cole plot is shown in the results and discussion part.

The dipole moments of dilute systems were calculated from Higasi's method.

$$\mu^2 = \frac{27kTM_2 \left(a_0 - a_\infty \right)}{4\pi Nd_1 \left(\varepsilon_1 + 2 \right)^2} \qquad (2)$$

where M_2 is molecular weight of solute, a_0 and a_∞ are respectively the slopes of ε_{static} and ε_∞ with respect to the weight fraction of the solute, d_1 is density of solvent, ε_1 is the static dielectric permittivity of solvent (benzene). The average uncertainty in the measurement of dipole moment is ± 0.02 Debye.

The excess dipole moments ($\Delta\mu$) of the binary systems are determined [11] by the equation,

$$\Delta\mu = \mu_{12} - \mu_1 - \mu_2 \qquad (3)$$

where μ_1 is the dipole moment of propan-2-ol, μ_2 is the dipole moment of either heptyl *p*-hydroxy benzoate or nonyl *p*-hydroxy benzoate and μ_{12} is the dipole moment of the equimolar solute mixture propan-2-ol + Heptyl *p*- hydroxy benzoate (system 1) or propan-2-ol + Nonyl *p*- hydroxy benzoate (system 2).

Minimum energy structures of the pure monomers of propan-2-ol, Heptyl *p*- hydroxy benzoate, Nonyl *p*-hydroxy benzoate and the equimolar hydrogen bonded complexes are obtained from semi-empirical calculations such as Austin Model 1 (AM1), Parameterized Model number 3 (PM3) and Modified Neglect of Differential Overlap (MNDO) Hamiltonian quantum mechanical calculations with optimized converged geometry optimization procedure using PC Spartan modeling software.

4. Results and discussion

The Dielectric data ε_{static}, $\varepsilon^* = \varepsilon' - j\varepsilon''$, ε_∞ and relaxation times for the systems IPA+7HB (system 1) and IPA+9HB (system 2) with various volume fractions in the solution are given in Tables 1 and 2 respectively. The relaxation times are found to increase in magnitude for a given mole fraction of n-alkyl *p*-hydroxy benzoate in propan-2-ol with the increase of solute volume fraction which shows that the molecules are unable to rotate freely as benzene concentration decreases in the solution. In general, the magnitude of average relaxation time is increasing with the increase of MF of n-alkyl *p*-hydroxy benzoate in system 1 and also in system 2, which may be attributed to the formation of hydrogen bonding between the compounds of solute systems. A representative Cole-Cole plot for 0.01% MF of 7HB in propan-2-ol with 40% volume fraction is shown in Figure 1.

The dipole moment (μ) values for pure and equimolar mixture systems are determined experimentally with Higasi's method and are given in Table 3. The theoretical dipole moment (μ) values (pure and equimolar systems) are determined with Hamiltonian quantum mechanical semi-empirical calculations AM1, PM3, MNDO and the corresponding values are given in Table 4.

Table 1: Dielectric constant data from static, microwave, optic and relaxation time for various concentrations of (IPA+7HB)

MF of 7HB in IPA	Volume fraction of solute (IPA+7HB) in solvent (benzene)	ε_{static}	$\varepsilon^* = \varepsilon' - j\varepsilon''$	ε_∞	τ (pico sec)
0.01%	10	2.64	2.59-j0.34	2.229	05.12
	20	3.58	2.90-j0.37	2.184	10.34
	30	4.61	3.13-j0.73	2.143	24.76
	40	5.38	3.44-j1.48	2.107	38.42
0.02%	10	2.76	2.73-j0.33	2.229	07.24
	20	3.46	3.00-j0.46	2.187	15.63
	30	4.53	3.14-j0.69	2.143	36.74
	40	5.61	3.41-j1.01	2.102	49.12
0.03%	10	2.84	2.64-j0.27	2.229	09.23
	20	3.53	2.89-j0.50	2.188	21.45
	30	4.69	3.14-j0.69	2.146	42.54
	40	5.50	3.39-j1.13	2.109	59.23
0.04%	10	2.64	2.58-j0.23	2.226	12.56
	20	3.53	2.89-j0.49	2.187	28.46
	30	4.57	3.11-j0.88	2.143	53.72
	40	5.35	3.41-j0.96	2.109	73.32

Table 2: Dielectric constant data from static, microwave, optic and relaxation time for various concentrations of (IPA+9HB)

MF of 9HB in IPA	Volume fraction of solute (IPA+9HB) in solvent (benzene)	ε_{static}	$\varepsilon^* = \varepsilon' - j\varepsilon''$	ε_∞	τ (pico sec)
0.01%	10	2.76	2.68-j0.29	2.229	06.85
	20	3.07	2.98-j0.62	2.190	12.14
	30	4.30	3.12-j0.87	2.150	30.15
	40	5.35	2.61-j1.07	2.114	44.11
0.02%	10	2.64	2.61-j0.17	2.229	08.46
	20	3.42	3.09-j0.39	2.193	20.21
	30	4.92	2.95-j0.43	2.157	48.07
	40	5.00	2.74-j0.62	2.122	55.12
0.03%	10	2.71	2.68-j0.21	2.232	10.26
	20	3.42	2.82-j0.49	2.190	32.46
	30	4.91	2.89-j0.59	2.175	67.96
	40	5.28	2.78-j0.48	2.128	79.76
0.04%	10	2.77	2.69-j0.12	2.229	14.57
	20	3.23	2.83-j0.43	2.187	44.12
	30	4.23	2.99-j0.48	2.166	78.92
	40	5.30	3.12-j0.87	2.134	95.23

Table 3: Experimental dipole moment values for various mole fractions of 7HB and 9HB in IPA

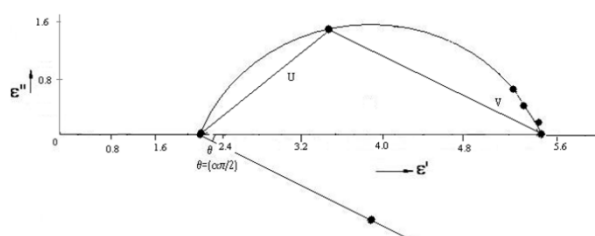| MF of n-alkyl *p*-hydroxy benzoate in propa-2-nol	IPA+7HB	IPA+7HB
0.01%	5.228	5.39
0.02%	5.279	5.19
0.03%	5.095	5.10
0.04%	5.052	5.08

Figure 1. Cole – Cole plot for 0.01% MF of 7HB in propan-2-ol with 40% volume fraction

It is very clear from Table 4, the theoretical dipole moment values, that there is an increase in the dipole moment of equimolar binary mixture compared to that of the pure compounds.

This may be due to the formation of hydrogen bonding between the compounds of the mixture systems [11].

Table 4: Theoretical dipole moment (μ) and excess dipole moment ($\Delta\mu$) values in Debye for pure IPA, 7HB, 9HB and equimolar systems (IPA+7HB, IPA+9HB)

Compound	Theoretical (PC Spartan)					
	AM1		PM3		MNDO	
	μ	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$
IPA	1.62	---	1.53	---	1.44	---
7HB	1.22	---	1.42	---	1.61	---
9HB	1.25	---	1.46	---	1.64	---
IPA+7HB	3.17	0.33	3.90	0.95	2.55	-0.50
IPA+9HB	3.23	0.36	3.89	0.95	2.62	-0.46

Table 5: Experimental and theoretical FT-IR analysis for the pure and binary mixtures of propan-2-ol (IPA) with Heptyl *p*-hydroxy benzoate (7HB) and Nonyl *p*-hydroxy benzoate (9HB).

| Compound	Band	Experimental		Theoretical (PC Spartan)					
				AM1		PM3		MNDO	
		ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})
IPA	OH	3550	---	3503	---	3903	---	4006	--
7HB	OH	3432	---	3449	---	3864	---	3980	---
9HB	OH	3433	---	3451	--	3873	---	3985	---
IPA+7HB	OH–OH	3541 / 3384	09--(IPA) / 48--(7HB)	3495 / 3399	08--(IPA) / 50--(7HB)	3884 / 3839	19--(IPA) / 25--(7HB)	3935 / 3934	71--(IPA) / 46--(7HB)
IPA+9HB	OH–OH	3538 / 3401	12--(IPA) / 32--(9HB)	3492 / 3397	11--(IPA) / 54--(9HB)	3878 / 3811	25--(IPA) / 62--(9HB)	4098 / 4066	92--(IPA) / 81--(9HB)
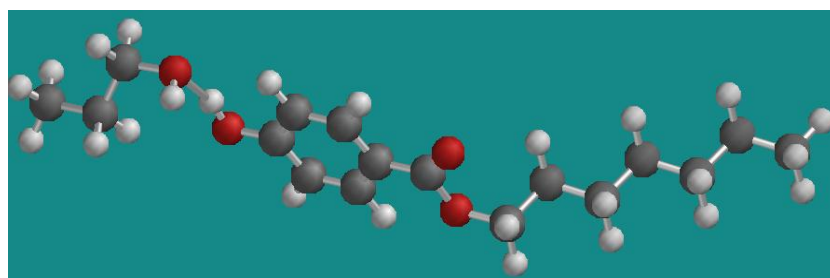
Fig. 2 Optimized geometrical structure of hydrogen bonded propan-2-ol and Heptyl *p*-hydroxy benzoate.

The excess dipole moment ($\Delta\mu$) values, obtained theoretically, are given in Table IV. It is observed that the values of $\Delta\mu$ are low and even negative which indicates the absence of any contribution from ionic structure of the binary mixture system to the total dipole moment because, the formation of ionic structure involves very high positive value of $\Delta\mu$ [18]. The excess dipole moment value is a qualitative index for the presence of hydrogen bonding in both the mixture systems (system1 and system 2).

Observing the experimental FT-IR spectra for the solute mixture of system 1(IPA+7HB), there is a shift of ≈ 09 cm^{-1} wave number for the mixture compared with the pure spectrum of IPA and a shift of ≈ 48 cm^{-1} wave number in the position of –OH for the mixture compared with the pure spectrum of 7HB. Similarly the FT-IR spectra for the solute mixture of system 2 (IPA+9HB), there is a shift of ≈ 12 cm^{-1} wave number for the mixture compared with the pure spectrum of IPA and a shift of ≈ 32 cm^{-1} wave number in the position of –OH for the mixture compared with the pure spectrum of 9HB. This shift is caused by the strong interaction between the high electro-negative charge of oxygen in the benzoate group and the hydrogen of IPA [19]. Thus the IR analysis convinces intermolecular hydrogen bonding between the compounds of the binary mixtures in system 1 and system2 effectively with proportionate variations in stretching frequencies of –OH compared to their respective pure spectrums. The experimental and theoretical FT-IR values, which are in good agreement, for –OH group of pure compounds IPA, 7HB, 9HB and solute mixture systems (system 1 and system 2) are shown in Table V. The optimized geometrical structure representing the formation of hydrogen bonding between propan-2-ol and 7HB (system 1), which is obtained from Hamiltonian quantum mechanical calculation [20], is shown in Figure 2.

5. Conclusions

In this paper, the dielectric properties of hydrogen bonded complexes formed by n- alkyl *p*-hydroxy benzoates (n=7 and 9) with propan-2-ol have been studied by computing experimental, theoretical dipole moments and relaxation times for various mole fractions. The formation of hydrogen bond between n- alkyl *p*-hydroxy benzoates (n=7 and 9) and propan-2-ol, which causes an increase in dipole moment values when compared to that of individual compounds and also considerable changes in relaxation times is confirmed through FT-IR spectra. The absence of ionic contribution to the structure is confirmed by the excess dipole moment values.

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