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RESEARCH ARTICLE

Dielectric Relaxation Study of Binary Mixtures of Benzamide and 1-propanol at a Microwave Frequency

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Abstract

The variation of dielectric parameters of the binary mixtures of benzamide and 1-propanol in dilute solutions with benzene is studied at four different temperatures. The investigations are being done for three different mole fractions of benzamide in 1-propanol at a microwave frequency of 9.385 GHz. The values of dielectric constant (ϵ') and dielectric loss (ϵ'') are calculated by using the method given by Heston et al. Permittivity at an optical frequency (ϵ_∞) and at a static frequency (ϵ_0) are measured with the help of Abbe's refractometer and dipolemeter respectively. The values of relaxation times for molecular and intramolecular rotations are calculated by using Higasi's method. It has been observed from the calculations that values of various relaxation times τ_1, τ_2 and τ_0 for binary mixtures decrease systematically with increase in temperature. The rate of decrease of τ_2 with the rise in temperature has been found to be more significant in comparison to τ_1 values. This suggests that relaxation time corresponding to intramolecular rotation falls off at faster rate with temperature as compared to the internal group rotation.

Key words

Benzamide, Binary mixtures, Dielectric parameters, Relaxation time

Introduction

Increasing use of microwaves in diverse fields such as communication, radar, medicine, biology, agriculture, and industrial process demands accurate data on dielectric properties of materials. Dielectric parameters at microwave frequencies for binary mixtures of polar liquids in dilute solutions of non-polar solvents provide an adequate opportunity for exploring the presence of solute-solute and solute-solvent interactions. 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. To investigate the structural behaviour of molecules, it is necessary to examine various dielectric parameters that are related with inter and intramolecular association and internal rotation with temperature variation. Now a days, dielectric relaxation behaviour of mixtures of different industrially and biologically useful polar solvent molecules (Sengwa *et al*, 2008; Khan *et al*, 2008; Sengwa *et al*,2009; Kalaivani and Krishnan 2009; Sengwa *et al*, 2010) under varying condition of composition have evoked considerable interest because it helps in formulating adequate models of liquid relaxation and obtaining information about the relaxation process in polar mixtures. The thermodynamics of dielectric relaxation is used to study the disturbances in the local structure of the medium.

Therefore, to provide experimental data and to understand relaxation mechanism in binary mixtures of benzamide & 1-propanol, we have made investigations on their binary mixtures. Benzamide is an off-white solid with the chemical formula of $C_6H_5CONH_2$. Its molecular structure can be seen from figure 1. It is the simplest aromatic carboxylic amide, used in the synthesis of various organic compounds. Benzamide is the most potent poly (ADP-ribose) polymerase (PARP) inhibitor in the family of benzamide. Benzamide acts as a neuroprotectant since it inhibits PARP, an enzyme activated by nitric oxide.

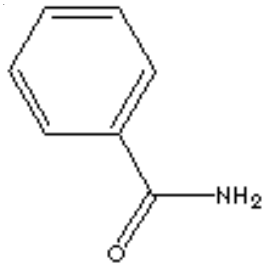

Fig.1. Molecular structure of benzamide

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1-Propanol (CH_3-CH_2-CH_2-OH) is very effective (Narwade *et al*, 2005) against a broad spectrum of microorganism including bacteria, fungi, and viruses such as HIV, hepatitis-B and respirator syncytial viruses.

It is expected that relaxation behaviour of mixtures must depend on the concentration of individual components and temperature of the mixtures.

Material and Methods

In this study, the binary mixtures of benzamide and 1-propanol in dilute solutions with benzene are observed. All of the above compounds have been procured from M/s SRL Pvt Ltd, Mumbai, India. The compounds taken for investigation are AR grade and are used without further purification.

The benzamide and 1-propanol are mixed in the calculated proportions, such that the sum of the mole fractions of each compound in the mixture is equal to one mole. In the present study we have taken three different mole fractions of benzamide viz. 0.01, 0.015 and 0.02 mixed with the 0.99, 0.985 and 0.98 mole fractions of 1-propanol to prepare binary mixtures.

These prepared binary mixtures with different weight fractions are then dissolved in benzene to make dilute solutions. Five different weight factions of each binary mixture have been observed in dilute solutions with benzene. The dielectric relaxation study is done at a frequency of 9.385 GHz considering four different temperatures ranging from 303K to 333K.

We have taken our observations on X- band microwave bench for calculating the dielectric constant (ϵ') and dielectric loss (ϵ'') using Heston et al (Sisodia and Raghuvanshi, 2007) method by using the following equations:

$$\epsilon' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \quad (1)$$

$$\epsilon'' = \frac{2}{\pi}\left(\frac{\lambda_g}{\lambda_d}\right)\left(\frac{\lambda_0}{\lambda_d}\right)^2\left(\frac{d\rho}{dn}\right) \quad (2)$$

where

$$\rho = \frac{\sin\theta}{(2-\cos^2\theta)^{1/2}} \quad (3)$$

and

$$\theta = \frac{\pi\Delta x}{\lambda_g} \quad (4)$$

Here λ_c is the cut-off wavelength, λ_0 is the free space wavelength, λ_d is the wavelength in the dielectric medium and λ_g is the wavelength in the empty waveguide. Parameter 'ρ' is the inverse voltage standing wave ratio, 'n' is the number of minima and Δx is the double minima width. The values of dielectric permittivity at static frequency (ϵ_0) and at optical frequency (ϵ_∞) are determined by using a dipolemeter and Abbe's refractometer respectively. All the measurements are performed at different temperatures using a constant temperature circulating water bath fitted with a thermostat having temperature stability of the order of ± 0.1°C.

For dilute solutions in non-polar solvents ϵ', ϵ'', ϵ_0 and ϵ_∞ can be expressed as linear functions of concentrations (Franklin *et al*, 1950; Higasi, 1966) in the following manner:

$$\epsilon' = \epsilon_1' + a'W_2 \quad (5)$$

$$\epsilon'' = a'' W_2 \quad (6)$$

$$\epsilon_0 = \epsilon_{10} + a_0 W_2 \quad (7)$$

$$\epsilon_\infty = \epsilon_{1\infty} + a_\infty W_2 \quad (8)$$

Here subscript 1 refers to the pure solvent, 2 to the solute, while 0 refers to the static or low frequency case and ∞ refers to the infinite or optical frequency case, W_2 is taken as the weight fraction of the solute. a', a'', a_0 and a_∞ are the slopes of above mentioned linear equations.

The values of the relaxation times τ_0, τ_1, and τ_2 are calculated by using the method given by Higasi *et al* (Higasi *et al*, 1971). The relaxation time for overall molecular rotation (τ_1) is defined by

$$\tau_1 = \frac{a''}{\omega(a'-a_\infty)} \quad (9)$$

While the relaxation time for intramolecular rotations (τ_2) is given by

$$\tau_2 = \frac{(a_0 - a')}{\omega a''} \quad (10)$$

Here ω is the angular frequency. The most probable relaxation time (τ_0) is then obtained by employing the following relation:

$$\tau_0 = \frac{1}{\omega}\left(\frac{A^2+B^2}{C^2}\right)^{\frac{1}{2(1-\alpha)}} \quad (11)$$

and

$$1-\alpha = \frac{2}{\pi}\tan^{-1}\frac{A}{B} \quad (12)$$

Where

$$A = a''(a_0 - a_\infty)$$
$$B = (a_0 - a')(a' - a_\infty) - (a'')^2$$
$$C = (a' - a_\infty)^2 - (a'')^2$$

The value of the dipole moment (μ) of the solute molecules is calculated by using Higasi's method. According to this method the value of dipole moment is given by

$$\mu = \left(\frac{27kTM_2}{4\pi N(\varepsilon_{01}+2)^2 d_1} \right)^{1/2} (a_0 - a_\infty)^{1/2} \qquad (13)$$

Where M_2 is the molecular weight of solute, d_1 is the density of solvent, k is the Boltzmann constant, N is the Avogadro's number and T is the temperature at which the experiment is performed. Thus knowing the value of a_0 and a_∞ , μ can be obtained from equation (13) at different temperatures.

Results and Discussion

On investigating the dielectric properties of the binary mixture of benzamide & 1-propanol, we observe that all dielectric permittivities are decreasing with temperature and increasing with the weight fraction of solute, which can be seen from Tables 1-3 for three different mole fractions. These tables contain the experimentally observed values of dielectric constant ϵ' and dielectric loss ϵ'' at 9.385 GHz at different temperatures, dielectric constant ϵ_0 at static frequency and dielectric constant ϵ_∞ at optical frequency of the binary mixtures of benzamide and 1-propanol at different mole fractions.

Table 1. Values of the dielectric parameters, for binary mixture of 0.01 mole of benzamide and 0.99 mole of 1-propanol at different temperatures and different weight fractions of solute in dilute solution of benzene.

Weight fraction (W_2)	ε'	ε''	ε_0	ε_∞	τ_1 (ps)	τ_2 (ps)	τ_0 (ps)	μ (Debye)	α
Temperature:303K									
0.00933	2.2763	0.0561	2.3076	2.2167	2.16	3.70	2.46	1.58	0.056
0.01244	2.2945	0.0579	2.3245	2.2216					
0.01556	2.3162	0.0595	2.3456	2.2313					
0.01867	2.3354	0.0612	2.3651	2.2367					
0.02179	2.3551	0.0630	2.3884	2.2418					
Temperature : 313 K									
0.00933	2.2594	0.0538	2.2943	2.2155	2.09	3.21	2.30	1.71	0.041
0.01244	2.2806	0.0556	2.3186	2.2208					
0.01556	2.2987	0.0575	2.3348	2.2261					
0.01867	2.3196	0.0593	2.3567	2.2327					
0.02179	2.3425	0.0612	2.3796	2.2371					
Temperature : 323 K									
0.00933	2.2441	0.0517	2.2834	2.2145	2.06	3.02	2.23	1.72	0.035
0.01244	2.2635	0.0535	2.3065	2.2197					
0.01556	2.2827	0.0553	2.3259	2.2243					
0.01867	2.3033	0.0573	2.3448	2.2306					
0.02179	2.3244	0.0590	2.3661	2.2329					
Temperature : 333 K									
0.00933	2.2348	0.0516	2.2748	2.2129	1.85	2.85	2.02	1.76	0.035
0.01244	2.2518	0.0533	2.2967	2.2173					
0.01556	2.2734	0.0552	2.3175	2.2231					
0.01867	2.2965	0.057	2.3387	2.2297					
0.02179	2.3107	0.0578	2.3534	2.2314					

Table 2. Values of the dielectric parameters, for binary mixture of 0.015 mole of benzamide and 0.985 mole of 1-propanol at different temperatures and different weight fractions of solute in dilute solution of benzene.

Weight fraction (W_2)	ε′	ε''	ε_0	ε_∞	τ_1 (ps)	τ_2 (ps)	τ_0 (ps)	μ (Debye)	α
Temperature:303K									
0.00942	2.2837	0.0580	2.3214	2.2375	2.55	4.05	2.87	1.44	0.053
0.01259	2.3061	0.0595	2.3458	2.2474					
0.01573	2.3273	0.0613	2.3667	2.2568					
0.01889	2.3488	0.0631	2.3859	2.2652					
0.02204	2.3685	0.0646	2.4095	2.2789					
Temperature : 313 K									
0.00942	2.2617	0.0558	2.3024	2.2217	2.38	3.74	2.66	1.56	0.049
0.01259	2.2853	0.0574	2.3241	2.2325					
0.01573	2.3078	0.0592	2.3472	2.2413					
0.01889	2.3283	0.0612	2.3688	2.2508					
0.02204	2.3505	0.0628	2.3923	2.2599					
Temperature : 323 K									
0.00942	2.2516	2.2516	2.2886	2.2269	2.20	3.42	2.43	1.57	0.044
0.01259	2.2742	2.2742	2.3178	2.2365					
0.01573	2.2955	2.2955	2.3364	2.2457					
0.01889	2.3177	2.3177	2.3575	2.2546					
0.02204	2.3394	2.3394	2.3799	2.2659					
Temperature : 333 K									
0.00942	2.2391	2.2391	2.2825	2.2212	2.10	3.10	2.28	1.72	0.036
0.01259	2.2574	2.2574	2.3035	2.2284					
0.01573	2.2783	2.2783	2.3244	2.2336					
0.01889	2.3012	2.3012	2.3457	2.2397					
0.02204	2.3221	2.3221	2.3679	2.2493					

Table 3. Values of the dielectric parameters, for binary mixture of 0.02 mole of benzamide and 0.98 mole of 1-propanol at different temperatures and different weight fractions of solute in dilute solution of benzene

Weight fraction (W_2)	ε′	ε''	ε_0	ε_∞	τ_1 (ps)	τ_2 (ps)	τ_0 (ps)	μ (Debye)	α
Temperature:303K									
0.00952	2.2946	0.0589	2.3292	2.2421	2.72	4.62	3.15	1.37	0.067
0.01270	2.3155	0.0603	2.3517	2.2535					
0.01587	2.3361	0.0620	2.3736	2.2644					
0.01905	2.3564	0.0637	2.3942	2.2753					
0.02223	2.3783	0.0653	2.4143	2.2851					
Temperature : 313 K									
0.00952	2.2946	0.0589	2.3292	2.2421	2.54	3.97	2.84	1.43	0.051
0.01270	2.3155	0.0603	2.3517	2.2535					
0.01587	2.3361	0.0620	2.3736	2.2644					
0.01905	2.3564	0.0637	2.3942	2.2753					
0.02223	2.3783	0.0653	2.4143	2.2851					
Temperature : 323 K									
0.00952	2.2577	0.0549	2.3017	2.2321	2.34	3.68	2.61	1.45	0.048
0.01270	2.2805	0.0566	2.3241	2.2438					
0.01587	2.3014	0.0574	2.3436	2.2544					
0.01905	2.3233	0.0593	2.3654	2.2651					
0.02223	2.3436	0.0607	2.3899	2.2769					
Temperature : 333 K									
0.00952	2.2418	0.0542	2.2841	2.2259	2.25	3.28	2.45	1.54	0.037
0.01270	2.2625	0.0557	2.3077	2.2376					
0.01587	2.2854	0.0570	2.3285	2.2481					
0.01905	2.3068	0.0587	2.3493	2.2598					
0.02223	2.3285	0.0602	2.3736	2.2671					

The values of relaxation time τ_1 due to individual rotation of molecules, relaxation time τ_2 due to whole or overall rotation of the molecule, the most probable relaxation time τ_0, the distribution parameter α and the dipole moment values μ at different temperatures are also displayed in Tables 1-3 for binary mixtures of benzamide and 1-propanol at different mole fractions.

It is evident from these tables that the values of various relaxation times τ_1, τ_2, and τ_0 for binary mixtures decrease systematically with increase in temperature (Kumar *et al* 2006). With rise in temperature, viscosity of liquid samples decrease and hence frictional resistance for dipolar orientation reduces. For each sample, the rate of decrease of τ_2 with the rise in temperature is more significant in comparison to τ_1 values. This suggests that relaxation time corresponding to intramolecular rotation falls off at faster rate with temperature as compared to the internal group rotation. This confirms the fact that in polar liquids the intramolecular relaxation process is more dominating though significant values of τ_1 also show some contribution of the intermolecular relaxation.

From the tables we also observe that the finite values of α, the distribution parameter for all the three binary mixtures suggest the presence of more than one relaxation process (Gupta *et al*, 2004) in these mixtures. The difference between $\tau_1$and τ_2 indicates the existence of an intramolecular relaxation process in addition to the overall relaxation process and it is further verified by the finite values of α. On examining Tables 1-3, we find that the values of distribution parameter for all binary mixtures decrease with increase in temperature, which shows that at higher temperature due to expansion of liquids, molecular rotation of liquids molecules, become faster and uniform in the solution.

Again on observing Tables 1-3, we find that the dipole moment values for a particular mole fraction increases with increase in temperature. This may be because of the fact that with temperature the length of the dipole increases.

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