



Intermolecular Interactions of Chlorpheniramine with 1-Methanol at 303K, 308K and 313K using Time Domain Reflectometry

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ABSTRACT

Intermolecular interactions of chlorpheniramine with 1-methanol have been reported at various concentrations in the frequency range 10 MHz to 10 GHz at 303K, 308K and 313K using Time Domain Reflectometry (TDR). Excess inverse relaxation time and dielectric relaxation time were computed by Higasi's Method and interoperated in terms of the molecular interaction of the liquid mixture. The relaxation time and dielectric constant were decreased with increase in concentration of chlorpheniramine. Cole-Cole method was used to determine the non-linearity of the interactions with ideal values. Deviations in such parameters at all the temperatures implies that the existence of solute-solvent interaction due to rotation of dipoles present in the selected liquid system. Hence the experimental observations suggested hetero interaction which may be due to hydrogen bonding of the -OH group of alcohol with N-H of the chlorpheniramine. The intermolecular interaction was obtained in the order of 303K > 308K > 313K.

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Introduction

Chlorpheniramine is used in common cold, allergic rhinitis. It is an amine group compound. 1-methanol is a polar and self associated with hydrogen bonding in pure state. Dielectric relaxation studies in binary mixtures take a vital role for elucidating intermolecular interactions through hydrogen bonding in the liquid system [1-6]. Dharmalingam *et al.* [7] reported the dielectric parameters for methyl acrylate-alcohol mixtures at various temperatures and concentrations. Present work is to study intermolecular interaction in chlorpheniramine and 1-methanol mixtures in microwave region (10 MHz to 10 GHz) with various concentrations (0% to 100%) using Time Domain Reflectometry technique at 303K, 308K and 313K. Dielectric relaxation of the liquid mixtures was determined by the Debye model. Excess inverse relaxation time was also determined. Molecular orientation in the mixture was determined using Kirkwood correlation factor.

Materials and Methods

All the chemicals were acquired from S.D. Fine Chemicals; India. All chemicals were in analytical grade used without further purification. Hewlett-Packard HP 54750 oscilloscope with HP 54754 A TDR plug-in module was used to determine the complex dielectric constant spectra. Based on the interaction the reflected pulse varied and analysed by sampling oscilloscope. Dielectric constant (ϵ') and dielectric loss (ϵ'') were determined by oscillator of frequency 9.36 GHz. Refractive indices (μ) of solution was measured by using Abbe's refractometer. Viscosities of the liquid mixture were determined by Ostwald's. Densities were determined by using 5cc specific gravity bottle. All measurements are made using a constant temperature bath [INSREF model IRI-016C, India] by circulating water from the thermostat with accuracy ± 0.01 K.

Theory

Higasi's Method:

Dielectric relaxation time (τ) was calculated by Higasi's method [8]. Let ϵ_0 , ϵ' , ϵ'' , ϵ_∞ linearly change with solute concentration. Slopes a_0 , a' , a'' and a_∞ were calculated from experimental data. Here

$$\epsilon_0 = \epsilon_1 + a_0 w_2 \quad \text{--- (1)}$$

$$\epsilon' = \epsilon_1 + a' w_2$$

$$\epsilon'' = a'' w_2$$

$$\epsilon_\infty = \epsilon_{1\infty} + a_\infty w_2$$

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

$$\tau_{(2)} = \frac{(a_0 - a')}{\omega a''}$$

$$\tau_{(0)} = \sqrt{\tau_{(1)} \tau_{(2)}} \quad \text{--- (2)}$$

Dielectric relaxation ΔF , τ , Mean relaxation time (τ_0), and viscous flow were determined by Eyring's equation.

$$\tau = \left(\frac{h}{kT}\right) \exp\left(\frac{\Delta F_\tau}{RT}\right) \quad \text{---- (3)}$$

$$\eta = \left(\frac{Nh}{V}\right) \exp\left(\frac{\Delta F_\eta}{RT}\right) \quad \text{---- (4)}$$

Cole-Cole Method:

Calculated values of ϵ_0 , ϵ' , ϵ'' and ϵ_∞ were fitted in a graph. Diameter angle with respect to centre from ϵ_∞ point and abscissa axis is equal to $\pi\alpha/2$. Relaxation time τ was determined by

$$(\omega\tau)^{1-\alpha} = V/U \quad \text{---- (5)}$$

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Table 1. Dielectric constant (ϵ_0), relaxation time (τ) of Chlorpheniramine with 1-methanol.

Volume % of alcohols	ϵ_0	ϵ'	ϵ''	ϵ_∞	Relaxation Time τ (ps)				Activation energy	
					Higasi's			Cole-Cole	ΔF_τ kJ/mol	ΔF_η kJ/mol
					$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$			
Temperature : 303K										
0	3.3063	2.7527	0.9945	2.4123	12.9955	20.1705	16.2155	19.0050	7.4235	3.3063
25	3.1978	2.7352	0.9749	2.4060	11.9175	16.9295	14.2135	15.0241	7.2065	3.1978
50	3.1733	2.7359	0.9721	2.4081	12.0225	16.8105	14.2275	19.7939	7.3675	3.1733
75	3.1558	2.7310	0.9686	2.4004	11.1265	14.1085	12.5335	14.6804	6.7305	3.1558
100	5.0334	4.624	2.9008	4.3361	13.0139	15.2399	14.0779	22.5234	8.9119	5.0334
Temperature : 308K										
0	3.9336	3.3429	2.2994	3.6031	12.5504	17.7864	14.9724	16.7945	8.1404	3.9336
25	3.8363	3.3415	1.5868	3.5058	11.2694	14.6154	12.8374	12.0786	7.9724	3.8363
50	3.8349	3.3408	1.5875	3.5058	10.9824	15.9314	13.2364	17.5281	6.6494	3.8349
75	3.7600	3.3268	1.5784	3.4302	10.5554	12.4524	11.4654	11.5739	7.5104	3.7600
100	3.7586	3.3331	1.5798	3.4281	10.5414	13.1944	11.7944	18.3345	7.7204	3.7586
Temperature : 313K										
0	4.3923	3.7505	1.9636	3.3457	10.9693	13.8463	12.2923	5.5632	8.2253	4.3923
25	4.3069	3.7750	1.9783	3.3429	11.3823	14.2243	12.7263	5.9209	8.5263	4.3069
50	4.2327	3.7792	1.9986	3.3576	12.6493	14.7423	13.6573	7.9425	8.8833	4.2327
75	4.1340	3.7638	1.9888	3.3499	11.1443	14.7983	12.8453	8.6880	8.5893	4.1340
100	4.0717	3.7463	1.9811	3.3387	10.8573	13.7203	12.2083	9.1115	8.1553	4.0717

Result and Discussion

From the experimental observations, dielectric constants (ϵ_0 , ϵ' , ϵ'' and ϵ_∞) of chlorpheniramine and 1-methanol in various concentrations at 303K, 308K and 313K were computed. Table 1 listed the variation of dielectric constant, relaxation time and activation energy with respect to the 1-methanol concentrations. It was noticed that dielectric parameters increased with the 1-methanol concentrations. Furthermore, such parameters decreased with increase in temperature of the liquid mixtures. It suggested that hetero interaction present in the selected liquid system [9]. It was interesting to notice that dielectric constant values increased at the chlorpheniramine rich concentrations. Obviously reverse trend observed with the 1-methanol concentrations. It suggested that the dissociation of the liquid mixture was more with the 1-methanol concentrations. Increasing concentrations of chlorpheniramine increase the solute and solvent interactions. This trend noticed due to the increasing trend of dipoles while mixing the chlorpheniramine in the liquid mixture. But increasing the temperature from 303K to 313K, rotatory motion of the dipoles ruptured. Therefore, dissociation took part with increasing the temperature [10, 11]. Increasing concentrations of chlorpheniramine act as a barrier of the rotator dipoles in the liquid mixtures. Significant variations were noticed in the relaxation time with 1-methanol concentrations. It simulated cluster of molecules, relaxation time dependent on size of the molecules [12]. This trend may due to the disturbance in their equilibrium state. It affected the re orientation of the dipoles existing in the binary liquid mixture. When proton donation increased with the chlorpheniramine with respect to 1-methanol, relaxation time correspondingly increased in the liquid system which was determined by Higasi's method. This kind of variations in the relaxation time supported the presence of solute-solvent interaction between chlorpheniramine and 1-methanol molecules. In this present study, it is observed that decreasing trend of the relaxation with the temperature from 303K to 313K, reveals that variation in the effective length of the dipole, viscosity and molar volume of the liquid mixtures. These variations suggested the leading thermal agitation of the system [13-15]. Similar compared with Cole-Cole method as listed in Table 1. In all the concentrations, viscous flow (ΔF_η) of the liquid system was greater than dielectric

relaxation (ΔF_τ) of the liquid mixture. Thus viscous flow changed with translation vibrations and rotational motion of the molecules. It implies that formation of hydrogen bonding between the presence of -NH group chlorpheniramine and -OH group of the 1-methanol. More over dissociation due to the increase in temperature suggested that strength of the intermolecular interactions were noticed in the order of 313K < 308K < 303K.

Conclusion

Intermolecular interaction between binary mixtures consists of chlorpheniramine and 1-methanol in various concentrations was determined at 303K, 308K and 313K by Time Domain Reflectometry method. Dielectric constants, relaxation time and activation energy were varied with the concentration of the 1-methanol and variation in the corresponding temperatures. Such non linear variations in the dielectric parameters with chlorpheniramine and 1-methanol suggested that strength of intermolecular interaction between the selected liquid system was obtained as 313K < 308K < 303K.

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