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Molecular Interaction Studies of Methyl Formate with Primary Alcohols at 303K Using Time Domain Reflectometry

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Abstract : Dielectric relaxation studies of methylformate with 1-methanol, 1-ethanol and 1-propanol have been carried out at micro frequency range 9.36 GHz at temperature of 303K.Different dielectric parameters like dielectric constant, dielectric loss, Static dielectric constant and dielectric constant at optical frequency have been determined. The Relaxation time has been obtained by Higasi and Cole-Cole method. The dielectric constant and relaxation time decreased with increasing the concentration of ethylformate in alcohol system. The relaxation time increased with increase in chain length of the alcohols. The result shows that the strength of this molecular interaction depends upon the carbon chain length of the alcohols. Hence the proton donating ability of alcohols is in the order of 1-methanol<1-ethanol<1-propanol.

Key Words : methyl formate, Dielectric relaxation, Alcohols.

Introduction

Molecular interaction between the liquid mixtures consisting of polar and non polar components takes place a vital role in physical and chemical properties of the liquid system[1-3]. The dielectric relaxation studies are one of the useful techniques to elucidate the nature of interactions that exist in solute-solvent component of a system. [4-6] Methyl formate is used in the lacquer industry as a solvent for cellulose nitrate. It is also used as fumigant and larvacide or tobacco. It is a highly attractive option for bulk disinfestations of unprocessed dried fruit during ware housing. Alcohols are highly polar and self associated through hydrogen bonding. The carbonyl group (C=O) present in the methyl formate tends to participate in hydrogen bonding interactions with hydroxyl (OH^-) group of alcohols. The present work is an attempt to study the molecular interactions between of methyl formate with1-methanol, 1-ethanol and1-propanol using time domain reflectometry technique at 303K.

Materials and Methods

Methylformate and alcohols of AR grade were obtained from E-Merck India and used with out further purification. The purity of liquids analysed with the standard physical quality values. The dielectric constant (ε') and dielectric loss (ε'') have been measured using X-band microwave frequency oscillator of frequency 9.36 GHz at 303K.The refractive index (μ) of all the solutions has been measured by Abbe's refractometer.The viscosities were measured with the help of Ostwald's viscometer. The densities were measured by using 5cc specific gravity bottle.

Methods

Higasi's Method:

The dielectric relaxation time (τ) was calculated using Higasi's method [6].Assuming ϵ_0 $\epsilon_,^{'}$ $\epsilon^{''}$ and ϵ_∞ vary linearly with weight fraction w_2 of the solute. The slopes a_0,$a^{'}$,$a^{''}$ and a_∞ determined from the determined values. We have

$$\varepsilon_0 = \varepsilon_1 + a_0 w_2$$
$$\varepsilon^{'} = \varepsilon_1 + a^{'} w_2$$
$$\varepsilon^{''} = a^{''} w_2$$
$$\varepsilon_\infty = \varepsilon_{1\infty} + a_\infty w_2 \qquad \text{--- (1)}$$

$$\tau_{(1)} = \frac{a^{''}}{\omega(a^{'} - a_\infty)}$$
$$\tau_{(2)} = \frac{(a_0 - a^{'})}{\omega a^{''}}$$
$$\tau_{(0)} = \sqrt{\tau_{(1)}\tau_{(2)}} \qquad \text{--- (2)}$$

Here (τ_0) is the mean relaxation time. The free of activation of dielectric relaxation ΔF_τ and viscous flow have been calculated using Eyring's equation [7]

$$\tau = (\frac{h}{kT})\exp(\frac{\Delta F_\tau}{RT}) \qquad \text{----- (3)}$$
$$\eta = (\frac{Nh}{V})\exp(\frac{\Delta F_\eta}{RT}) \qquad \text{---(4)}$$

Where h is Planck's constant .k is Boltzmann constant, N is Avogadro number and V is the molar volume.

Cole-Cole Method: The measured values of ε_0, $\varepsilon_,^{'}$ $\varepsilon^{''}$ and ε_∞ are fitted in a complex plane plot with depress circular arc. The angle made by the diameter d drawn through the centre from the ε_∞ point and the abscissa axis is equal to πα/2.From the Cole-Cole arc, the relaxation time τ can be found using the equation

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

Where ω is the angular frequency of the micro wave and α can be obtained from the Cole-Cole plot.

Result and Discussion

The dielectric parameters of the liquid mixtures have been listed as shown in the Table-1. The relaxation time varies with size and shape of the rotating molecular entities in liquid mixture.

Table 1-Values of dielectric constant($\varepsilon_{0)}$,relaxation time(τ) of methylformate with alcohols at 303K

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
					$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$	τ		
System : Ethylformate + 1-Methanol										
0	2.2701	1.8494	0.1736	1.5533	11.046	13.923	12.369	5.6399	8.302	9.485
25	2.1847	1.8739	0.1883	1.5505	11.459	14.301	12.803	5.9976	8.603	9.786
50	2.1105	1.8781	0.2086	1.5652	12.726	14.819	13.734	8.0192	8.96	9.975
75	2.0118	1.8627	0.1988	1.5575	11.221	14.875	12.922	8.7647	8.666	9.807
100	1.9495	1.8452	0.1911	1.5463	10.934	13.797	12.285	9.1882	8.232	9.464
System : Methylformate + 1-Ethanol										
0	2.1483	1.7787	0.8463	2.1476	12.964	18.2	15.386	17.2081	8.554	9.744
25	2.0510	1.7773	0.1337	2.0503	11.683	15.029	13.251	12.4922	8.386	9.044
50	2.0496	1.7766	0.1344	2.0503	11.396	16.345	13.65	17.9417	7.063	8.967
75	1.9747	1.7626	0.1253	1.9747	10.969	12.866	11.879	11.9875	7.924	9.128
100	1.9733	1.7689	0.1267	1.9726	10.955	13.608	12.208	18.7481	8.134	7.875
System : Methylformate + 1-Propanol										
0	2.1329	1.8004	0.1533	1.5687	14.021	21.196	17.241	20.0305	8.449	9.779
25	2.0244	1.7829	0.1337	1.5624	12.943	17.955	15.239	16.0496	8.232	9.275
50	1.9999	1.7836	0.1309	1.5645	13.048	17.836	15.253	20.8194	8.393	8.624
75	1.9824	1.7787	0.1274	1.5568	12.152	15.134	13.559	15.7059	7.756	9.058
100	1.9236	1.7353	0.1232	1.5561	12.103	14.329	13.167	21.6125	8.001	8.540

In this present work, relaxation time (τ) values increased with increase in the concentration of alcohols. This trend may show that the hydrogen bond formation between the C=O group of methyl formate and the O-H group of the alcohol. Table-1 signified that the ε_0 value gradually decreased with increasing the carbon chain length of the alcohols. This trend signifies that the decrease in the number of dipoles in the complex, which lead to a decrease in the molar volume of the rotated molecules. It is evident from this study that the molar free energy of activation for viscous flow (ΔF_η) is greater than the free energy activation over dielectric relaxation (ΔF_τ) .It may reveal that the viscous flow involved both the rotational and translation form of motion. Similar results were reported as earlier [7-10]. The result shows that the strength of this molecular interaction depends upon the carbon chain length of the alcohols. Hence the proton donating ability of alcohols is in the order of 1-methanol<1-ethanol<1-propanol.

Conclusion

Dielectric relaxation parameters have been determined for primary alcohols with methylformate in various concentrations at 303K.The relaxation time increases with increasing acidity of proton donor complex systems. The deviation in dielectric parameters with alcohols reveal that the proton donating ability of alcohols is in the order of 1-methanol<1-ethanol<1-propanol.

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