



## Intermolecular Interaction Studies of Binary Liquid Mixtures Using Time Domain Reflectometry at 303K

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**Abstract :** Intermolecular interactions of propylformate with 1-methanol, 1-ethanol and 1-propanol have been studied at micro frequency range 9.36 GHz at 303K. Dielectric constant, dielectric losses were determined. Relaxation time was calculated using Higasi and Cole-Cole method. Dielectric constant and Relaxation time decreased while concentration of alcohols in propyl formate system. Strength of dissociation of liquid mixtures was based on the carbon chain length of alcohols with propyl formate which was in the order of 1-methanol<1-ethanol<1-propanol.

**Key Words:** propyl formate, Dielectric relaxation, Alcohols.

### Introduction

Molecular interaction depends the physical and chemical properties of the liquid system which consists of polar and non polar molecules<sup>1-3</sup>. Time domain reflectometry is one of the useful techniques to identify the nature of interactions of a liquid system.<sup>4-6</sup> Propyl formate is used as a solvent for cellulose nitrate. It is also used as larvacide and fumigant. It is also used 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 propyl formate tends to interaction with hydroxyl (OH<sup>-</sup>) group of alcohols. The present work is an attempt to analyse the molecular interactions among propyl formate with 1-methanol, 1-ethanol and 1-propanol using time domain reflectometry technique at 303K.

### Materials and Methods

Propyl formate 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 ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) have been measured using X-band microwave frequency oscillator of frequency 9.36 GHz at 303K. The refractive index ( $\mu$ ) 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.

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## Methods

### Higasi's Method:

The dielectric relaxation time ( $\tau$ ) was calculated using Higasi's method<sup>6</sup>. Assuming  $\epsilon_0, \epsilon', \epsilon''$  and  $\epsilon_\infty$  vary linearly with weight fraction  $w_2$  of the solute. The slopes  $a_0, a', a''$  and  $a_\infty$  determined from the determined values. We have

$$\begin{aligned}\epsilon_0 &= \epsilon_1 + a_0 w_2 \\ \epsilon' &= \epsilon_1 + a' w_2 \\ \epsilon'' &= a'' w_2 \\ \epsilon_\infty &= \epsilon_{1\infty} + a_\infty w_2\end{aligned}\quad \text{--- (1)}$$

$$\begin{aligned}\tau_{(1)} &= \frac{a''}{\omega(a' - a_\infty)} \\ \tau_{(2)} &= \frac{(a_0 - a')}{\omega a''} \\ \tau_{(0)} &= \sqrt{\tau_{(1)} \tau_{(2)}}\end{aligned}\quad \text{--- (2)}$$

Here ( $\tau_0$ ) is the mean relaxation time. The free of activation of dielectric relaxation  $\Delta F_\tau$  and viscous flow have been calculated using Cernuschi and Eyring's equation<sup>7</sup>

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

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

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  $\epsilon_0, \epsilon', \epsilon''$  and  $\epsilon_\infty$  are fitted in a complex plane plot with depress circular arc. The angle made by the diameter  $d$  drawn through the centre from the  $\epsilon_\infty$  point and the abscissa axis is equal to  $\pi\alpha/2$ . From the Cole-Cole arc, the relaxation time  $\tau$  can be found using the equation

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

Where  $\omega$  is the angular frequency of the micro wave and  $\alpha$  can be obtained from the Cole-Cole plot.

## Result and Discussion

Dielectric parameters of the selected liquid system have been listed as shown in the Table-1. Relaxation time changes with shape and size of the rotating molecular present in the liquid mixture. In this study, Dielectric relaxation time ( $\tau$ ) values changes with the concentration of alcohols. It also increased with concentration of alcohols. It may reveals that hydrogen bond formation between the carbonyl group of propyl formate and hydroxyl group of the alcohol. Table-1 listed that the  $\epsilon_0$  value gradually decreased with increasing the carbon chain length of the alcohols.

**Table 1-Dielectric constant( $\epsilon_0$ ),relaxation time( $\tau$ ) of propylformate with alcohols at 303K**

Volume % of alcohols	$\epsilon_0$	$\epsilon'$	$\epsilon''$	$\epsilon_\infty$	Relaxation Time $\tau$ ( $10^{-12}$ s)				Activation energy	
					Higasi's			Cole-Cole	$\Delta F_\tau$ kJ/mol	$\Delta F_\eta$ kJ/mol
					$\tau_{(1)}$	$\tau_{(2)}$	$\tau_{(0)}$	$\tau$		
<b>System : Propylformate + 1-Methanol</b>										
0	1.3912	0.9705	0.7053	0.6744	10.1671	13.0441	11.4901	4.761	7.4231	8.6061
25	1.3058	0.9950	0.6906	0.6716	10.5801	13.4221	11.9241	5.1187	7.7241	8.9071
50	1.2316	0.9992	0.6703	0.6863	11.8471	13.9401	12.8551	7.1403	8.0811	9.0961
75	1.1329	0.9838	0.6801	0.6786	10.3421	13.9961	12.0431	7.8858	7.7871	8.9281
100	1.0706	0.9663	0.6878	0.6674	10.0551	12.9181	11.4061	8.3093	7.3531	8.5851
<b>System : Propylformate + 1-Ethanol</b>										
0	1.2694	0.8998	0.0326	1.2687	12.0851	17.3211	14.5071	16.3292	7.6751	8.8651
25	1.1721	0.8984	0.7452	1.1714	10.8041	14.1501	12.3721	11.6133	7.5071	8.1651
50	1.1707	0.8977	0.7445	1.1714	10.5171	15.4661	12.7711	17.0628	6.1841	8.0881
75	1.0958	0.8837	0.7536	1.0958	10.0901	11.9871	11.0001	11.1086	7.0451	8.2491
100	1.0944	0.89	0.7522	1.0937	10.0761	12.7291	11.3291	17.8692	7.2551	6.9961
<b>System : Propylformate + 1-Propanol</b>										
0	1.254	0.9215	0.7256	0.6898	13.1421	20.3171	16.3621	19.1516	7.5701	8.9001
25	1.1455	0.904	0.7452	0.6835	12.0641	17.0761	14.3601	15.1707	7.3531	8.3961
50	1.121	0.9047	0.7480	0.6856	12.1691	16.9571	14.3741	19.9405	7.5141	7.7451
75	1.1035	0.8998	0.7515	0.6779	11.2731	14.2551	12.6801	14.827	6.8771	8.1791
100	1.0447	0.8564	0.7557	0.6772	11.2241	13.4501	12.2881	20.7336	7.1221	7.6611

It suggests that the number of dipoles in the complex decreased with increasing concentration of alcohols. It is noticed that the molar free energy of activation for viscous flow ( $\Delta F_\eta$ ) is greater than the free energy activation over dielectric relaxation ( $\Delta F_\tau$ ). It elucidates that the viscous flow involved both the rotational and translation vibration of the molecules.<sup>7-10</sup> The result reveals that the strength of molecular interaction depends upon proton donating ability of alcohols which is obtained in the order of 1-methanol<1-ethanol<1-propanol.

## Conclusion

Dielectric relaxation parameters have been obtained for 1-methanol,1-ethanol and -propanol with propylformate in various concentrations at 303K. Dielectric relaxation time increased with increasing acidity of proton donor in the liquid mixture. Deviations in dielectric parameters with alcohols reveal that the intermolecular interaction of alcohols with propyl formate is in the order of 1-methanol<1-ethanol<1-propanol.

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## References

1. Kompaneets V. V and Vasilieva I. A., The influence of the nature of a substituent on the parameters of the intra- and intermolecular interactions in molecules of cross-conjugated ketones, *Opt. Spectrosc.*, 2017, 123, 245-254.
2. Mohan A., Malathi M., Shaikh S.S and Kumbharkhane A.C., Thermodynamic and Molecular Dielectric Relaxation Studies of Polar–Polar Binary Mixtures Using Time Domain Reflectometry Technique, *J. Solution. Chem.*, 2016, 45, 221-234.
3. Zhuravlev V.I., Dielectric properties of multiatomic alcohols: 1, 4-butanediol, *Russ.J Phys Chem A.*, 2015, 89, 2213–2221.
4. Mezhevoi I.N and Badelin V. G., Thermochemical study of glycyglycine interaction with polyhydric alcohols in aqueous solution, *Russ. J. Gen Chem.*, 2015, 85, 816-819.
5. Elangovan S., Molecular interaction studies of methyl formate with primary alcohols at 303k using time domain reflectometry, *Int. J Chem Tech. Res.*, 2017, 10, 640-643.
6. Higasi K. A, Koga Y and Nakamura M., Dielectric relaxation and molecular structure. Application of the single frequency method to systems with two Debye dispersions, *Bull. Chem. Soc. Jpn.*, 1971, 44, 988-992.
7. Cernuschi F and Eyring H., An elementary theory of condensation, *J. Chem Phys.*, 1939, 7, 547-551.
8. Rander D. N, Joshi Y. S, Kanse K .S and Kumbharkhane A.C., Dielectric relaxation and hydrogen bonding interaction in xylitol–water mixtures using time domain reflectometry, *Indian J. Phys.*, 2016, 90, 67-72.
9. Kumar S, Periyasamy P and Jeevanandham P., Dielectric relaxation studies of binary liquid mixtures of a few glycols with 1,4 – dioxane., *Int. J. Chem Tech. Res.*, 2011,3, 369-375.
10. Rawal A, Mahavar, Tanwar A and Singh P. J., Dielectric relaxation studies of polyvinylpyrrolidone (PVP) and polyvinylbutyral (PVB) in benzene solutions at microwave frequency, *Indian J. Pure Ap. Phy.*, 2014, 52, 632-636.

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