

Molecular Interaction Study of DMA and NMA with Primary alcohols Systems by X-band Microwave

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Abstract

Molecular interaction between NMA (N-methylacetamide) with 1- Alcohols and DMA (N, N-dimethylacetamide) with Primary Alcohols (1-Propanol, 1-Butanol, 1-Pentanol) has been studied in carbon tetrachloride by using X-band microwave bench at 936Ghz and the orientation of molecular dipoles have been identified by Kirkwood correlation factor (g). The dielectric relaxation time τ of the binary system are obtained by both Higasi's method and Gopalakrishna method. The results show that the most likely interaction between alcohols and amides is 1:1 complex through the free hydroxyl group of the alcohol and the carbonyl group of amide and the alkyl chain-length of both the alcohols and amide plays an important role in the determination of the strength of hydrogen bond (O-H: C=O) formed.

Key words: Relaxation time, X-band Microwave, Primary Alcohols, Kirkwood correlation factor, Dipolement, Amides and Hydrogen bonding

Introduction

Molecular interaction study between associated and non-associated solution in inert media gives valuable information about solute–solute interaction. An alcohol is an important scientific and industrially organic compound and the hydroxyl group largely determines their physical and chemical properties. Dielectric properties provide important information about the interaction of C=O group and -OH group. A literature survey [1-3] reveals that only limited amounts of work has been carried out on some binary system of alcohols. With these considerations, the authors have investigated the relaxation behavior of the binary liquid systems of 1-Propanol, 1-Butanol and 1-Pentanol in dilute solution of carbon tetrachloride. The selection of these alcohols as solutes play an important role in many chemical reactions due to the

ability to undergo self-association with manifold internal structures and are in wide use in industry and science as reagents, solvents and fuels [4].

The present work deals with the dependence of strength of hydrogen bond formation between alcohol and amides on the alkyl chain-length of both the alcohols and amides.

Experimental

The measurement of dielectric constant at an angular frequency (ϵ') and dielectric loss factor (ϵ'') were carried out from the X-band microwave bench of oscillating frequency 9.36Ghz [5]. The static dielectric constants were determined from the instrument, Dipole meter DM01, supplied by Wissenschaftlich Technische Werkstatter, Germany operated at 220 Volts. The refractive indices were measured by an Abb'e refractometer. The temperatures of the measurement are at 303K. The chemicals used were of A.R.grade and were purified by standard methods. The density measurements were carried out with the help of 10cc specific gravity bottle and redistill before use.

Dielectric measurements

Experimental details and theory

For a small volume of solution the total polarization depends on the total energy of interaction between molecules. By using the reaction field theory, the dipolar interaction in a solution containing an associated species in an inert solvent may be given by Kirkwood correlation factor (g).

$$g = \frac{9KM_2T}{4\pi NAW_2\mu_2^2(\epsilon_\infty + 2)^2} \left(\frac{(\epsilon_o - \epsilon_\infty)(2\epsilon_o + \epsilon_\infty)}{\epsilon_o d} \frac{W_1(\epsilon_1 - \epsilon_{1\infty})(2\epsilon_1 - \epsilon_{1\infty})}{\epsilon_1 d_1} \right) \dots\dots(1)$$

Where ϵ_o is the static dielectric constant and ϵ_∞ is the dielectric constant at infinite frequency for the solution. ϵ_1 and $\epsilon_{1\infty}$ are the dielectric constant and refractive index of the solvent respectively. W_2 and M_2 are weight fraction and molecular weight of alcohol species respectively. μ_2 is the dipole moment of alcohol in gaseous state. d and d_1 are the densities at the temperature T for solution and solvent respectively. K is the Boltzmann constant and NA is the Avogadro number.

The Kirkwood correlation factor (g) measures the angular correlation of the dipole vector of the molecule with the neighboring molecules in the solution.

According to Higasi's method [6], the individual relaxation time $\tau_{(1)}$ is described by

$$\tau_{(1)} = \frac{a''}{\omega(a' - a_\infty)} \dots\dots(2)$$

While the overall dielectric relaxation $\tau_{(2)}$ is given by,

$$\tau_{(2)} = \frac{(a_0 - a')a''}{\omega a''} \dots\dots\dots(3)$$

The average relaxation time τ is given by

$$\tau = \sqrt{\tau_{(1)}\tau_{(2)}} \dots\dots\dots(4)$$

Where ω is the angular frequency and a_0, a', a'' and a_∞ are Higasi's parameters defined by Eqs (3)

The dielectric constant ϵ' is given by

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

The dielectric loss ϵ'' will be given by

$$\epsilon'' = \frac{2}{\pi} \left(\frac{\lambda_0^2 \lambda_g}{\lambda_d^3}\right) \left(\frac{d\rho_{measured}}{dn}\right)$$

Where ω is the angular frequency a_0, a', a'' and a_∞ are defined by Eqs (3)

$$\epsilon_0 = \epsilon_{01} + a_0 w_2$$

$$\epsilon' = \epsilon'_{1} + a' w_2$$

$$\epsilon_\infty = \epsilon_{1\infty} + a_\infty w_2 \dots\dots\dots(5)$$

In which subscript 1 refers to the pure solvent and 2 refers to the solute, 0 refers to the static frequency and ∞ refers to the infinite or optical frequency measurements and w_2 is the weight fraction of the solute.

Gopalakrishna gives a single frequency concentration variation method by using

the relations,
$$x = \frac{\epsilon'(\epsilon'+1) + \epsilon''^2 - 2}{(\epsilon'+2)^2 + \epsilon''^2}$$

$$y = \frac{3\epsilon''}{(\epsilon'+2)^2 + \epsilon''^2}$$

$$\tau = \frac{\lambda}{2\pi c} \left[\frac{dy}{dx} \right]$$

Where λ is the wavelength in free space. The relaxation time (τ) is obtained by plotting a graph between x and Y values. dy/dx is obtained by plotting a graph between x and y values

Results and discussion

The alcohol's like 1-propanol, 1-butanol and 1-pentanol are chooses for the study of molecular interaction with the non-polar solvent carbon tetrachloride. The kinetic process responsible for the dielectric behavior of these alcohols is analyzed on the basis on significant structure model of associated liquids.

Kirkwood correlation factor (g)

The value of 'g' gives important information regarding the orientation of the dipoles in liquid [8]. In alcohol the formation of hydrogen bonds leads to association of a restricted numbers of molecules, often called multimers. The linear correlation factor in an associated liquid in its mixture with a non-polar liquid reflects on the nature of multimers.

The Kirkwood correlation factor (g) greater than one indicates predominance of α -multimers with parallel dipole orientation and 'g' less than one indicates predominance of β -multimers with anti parallel orientation [9]

For 1-Propanol, 1-Butanol and 1-Pentanol in CCl_4 system, the values of 'g' is less than unity is observed for all concentration of solute. This result indicates the predominance of β -multimers with anti parallel orientation present in these systems. Similar results are obtained by Rana et al [10]

For NMA and DMA in carbon tetrachloride system. The 'g' values are higher than one are observed for all the molar concentration of solute. This may conforms the parallel alignment of neighboring dipole that is α -multimers form. Similar results for NMA and DMA in chlorobenzene were observed by Powar et al [11,12].

The dilute effect on Kirkwood correlation factor has extensively studied for monoalcohols by Gestblom et al [13] In the case of 1-Propanol, 1-Butanol and 1-Pentanol with CCl_4 system, the 'g' value decreases at the initial dilution, then the progressively increases as the molar concentration of alcohol increases. Similar results were reported by srivastava et al [14].

It is observed from the result as the chain length of alcohol increases, the g values get decreased. it would be interesting to extend the dielectric studies to the relaxation mechanisms of these alcohols.

Dielectric relaxation time

The value for static dielectric constant (ϵ_0), dielectric constant at infinite dilution (ϵ_∞), dielectric constants at an angular frequency (ϵ'), dielectric loss factor (ϵ''), the dielectric relaxation time for individual molecular rotation (τ_1), dielectric relaxation time for overall rotation (τ_2) and average relaxation time (τ) are calculated by using the Higasi's method and Gopalakrishna's method are reported in the table.

The relaxation time by Higasi's method were determined [15,16] the vales for the binary systems were determined and the values are appreciable, which implies the existence of more than one relaxation mechanisms. In the present study Higasis and Gopalakrishna method have been used. This will enable one to study quantitatively the relaxation mechanisms involved in the present systems.

From the table it is observed that the values for ϵ_0 , ϵ_∞ , ϵ' , ϵ'' are increase with molar concentration of Primary alcohol increases. The relaxation time for individual molecular rotation, dielectric relaxation time for overall rotation and average relaxation time are also increase with increasing the molar concentration of the proton donor (alcohol's). This confirms the association between the proton donor and solvent.

Table: Values of Dielectric constant, relaxation time (τ), Kirkwood correlation factor (g), for different mole fractions (f_2) of solute and solvent at 303 K.

f_2	ϵ'	ϵ''	ϵ_0	ϵ_∞	Higasi's method			Gopalakrishna's method	Kirkwood correlation factor
					τ_1 (Ps)	τ_2 (Ps)	τ (Ps)	τ (Ps)	g
Systems	1-Propanol with CCl ₄								
0.02	2.2788	0.021	2.2971	2.2011	7.81	14.8	10.8		0.9439
0.04	2.2814	0.026	2.3048	2.2032	9.57	15.3	12.1		0.9472
0.06	2.2897	0.03	2.3183	2.2094	10.6	16.2	13.1	13.32	0.9517
0.08	2.2922	0.036	2.3297	2.2121	12.7	17.7	15		0.9556
0.1	2.2961	0.041	2.3396	2.2173	14.9	18	16.4		0.9583
	1-Butanol with CCl ₄								
0.02	2.2764	0.02	2.2958	2.2026	8.13	16.5	11.6		0.9229
0.04	2.2818	0.024	2.3062	2.2056	9.23	17.3	12.6		0.9272
0.06	2.2878	0.032	2.3219	2.2099	11.9	18.1	14.7	14.9	0.9317
0.08	2.2911	0.038	2.3367	2.2111	13.5	20.4	16.6		0.9356
0.1	2.2968	0.048	2.3595	2.2148	16.3	22.2	19		0.9383
	1-Pentanol with CCl ₄								
0.02	2.2735	0.019	2.2932	2.2068	9.31	17.6	12.8		0.9439
0.04	2.2782	0.026	2.307	2.2098	12.1	18.8	15.1		0.9472
0.06	2.2826	0.032	2.3201	2.2128	14.4	19.9	16.9	16.91	0.9517
0.08	2.2862	0.036	2.3322	2.2159	16	21.7	18.6		0.9556
0.1	2.2881	0.042	2.3502	2.2168	18.2	25.1	21.4		0.9583
	NMA with CCl ₄								
0.02	2.2901	0.02	2.3129	2.2182	8.52	19.4	12.9		1.0921
0.04	2.2995	0.025	2.3291	2.2214	9.22	20.1	13.6		1.0947
0.06	2.3017	0.029	2.3383	2.2258	11.2	21.5	15.5	14.3419	1.0967
0.08	2.3063	0.035	2.3557	2.2309	13.7	24	18.1		1.0979
0.1	2.3081	0.042	2.3752	2.2338	16.9	27.2	21.4		1.0993
	DMA with CCl ₄								
0.02	2.3589	0.0425	2.4127	2.2228	5.9	9.97	7.65		1.0827
0.04	2.4125	0.0531	2.6534	2.2229	6.68	14.57	11.9		1.0852
0.06	2.4539	0.0555	2.7659	2.2232	8.63	17.35	13.6	11.186	1.0871
0.08	2.4706	0.0583	2.9674	2.2234	10.3	18.25	19.2		1.0885
0.1	2.5301	0.0612	3.0534	2.2398	11.1	20.23	21.4		1.0891

The relaxation time τ for alcohol and solvent system are found to be larger in 1-Pentanol with CCl_4 when comparing with the remaining two binary systems (1-Propanol and 1-Butanol). This may be due to longer chain length of 1-Pentanol. This reveals that molecular interaction between the OH group of the alcohol and solvent is greater in 1-Pentanol-solvent systems than others binary system.

For DMA and NMA, The relaxation time due to individual molecular rotation. Overall rotation and average relaxation time are increase with increasing molar concentration of the solute. This confirms the molecular interaction between carbonyl and hydroxyl group in solvent increases. The free rotation $\text{C}=\text{O}$ in DMA and NMA must be restricted due to the resonance structure's. As the molar concentration of solute further increases the hydrogen-bonded complex stabilized by resonance structure breaks. Such processes are arrested due to the basicity of the CCl_4 , which is having a better hydrogen bonding ability with DMA.

In the present study the relaxation time of amides and Primary alcohol are varying in the order of

$$\text{DMA} > \text{NMA} > \text{1-Pentanol} > \text{1-Butanol} > \text{1-Propanol}.$$

The trend indicates that the solute and solvent interactions are more predominant in NMA than DMA system.

The relaxation time calculated for the alcohols with CCl_4 by Gopalakrishna method shows slightly higher values when compared with the Higasi's method.

A perusal of Table shows that, the value of relaxation time increases with increasing chain length of alcohols and Amides and offers hindrance to the rotation of the molecule. The increase in relaxation time may be due to the increase in effective radius of the rotating unit. The value of relaxation time for DMA is greater than that of the other. This may be due to the fact that the increase of the size of the molecule with alkyl chain may cause hindrance to the group rotation, which may give rise to increased relaxation time.

From table it is observed that as the mole concentration of proton donor increases the value of ϵ_0 , ϵ_∞ , ϵ' , ϵ'' are goes on increasing. The relaxation time for individual molecular rotation τ_1 , dielectric relaxation time for overall rotation τ_2 and average relaxation time τ_0 are also increase with increasing the molar concentration of the proton donor (alcohol's). This confirms the association between the proton donor and solvent.

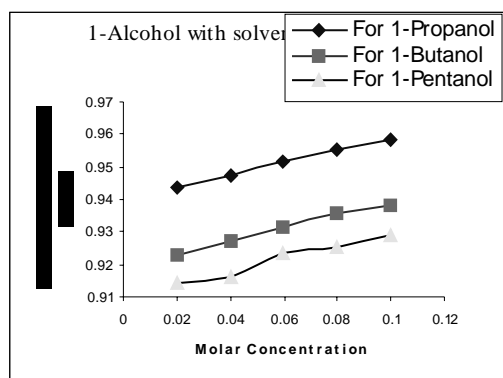


Figure 1: Variation of Kirkwood correlation factor (g) with molar concentration of 1-alcohol.

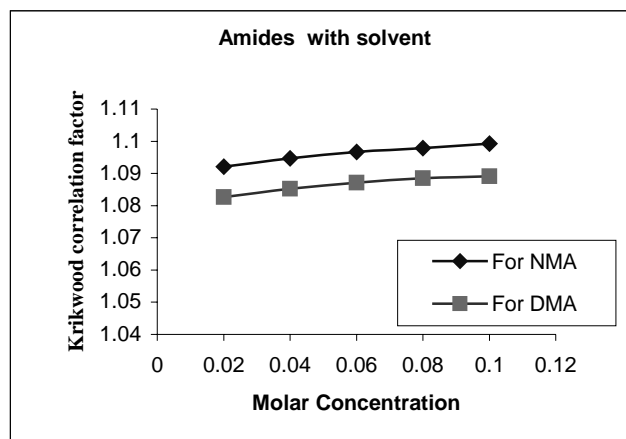


Figure 2: Variation of Kirkwood correlation factor (g) with molar concentration of Amide.

Conclusion

The hydrogen bonding interaction between Amides, namely DMA, NMA and Primary alcohol (1-propanol, 1-butanol, 1-pentanol) were studied in carbon tetrachloride solution by using Microwave method and dielectric methods at 303 K. From this study, it may be concluded that the higher chain alcohol have relatively more tendency of complex formation than the other lower chain alcohols. The study from microwave systems shows that the strength of hydrogen bonding is depending on the chain length of alcohols and amides with solvent.

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