

Solvent effect on linear correlation factor and dielectric relaxation time of butyl alcohol

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The relaxation time (τ) of butyl alcohol with some non-polar solvents like benzene, carbon tetrachloride and 1,4 dioxane have been calculated from Higasi's method. The linear correlation factor (g) and the thermodynamic parameter like molar free energy of activation for viscous flow (ΔF_{η}) and the free energy of activation for dielectric relaxation (ΔF_{τ}) also have been calculated.

[**Keywords:** Dielectric relaxation, Relaxation time, Kirkwood correlation factor, Thermodynamic parameters]

1 Introduction

The structure of alcohols has been the subject of many investigations because of its having a possible hydrogen bonding between adjacent molecules. Alcohols as solvents play important role in many chemical reactions due to their ability to undergo self-association with manifold internal structure. For reactions in which the rates are comparable to or faster than solvent fluctuations, the details of the motion and structure of surrounding solvent play an important role in the rates of chemical reaction. Marsch & Kohler¹ have studied the molecular association of alcohols. The influence of association on the dielectric behaviour of a liquid is often expressed through g , the Kirkwood correlation factor². However, it cannot give specific information as to the size of the multimers. Schuster *et al.*³ have reviewed the work in this direction. Dielectric relaxation measurements provide a different approach to this problem. Debye's⁴ relaxation times of alcohols are commonly associated with at least three important molecular motions namely, the hydrogen bonded dynamics of the aggregates, the monomer rotation and the rotation of the terminal O-H group⁵. Physical parameters like g , viscosity and relaxation times of butanol in benzene, carbon tetrachloride and 1,4 dioxane have been measured to have information on the fluid structure of butyl alcohol in this paper.

2 Experimental Details

Dielectric constant at an angular frequency (ϵ') and dielectric loss factor (ϵ'') were measured at 9.43 GHz using standard liquid cell, supplied by Electronic Corporation of India Ltd, Hyderabad, in conjunction with standard X-band microwave set-up. The static dielectric constant (ϵ_0) measurements were carried out at 303K, using a commercial instrument Dipolemeter DM 01, supplied by Wissenschaftlich Technische Werkstatter, Germany. It has a measuring frequency of 2 MHz. Abbe's refractometer was used to measure the refractive indices for sodium D line. Ostwald's viscometer was used to determine the viscosity of liquid and liquid mixtures. The densities were measured with 5cc specific gravity bottle.

3 Kirkwood Correlation Factor

The total polarization of a small volume of solution depends on the total energy of interaction between molecules viz. solvent-solvent, solvent-solute and solute-solute molecules. Using the reaction field theory, the dipolar interaction in a solution containing an associated species in an inert solvent may be given by the Kirkwood correlation factor g , given by:

$$g = \frac{9kT(2\epsilon_{12} + \epsilon_{12\infty})^2}{4\pi N\mu_2^2 f_2 (\epsilon_{12\infty} + 2)^2 (2\epsilon_{12} + 1)}$$

$$\left[v_{12} \frac{\epsilon_{12} - 1}{\epsilon_{12}} - \frac{3f_1 v_1 (\epsilon_{1\infty} - 1)}{(2\epsilon_{12} + \epsilon_1)} - \frac{3f_2 v_2 (\epsilon_{2\infty} - 1)}{(2\epsilon_{12} + \epsilon_{2\infty})} \right]$$

where v_{12} is the molar volume of the solution, ϵ_{12} the dielectric constant of the solution, f_1 and v_1 are the mole fraction and the molar volume of the solvent, f_2 and v_2 those of the solute, respectively. μ_2 is the dipole moment of alcohol in the gaseous state, ϵ_{∞} , $\epsilon_{1\infty}$ and $\epsilon_{2\infty}$ the dielectric constants at infinite frequency for the solution, solvent and solute, respectively. k is the Boltzmann constant, N_A the Avogadro number and T the temperature.

4 Relaxation Time

The following expressions⁶ were used for measuring ϵ' and ϵ'' :

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

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

where λ_d is the wavelength in the dielectric medium, λ_g the guide wavelength, λ_0 the free space wavelength, λ_c the cut-off wavelength and $1/\rho$ the standing wave ratio obtained by using a short circuited movable plunger. The uncertainties in the

measurement of ϵ_0 , ϵ_{∞} and ϵ' were 1% and in ϵ'' it was 5%.

The relaxation time for different dilute solutions of butyl alcohol of weight fraction w_2 was also measured in terms of two Debye relaxation mechanisms with the help of the following equations^{7,8}:

$$\epsilon_0 = \epsilon_1 + w_2 a_0; \quad \epsilon' = \epsilon_1 + w_2 a'$$

$$\epsilon'' = a'' w_2; \quad \epsilon_{\infty} = \epsilon_{1\infty} + a_{\infty} w_2$$

$$\tau_{(1)} = \frac{a''}{\omega(a' - a_{\infty})}; \quad \tau_{(2)} = \frac{a_0 - a'}{\omega a''}$$

where ω is the angular frequency.

The free energy of activation for dipolar and viscous forces have been calculated by using Eyring's equation⁹.

$$\tau = \frac{h}{kT} \exp \left(\frac{\Delta F_{\tau}}{RT} \right), \quad \frac{Nh}{V} \exp \left(\frac{\Delta F_{\eta}}{RT} \right)$$

5 Results and Discussion

The variation of g with mole fraction of butyl alcohol in carbon tetrachloride, benzene and 1,4 dioxane are shown in Table 1. The g value of butyl alcohol in the solvents like, benzene and carbon tetrachloride decreases rapidly at the initial

Table 1 — Values of dielectric constant, relaxation time and activation energies for different mole fractions of butyl alcohol at 303K

Compound	x_2	ϵ_0	ϵ_{∞}	ϵ'	ϵ''	$\tau_{(1)}^*$ ps	$\tau_{(2)}^*$ ps	$\tau_{(0)}^*$ ps	g	ΔF_{τ} KJ/m	ΔF_{η} KJ/m	
Butyl alcohol +	0.02	2.37	2.21	2.34	0.03	4.80	1520	8.54	1.600	10.4	12.59	
	0.04	2.50	2.20	2.43	0.08	6.61	15.41	10.09	1.458	10.46	12.61	
	Benzene	0.06	2.58	2.20	2.45	0.14	10.11	15.94	12.70	1.301	11.04	12.65
		0.08	2.68	2.19	2.49	0.19	11.43	17.06	13.96	1.292	11.28	12.76
	0.10	2.89	2.18	2.54	0.24	11.93	24.84	13.21	1.537	11.81	12.86	
Butyl alcohol +	0.04	2.38	2.10	2.34	0.05	5.75	14.52	9.14	1.281	10.22	13.89	
	0.08	2.47	2.10	2.39	0.08	6.77	16.04	10.42	0.991	10.54	13.98	
	Carbon tetrachloride	0.12	2.53	2.09	2.41	0.11	8.28	18.45	12.36	0.895	10.98	14.14
		0.15	2.65	2.09	2.44	0.14	9.20	24.97	15.16	0.840	11.49	14.22
	0.19	2.77	2.09	2.48	0.18	10.14	27.20	16.61	0.842	11.72	14.33	
Butyl alcohol +	0.02	2.37	2.00	2.36	0.03	2.92	3.38	3.14	1.865	7.52	14.06	
	0.05	2.47	1.99	2.45	0.05	3.15	7.83	4.97	1.775	8.68	14.09	
	1,4dioxane	0.07	2.66	1.99	2.61	0.09	3.53	8.63	5.52	1.690	8.95	14.18
		0.09	2.77	1.99	2.69	0.10	3.29	12.99	6.54	1.600	9.37	14.20
		0.11	2.83	1.98	2.73	0.13	3.95	13.64	7.34	1.514	9.66	14.30

*These were calculated by Higasi's method

concentration of butyl alcohol and reaches a minimum and then increases at higher concentration.

The dip value of g for benzene, carbon tetrachloride with butyl alcohol suggests that, the smallest multimers are linear, somewhat greater ones are cyclic, and greatest multimers are linear again. The rapid fall of g with dilution can be explained by assuming conversion of α -multimers to β -multimers. This is significantly absent in 1,4 dioxane.

The relaxation behaviour of butyl alcohol, at the lower concentration range, in all these three solvents give useful information. The value of relaxation times, $\tau_{(1)}$ and $\tau_{(2)}$ for all the systems were calculated by Higasi's method and are reported in Table 1. It is observed that, $\tau_{(2)}$ increases with increase of concentration, perhaps due to the increase in the frictional resistance for dipolar rotation of the whole molecule and is far more distributed with increase of concentration. The relaxation time $\tau_{(2)}$ is found to be maximum in carbon tetrachloride which may be due to the hindrance offered by the bulky carbon tetrachloride molecule for free rotation. The relaxation time $\tau_{(1)}$ is lowered in 1,4 dioxane with butanol. This may be due to the fact that, there is a non-specific interaction¹⁰ between the solute and the solvent inhibiting intra-molecular rotation.

It is evident from our data that, the molar-free energy of activation for viscous flow ΔF_{η} is greater than ΔF_{τ} , the free energy of activation for dielectric relaxation. This is in agreement with the fact that, the process of viscous flow involved greater

interference by neighbours than does dielectric relaxation, as the latter takes place by rotation only, whereas the viscous flow involved both the rotational and translational forms of motion. It is further suggested that, for non-associated polar liquids and free energy of activation for rotation and for viscous flow would be:

$$\Delta F_{\tau} < 0.5 \Delta F_{\eta}$$

In the present study, ΔF_{τ} is larger than expected. This suggests that, the aggregates of H-bonded alcohols can no longer be considered as spherical and the rotation necessarily requires a translational motion of the neighbours.

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