

An Empirical Relation for the Evaluation of the Dielectric Relaxation Time of Certain Polar Liquids Using a Single Microwave Frequency

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Abstract

An empirical relation is proposed for the determination of the dielectric relaxation time τ of polar liquids with nearly spherical molecules from measurements of the dielectric constants at a single microwave frequency. The relation is obtained by introducing a concentration factor as a parameter in the expression for τ derived by Eyring *et al.* (1941). Its validity for suitable polar liquids is demonstrated by comparison of results with previously reported values. Thermodynamic parameters for a number of liquids at various concentrations have also been evaluated from experimental data using the relation.

Introduction

The macroscopic dielectric relaxation time τ of a polar molecule in a pure liquid state at a given temperature is normally determined by drawing a Cole-Cole plot (Cole and Cole 1941; Cole 1955). Such a determination requires the evaluation of the static dielectric constant ϵ_s and the dielectric constant ϵ' and dielectric loss ϵ'' of the liquid at different microwave frequencies. Although single-frequency methods of determining the value of τ for a polar liquid in a nonpolar solvent are described in the literature, none of these methods are applicable to an undiluted compound at a given temperature. An empirical relation to enable the evaluation of τ for a pure polar liquid is therefore proposed here and its validity is tested against previous experimental data for a number of such substances.

Eyring *et al.* (1941) treated dipolar relaxation as a rate process and deduced an equation for the relaxation time τ of the form

$$\tau = (h/kT)\exp(\Delta F/RT), \quad (1)$$

where h , k and R are the Planck, Boltzmann and gas constants respectively, T is the temperature and ΔF is the molar free energy of activation for dipolar relaxation. The fact that a plot of τ versus concentration for a polar liquid in a nonpolar solvent is found to be nonlinear suggests that the dipole-dipole interaction increases with the concentration of the polar liquid. A similar nonlinear relation for polar liquids has been observed between the distribution parameter α and the temperature, and in this case Lakshminarayana (1961) suggested evaluation of α from the expression

$$\alpha = A \exp(B/T), \quad (2)$$

which is similar to the Eyring *et al.* equation (1) for τ . Subsequently Muralidhara

Rao (1963) modified the relation (2) to

$$\alpha = (A/T)\exp(B/T) \quad (3)$$

and obtained a linear plot between $\log \alpha T$ and T^{-1} which was valid over a wide range of temperature.

The above results suggested that an analogous procedure might be followed in order to obtain a linear relation between the relaxation time and the concentration of a polar solute in a nonpolar solvent by introducing a concentration factor C into equation (1) to give

$$\tau = (h/kCT)\exp(\Delta F/RCT). \quad (4)$$

Since $\Delta F = \Delta H - T\Delta S$ where ΔH and ΔS are respectively the enthalpy and entropy of activation for dipolar relaxation, we have from equation (4)

$$\ln CT\tau = X + (\Delta H/R)(CT)^{-1}, \quad (5)$$

with

$$X = \ln(h/k) - \Delta S/RC,$$

which is the relation we propose. C is defined as the concentration (volume fraction in solution) of the polar liquid in the nonpolar solvent. Plots of $\log CT\tau$ against $(CT)^{-1}$ for a number of solutions have shown that the linear relation (5) holds for concentrations above 0.5. Extrapolation of the graphs at known temperature T to obtain the value of $\log CT\tau$ when $C = 1$ then allows a determination of the value of τ for the pure liquid.

Experimental Details

The dielectric constant ϵ' and loss factor ϵ'' of a number of solutions of a polar liquid in a nonpolar solvent were measured at a single microwave frequency in the X-band using the method described by Poley (1955), with a similar experimental set-up, while the static dielectric constant ϵ_s was determined at 1 MHz using a Marconi Q-meter (TF 1245A) in combination with a standard variable capacitor (GM 4353). The relaxation time was then calculated at each concentration from the relation

$$\tau = \omega^{-1}(\epsilon_s - \epsilon')/\epsilon'', \quad (6)$$

where $\omega = 2\pi f$, f being the microwave frequency used. The expression (6) is obtained from Debye's equations for ϵ' and ϵ'' by eliminating the high frequency dielectric constant ϵ_∞ and the resulting error in the relaxation time is of the same order as when ϵ_∞ is estimated by drawing a Cole-Cole plot. In this latter procedure the errors in the individual measurements of τ at different frequencies are averaged out to yield the most probable value. In the graphical method proposed here the errors in the individual values of τ at the various concentrations are also averaged out and the result gives the most probable τ value for the pure liquid.

All the chemicals investigated were of reputed make and were dried and re-distilled before use. The solutions were stored in flasks with ground-glass joints to prevent absorption of moisture.

Table 1. Results for polar liquids at various concentrations

Polar solute in solvent	Fre- quency (GHz)	Concen- tration C	$\log_{10} CT\tau$ +9	τ for $C = 1^*$ (10^{-12} s)	Temp. T^* (K)	ΔH (kcal mole $^{-1}$)	ΔF (kcal mole $^{-1}$)	ΔS (cal mole $^{-1}$)
Nitrobenzene in benzene	8.2	1.0	1.1000	41.3	306	0.97	3.38	-7.96
		0.9	0.9631	[46.0] ⁽¹⁾	[293] ⁽¹⁾	2.93	-6.48	
		0.8	0.8833			2.48	-4.97	
		0.7	0.7847			2.04	-3.87	
		0.6	0.6245			1.63	-2.19	
		0.5	0.3941			1.17	-0.67	
Methyl alcohol in benzene	8.2	1.0	1.2000	53.1	305	0.72	3.52	-9.15
		0.9	1.1368	[53.0] ⁽¹⁾	[293] ⁽¹⁾	3.09	-7.56	
		0.8	1.0450			2.66	-6.35	
		0.7	0.9905			2.24	-4.98	
		0.6	0.8545			1.82	-3.61	
		0.5	0.6780			1.39	-2.21	
Ethyl benzoate in carbon tetra- chloride	9.173	1.0	0.9100	28.0	305	0.88	3.14	-7.44
		0.9	0.8542	[31.0] ⁽¹⁾	[301] ⁽¹⁾	2.71	-6.02	
		0.8	0.7312			2.30	-4.70	
		0.7	0.6324			1.90	-3.40	
		0.6	0.5039			1.55	-2.22	
<i>o</i> -Toluidine in <i>n</i> -heptane	8.2	1.0	0.8800	25.1	301	1.66	2.93	-4.21
		0.9	0.7525			2.57	-3.02	
		0.8	0.5783			2.09	-1.44	
		0.7	0.3326			1.59	+0.23	
		0.6	0.0647			1.14	+1.73	
Diethylaniline in benzene	8.2	1.0	1.2600	59.7	305	1.22	3.61	-7.86
		0.9	1.1839	[60.9] ⁽²⁾	[303] ⁽²⁾	3.17	-6.41	
		0.8	0.9884			2.62	-4.62	
		0.7	0.8366			2.12	-2.96	
		0.6	0.7180			1.68	-1.53	
Diethylaniline in <i>n</i> -heptane	8.2	1.0	1.1350	57.1	301	0.67	3.38	-8.98
		0.9	1.0914			2.98	-7.65	
		0.8	0.9925			2.57	-6.28	
		0.7	0.8968			2.15	-4.90	
		0.6	0.7974			1.75	-3.57	
		0.5	0.6413			1.35	-2.25	
Methyl benzoate in <i>n</i> -heptane	8.2	1.0	0.9700	30.6	305	0.94	3.21	-7.43
		0.9	0.9128	[26.4] ⁽¹⁾	[301] ⁽¹⁾	2.82	-6.17	
		0.8	0.7810			2.39	-4.74	
		0.7	0.6925			1.98	-3.39	
		0.6	0.5423			1.53	-1.95	
		0.5	0.3087			1.13	-0.62	
Methyl benzoate in carbon tetra- chloride	9.173	1.0	0.9467	29.0	305	0.74	3.16	-7.94
		0.9	0.8834			2.77	-6.64	
		0.8	0.7677			2.39	-5.39	
		0.7	0.6652			1.98	-4.05	
		0.6	0.5877			1.60	-2.81	

Table 1 (Continued)

Polar solute in solvent	Fre- quency (GHz)	Concen- tration <i>C</i>	$\log_{10} CT\tau$ +9	τ for $C = 1^*$ (10^{-12} s)	Temp. T^* (K)	ΔH (kcal mole ⁻¹)	ΔF (kcal mole ⁻¹)	ΔS (cal mole ⁻¹)
Methyl benzoate in carbon tetra- chloride	8.2	1.0	1.0400	39.9	275	0.63	2.97	-8.50
		0.9	0.9981				2.62	-7.24
		0.8	0.9531				2.26	-5.92
		0.7	0.8337				1.90	-4.59
		0.6	0.6893				1.54	-3.29
	0.5	0.6024	1.18	-2.00				
	8.2	1.0	0.8537	21.9	323	0.89	3.21	-7.15
		0.9	0.7414				2.74	-5.70
		0.8	0.6734				2.36	-4.53
		0.7	0.5811				1.97	-3.32
0.6		0.4556	1.57				-2.11	

* Values in square brackets are previously reported measurements of τ for the pure liquid at the indicated temperatures by (1) Syamalamba and Premaswarup (1965) and (2) Lakshminarayana (1958).

Results and Discussion

The experimental data for the substances investigated, which include polar liquids with nearly spherical molecules of low and high viscosity and low and high dipole moment, an associated liquid, and mono- and di-substituted benzene compounds, are given in Table 1. The values of τ at $C = 1$ derived by the extrapolation method proposed above are compared, where possible, with previously reported measurements for the pure solutes (values enclosed in square brackets). It can be seen that in all cases investigated the method yields acceptable values of τ .

Solutions of diethylaniline and methyl benzoate in *n*-heptane have been studied in order to determine the influence of the viscosity of the solvent on the derived value of τ . Since the results agree within the limits of experimental error with the values obtained in different solvents, it can be inferred that the empirical relation (5) is not affected by the viscosity of the solvent, provided it is lower than that of the polar liquid.

Methyl benzoate has also been investigated at different temperatures using carbon tetrachloride as solvent. The values of $\tau(C = 1)$ obtained at $T = 275, 305$ and 323 K are found to yield a linear plot of $\log T\tau$ versus T^{-1} , which not only indicates that the τ values are satisfactory but also that the method is applicable at different temperatures, provided care is taken to ensure that the concentration of the solution does not change during the experiment.

The value of ΔH obtained from the slope of the $\log CT\tau$ versus $(CT)^{-1}$ graph, as indicated by equation (5), together with the results for ΔF from equation (4) and the corresponding ΔS at each concentration are included in Table 1. It can be seen that ΔF increases with the concentration of the polar solute. Since a higher value of ΔF indicates a reduced probability for dipoles to switch from one orientation to another, there is an accompanying increase in relaxation time. The results for ΔS in Table 1 show that its value becomes more negative as the concentration is increased.

We can infer from the negative values of entropy that there are fewer possible dipole configurations than in the normal random distribution of the molecules and hence that the solutions are in a more-ordered, activated state. The decrease in ΔS with higher solute concentration can be explained in terms of the increase in cooperative orientations of molecules resulting from either steric forces or dipole-dipole interactions (Branin and Smyth 1952). For the enthalpy ΔH , its value is found to depend on the viscosity of the solvent and to a lesser extent on the temperature. The latter dependence can be attributed to changes in viscosity with temperature. Because of the greater variation of viscosity with increasing concentration, the value of ΔH obtained from the slope of a $\log CT\tau$ versus $(CT)^{-1}$ graph may be lower than the corresponding value derived from a plot of $\log T\tau$ versus T^{-1} .

From equation (5), the quantity X is equivalent to the intercept on a graph of $\log CT\tau$ versus $(CT)^{-1}$. However, owing to the empirical nature of the proposed relation, the significance of X is not explicitly revealed by this investigation.

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