

DIELECTRIC RELAXATION—EFFECT OF TEMPERATURE

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ABSTRACT. Dielectric relaxation times were determined over a wide range of temperatures for benzophenone, ethyl benzoate, *o*-nitro-naphthalene and ethyl adipate dissolved in heptane and ethyl adipate in decalin. The results have been discussed in the light of Eyring's theory on dipole rotation.

INTRODUCTION

Recent approaches to the problem of dielectric relaxation have involved the supposition that the dipole actually rotates between two positions of equilibrium separated by a potential energy barrier. If the height of the potential energy barrier is H_τ , then Frohlich (1949) has shown that the dielectric relaxation time τ , considered as a measure of the transition probability, is given by a relation of the form

$$\tau = \frac{C}{\omega_a} e^{H_\tau/KT} \quad \dots (1)$$

where C is temperature-dependent to some extent, π/ω_a the average time required by an excited molecule to turn from one equilibrium direction to the other.

Eyring (1941), postulating an analogy between the processes of dipole rotation and of unimolecular chemical reactions, identifies H_τ with ΔF , the thermodynamic standard free energy associated with these processes. His theory leads to a value h/KT for the factor C/ω_a , h being the Planck's constant, and equation (1) can be written as

$$\tau = \frac{A}{T} e^{H_\tau/KT} \quad \dots (2)$$

where $A/T = C/\omega_a$.

As in the dielectric relaxation, the conception of viscous flow as involving the surmounting by each molecule of a potential energy barrier of height H_η say, each time it moves, leads to a relation of the form

$$\eta = B e^{H_\eta/KT} \quad \dots (3)$$

Eyring (1941) identified B with the factor hN/V , where h is the Planck's constant, N the Avogadro's number and V the molar volume.

This approach by Eyring to the understanding of relaxation as a rate process was investigated by Whiffen and Thompson (1946) by carrying out measurements on dilute solutions of chloroform, camphor, etc., in heptane. They observed a linear relationship between the logarithm of the relaxation time and the reciprocal of the absolute temperature. They pointed out, however, that a slight curvature to the graph, expected on the basis of Eyring's theory, could not be detected due to insufficient accuracy in their experimental results. Their observations indicated further an approximate equality of H_τ and H_η . They evaluated also the entropy change (ΔS) and heat content change (ΔH) for the process of activation and noticed that the entropy changes of activation were all small and negative. They said that the physical significance of such negative values should be left for later consideration but however indicated that this data might be informative about the packing of the molecules when compared with the corresponding values for other systems. Similar conclusions were drawn by Smyth *et al.* (1948) in their study on alkyl bromides. Recent investigation by Saxton (1952) on the effect of temperature on dielectric relaxation in the case of pure polar liquids, indicated a linear relationship between $\log T\tau$ and $1/T$ in the case of methyl and ethyl alcohols but a curvature in the case of water. In all the three liquids he found the plot of $\log T\tau$ versus $\log \eta$ to be a perfect straight line with slope unity, thus showing that H_τ is identical with H_η . Further his observations on the two factors A and B indicated that, though they remained fairly constant over a wide range of temperatures in the case of alcohols, the values of the latter were found to be in reasonable agreement and those of the former to be significantly greater than the values predicted by Eyring. In the case of water he did not observe any constancy in the values of A and B , and this peculiar behaviour was attributed to the change of its co-ordinated structure with change in temperature.

A study of these observations on the effect of temperature on dielectric relaxation, so far recorded, seems to indicate that Eyring's theory on dipole rotation still remained open to discussion and requires a bulk of experimental data before any attempt is made to draw definite conclusions on this subject. Hence the present work has been undertaken with a view to studying Eyring's approach in understanding dielectric relaxation. Observations are recorded on benzophenone, ethyl benzoate, α -nitronaphthalene and ethyl adipate dissolved in heptane and ethyl benzoate in decalin. H_τ is found approximately equal to H_η in all the cases studied. The values for the factors A and B calculated from experimental observations are found to be constant in each liquid, and they are of the same order of magnitude though not in agreement, with those predicted by Eyring (1941).

EXPERIMENTAL

All the measurements on the effect of temperature were made at a wavelength of 3.28 cms.

The value of the dielectric relaxation time is evaluated at various temperatures by assuming Debye's equation for the complex dielectric constant as a function of frequency for a dilute solution of a polar compound in a non-polar solvent which can be written as

$$\frac{\epsilon^* - 1}{\epsilon^* + 2} - \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} + \frac{4\pi n\mu^2}{9KT} \cdot \frac{1}{1 + i\omega\tau}$$

where n is the number of dipole molecules per c.c., ϵ^* is the complex dielectric constant of the solution.

Splitting the above expression into its real and imaginary parts, we obtain for the coefficient of imaginary part

$$\frac{3\epsilon''}{(\epsilon' + 2)^2 + \epsilon''^2} = \frac{4\pi n\mu^2}{9KT} \cdot \frac{\omega\tau}{1 + \omega^2\tau^2} \quad \dots \quad (4)$$

where ϵ' and ϵ'' are dielectric constant and loss of the solution.

This equation can be written as

$$\frac{T\epsilon''}{\{(\epsilon' + 2)^2 + \epsilon''^2\}d_{12}} = \frac{4\pi N\mu^2 W}{27KT M} \cdot \frac{\omega\tau}{1 + \omega^2\tau^2} \quad \dots \quad (5)$$

since $n = Nd_{12}W/M$, where W is the weight fraction of the solute and M its molecular weight and N the Avogadro's number.

It can be seen that $T\epsilon''/\{(\epsilon' + 2)^2 + \epsilon''^2\}d_{12}$ is maximum, when $\omega\tau = 1$, which gives the value of τ at that temperature. At any other temperature the ratio of the value of $T\epsilon''/\{(\epsilon' + 2)^2 + \epsilon''^2\}d_{12}$ to its maximum value will be $2\omega\tau/(1 + \omega^2\tau^2)$ in which τ is the relaxation time at that temperature. The choice between the two possible values of τ for one value of this ratio is determined by whether the temperature is above or below that corresponding to the maximum value.

It may be mentioned here that Whiffen and Thompson (1946) adopted this procedure in their temperature measurements, but they have taken the following equation as the basis.

$$\tan \delta = \frac{(\epsilon + 2)^2}{\epsilon} \frac{4\pi\mu CN}{27KT} \cdot \frac{\omega\tau}{1 + \omega^2\tau^2}$$

where ϵ is the dielectric constant of the solvent. This can be deduced from equation (4) if ϵ' , the dielectric constant of the solution is assumed to be equal to that of the solvent and ϵ''^2 is neglected in comparison with $(\epsilon' + 2)^2$. Further,

in their measurements, the dielectric constants of the solvent at different temperatures were estimated from that at 20°C by assuming that the molecular

polarisability $\frac{\epsilon-1}{\epsilon+2} \cdot \frac{M}{\rho}$ is independent of temperature.

In the present work, no such approximations were made, and equation (4) was taken as the basis for the calculation. The values of ϵ' and ϵ'' of the solution at different temperatures were computed from the standing wave measurements by the method indicated by the author (1956).

The experimental set-up consists of Philips 55391 klystron oscillator with a frequency range 8500-9600 Mc/s fed by a stabilised power supply. In series with it are a matching unit a variable attenuator, a standing wave indicator and a silvered dielectric cell. The probe position in the standing wave indicator can be read to 0.002 cm. The dielectric cell and the standing wave indicator are vertically mounted to facilitate introduction of several temperature baths at the dielectric end without disturbing the main set-up. The design of the dielectric cell is such as to maintain constant thickness of the dielectric irrespective of the temperature for which it is exposed. A piece of waveguide, connected between the standing wave indicator and the dielectric cell, reduced to a great extent the transfer of heat to the crystal. In addition to this, forced air was blown at the extension guide which was found necessary to obtain reproducible results. The required temperatures were obtained by hot water, ice and pre-cooled alcohol.

The densities of the solution at different temperatures were measured by a Westphal balance, which are accurate to one unit in the third decimal place.

RESULTS AND DISCUSSION

The experimentally obtained values of ϵ' , ϵ'' , and density together with the values, τ , $\log T\tau$, and $1/T$ obtained on calculation for ethyl adipate, α -nitronaphthalene, ethyl benzoate and benzophenone dissolved in heptane and ethyl benzoate in decalin are given in Table I.

The values of the dipole moments are calculated from the maximum of $Te''/((\epsilon'+2)^2 + \epsilon''^2)d_{12}$, since at that point its value will simply be $2\pi N\mu^2W/27KM$. The dipole moments calculated thus are compared with those taken from R.F. measurements (Tables of dipole moments, Wesson, 1948) in the following Table II

A reasonable agreement is found in all the cases and this can be taken as a satisfactory justification for using the Debye equations in calculating the values of τ .

The values of viscosity at various temperatures for the two solvents heptane and decalin are presented in Table III. The values of heptane are taken from

TABLE I

Temp °C	ϵ'	ϵ''	Density	τ	$10 + \log T\tau$	$1/T$
1. <i>Ethyl adipate in heptane</i> (Weight fraction of the solute = 0.0454)						
-50	2.70	0.0711	0.794	27.5	1.788	4.48
-40	2.70	0.0724	0.784	21.8	1.706	4.20
-30	2.70	0.0704	0.775	17.4	1.626	4.12
-20	2.70	0.0656	0.766	14.4	1.561	3.95
-10	2.69	0.0593	0.757	12.0	1.500	3.80
0	2.69	0.0536	0.748	10.6	1.461	3.66
10	2.68	0.0498	0.739	8.5	1.381	3.53
20	2.66	0.0384	0.730	7.2	1.326	3.41
30	2.64	0.0330	0.721	6.4	1.286	3.30
40	2.63	0.0285	0.712	5.7	1.248	3.20
60	2.60	0.0201	0.694	4.2	1.148	3.00
70	2.56	0.0177	0.686	3.9	1.125	2.92
2. α -nistranaphthalene in heptane (Weight fraction of the solute = 0.0215)						
-20	2.78	0.1100	0.767	33.3	1.925	3.95
-10	2.75	0.1120	0.757	28.3	1.872	3.80
0	2.72	0.1127	0.748	23.6	1.810	3.66
10	2.69	0.1096	0.739	20.8	1.770	3.53
20	2.68	0.1056	0.730	17.4	1.707	3.41
30	2.67	0.0976	0.721	14.9	1.661	3.30
40	2.66	0.0927	0.711	13.7	1.632	3.20
50	2.58	0.0811	0.703	11.5	1.568	3.10
60	2.60	0.0722	0.694	10.5	1.542	3.00
70	2.46	0.0638	0.684	9.3	1.505	2.92
80	2.43	0.0560	0.675	8.2	1.462	2.83
3. <i>Ethyl benzoate in heptane</i> (Weight fraction of the solute = 0.0520)						
-40	2.69	0.0732	0.786	32.5	1.880	4.29
-30	2.69	0.0757	0.777	27.3	1.821	4.12
-10	2.68	0.0745	0.759	19.6	1.712	3.80
0	2.67	0.0712	0.750	17.4	1.677	3.66
10	2.67	0.0648	0.741	12.9	1.562	3.53
25	2.65	0.0568	0.728	10.9	1.510	3.36
40	2.62	0.0481	0.714	9.3	1.463	3.20
50	2.61	0.0423	0.705	8.1	1.420	3.10
60	2.59	0.0369	0.696	7.2	1.378	3.00
70	2.40	0.0315	0.688	6.5	1.347	2.92

TABLE I (contd.)

Temp °C	ϵ'	ϵ''	Density	τ	$10 + \log T\tau$	$1/T$
4. <i>Benzophenone in heptane</i> (Weight fraction of the solute = 0.0407)						
0	2.65	0.0948	0.743	27.3	1.872	3.66
10	2.64	0.0952	0.734	23.5	1.823	3.53
20	2.63	0.0937	0.724	20.1	1.770	3.41
25	2.62	0.0912	0.719	19.0	1.753	3.36
30	2.61	0.0891	0.714	17.4	1.722	3.30
35	2.60	0.0864	0.710	16.7	1.711	3.25
40	2.56	0.0829	0.706	16.3	1.680	3.20
45	2.54	0.0800	0.702	14.9	1.675	3.15
50	2.52	0.0765	0.697	13.9	1.650	3.10
60	2.46	0.0692	0.688	12.4	1.615	3.00
70	2.45	0.0631	0.679	11.0	1.576	2.92
80	2.43	0.0568	0.671	9.8	1.538	2.83
<i>Ethyl benzoate in decalin</i> (Weight fraction of the solute = 0.0829)						
-20	2.23	0.0491	0.928	86.4	2.340	3.95
-10	2.21	0.0535	0.918	66.7	2.244	3.80
0	2.21	0.0663	0.908	54.3	2.171	3.66
10	2.20	0.0604	0.898	48.0	2.133	3.53
22.5	2.19	0.0700	0.885	36.5	2.033	3.39
29	2.17	0.0868	0.879	28.8	1.939	3.31
40	2.17	0.0915	0.868	21.1	1.819	3.20
49	2.15	0.0890	0.859	17.4	1.747	3.11
58	2.13	0.0818	0.850	13.1	1.637	3.02
70	2.12	0.0734	0.838	11.3	1.588	2.92
80	2.11	0.0661	0.828	10.0	1.546	2.83

TABLE II

Substance	Present investigation	R. F. measurements
Ethyl adipate	2.10	2.40
α -nitronaphthalene	3.92	3.88
Ethyl benzoate in heptane	1.84	1.82
in decalin	1.88	
Benzophenone	2.81	2.5 to 3.0

"Physico-Chemical constants" (Timmermans). The viscosity of decalin was determined using Ostwald type of viscometer, the accuracy of which may be within 2 per cent.

TABLE III

<i>n</i> -heptane		Decalin	
Temp. °C	Viscosity $\times 10^5$	Temp °C	Viscosity $\times 10^5$
6.6	480	0	3400
13.5	442	10	2590
21.7	403	14	2370
30.3	369	20	2170
38.3	340	27	1730
47.3	311	35	1430
55.0	289	45	1200
62.0	271	55	940
70.1	253	65	740
77.1	237		
85.5	222		

It is observed that the plots of $\log T\tau$ versus $1/T$ yield a straight line, which means that H_τ is constant. The plots of $\log \eta$ and $1/T$ fall on a good straight line, indicating H_η to be constant. The values of H_τ and H_η , calculated from the slopes of the respective graphs $\log T\tau$ versus $1/T$ and $\log \eta$ versus $1/T$ for the substances investigated at present, are given in Table IV.

TABLE IV

	$H_\eta \times 10^{13}$	$H_\tau \times 10^{13}$	
			ergs
Ethyl adipate	1.35	1.36	} Heptane
α -nitronaphthalene	1.32	1.36	
Ethyl benzoate	1.31	1.36	
Benzophenone	1.28	1.36	
Ethyl benzoate	2.45	2.81	

It can be seen that in all cases H_τ is approximately equal to H_η , and the difference is almost within the possible experimental error. It would thus appear that the heights of the potential energy barriers to be surmounted in the two processes of viscous flow and dipole rotation are almost equal.

The factors *A* and *B*

The values of the factors *A* and *B*, according to Eyring, as mentioned earlier, must be h/K and hN/V respectively. On this basis we might therefore expect *A* to be a constant for all the liquids, and *B* also for any liquid except for the small variation of the molar volume *V*, with temperature. This aspect of Eyring's theory was also studied in the present investigation.

The value of A is calculated at each temperature for the investigated molecules from equation (2) using the value of H_τ obtained from the slopes of the plots $\log T\tau$ versus $1/T$. The results are given in Table V. It is observed that the values of A are fairly constant for each liquid, and they are in the same order of magnitude, but not in agreement, with the value h/K , which is 4.8×10^{-11} . It may be mentioned here that these observations are in accordance with those of Saxton (1952) in his studies on methyl and ethyl alcohols. His experimental results indicated that the values of A (average value 4.1×10^{-10} and 1.7×10^{-10} in methyl and ethyl alcohols respectively), though observed to be constant over the temperature range -10°C . to 50°C are significantly greater than h/K (4.8×10^{-11}).

The values of B (shown in Table VI) are also calculated from equation (3) using the values of H_η obtained from the slopes of the plots $\log \eta$ and $1/T$. In the case of the solvent decalin, the value of B (2.13×10^{-5}) is in reasonable agreement with the hN/V value calculated at 20°C which is 2.53×10^{-5} . But in the case of the solvent heptane, the experimentally determined value for B (1.45×10^{-4}) is greater than hN/V value calculated at 20°C which is 2.72×10^{-5} . Reference may again be made to the work of Saxton (1952), in the two alcohols, the values of which are presented below.

TABLE V
Values for factor A

Temp $^\circ\text{C}$	Ethyl adipate	Ethyl benzoate	α -nitronaphthalene	Benzo-phenone	Ethyl benzoate in decalin
	in heptane $A \times 10^9$				
-50	7.60	—	—	—	—
-40	7.59	14.2	—	—	—
-30	7.50	13.5	—	—	—
-20	7.57	—	19.5	—	1.98
-10	7.64	14.1	19.9	—	2.08
0	7.99	14.9	19.7	25.4	2.24
10	7.55	12.9	20.3	25.4	2.59
20	7.48	13.5 (25 $^\circ\text{C}$)	19.7	25.2	2.67 (22.5 $^\circ\text{C}$)
30	7.62	14.5	19.7	25.0	2.45 (29 $^\circ\text{C}$)
40	7.75	14.1	20.4	25.1	2.29
50	—	14.0	19.4	25.6	2.27
60	7.43	13.9	19.9	25.7	2.04 (58 $^\circ\text{C}$)
70	7.67	14.1	19.9	25.5	2.20
80	—	—	19.5	25.2	2.32

TABLE VI
Values for factor B

Decalin		Heptane	
Temp. °C	$B \times 10^6$	Temp. °C	$B \times 10^4$
0	2.00	6.6	1.44
10	1.98	13.5	1.45
14	2.00	21.7	1.45
20	2.13	30.3	1.46
27	1.98	38.3	1.46
35	1.96	47.3	1.46
45	2.20	55.0	1.46
55	1.93	62.0	1.46
65	1.83	70.1	1.46
		77.1	1.45
		85.5	1.44
	Experimental observations	hN/V	
Methyl alcohol	8.7×10^{-5}	10^{-4}	
Ethyl alcohol	4.5×10^{-5}	6.9×10^{-5}	

The values show a somewhat reasonable agreement in the two cases, and not as so in decalin.

Further, it may be seen for all the five solutions examined that the values of B are very much greater than A ; thus, although H_r is equal to H_v approximately molecular jumps over the potential energy barrier in viscous flow are accomplished more readily than those associated with dipole rotation.

Lastly, it may be mentioned that the suggestion put forth by Eyring for the possible separation of H_r into internal energy change (ΔH) and entropy change (ΔS) has not been discussed in the present investigation, since this procedure will sometimes lead to false deductions concerning their magnitudes, especially when $h \omega_a/2\pi > KT$, as pointed out by Pelzer (1946) and when the entropy varies rapidly with temperature (Saxton 1946).

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