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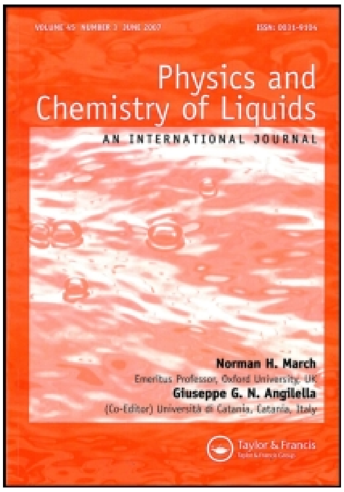

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Dielectric Relaxation of Some Rigid Molecules in Viscous Media

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To cite this Article Chauhan Miss, M. , Gupta Miss, M. , Saxena, S. K. and Shukla, J. P.(1981) 'Dielectric Relaxation of Some Rigid Molecules in Viscous Media', Physics and Chemistry of Liquids, 10: 4, 335 — 346

To link to this Article: DOI: 10.1080/00319108108079089

URL: http://dx.doi.org/10.1080/00319108108079089

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Phys. Chem. Liq., 1981, Vol. 10, pp. 335–346
0031-9104/81/1004–0335$06.50/0

Printed in the U.S.A.

Dielectric Relaxation of Some Rigid Molecules in Viscous Media

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(*Received December 12, 1980*)

The dielectric relaxation times(τ) have been evaluated from the measured values of dielectric constant(ε') and loss (ε'') of four rigid molecules in paraffin oil + benzene mixtures of varying viscosity extending from moderate to high values. Two of the rigid systems are nearly spherical in nature. An attempt has been made to find out the suitable viscosity term describing the dipolar rotation by applying the measured parameters to the earlier models as proposed by Debye, Hill and Kalman. Hill's model which describes the motion by a mutual viscosity (η_{AB}) term has been found to yield negative values showing its inadequacy for the systems rotating in high viscosity media. A comparison of Kalman's equation with Debye shows that the former gives better results for the region investigated both in high and low viscosity media. Even the systems having spherical symmetry give more satisfactory results when applied to Kalman's equation. In the process, the thermodynamical parameters and dipole moments of the molecules have also been evaluated and discussed.

INTRODUCTION

The Debye relation[1] between the dielectric relaxation time τ and viscosity η was found inadequate to define correctly the relaxation mechanism by several workers.[2–4] The discrepancy arising due to presumption of spherical shape of molecules and internal viscosity concept entailed the Debye relation to be modified. The discrepancy was more pronounced in highly viscous media.[5,6] The modified equations[7,8] have been tested for various polar molecules in solutions.

The models based on the concept of mutual viscosity and averaged mutual viscosity were proposed by Hill[9] and Vaughan *et al.*[10] respectively. These models have been successfully tested for a few systems. However, in

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some cases these have been found inadequate. An empirical relation between τ and η of the type $\tau = A\eta^{\alpha}$ was proposed by Higasi[11] and was examined for about eight molecules in various solutions. Kalman and Smyth[12] using Eyring's rate equations,[13] derived a relation of the type $\tau = (C/T)\eta^{\alpha}$, which gave satisfactory results over a small temperature range for some systems. The proposed models have been applied for systems comprised of numerous molecules of different shapes and sizes in several non-polar media.

The relaxation behaviour of 1-butanol and 1-decanol in highly viscous media has been studied by Crossley *et al.*[14] and the effect of viscosity on group process has been examined. Recently Crossley *et al.*[15] have studied some aromatic methoxy compounds for their molecular and intramolecular rotational behaviour and found that the group process is independent of viscosity. In view of the limited studies reported for the systems rotating in highly viscous media it was considered worthwhile to undertake an investigation on some rigid polar molecules, both spherical and slightly elongated in shape, in high viscosity media comprising of the mixture of paraffin oil (p.o.) and benzene. The molecules investigated were pyridine, quinoline, bromobenzene and iodobenzene. It was aimed to investigate the applicability of the earlier proposed equations correlating the dilectric relaxation time and viscosity of the medium. Such a study is expected to be useful in getting an expedient viscosity term.

The molecules chosen for investigation are rigid in nature and two of them are spherically symmetrical. Considering the Debye's model applicable for symmetrical systems, this would provide an opportunity to apply Hill's and Kalman's models to these systems and observe the changes occurring therein.

In the process, the thermodynamical parameters associated with the motion have also been determined and discussed. Dipole moments of various molecules have also been determined and compared with the available literature values.

Theory and method

The fixed frequency method of Gopala Krishna[16] has been adopted to determine the relaxation time. The technique employed was that of Roberts and Von Hippel.[17] The values of dielectric constant ε' and dielectric loss ε'' have been calculated with the help of Dakin and Works[18] method as described earlier.[19]

Eyring's rate equations[13] have been used to determine thermodynamical parameters, e.g. free energy ΔF_{ε}, enthalpy of activation ΔH_{ε}, ΔH_{η} and entropy ΔS_{ε}.

The mutual viscosity term η_{AB} proposed by Hill,[9] accounts for the solute solvent interaction and employs Andrade's[20] theory of viscosity in deriving the relation

$$\eta_m \sigma_m = x_A^2 \eta_A \sigma_A + x_B^2 \eta_B \sigma_B + 2x_A x_B \eta_{AB} \sigma_{AB}$$

where, η_m, η_A and η_B are coefficients of viscosity of solution, solvent and solute respectively; x_A, x_B are the mole fractions of solvent and solute and the σ's are the average intermolecular distances given as

$$\sigma_A = \left(\frac{M_1}{d_1 N}\right)^{1/2};\ \sigma_B = \left(\frac{M_2}{d_2 N}\right)^{1/2};\ \sigma_m = \left(\frac{x_A M_1 + x_B M_2}{d_m N}\right)^{1/2}$$

where M_1 and M_2 are the molecular weights of the solvent and solute molecules, d_1 and d_2 are the corresponding densities and d_m is the density of solution; σ_{AB} is the average separation of the solute and solvent molecules given by

$$\sigma_{AB} = \tfrac{1}{2}(\sigma_A + \sigma_B)$$

The following six solutions of varying viscosities were taken for the measurements for all the four molecules.

1) Pure benzene
2) 80% benzene + 20% paraffin oil (p.o.)
3) 60% benzene + 40% p.o.
4) 40% benzene + 60% p.o.
5) 20% benzene + 80% p.o.
6) 100% p.o.

at microwave frequency of 9.8 GHz.

Chemicals

All the chemicals used were of pure quality; pyridine, quinoline, bromobenzene and iodobenzene were obtained from B.D.H. (Ltd.), England. The medicinal paraffin oil was obtained from Liberty Pharmaceutical (Ltd.), Bombay (India), and the solvent benzene (A.R. Grade) was obtained from B.D.H. England. Benzene was distilled twice before use.

RESULTS AND DISCUSSION

The values of $\tau T/\eta$, $\tau T/\eta^{\alpha}$, η_{AB}, and the dipole moments have been listed in Table I. Table II and III contains thermodynamical parameters.

It is observed from Table I that the relaxation time τ shortens with increasing temperature as usual in all the investigated polar molecules. Also

TABLE I

Relaxation time(τ) viscosity(η) and their dependence on Debye and Kalman's equation with enthalpy ratio(α) and dipole moment(μ) (a) Pyridine

Solvent concentration	Temperature °K	$\tau \cdot 10^{12}$ sec.	α	η m.p.	η^{α} m.p.	$\frac{\tau T}{\eta} \cdot 10^{9}$	$\frac{\tau T}{\eta^{\alpha}} \cdot 10^{9}$	μ Debye obsd.	μ Debye lit.
Pure benzene	306	3.50	0.33	5.62	180.89	190.57	5.92	2.17	2.22
	314	3.10		4.78	171.48	203.6	5.68		
	322	3.00		3.31	151.89	291.8	6.36		
80% benzene +20% p.o.	306	5.00	0.35	10.79	204.83	141.8	7.47	1.69	
	314	4.90		8.80	190.81	174.8	8.06		
	322	—		6.64	172.89	—	—		
60% benzene +40% p.o.	306	5.32	0.51	16.34	122.68	99.6	13.27	1.96	
	314	4.94		12.04	104.73	128.8	14.81		
	322	4.60		8.93	90.14	165.9	16.43		
40% benzene +60% p.o.	306	5.83	0.65	28.71	99.52	62.1	17.93	1.57	
	314	5.32		20.73	80.50	80.6	20.75		
	322	5.20		15.88	67.67	105.4	24.74		
20% benzene +80% p.o.	306	6.60	0.78	104.57	171.85	19.3	11.75	1.77	
	314	5.80		95.09	159.55	19.2	11.41		
	322	5.50		78.48	137.49	22.6	12.88		
pure p.o.	306	7.30	0.77	483.40	571.34	4.6	3.91	1.83	
	314	6.30		384.60	479.19	5.1	4.13		
	322	5.76		240.30	333.51	7.7	5.56		
				($\eta_{AB} = -1.203$)					

η_{AB} is mutual viscosity calculated by Hill equation.[7] The molecular weight of p.o. (pure) is taken 440.[10]

TABLE I (*continued*)

(b) Quinoline

Solvent concentration	Temperature °K	$\tau \cdot 10^{12}$ sec.	α	η m.p.	η^x m.p.	$\frac{\tau T}{\eta} \cdot 10^9$	$\frac{\tau T}{\eta^x} \cdot 10^9$	μ Debye obsd.	μ Debye lit.
Pure	306	6.8		5.62	60.93	370.25	34.15	2.01	2.18
benzene	314	6.1	0.54	4.78	55.83	400.71	34.31		
	322	5.5		3.31	45.78	535.05	38.69		
80%	306	6.9		10.79	63.12	195.68	33.45	1.80	
benzene	314	6.3	0.61	8.80	55.74	224.80	35.49		
+20% p.o.	322	5.8		6.64	46.94	281.27	39.79		
60%	306	8.6		16.34	60.96	161.05	43.17	2.21	
benzene	314	7.8	0.68	12.04	49.53	203.42	49.45		
+40% p.o.	322	6.4		8.93	40.52	230.77	50.98		
40%	306	8.7		28.71	74.88	92.73	35.55	2.22	
benzene	314	8.0	0.73	20.73	59.04	121.18	42.55		
+60% p.o.	322	7.7		15.88	48.60	156.13	51.02		
20%	306	9.2		104.57	157.01	26.92	17.93	1.46	
benzene	314	8.4	0.82	95.09	145.23	27.74	18.16		
+80% p.o.	322	8.1		78.48	124.08	33.23	21.02		
Pure	306	10.0		483.40	563.12	6.33	5.43	1.57	
p.o.	314	8.6	0.79	384.60	470.06	7.02	5.74		
	322	8.4		240.30	324.19	11.26	8.34		

$(\eta_{AB} = -0.372)$

TABLE I (*continued*)

(c) Bromobenzene

Solvent concentration	Temperature °K	$\tau \cdot 10^{12}$ sec.	α	η m.p.	η^{α} m.p.	$\frac{\tau T}{\eta} \cdot 10^{9}$	$\frac{\tau T}{\eta^{\alpha}} \cdot 10^{9}$	μ Debye
Pure	306	8.6		5.62	47.03	468.26	55.96	1.88
benzene	314	7.5	0.59	4.78	42.74	492.68	55.10	
	322	—		3.31	34.41	—	—	
80%	306	9.2		10.79	50.33	260.91	55.93	2.13
benzene	314	7.8	0.66	8.80	43.99	278.32	55.68	
+20% p.o.	322	6.9		6.64	36.53	334.61	60.82	
60%	306	9.5		16.34	51.71	177.91	56.22	2.06
benzene	314	8.6	0.72	12.04	41.50	224.29	65.07	
+40% p.o.	322	7.7		8.93	33.47	277.65	74.08	
40%	306	10.6		28.71	56.36	112.98	57.55	2.10
benzene	314	9.5	0.81	20.73	43.30	143.90	68.89	
+60% p.o.	322	8.2		15.88	34.89	166.27	75.68	
20%	306	11.9		104.57	119.74	34.82	30.41	1.95
benzene+	314	10.0	0.94	95.09	109.51	33.02	28.67	
80% p.o.	322	8.6		78.09	91.43	35.29	30.29	
Pure	306	—		483.40	508.63	—	—	—
p.o.	314	11.5	0.93	384.60	411.21	9.39	8.78	
	322	9.5		240.30	265.52	12.73	11.52	

($\eta_{AB} = -0.376$)

TABLE I (*continued*)

(d) Iodobenzene

Solvent concentration	Temperature °K	$\tau \cdot 10^{12}$ sec.	α	η m.p.	η^{α} m.p.	$\frac{\tau T}{\eta} \cdot 10^9$	$\frac{\tau T}{\eta^{\alpha}} \cdot 10^9$	μ Debye
Pure	306	8.6		5.62	22.77	468.26	115.57	1.85
benzene	314	7.8	0.73	4.78	20.23	512.38	121.07	
	322	7.5		3.31	15.47	729.61	156.11	
80%	306	10.6		10.79	23.30	300.61	139.21	2.34
benzene	314	9.2	0.83	8.80	19.68	328.27	146.79	
+20% p.o.	322	8.2		6.64	15.57	397.65	169.58	
60%	306	11.5		16.34	26.77	215.36	131.45	1.71
benzene	314	10.0	0.88	12.04	20.46	260.80	153.47	
+40% p.o.	322	9.2		8.93	15.73	331.74	169.33	
40%	306	12.8		28.71	42.43	136.43	92.31	1.87
benzene	314	10.6	0.89	20.73	31.75	160.56	104.83	
+60% p.o.	322	9.7		15.88	25.05	196.69	124.69	
20%	306	13.8		104.57	106.96	40.38	39.48	2.03
benzene	314	11.5	0.99	95.09	97.35	37.97	37.09	
+80% p.o.	322	10.0		78.48	80.50	41.03	40.00	
pure	306	15.4		483.40	486.93	9.75	9.68	1.61
p.o.	314	13.8	0.99	384.60	388.29	11.27	11.16	
	322	12.6		240.30	243.75	16.88	16.64	

($\eta_{AB} = 0.331$)

TABLE II

Free energy of activation and entropy values calculated by using Eyring's equation

Solvent	Temperature °K	Pyridine ΔF_ε KJmol^{-1}	Pyridine ΔS_ε Jmol^{-1} deg^{-1}	Quinoline ΔF_ε KJmol^{-1}	Quinoline ΔS_ε Jmol^{-1} deg^{-1}	Bromobenzene ΔF_ε KJmol^{-1}	Bromobenzene ΔS_ε Jmol^{-1} deg^{-1}	Iodobenzene ΔF_ε KJmol^{-1}	Iodobenzene ΔS_ε Jmol^{-1} deg^{-1}
Pure	298	7.70		—		10.02		10.23	
benzene	306	7.87	−14.2	9.59	−14.4	10.18	−5.35	10.24	−1.36
	314	7.90		9.61		10.20		10.27	
	322	8.10		9.66		—		10.56	
80% benzene	298	8.7		9.58		10.10		10.60	
+20% p.o.	306	8.8	−16.4	9.62	−6.8	10.19	−5.2	10.70	0.86
	314	9.0		9.71		10.27		10.71	
	322	—		9.8		10.27		10.73	
60% benzene	298	8.9		10.15		10.23		10.88	
+40% p.o.	306	9.0	−10.6	10.20	−2.8	10.44	−3.06	10.92	2.64
	314	9.1		10.27		10.52		10.93	
	322	9.2		10.37		10.56		11.04	
40% benzene	298	9.20		10.23		10.58		—	
+60% p.o.	306	9.24	−5.2	10.24	−2.04	10.72	−0.86	11.10	3.20
	314	9.30		10.33		10.78		11.12	
	322	9.50		10.56		10.80		11.17	
20% benzene	298	9.45		—		10.88		11.30	
+80% p.o.	306	9.48	0.403	10.36	1.86	11.01	6.34	11.39	8.63
	314	9.50		10.46		10.92		11.28	
	322	9.66		10.64		10.88		11.34	
pure p.o.	298	10.0		10.55		11.03		11.60	
	306	9.76	0.67	10.57	2.52	—	8.7	11.67	11.24
	314	9.71		10.62		11.28		11.76	
	322	9.78		10.8		11.12		11.88	

TABLE III

Enthalpies ΔH_η, ΔH_ε and the ratio α

	Pyridine			Quinoline		
Solvent	ΔH_η	ΔH_ε	$\left(\frac{\Delta H_\varepsilon}{\Delta H_\eta}\right)$	ΔH_η	ΔH_ε	$\left(\alpha = \frac{\Delta H_\varepsilon}{\Delta H_\eta}\right)$
Pure benzene	10.56	3.48	0.33	10.56	5.74	0.54
80 % benzene +20 % p.o.	10.94	3.82	0.35	10.94	6.70	0.61
60 % benzene +40 % p.o.	11.34	5.74	0.51	11.34	7.66	0.68
40 % benzene +60 % p.o.	11.78	7.65	0.65	11.78	8.62	0.73
20 % benzene +80 % p.o.	12.25	9.57	0.78	12.25	10.05	0.82
pure p.o.	13.32	10.20	0.77	13.32	10.53	0.79
	Bromobenzene			Iodobenzene		
Pure benzene	10.56	6.22	0.59	10.56	7.66	0.73
80 % benzene +20 % p.o.	10.94	7.18	0.66	10.94	9.09	0.83
60 % benzene +40 % p.o.	11.34	8.14	0.72	11.34	10.05	0.88
40 % benzene +60 % p.o.	11.78	9.57	0.81	11.78	10.53	0.89
20 % benzene +80 % p.o.	12.25	11.49	0.94	12.25	12.14	0.99
pure p.o.	13.32	12.44	0.93	13.32	13.24	0.99

the relaxation time τ lengthens with the increase in viscosity but not in parallelism with viscosity. As seen from Table I, in case of pyridine molecule τ is observed to vary from 3.0 to 7.3 ps. where as the viscosity varies from 3.0–483.0 mp. It is because the pyridine molecule is spherical in shape showing rotational freedom over a wide range of temperature. This is in agreement with previous studies[12] exhibiting that nearly spherical molecules are less dependent on the viscosity of the medium. Similar is the case with the quinoline molecule. The relaxation time in this case varies from 5.5 to 10.0 ps.

in the same viscosity range. This shows that the relaxation times of pyridine and quinoline molecules which are spherically symmetrical, exhibit much less dependence on the medium viscosity.

The dielectric relaxation times of bromobenzene and iodobenzene molecules have been found to vary from 6.9 to 11.9 ps and 7.5 to 15.4 ps whereas the medium viscosity changes from 3.0 mp to 483 mp for both the systems respectively. In both the cases the variation in the relaxation time is very small with much larger changes occurring in the medium viscosity. This again shows that no direct correspondence between the τ and η values are observed. Also, the dielectric relaxation times of bromobenzene and idobenzene molecules are longer than that of pyridine and quinoline molecules. Further, τ values of iodobenzene for all the concentrations are longer than of bromobenzene in solutions. This indicates that the elongated systems experience greater hindrance to the dipolar rotation.

Application of Hill's concept of mutual viscosity to the p.o. solutions shows its inadequacy for these data. As can be seen from the Table I, the mutual viscosity parameter η_{AB}, at least in three systems, yielded negative values. This is inconsistent with the concept of the medium viscosity and indicates that the Hill's equation is no longer applicable for representing the medium viscosity for dipolar rotation in highly viscous media.

From Table I it is found that the pyridine molecule has the value of $\tau T/\eta$ ranging from (190.57–291.8) in pure benzene in the temperature range of 306–322°K. The large variation in $\tau T/\eta$ values with temperature is contrary to what was proposed by Debye. In the same temperature range $\tau T/\eta^{\alpha}$ values vary from (5.92–6.36) showing a slight difference in $\tau T/\eta^{\alpha}$ values. The constancy in $\tau T/\eta^{\alpha}$ has been observed in all the four investigated molecules in pure benzene at temperature range 306–322°K. Although the variation in $\tau T/\eta^{\alpha}$ values with temperature is a bit more in the case of iodobenzene yet it gives a better constancy over $\tau T/\eta$ values.

There occurs no appreciable difference in $\tau T/\eta^{\alpha}$ values in a small temperature range with increased solvent concentration up to 40% benzene +60% p.o. in all the investigated molecules. This behaviour supports the effectiveness of Kalman's relation over Debye's.

In pure paraffin oil Kalman's relation yields the values of $\tau T/\eta^{\alpha}$ varying from (3.91–5.56) for pyridine molecule whereas $\tau T/\eta$ lies in the range (4.6–7.7) at the temperature range 306–322°K. There does not seem any significant change in both the relations of Debye and Kalman for high values of α, approaching 1. Similar is the case observed in the other investigated molecules in highly viscous p.o.

A comparison of Debye, Hill[9] and Kalman[12] relations for viscosity and dielectric relaxation times indicates that the Hill's model is not suitable for the systems rotating in high viscous media where as the Debye's model seems to be approximately true for spherically symmetrical systems. Among the three models suggested the Kalman's relation seems to give better results for low and high viscosity media in the temperature range investigated here. It may be pointed out that as the factor $\alpha(=\Delta H_\varepsilon/\Delta H_\eta)$ approaches unity, the Kalman's relation terminates into Debye's relation which is indicated by observing similar values of $\tau T/\eta^\alpha$ and $\tau T/\eta$ in high viscosity region.

Thermodynamical parameters

It has been observed that the free energy of activation ΔF_ε of quinoline molecule is higher than that for pyridine. It was the effect of its bigger molecule size and hence, it experiences greater hindrance to the dipolar rotation. ΔF_ε values increase with the increase in temperature in all the cases of investigated polar molecules. It is because the increase in temperature enhances thermal agitation and, hence, dipoles require more energy to attain equilibrium with the applied field. Similar results have been reported by earlier workers.[19,21]

ΔF_ε values have been found to exceed the enthalpy of activation ΔH_ε, thus, giving negative values of entropy ΔS_ε which shows more orderliness in the activated state than in normal state. These states are getting disordered as the viscosity is increased.

The entropy values ΔS_ε are higher for the elongated systems than for spherically shaped molecules which can be interpreted as due to the greater hindrance caused by the surrounding molecules to dipolar rotation. Similar results have been observed by Kalman.[12]

The enthalpy values for dielectric relaxation ΔH_ε are found to increase from spherically shaped molecules to the elongated ones. The enthalpy for viscous flow ΔH_η are always higher than ΔH_ε as expected because viscous flow takes along both the rotation and translation where as it is only rotation involved in the relaxation process.

The dipole moment μ has been found to be 2.17 and 2.01 D in pure benzene for pyridine and quinoline molecule respectively which is in agreement with the literature value.[22,23] Dipole moment changes irregularly with the increase in viscosity parameter. The irregular trend in dipole moment values with viscosity has been observed in all the four molecules.

CONCLUSION

Present investigations on the rotational behaviour of some rigid (spherical and elongated) molecules as regards to the mdium viscosity, indicates that the Debye equation is applicable only to the spherical systems. The Hill's suggestion of mutual viscosity appears to be quite unsatisfactory in high viscous medium as can be seen from the observed negative values for η_{AB} in p.o. solutions, at least in three cases. Kalman *et al.*[12] have also observed similar results in solutions. The Kalman's equation gives better results for both the low and high viscosity region and as has been pointed out with $\Delta H_\varepsilon/\Delta H_\eta$ approaching 1, this equation becomes same as Debye's original equation. The energy parameters have been found to vary as usual, with higher entropy of activation in highly viscous media and also for elongated systems, in comparison to the spherically shaped molecules. It may be suggested that much further work is necessary for establishing a suitable representation of the viscous drag in highly viscous medium to understand the dipolar rotational process.

Acknowledgment

Thanks are due to Prof. M. C. Saxena for many helpful discussions, M. Gupta (Miss) and SKS are grateful to C.S.I.R. and U.G.C. respectively for providing the fellowships during the course of research work.

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