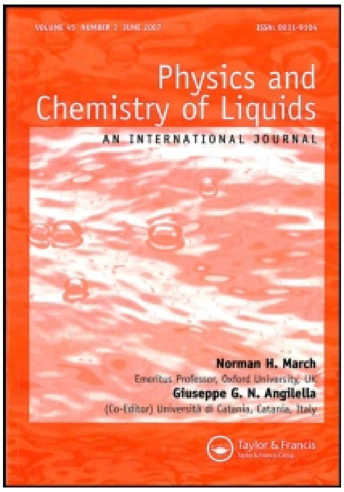

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On the effect of temperature on the dielectric relaxation time of some benzene derivatives and certain of their binary mixtures

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On the effect of temperature on the dielectric relaxation time of some benzene derivatives and certain of their binary mixtures

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Dielectric relaxation behaviour of polar molecules in a non-polar solvent, or mixtures of these substances at different microwave frequencies and over a range of temperatures and concentrations give an idea about inter- and intra-molecular forces. Also such studies enable one to calculate thermodynamic parameters such as, the change of activation energy for dipole orientation (ΔG^*), the enthalpy (ΔH^*) and entropy (ΔS^*) of activation. Such studies in the case of binary, ternary, etc. mixtures of polar molecules in pure liquid phase or in dilute solution phase of them in a non-polar solvent help in drawing certain quantitative conclusions regarding their relaxation behaviour as to whether a single component is responsible for observed microwave absorption, or a cooperative phenomenon (average) by all the dipoles of the mixture contribute to it. An experimental investigation is here performed on typical systems. With this in view, systematic dielectric measurements in a range of temperatures are carried out at a single microwave frequency on a single weight fraction in benzene of the four substituted phenols, namely, *p*-fluorophenylacetonitrile, *p*-bromonitrobenzene, *m*-bromonitrobenzene and 2-chloro-6-fluoro-benzaldehyde and on binary (1 : 1) mixtures of [*p*-2-chloro-6-fluoro-benzaldehyde + *o*-ethylphenol] and [*p*-fluorophenylacetonitrile + 2-*n*-butyl phenol] in benzene as solvent at different temperatures. The results are presented and discussed.

Keywords: Dielectric relaxation; Enthalpy; Entropy; Activation energy; Microwave; Substituted benzenes

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1. Introduction

In the recent past, studies on dielectric relaxation behaviour of polar molecules in a pure liquid phase and in dilute solutions, and their mixtures at microwave frequencies and over a range of temperatures have been reported by the authors of Refs. [1–7] and others [14–17,19–21,28], as such studies give useful information about this structure. These studies are motivated by the fact that the phenomenological electric properties

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of matter can be described in terms of polarization, magnetization and conduction, which can be interpreted in terms of the stand point of molecular theory [1–29]. The polarization (a complex quantity in itself) can be understood from the electric dipole moment per unit volume of the dielectric and dielectric relaxation studies. The molecular parameters associated with these studies are mainly, the electric dipole moment (μ), the relaxation time (τ), and the loss angle (δ), which can be determined experimentally, by measuring the real and imaginary parts of the complex dielectric constant. Similar studies on the liquid mixtures of the polar substances on one hand, or a polar solute in a non-polar solvent, or mixtures of these substances at different microwave frequencies and over a range of temperatures and concentrations give an idea about inter- and intra-molecular forces. On the other hand, such studies enable one to calculate thermodynamic parameters such as the change of activation energy for dipole orientation (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) of activation. Dielectric measurements carried out at a single microwave frequency over a temperature range at a single concentration of polar solute molecules and their mixtures in a non-polar solvent do also help in obtaining thermodynamic parameters, the size of the orienting unit, distribution parameters and the nature of the relaxation processes involved which in turn provide insight into inter- and intra-molecular forces. Particularly, this applies to the case of binary, ternary, etc. mixtures of polar solutes in pure liquid phase, or with different weight fractions of them in a non-polar solvent. Such studies help in drawing certain quantitative conclusions regarding their relaxation behaviour as to whether a single component is responsible for the observed microwave absorption or a cooperative phenomenon (average) by all the dipoles of the mixture contribute to it.

Schallamach [8], basing his observations on several binary mixtures of some polar liquids, found that the curve of dielectric constant showed a single dispersion region and the dielectric loss showed a single maximum if both the components of the mixture were either associated or unassociated liquids. Further, on the basis of the fact that the dielectric relaxation process is not directly connected with individual molecules, but is a disturbance of an appreciable region in the liquid [9–11], any liquid which is microscopically homogenous, albeit a mixture, would be characterized by a single relaxation time and further, a mixture of an associated and non-associated liquid which is not microscopically homogenous show two relaxation processes. Ritson [11] suggested that the relaxation of a mixture need not be the sum of the relaxation effects of each component, if independent of each other. An empirical equation for the calculation of the relaxation time of a binary mixture and its application is available in the literature [13,14] along with experimental work carried in recent past [15–23]. We here present the results of an experimental investigation carried out on typical systems, to quantitatively test some of the aforesaid assumptions.

With this in view, systematic dielectric measurements in a range of temperatures are carried out at a single microwave frequency on a single weight fraction in benzene of each of the four substituted benzenes, namely, *p*-fluorophenylacetonitrile, *p*-bromonitrobenzene, m-bromonitrobenzene and 2-chloro-6-fluoro-benzaldehyde and also on binary (1 : 1) mixtures of [*p*-2-chloro-6-fluoro-benzaldehyde + *o*-ethylphenol] and [*p*-fluorophenylacetonitrile + 2-*n*-butyl phenol] in benzene as solvent at different temperatures. The data on binary (1 : 1) mixtures of *p*-bromonitrobenzene + *m*-bromonitrobenzene are also presented from the earlier published work of the authors [1] along with present work and the results are discussed.

2. Experimental

An X-band microwave set-up (supplied by Mrs Scanner Ltd, UK) was used to measure the dielectric constant and dielectric loss at 9.98 GHz frequency. However, for microwave generation a gun oscillator supplied by Mrs Vidut Yantra Ltd, India operating in H_{01} mode was used instead of klystron (R-302). The frequency 9.98 GHz was fixed such that the intensity is maximum at the output. The technique adopted for these measurements is due to Roberts and Von Hippel [23], modified later by Dakin and Works [24].

For the evaluation of the relaxation time τ at a given temperature T, the expression for $\tan\delta$ (loss tangent) computed by the measured values of ε' (real part of the dielectric constant) and ε'' (imaginary part of the dielectric constant) were used as are employed by Whiffen and Thompson and others [22–24], in which it is assumed that the polar molecules under investigation conforms closely to Debye theory [12].

The thermodynamic parameters ΔG^*, ΔH^* and ΔS^* for the dielectric relaxation process are evaluated using Eyring's equation for the rate process in the following way:

$$\tau = (h/KT)\exp(\Delta G^*/RT) \qquad (1)$$

That is,

$$\Delta G^* = 2.303RT\log(\tau KT/h) \qquad (2)$$

With, $\Delta G^* = \Delta H^* - \mathrm{T}\,\Delta S^*$, one can write from equation (1),

$$\ln(\tau T) = \ln(h/K) + (\Delta H^* - T\,\Delta S^*)/RT = [\ln(h/K) - (\Delta S^*/R)] + [(\Delta H^{*)}/RT]$$

Thus, the slope of the linear plot between $\ln(\tau T)$ and $(1/T)$ gives $(\Delta H^*)/2.303R$.

With the value obtained for ΔH^*, ΔS^* can be calculated and ΔG^* is determined with the relation

$$\Delta G^* = \Delta H^* - T\,\Delta S^*.$$

3. Results and discussion

The measured values of ε' (real part of the dielectric constant) and ε'' (imaginary part of the dielectric constant) at various temperatures for four substituted benzenes are presented in table 1 (the experimental data is part of the unpublished PhD work of the first author, along with the values determined for τ. In this table are also presented the thermodynamic parameters obtained using relevant equations mentioned earlier. In table 2 the data for three binary mixtures are presented. The plots of $\log(\tau T)$ *versus* $(1/T)$ in case of *p*-fluorophenylacetonitrile and in the case of binary mixture of *p*-fluorophenylacetonitrile + 2-*n*-butylphenol are shown in figure 1 as an illustration.

It is seen that the τ values for the four samples under study in benzene as solvent, at specified temperature agree well with those obtained from Gopal Krishna [25] procedure at room temperature [2] quite within possible experimental errors, and this can be taken as a satisfactory justification for using the Debye equation for the evaluation of τ. Further, the plots of $\log(\tau T)$ *versus* $(1/T)$ given in figure 1 indicate that they are linear up to a certain value of the temperature, but beyond this a slight

Table 1. The measured values of ε' (real part of the dielectric constant) and ε'' (imaginary part of the dielectric constant) and determined parameters at various temperatures for samples under study.

T (K)	ε'	ε''	τ (ps)	ΔG^* Kcal mol^{-1}	ΔS^* Kcal mol^{-1}
p-Fluorophenylacetonitrile; $\Delta H^* = 1.22$ Kcal mol^{-1}; $\Sigma\,\Delta \mathrm{G}^*/n = 2.86$; $\Delta \mathrm{S}^*/n = -5.10$					
301	2.450	0.0199	20.1	2.89	−5.56
308	2.437	0.0202	16.6	2.86	−5.33
313	2.429	0.0198	14.0	2.81	−5.08
318	2.405	0.0191	12.5	2.79	−4.95
323	2.398	0.0188	12.0	2.82	−4.95
328	2.390	0.0185	11.5	2.84	−4.96
333	2.376	0.0182	11.3	2.89	−5.01
338	2.358	0.0178	10.8	2.91	−5.01
343	2.350	0.0175	10.4	2.94	−5.01
p-Bromonitrobenzene; $\Delta H^* = 2.40$ Kcal mol^{-1}; $\Sigma\,\Delta G^*/n = 2.46$; $\Delta S^*/n = -0.66$					
310	2.308	0.0213	16.5	2.88	−1.52
313	2.308	0.0180	9.1	2.54	−0.43
319	2.307	0.0145	6.5	2.39	0.06
323	2.297	0.0137	6.0	2.38	0.08
328	2.291	0.0121	5.2	2.33	0.24
333	2.276	0.0115	4.9	2.34	0.21
338	2.269	0.0113	4.8	2.37	0.11
343	2.246	0.0112	4.8	2.42	−0.04
m-Bromonitrobenzene; $\Delta H^* = 2.40$ Kcal mol^{-1}; $\Sigma\,\Delta G^*/n = 2.94$; $\Delta S^*/n = -1.64$					
308	2.382	0.0152	20.2	2.98	−1.86
314	2.381	0.0155	16.5	2.92	−1.64
319	2.373	0.0153	14.2	2.88	−1.50
323	2.368	0.0152	13.6	2.90	−1.53
328	2.367	0.0150	12.9	2.92	−1.58
333	2.359	0.0148	12.4	2.95	−1.63
338	2.348	0.0144	11.5	2.95	−1.62
343	2.346	0.0143	11.4	3.00	−1.74
2-Chloro-6-fluoro-benzaldehyde; $\Delta H^* = 3.22$ Kcal mol^{-1}; $\Sigma\,\Delta G^*/n = 2.78$; $\Delta S^*/n = 1.38$					
303	2.442	0.0393	22.3	2.98	0.81
308	2.438	0.0409	17.2	2.88	1.12
313	2.433	0.0409	16.6	2.92	0.99
318	2.427	0.0384	11.7	2.75	1.49
323	2.426	0.0363	10.2	2.71	1.59
328	2.424	0.0344	9.1	2.69	1.62
333	2.423	0.0326	8.3	2.69	1.62
338	2.402	0.0309	7.8	2.69	1.59
343	2.391	0.0294	7.2	2.69	1.56

curvature (not shown in the figure) in the graph can be noted as is expected on the basis of Eyring theory and as suggested by Whiffin and Thompson [22]. However, for the estimation of ΔH^* value, the slope of the linear portion of such plots are used in the present work. The τ value in each case of the solute molecule decreases as the temperature surrounding the dielectric medium increases. This is not unexpected on the basis of Debye theory, that τ is inversely proportional to the absolute temperature. This decrease in τ value with the increase in temperature can be explained on the basis of Eyring's theory of dielectric relaxation as a rate process.

In the light of this fact, in an ideal situation, the decrease in the value of τ is expected to be compensated by an increase in the value of temperature, so that a constant value of $\log(\tau T)$ results for any temperature and that only one value for each of the

Table 2. The measured values of ε' (real part of the dielectric constant) and ε'' (imaginary part of the dielectric constant) and determined parameters at various temperatures for three binary mixtures.

T (K)	ε'	ε''	τ (ps)	ΔG^* Kcal mol^{-1}	ΔS^* Kcal mol^{-1}
p-Bromonitrobenzene + *m*-bromonitrobenzene (1 : 1); $\Delta H^* = 1.17$ Kcal mol^{-1}; $\Sigma\,\Delta G^*/n = 2.74$; $\Delta S^*/n = -4.85$					
304	2.355	0.0142	18.0	2.86	−5.55
309	2.350	0.0143	16.5	2.86	−5.47
313	2.347	0.0129	10.6	2.63	−4.67
318	2.346	0.0124	9.7	2.63	−4.51
323	2.345	0.0123	9.5	2.67	−462
328	2.343	0.0121	9.3	2.71	−4.67
333	2.328	0.0119	9.1	2.74	−4.17
338	2.230	0.0118	8.9	2.78	−4.75
343	2.269	0.0110	8.3	2.78	−4.68
p-2-Chloro-6-fluoro-benzaldehyde + *o*-ethylphenol (1 : 1); $\Delta H^* = 2.47$ Kcal mol^{-1}; $\Sigma\,\Delta G^*/n = 2.70$; $\Delta S^*/n = -0.72$					
306	2.399	0.0324	23.9	3.06	−1.92
308	2.396	0.0346	16.6	2.86	−1.72
313	2.396	0.0309	10.2	2.61	−0.46
318	2.393	0.0294	9.3	2.61	−0.43
323	2.386	0.0281	8.6	2.61	−0.42
328	2.378	0.0269	8.0	2.61	−0.44
333	2.374	0.0258	7.6	2.62	−0.45
338	2.371	0.0248	7.1	2.63	−0.48
343	2.348	0.0242	7.0	2.66	−0.57
p-Fluorophenylacetonitrile + 2-*n*-butyl phenol (1 : 1); $\Delta H^* = 2.11$ Kcal mol^{-1}; $\Sigma\,\Delta G^*/n = 2.80$; $\Delta S^*/n = -2.16$					
305	2.398	0.0194	23.4	3.03	−3.03
308	2.395	0.0205	16.6	2.86	−2.44
313	2.388	0.0193	11.9	2.71	−1.91
318	2.385	0.0190	11.4	2.73	−1.97
323	2.379	0.0184	10.6	2.74	−1.96
328	2.361	0.0178	10.0	2.76	−1.97
333	2.357	0.0173	9.5	2.77	−1.99
338	2.345	0.0168	9.1	2.79	−2.02
343	2.326	0.0165	8.9	2.83	−2.11

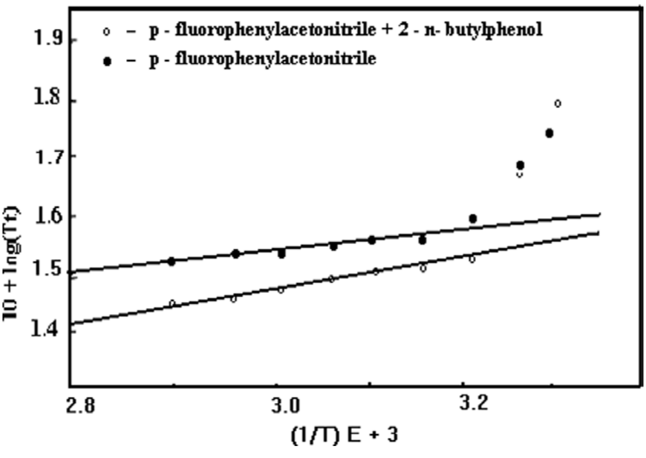

Figure 1. Plot of log $(T\tau)$ *vs.* $(1/T)$ of (*p*-fluorophenylacetonitrile + 2-*n*-butylphenol) and *p*-fluorophenylacetonitrile.

thermodynamic parameters, such as a change of activation energy for dipole orientation (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) of activation, can be specified. But in the present work, ΔG^* is calculated using equation (2) and ΔH^* from the slope of the plot (single value) of $\log(\tau T)$ *versus* $(1/T)$. This has probably resulted in fluctuations of the values of ΔG^* and ΔS^*, and hence an average value is specified for these two parameters for ease of comparison with such values for other molecules. In other words, if the decrease in the value of τ is fully compensated by an increase in temperature, which is an ideal behaviour, there would have been no fluctuation of this kind in the values of (ΔG^*), enthalpy (ΔH^*) and hence in entropy (ΔS^*).

As stated earlier, Eyrings equation for the rate process (dielectric relaxation) can be expressed in the form $\ln(\tau T) = ((\ln(h/k) - ((\Delta S^*)/R)) + CT)$. This is the equation of a straight line with slope $(\Delta H^*)/R$ and intercept $(\ln(h/k) - ((\Delta S^*)/R))$. Thus, both enthalpy ΔH^* and entropy ΔS^* (unique values) can be computed. Using these values the free energy of activation ΔG^* at various temperatures can be determined by the defining relation $\Delta G^* = \Delta H^* - T\Delta S^*$. Alternatively, the value of ΔH^* can be determined from the slope, while ΔG^* can be determined by the relation $\Delta G^* = 2.303\, RT \log(\tau kT/h)$ and ΔS^* by the earlier-mentioned defining relation. Here, any ambiguity in determining the intercept and hence ambiguity in ΔS^* may be avoided. However, it may be noted that these thermodynamic parameters may not have any special significance, except that they only indicate whether a highly ordered molecular arrangement is maintained in the activated state. Thus, the values of these parameters have the same merit of consideration when determined following either of these two methods.

It can be observed from table 1 that the enthalpies of activation ΔH^* are less than the corresponding values of free energies of activation, ΔG^*, thus leading to a negative entropy of activation ΔS^*. Whiffen and Thompson [22], Smyth *et al.* [26] and others [27–29] have explained the physical significance of such negative values. It is concluded that the sign is informative about the packing of the molecules when compared with the corresponding values of the other systems. This leads to the inference that smaller molecules in the configuration involved in a system in dipole orientation have an activated state of greater molecular order. Further, it may be noted that ΔG^* values are in phase with molecular weights as observed in earlier works.

The dielectric data on the three binary mixtures [*p*-2-chloro-6-fluorobenzaldehyde + *o*-ethylphenol]; [*p*-fluorophenylacetonitrile + 2-*n*-butyl phenol] and [*p*-bromonitrobenzene + *m*-bromonitrobenzene] in benzene studied are analyzed in a similar manner as for the single component solutions. Again the τ value of mixtures decreases as the temperature is increased. Taking the appropriate τ value out of the two possible values based on the equation $\tan\delta = [(\varepsilon' + 2)^2/\varepsilon'][4\pi CN\mu^2/27kT][\omega\tau/(1 + \omega^2\tau^2)]$, where the different terms have the same usual meaning and the individual values of polar components of the mixtures, for the molecules *p*-fluorophenylacetonitrile, *p*-bromonitrobenzene, *m*-bromonitrobenzene and 2-chloro-6-fluoro-benzaldehyde [2], the observed values of the mixtures at all temperatures tend to follow the average value of the component of the mixtures within possible experimental errors. This may be partially due to the fact that the individual τ values do not differ much from one another.

Following Schallamach [8], the mixtures *p*-2-chloro-6-fluoro-benzaldehyde + *o*-ethylphenol and *p*-bromonitrobenzene + *m*-bromonitrobenzene studied belong to the case of microscopically homogenous media while the second *p*-fluorophenylacetonitrile + 2-*n*-butyl phenol system containing associated and non-associated polar component can be assumed to belong to a microscopically inhomogenous medium so that one will be able to observe two absorption maxima. However, because of the closeness of the relaxation times of the molecules under study, although two peaks are expected to occur, they may not be resolved, thus giving a rather broad unresolved peak. In view of all these, the observed τ will possibly correspond to this seemingly single but unresolved peak and is expected to be rather close to the average of the component values as reported in our earlier work.

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