

Activation energy (ΔG^*), enthalpy (ΔH^*), and entropy (ΔS^*) of some indoles and certain of their binary mixtures

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Abstract Thermodynamic parameters, like, change of activation energy for dipole orientation (ΔG^*), enthalpy (ΔH^*), and entropy (ΔS^*) of activation in the case of binary-, ternary-, etc. mixtures of polar molecules in pure liquid phase or in dilute solution phase in a non polar solvent helps in drawing certain quantitative conclusions regarding their relaxation behavior 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. Dielectric relaxation behavior 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 a method of determining these quantities. Such an experimental investigation on verity of systems is necessary to draw quantitative conclusions regarding the system of the molecules which are not studied so as to examine if the results obtained are in favor or against the general conclusions already arrived at, in other 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 indoles, namely, 5-Bromoindole, 5-Fluoroindole, 2,3-Dimethylindole, 2,5-

Dimethylindole and on binary (1:1) mixtures of 2,5-Dimethylindole + 5-Bromoindole and 2,3-Dimethylindole + 5-Fluoroindole in benzene as solvent at different temperatures. The results are presented and discussed.

Keywords Dielectric relaxation · Enthalpy · Activation energy

Introduction

Studies involving dielectric measurements have become the basis of study of thermodynamic functions [1–4]. Dielectric measurements have been also been exploited to measure different thermodynamic functions through relaxation behavior of polar molecules in a pure liquid phase in dilute solutions with their mixtures at microwave frequencies. The range of temperatures a was given by the authors [5–12] and others [13–36]. Especially, study of the temperature variation of dielectric dispersion and dielectric loss of polar liquids and their dilute solutions in non-polar solvent at microwave frequency can yield valuable information regarding the structure of the molecule and the process of dipole orientation. Such studies on liquid mixtures of the polar substances in non-polar solvents at several microwave frequencies and over a range of temperatures and concentrations also give an idea about inter- and intra-molecular forces. Further, they enable one to calculate thermodynamic parameters such as change in activation energy for dipole orientation ΔG^* , enthalpy ΔH^* , entropy of activation ΔS^* , and the other temperature dependent parameters such as relaxation time τ , the distribution parameter α , and the dielectric constant at an infinitely high frequency. Smyth and his collaborators have previously carried out investigation on the variation of τ using a number of polar liquids and solutions. The values

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of τ for the pure liquid and also in solution are found to decrease with increasing temperature, which indicates an increase in uniformity of potential barriers hindering molecular rotation throughout the liquid. Smyth and his collaborators have suggested that expansion of the liquid may have reduced the effect of the environment on the orientation process. A change of temperature might alter the location of the molecules surrounding a particular orienting molecule or the particular molecule might orient itself in several ways depending on the distribution of internal energy.

However, dielectric measurements carried out at a single microwave frequency and a range of temperatures on a single concentration of polar molecule or their mixtures, in a non-polar solvent are also expected to give useful information regarding inter-, intramolecular forces, thermodynamic parameters, size of the orienting unit, distribution parameter, the nature of the relaxation process involved, etc., particularly, in the case of binary, ternary-, etc., mixtures of the polar molecules in pure liquid phase or in a nonpolar solvent. Such studies have helped in drawing certain quantitative conclusions regarding their relaxation behavior as to whether a single component is responsible for the observed microwave absorption or a co-operative phenomenon by all the dipoles on the mixture contribute to it. Binary liquid mixture, in which both the components are either associated or non-associated, exhibits a single relaxation time, whereas two distinct relaxation times are observed in mixtures in which one component is associated and the other is non-associated. Such studies also help in understanding the nature of the systems involved.

Although a good deal of work on the study of dielectric relaxation in relation to temperature of a variety of polar substances is reported in the literature, such studies still seem to be warranted on some other molecules, especially, heterocyclic compounds which are least studied, chosen in the present investigation. These studies are carried with a view to examine if the conclusions arrived are in favor or against the general conclusions. With this end in view, systematic dielectric measurements in a range of temperatures (299–343 K) are carried out at a single microwave frequency on a single weight fraction in benzene of each of the following pure organic molecules, namely, 5-Bromoindole, 5-Fluoroindole, 2,3-Dimethylindole, 2,5-Dimethylindole, and also on the binary mixture (1:1) of 2,5-Dimethylindole + 5-Bromoindole and 2,3-Dimethylindole + 5-Fluoroindole in benzene in the said temperature range. The result obtained are presented here and discussed.

Methods and experimental procedures

The phenomenon of dielectric relaxation can be viewed as the dipole actually rotating between two positions of

equilibrium, separated by a potential barrier. The dielectric relaxation time τ depends on this height of the potential barrier, a temperature-dependent constant, and the average time required by an excited molecule to rotate from one equilibrium position to the other. Postulating on the analogy between the processes of the dipole rotation and unimolecular chemical reactions, Eyring identified a relation with molar free activation energy ΔG^* . His theory leads to an expression for τ as

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

that is,

$$\Delta G^* = 2.303 RT \log(\tau K T/h) \quad (2)$$

With, $\Delta G^* = \Delta H^* - T\Delta S^*$, one can write from Eq. 1,

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

Thus, the slope of the linear plot between $\ln(\tau T)$ and $(1/T)$ gives $(\Delta H^*)/2.303R$. With obtained value of ΔH^* , ΔS^* can be calculated and ΔG^* can be calculated with the following relation

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

For the evaluation of the relaxation time τ at any 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) are used; as are employed by Whiffen and Thompson and others [20–23], in which it is assumed that the polar molecules under investigation conforms closely to Debye theory [27]. For the evaluation of τ from single concentration with frequency measurements, the following expression for loss tangent can be used as a fair approximation.

$$\tan\delta = \left[\frac{(\epsilon' + 1)^2/\epsilon'}{[\omega\tau/(1 + \omega^2\tau^2)]} \right] \left[\frac{(4\pi CN\mu^2)/(27VKT)}{[\omega\tau/(1 + \omega^2\tau^2)]} \right] \quad (1)$$

where all the quantities in the equation have their usual meaning explained earlier [5–9].

The X-band microwave set-up was used to measure the dielectric constant and dielectric loss at 9.98 GHz frequency. Mrs Scanner Ltd, England, supplied this microwave bench with all necessary parts used. However, for microwave generation, a gun oscillator supplied by Mrs Vidut Yantra Ltd, India operating in H01 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 was due to Roberts and Von Hippel [21], modified later by Dekin and Works [22]. The solvent benzene and the polar substances used in the investigation were stated to be of high purity by

Table 1 ϵ' and ϵ'' at different temperatures with the values of τ and the thermodynamic parameters ΔG^* , ΔH^* , and ΔS^* for 5-bromoindole, 5-fluoroindole, 2,3-dimethylindole, and 2,5-dimethylindole, single component systems in benzene

Compound	Temp/K	ϵ'	$\epsilon'' \times 10^3$	τ/ps	$\Delta G^*/\text{kcal/mole}$	$\Delta H^*/\text{kcal/mole}$	$\Delta S^*/\text{cal/mole/K}$
5-Bromoindole	303	2.350	18.71	26.1 (27.3)	2.867	2.445	-1.394
	308	2.346	19.36	22.6	2.874		
	313	2.339	19.69	18.6	2.881		
	318	2.331	19.16	14.9	2.888		
	323	2.324	18.24	12.7	2.895		
	328	2.316	17.28	11.2	2.902		
	333	2.303	16.21	10.0	2.909		
	338	2.297	15.55	9.4	2.916		
	343	2.289	14.72	8.6	2.923		
5-Fluoroindole	303	2.423	15.87	18.6 (20.5)	2.790	2.354	-1.438
	308	2.415	15.69	16.5	2.797		
	313	2.403	15.52	15.7	2.804		
	318	2.396	14.83	13.2	2.811		
	323	2.385	14.12	11.8	2.818		
	328	2.371	13.51	10.9	2.825		
	333	2.357	12.75	9.8	2.832		
	338	2.338	12.04	9.0	2.840		
	343	2.303	11.51	8.6	2.847		
2,3-Dimethylindole	303	2.364	49.88	22.3 (21.8)	2.915	2.487	-1.412
	308	2.351	50.07	20.9	2.922		
	313	2.344	50.39	18.6	2.929		
	318	2.326	49.54	16.4	2.936		
	323	2.319	48.93	15.5	2.943		
	328	2.307	47.06	13.5	2.950		
	333	2.294	45.19	12.2	2.957		
	338	2.285	42.27	10.6	2.964		
	343	2.271	40.42	9.9	2.971		
2,5-Dimethylindole	303	2.341	11.54	22.2 (19.9)	2.809	2.389	-1.385
	308	2.336	11.70	18.6	2.816		
	313	2.323	11.61	16.5	2.823		
	318	2.317	11.19	14.2	2.829		
	323	2.308	10.82	12.9	2.836		
	328	2.298	10.42	10.9	2.843		
	333	2.287	9.26	9.5	2.850		
	338	2.279	8.50	8.3	2.857		
	343	2.268	7.96	7.6	2.864		

the manufacturers and therefore, they were used directly in the work without any further purification.

Results and discussion

The high frequency dielectric parameters ϵ' and ϵ'' obtained at different temperatures along with the values of τ and the thermodynamic parameters ΔG^* , ΔH^* , and ΔS^*

for 5-Bromoindole, 5-Fluoroindole, 2,3-Dimethylindole, and 2,5-Dimethylindole, single component systems in benzene are presented in Table 1. Similar parameters for the two binary systems studied, namely, binary mixture (1:1) of 2,5-Dimethylindole + 5-Bromoindole and 2,3-Dimethylindole + 5-Fluoroindole are given in Table 2. The values of the single component systems determined at room temperature, which are published already elsewhere [12], are included in parenthesis for the sake of ready

Table 2 ϵ' and ϵ'' at different temperatures with the values of τ and the thermodynamic parameters ΔG^* , ΔH^* , and ΔS^* for binary mixture (1:1) of 2,5-dimethylindole + 5-bromoindole and 2,3-dimethylindole + 5-fluoroindole systems in benzene

Compound	Temp/K	ϵ'	$\epsilon'' \times 10^3$	τ/ps	$\Delta G^*/\text{kcal/mole}$	$\Delta H^*/\text{kcal/mole}$	$\Delta S^*/\text{cal/mole/K}$
5-Bromoindole + 2,5-dimethylindole	303	2.339	25.79	21.7	2.866	2.430	-1.438
	308	2.331	26.01	18.6	2.873		
	313	2.327	25.75	16.3	2.880		
	318	2.319	24.85	14.0	2.887		
	323	2.331	23.96	12.6	2.894		
	328	2.305	23.98	11.8	2.901		
	333	2.294	22.71	11.3	2.908		
	338	2.283	21.92	10.6	2.915		
	343	2.272	21.44	10.3	2.923		
	5-Fluoroindole + 2,3-dimethylindole	303	2.382	25.08	18.6		
308		2.373	24.70	15.9	2.731		
313		2.359	23.25	13.2	2.738		
318		2.341	22.09	11.6	2.745		
323		2.328	20.76	10.3	2.752		
328		2.316	19.43	9.2	2.759		
333		2.305	18.12	8.3	2.766		
338		2.291	16.77	7.5	2.773		
343		2.278	15.56	6.8	2.780		

reference. The relevant plots used for the determination of the thermodynamic parameters are shown in Figs. 1, 2, and 3.

It is noticed from the results in table that the observed values at 303 K in each case are in fair agreement with that of its room temperature value and thus serves as reference value at this temperature. The subsequent values of different elevated temperatures decrease and the rate of decrease is different for different molecules but for the two dimethyl indole isomers, they are nearly equal. This indicates that the decrease in the value of τ as temperature increases does not depend on the location of dipole in the case of isomeric molecules. Further, in the light of Debye equation for τ , namely, $\tau = 4\pi\eta a^3/kT = A (\eta/T)$, where A can be treated as constant provided that the shape and size of molecule does not change while heating, that is, one can say that the change in the value of the microscopic viscosity of the medium for isomeric molecules with temperature may be in equal amount so that the same rate of change in the τ values results. Contrary to this, in the case of non-isomeric media, the change in the value τ as the temperature is changed depends on the nature and location of dipoles and the structure (rigid or non-rigid) of the molecule and hence non-equal values for the rate of change in which temperature may not be unexpected.

It may be emphasized that while assigning the τ value at different temperatures in the molecules, it is implicit that the general behavior obeyed is that τ is inversely proportional to absolute temperature, which is essence of the

Debye relation between τ and T . In the present study, values for all the molecules studied in benzene at the specified room temperature agree well with those obtained from two frequency-single concentration methods at room temperature quite within possible experimental errors. Further, the plots of $\log(T\tau)$ versus $1/T$ indicate that they are linear. The thermodynamic parameters estimated by the values of the slopes of the linear portion of such plots are found to give physically meaningful values. All these considerations seem to lead to a conclusion that there is a satisfactory justification for using the Debye equation for the evaluation τ at least in the case of some molecules. It is noticed from the table that in all the cases the enthalpies of activation are less than the corresponding free energies of activation, thus leading to negative values for the entropy of activation. It is suggested by several workers that the sign of ΔS^* plays an important role in drawing conclusions about the packing of the molecules when compared with the corresponding values for other systems. However, these authors further suggest that in the absence of sufficient information regarding the temperature dependence of these values, may not have any special significance but may indicate that at least for these molecules the configurations involved in dipole orientation have an activated state of greater local molecular order. In view of these considerations, the observed values of ΔG^* , ΔH^* , and ΔS^* may be treated to indicate qualitative trends if not quantitative.

It has been shown by Schallamach [13] and other workers that binary liquid mixture, in which both the

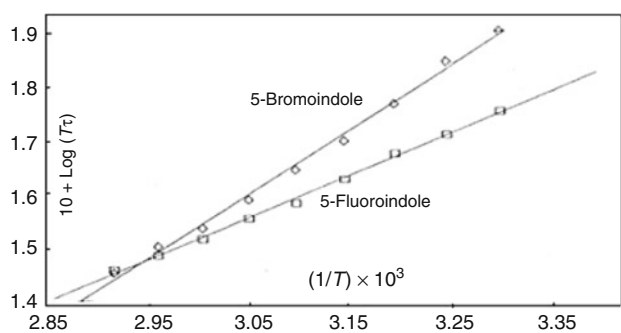


Fig. 1 Plots for determination of ΔH^* of 5-bromoindole and 5-fluoroindole

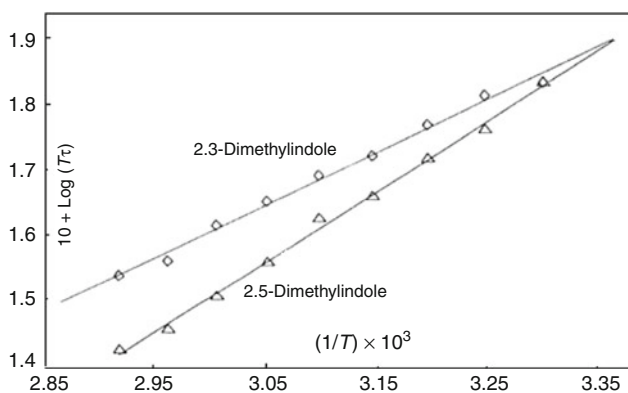


Fig. 2 Plot for determination of H^* of 2,3-dimethyl- and 2,5-dimethyl-indole

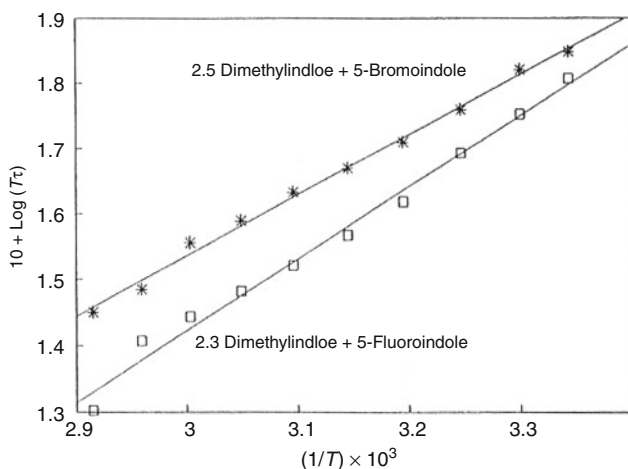


Fig. 3 Plots for determination of H^* of two binary mixtures

components are either associated or non-associated, exhibits a single relaxation time, whereas two distinct relaxation times are observed in mixtures in which one component is associated and the other is non-associated. When a dipolar mixture is studied in dilute solution of a non-polar solvent, the complex dielectric constant can be

represented by a simple sum of the complex dielectric constant of the individual components. If there happens to be an association or complex formation in the mixture, the value of complex dielectric constant of the system will roughly give an idea about the type of complex species that are present in the mixture. 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, so that any liquid which is microscopically homogeneous, even if a mixture, would be characterized by a single relaxation time, Schallamach [13] concluded that a mixture of two associated- or non associated liquids may be treated as microscopically homogeneous and is expected to show a single relaxation process, while a mixture of a associated- and a non-associated liquid, which is not microscopically homogeneous shows two relaxation processes. A review work by Coffey [1] suggests that the relaxation of a mixture need not be the sum of the relaxation effects, which each component would have if independent of the other.

The two binary mixture systems studied in the present study have their individual components as non-associated nature. Thus, they belong to the case of two non-associated components exhibiting microscopically homogeneous media. Further, the τ values at room temperature of the polar components forming the mixture in benzene do not differ well outside the experimental errors, e.g., 22.3, 18.7 ps for 2,3-dimethyl indole and 5-fluoro indole respectively and 22.3, 26.1 ps for 2,5-dimethyl indole and 5-bromoindole respectively at the same temperature of 303 K. Following Schallamach it is hardly possible to observe two separate absorption peaks for the mixtures studied in view of the nearness of relaxation times of the individual components forming the mixture and also due to certain limitations in the experimental conditions of these measurements in the present study, namely, single frequency, and narrow range of temperature (far removed from the boiling temperature of the solvent benzene). In other words, the individual components of the mixture are unable to maintain their identity during rotation but the observed absorption results due to cooperation phenomenon. Thus, the observed τ may possibly correspond to this seemingly single but unresolved peak and is expected to be rather close to the average of the component values.

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