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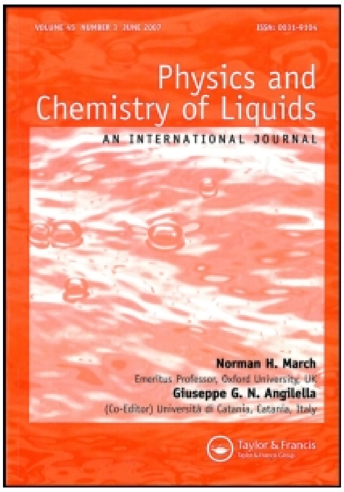

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Thermodynamics of *H*-Bond Through Dielectric Data Analysis

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Thermodynamics of *H*-Bond Through Dielectric Data Analysis

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The dielectric measurements on the mixtures of benzaldehyde with phenol and cresols as well as of acetophenone with *n*-butylalcohol and phenol in carbontetrachloride have been made in the temperature range (290–318)K. The relaxation time of the complexed species have been calculated using Higasi *et al.* method. With the help of the equation proposed previously in one of our earlier papers, the equilibrium constants along with thermodynamical parameters for association process have been evaluated using different values of constants A and B. The fairly good agreement between the calculated values of equilibrium constant (K) and its literature values shows the applicability and reliability of the proposed equation and also the importance of the need for a detailed study in this direction.

INTRODUCTION

The dielectric relaxation study have been utilised by many workers[1–4] to provide important information regarding the interaction between proton donor and proton acceptor molecules in ternary mixtures having an inert component as a solvent. In general, to evaluate the equilibrium constant of complexed species, the concentrations of all the three component (proton donor, proton acceptor and complex) molecules have to be determined somehow.

A different approach to evaluate the concentration values of all the com-components in equilibrium condition and thus the equilibrium constant of 1:1 hydrogen bonded complex with the help of the study of dielectric relaxation only at single microwave frequency was proposed by the authors[5] provided the dipole moment values for individual components and of the complex molecule are known. Another attempt[6] was made to calculate the equilibrium constant without considering the dipole moment of the complex, the concentration values. Thus latter approach has been made by establishing a relationship between the free energy of activation for dipolar rotation process (ΔG_ε) and the free energy of activation for association process (ΔG^0), which enabled us to calculate (K) at varying temperatures. This further leads to the determination of the thermodynamical energy parameters by simply analysing the dielectric measurements using single frequency concentration variation method of Higasi, Koga and Nakamura. To check the validity of the approach, further study[7] has been made to evaluate the equilibrium constant (K) and the thermodynamical parameters on complexes of some acetates with *o*-cresol as proton donor in the temperature range of (298–322) K.

With a view to extend the applicability of the earlier proposed equation, attempt has been made through the present study to evaluate the equilibrium constant (K) of benzaldehyde complexes with phenol and cresols and of acetophenone complexes with phenol and *n*-butyl alcohol as proton donors, individually. In the present study the linear relationship between ΔG^0 and ΔG_ε gives the values of constants A and B as 0.2 and 3.25 K cal/mole, quite different to the previously[6] determined value of $A(=0.4)$ and $B(=4.0$ K cal/mole). The different values of A and B provide the important information that these constants are not universal constants. A and B are characteristic parameters depending not only on the type of functional group and the structural configuration of the corresponding complexed species as was expected previously, but also on hydrogen bond length, packing of the molecules and other physical parameters which may have different values for the same type of functional group.

THEORY

Eyring's rate process theory[8] describes that the free energy of activation for dipolar rotation process (ΔG_ε), may be given by:

$$\Delta G_\varepsilon = 2.303RT \log \tau \cdot \frac{kT}{h} \tag{1}$$

Simultaneously, for the association process, the standard free energy change ΔG^0 is related with the equilibrium constant (K) as:

$$\Delta G^0 = -2.303RT \log K \tag{2}$$

The relationship between ΔG_ε and ΔG^0 is linear and the plot between these two results in a straight line as found earlier.[6] Hence,

$$\Delta G_\varepsilon = A \cdot \Delta G^0 + B \tag{3}$$

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where "A" represents the slope of the straight line and "B" is the intercept by the straight line on ΔG_ε axis. Introducing Eqs. (1) and (2) in Eq. (3) we obtain the final equation relating K with the dipolar rotational relaxation time as

$$\log \tau \cdot \frac{kT}{h} + \log K^{A} = \frac{B}{2{,}303RT} \tag{4}$$

To find the values of "A" and "B" for present systems, the values of ΔG_ε and ΔG^0 have been taken from Table IV which were calculated using the relaxation time values of Table II and the literature K values respectively. Thus the values of A and B have been found as 0.2 and 3.25 Kcal/mole Figure 1 which are quite different from the previously determined values. Having determined A and B, K at different temperatures for the same systems has been evaluated to determine further the energy parameters for association process by utilizing the known values of τ, A and B.

Likewise, for the dipolar rotation process, if ΔH^0 represents standard enthalpy change between the enthalpies of formation of products and reactants and ΔS^0 the entropy change of the same, then:

$$2.303 \log \mathrm{K} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{5}$$

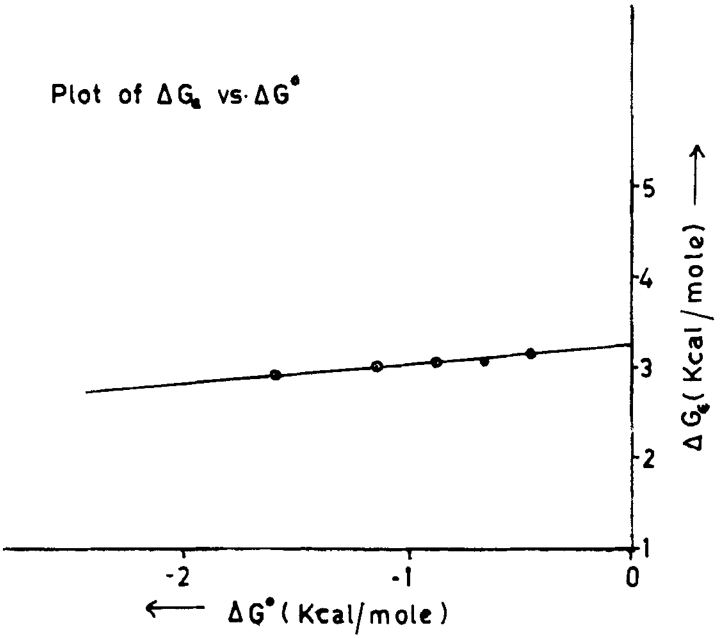

FIGURE 1

since

$$\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0 \quad (6)$$

Here, ΔH^0 is the slope of the straight line log K *vs.* $1/T$plot, ΔG^0 is determined using (2), and hence ΔS^0 by means of Eq. (6).

EXPERIMENTAL

The experimental part of the work essentially involves the dielectric constant measurements at different frequencies (statis, microwave and optical) as well as of dielectric loss measurements at 9.8 GHz frequency at different temperatures of various solutions containing different concentrations of the complexed system. The details about the experimental technique and the method of evaluating the slopes a_0, a', a'' and a_∞ have been reported in our

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TABLE I

Slope values for all ternary systems under investigation

System	Temp. (K)	a_0	a'	a''	a_∞
Benzaldehyde + Phenol	290	14.00	4.80	6.00	0.27
	299	12.75	5.16	5.87	0.25
	308	12.08	5.70	5.69	0.25
	318	11.18	6.21	5.21	0.21
Benzaldehyde + *O* cresol	290	11.80	4.01	4.15	0.42
	299	10.76	4.28	3.97	0.30
	308	9.40	3.95	3.93	0.27
	318	8.85	4.47	3.65	0.24
Benzaldehyde + *m*-cresol	290	13.33	4.00	4.71	0.40
	299	14.00	4.79	5.51	0.37
	308	12.22	4.74	4.91	0.27
	318	9.90	4.90	4.02	0.25
Benzaldehyde + *p*-cresol	290	13.00	4.00	4.21	0.43
	299	11.59	4.17	4.10	0.43
	308	10.62	4.66	3.87	0.41
	318	—	—	—	—
Acetophenone + Phenol	290	15.09	7.11	4.70	0.12
	299	14.05	6.95	4.54	0.05
	308	12.86	6.88	4.44	0.00
	318	11.43	6.67	4.00	0.00
Acetophenone + *n*-butyl alcohol	290	16.61	8.00	4.17	−0.33
	299	15.00	7.86	4.00	−0.33
	308	12.73	7.14	3.53	−0.32
	318	11.67	7.00	3.16	−0.29

earlier papers.[9–11] The slope values have been utilised for determining the different relaxation times and also for getting detailed information about the association phenomenon using the proposed equation.

RESULTS

The slope values (a_0, a', a'' and a_∞) for all the six systems are reported in Table I. The relaxation time values determined using Higasi[12] and Higasi *et al.*[13] method along with the free energy of activation for dipolar rotational process (ΔG_ε) have been reported in Table II. The equilibrium constant for association process i.e., the association constant (K) as well as the thermodynamical energy parameters for the corresponding process for complexed species have been given in Table III. Table IV, includes ΔG^0 and ΔG_ε values for graphical treatment primarily.

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TABLE II

Relaxation times evaluated using Higasi and Higasi *et al.* method along with distribution parameter and free energy of activation for dipolar rotational process

System	Temp. (K)	$\tau_{(1)}$ ps	$\tau_{(2)}$ ps	$\tau_{(0)}$ ps	α	$\tau_{(OH)}$ ps	G_ε (K cal/mole)
Benzaldehyde + Phenol	290	21.5	24.9	23.1	0.04	24.1	2.91
	299	19.4	21.0	20.2	0.02	20.3	2.92
	308	17.0	18.2	17.6	0.05	17.7	2.93
	318	14.1	15.5	14.8	0.03	14.7	2.95
Benzaldehyde + *o*-cresol	290	18.8	30.5	24.0	0.14	28.3	3.03
	299	16.3	26.5	20.8	0.15	23.2	3.05
	308	15.2	22.5	18.9	0.08	20.7	3.06
	318	14.0	19.5	16.5	0.10	16.6	3.09
Benzaldehyde + *m*-cresol	290	21.3	32.2	26.2	0.12	30.9	3.06
	299	20.3	27.2	23.5	0.09	25.7	3.07
	308	16.8	24.0	22.6	0.10	22.6	3.10
	318	14.0	20.2	16.8	0.12	18.9	3.12
Benzaldehyde + *p*-cresol	290	19.2	34.7	25.8	0.17	33.0	3.10
	299	17.8	29.4	22.2	0.15	26.7	3.12
	308	14.8	25.0	19.2	0.16	20.9	3.13
	318	—	—	—	—	—	—
Acetophenone + Phenol	290	10.9	29.3	17.9	0.30	24.0	3.00
	299	10.7	25.4	16.5	0.27	17.2	3.03
	308	10.5	21.9	15.1	0.23	14.4	3.05
	318	9.7	19.3	13.7	0.21	12.2	3.09
Acetophenone + *n*-Butylalcohol	290	8.1	33.5	16.5	0.42	17.0	3.08
	299	7.9	29.0	15.2	0.39	13.6	3.11
	308	7.7	25.7	14.1	0.36	11.5	3.15
	318	7.0	24.0	13.0	0.36	9.5	3.23

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TABLE III

Equilibrium constant values along with thermodynamical parameter for association process of all systems

Systems	Temp. (K)	K(1/mole)	$-\Delta H^0$ (K cal/mole)	$-\Delta G^0$ (K cal/mole)	$-\Delta S^0$ (cal/mole)
Benzaldehyde + Phenol	290	19.03	3.84	1.71	7.34
	299	16.47		1.68	7.22
	308	13.13		1.59	7.31
	318	10.90		1.52	7.30
Benzaldehyde + *o*-cresol	290	6.90	4.30	1.12	10.96
	299	5.15		0.98	11.10
	309	4.55		0.93	10.93
	318	3.46		0.79	11.03
Benzaldehyde + *m*-cresol	290	5.26	3.69	0.96	9.40
	299	4.52		0.90	9.33
	308	3.29		0.73	9.61
	318	2.89		0.68	9.47
Benzaldehyde + *p*-cresol	290	3.62	3.19	9.76	8.41
	299	3.06		9.73	8.43
	308	2.68		9.64	8.34
	318	—		—	—
Acetophenone + Phenol	290	8.43	5.18	1.24	13.59
	299	6.36		1.11	13.61
	308	5.20		1.02	13.51
	318	3.64		0.82	13.71
Acetophenone + *n*-butyl alcohol	290	4.32	9.21	0.85	28.83
	299	3.28		0.71	28.43
	308	2.34		0.52	28.20
	318	1.22		0.13	28.56

TABLE IV

Equilibrium constant values of literature, calculated and data for determining constants A and B

Complex	$K_{(\text{Kpted})}$	ΔG^0 (K cal/mole)	ΔG_ε (K cal/mole)	$K_{(\text{Calcd.})}$
Benzaldehyde + Phenol	13.16[15]	−1.59	2.93	13.13
Benzaldehyde + *C*-cresol	4.08[15]	−0.87	3.06	4.55
Benzaldehyde + *p*-cresol	2.50[15]	−0.56	3.13	2.68
Acetophenone + Phenol	6.85[21]	−1.14	3.03	6.36
Acetophenone + *n*-butyl alcohol	2.10[16]	−0.46	3.15	2.34

DISCUSSION

According to some workers[4,14] the distribution parameter of complex molecule is a measure of rigidity or flexibility of complexed species. For phenol and benzaldehyde system the low values of α can be interpreted on the basis that *H*-bond is stronger and no free rotation of individual component is possible about the *H*-bond axis. The values of distribution parameter for benzaldehyde complexes follows the order benzaldehyde + phenol< benzaldehyde + *m* cresol < benzaldehyde + *c*-cresol < benzaldehyde + *p*-cresol generally, following thus the reverse order of acidity indicating that with higher acidic strength relative to the same base, more rigid complex is formed. The distribution parameter values for acetophenon + phenol complex is less than of acetophenone + alcohol which is in agreement with the previous argument again, as alcohol has less proton donating strength than that of phenol, thus indicating the weak association for acetophenone + alcohol complexes and the association of highest strength for phenol + benzaldehyde complex. This is in agreement with the literature value of equilibrium constant of 13.16[15] at 35°C for phenol + benzaldehyde and 2.10[16] at 30°C for alcohol + acetophenone complex, while the equilibrium constant values for the rest of the four systems lie between these two limits in the temperature region (26–35)°C.

Wherever much lower value of $\tau_{(1)}$ and $\tau_{(2)}$ occurs it may correspond to the dielectric relaxation time of individual components as in the case of acetophenone complexes or simply to the sum of relaxation times of individuals altogether as in the case of complexes of benzaldehyde with cresol. Thus the lower value of $\tau_{(1)}$ pertains to the relaxation times of individual components and $\tau_{(2)}$ to complex molecule.

At all the temperatures chosen for the present study, the relaxation time $\tau_{(2)}$ for benzaldehyde complexes with phenol < with *o*-cresol < with *m* cresol < with *p* cresol i.e., this exactly follows the trend of individual species as relaxation time of phenol < *o*-cresol < *m*-cresol < *p*-cresol. For the rest of the two complexes relaxation time $\tau_{(2)}$ for Acetophenone with *n*-butyl alcohol > with phenol though the latter is heavier. This is in accordance with the view that the phenol system is compact while the former one is more elongated due to linear chain of *n*-butyl alcohol and also has greater possibility of the formation of dimer or trimer molecules which has to face greater hindrance in rotation process along *H*-bond axis and hence is responsible for high relaxation time.

Except *m*-cresol with benzaldehyde, the remaining three benzaldehyde complexes have their equilibrium constant 13.16, 4.55 and 2.68 at 35°C, having parallelism with the acidity of phenol > *o*-cresol > *p*-cresol. Similarly, for acetophenone + phenol system K is 6.36 at 26°C for second complex of

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acetophenone with the alcohol is 3.28 following the exact order as phenol has larger proton donating tendency then of *n*-butylalcohol. The anomaly presently found in the case of *m* cresol + benzaldehyde system is that K is 3.92 which is less than of *o*-cresol + benzaldehyde system at corresponding temperature though *m*-cresol is a litter stronger acid than *o*-cresol. This larger stability of *o*-cresol + benzaldehyde system than to *m*-cresol + benzaldehyde system might be due to the greater heat of formation of the former as has been observed from Table III. Such type of anomaly has been observed earlier[18] also regarding larger anomalous stability of *β*-naphthol complex to *α*-naphthol complex of amine. Hence the strength of *H*-bond though depends on relative acidic and basic strength of interacting components, but is simultaneously dependent on the structural configuration including the spatial arrangement as Sutton and his coworkers suggested that K does not exactly follow the ionisation constant of acids. Due to the greater number and complexity of molecular species found in the complex systems the experimental results are difficult to interpret and therefore consistantly demand a detailed study in this direction.

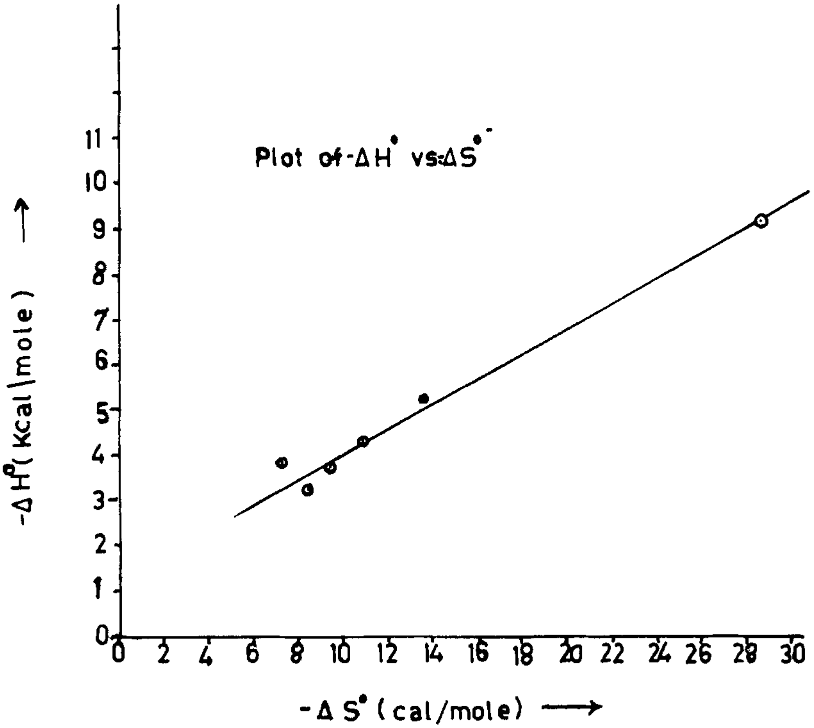

FIGURE 2

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The determined equilibrium constant values have been found to decrease regularly with increasing temperature favouring Lechatelierts principle as at higher temperature, larger K.E. tends to weaken the H-bond and to break the polar species held together through H-bond.

The thermodynamic parameters for association process provide important information regarding the association mechanism. The free energy of activation for association process ΔG^0 exactly follows the order of equilibrium constant. The appreciable negative values of ΔG^0 suggests that the reaction is going towards product i.e., favouring association mechanism between opposite polar species. The negative ΔH^0 values indicate the exothermic nature of chemical reaction i.e., of the present association processes. The negative values of ΔS^0 account for that the product state is more ordered than the states of reactants. The observed entropies are in agreement with the results of Clarks *et al.*,[18] that higher the entropy contribution, weaker would be the H-bond strength.

The presently evaluated values of ΔH^0 and ΔS^0 have been observed to produce a linear variation of entropy with the heat of association (Figure 2) supporting the linear relationship between them as suggested by many workers.[18–20]

The ΔH^0 value has been found maximum ($\Delta H^0 = 9.21$ Kcal/mole) for the acetophenone + n-butyl alcohol, though it is very weak complex. It may be presumed that this ΔH^0 value corresponds to the trimer of this complex having 3.07 Kcal/mole for monomer. The tendency for the formation of dimer or trimer is more for aliphatic alcohols than phenol.

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