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On the Determination of Equilibrium Constant and Thermodynamic Parameters for the Association Process of Hydrogen Bond Complexes Using Relaxation Parameters

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A dielectric study of H-bond complexes of three acetates namely ethyl acetate, butyl acetate, and benzyl acetate with the proton donor (O-Cresol) has been made. The equilibrium constant and the thermodynamic parameters for the association process as well as the dielectric relaxation process have been determined from the dielectric data using an equation, proposed in our earlier paper. The results obtained being in agreement with the literature values thus support the validity of the proposed equation.

INTRODUCTION

The study of hydrogen bond complexes is of significance from theoretical as well as experimental point of view. Magee and Walker¹ proposed that study on the complex formation can be made by investigating the relaxation time and distribution parameter. Determination of the relaxation time, dipole moment and distribution parameter were utilized to ascertain the behaviour of the complexed species in several systems.^{2,3} Saxena *et al.*⁴ while studying the complex formation of pyridine and quinoline with phenol correlated the relaxation time with the size and the shape of the complexed species. It may thus be suggested that dielectric relaxation study providing for the determination of the thermodynamical parameters, may be utilised for

understanding the complex formation, of a proton donor with an acceptor and its behaviour under applied field.

In general, an estimate of the equilibrium constant (K) of a complexed specie has been made from the known concentrations of the component molecules. An attempt was made to determine the equilibrium constant of a complexed system using the relaxation time data. In the process, a relationship between free energy of activation for dipolar rotation (ΔG_e) and free energy of activation for association process (ΔG^0) was proposed and the equilibrium constant and thermodynamic parameters of some sulphoxides and phenol were determined. The results were reported in our earlier paper.⁵

With a view to establish the applicability of the proposed equation for determining the 'K' and thermodynamical parameters, measurements were extended on complexes of ethyl acetate, butyl acetate and benzyl acetate with O-Cresol as proton donor in the temperature range of 298–322 K. The results obtained have been found to be in agreement with the reported literature values and thus support the validity of the relation proposed earlier.

THEORY

The Eyring's rate process theory⁶ considers the dipole rotational process as analogous to the chemical rate process. If 'A' be a proton donor molecule and 'B' the acceptor, both would contribute to form an activated complex 'AB', with minimum required amount of energy available for the reaction:
 $A + B \rightarrow AB$.

Thus, Eyring proposed a relation between specific reaction rate (k') and free energy of activation (ΔG_e) as:

$$k' = \left(\frac{kT}{h} \right) \exp. \left(- \frac{\Delta G_e}{RT} \right) \quad (1)$$

where ΔG_e , represents the difference of free energies of activated and normal state. 'k' was defined as the number of times per second the dipole acquires sufficient energy to cross over the potential barrier from one equilibrium position to the other and related with the relaxation time ' τ ' as

$$\tau = \frac{1}{k'} \quad (2)$$

Hence, combining (1) and (2)

$$\tau = \frac{h}{kT} \exp \frac{\Delta G_e}{RT} \quad (3)$$

The free energy of activation for dipole rotation ΔG_e , thus given by

$$\Delta G_e = 2.303RT \log \tau \frac{kT}{h} \quad (4)$$

may be determined.

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

$$\Delta G^0 = -2.303RT \log K \quad (5)$$

Some of the experimental results calculated using known parameters from Eq. (4) and (5) suggest a linear relationship between ΔG_e and ΔG^0 exhibiting a linear relation of the type

$$\Delta G_e = A \cdot \Delta G^0 + B \quad (6)$$

of which, the slope gives the value of 'A' and the intercept on y-axis provides the value of B.⁵

In Eq. (6); substituting, values of ΔG_e from (4) and ΔG^0 from Eq. (5) we obtain an equation relating the equilibrium constant and the relaxation time for dipolar rotation of the system

$$\log \tau \frac{kT}{h} + \log K^A = \frac{B}{2.303RT} \quad (7)$$

Having previously determined numerical values of A and B (A = 0.4 and B = 4.0 Kcal/mole); the equilibrium constant 'K' may be evaluated by simply having the knowledge of τ value.

If ΔH^0 represents standard enthalpy change between the enthalpies of formation of products and reactants; ΔS^0 the entropy change of the same, Eq. (7) reduces to the form.

$$2.303 \log K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (8)$$

$$\text{as } \Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (9)$$

Thus ΔH^0 being the slope of the straight line, $\log K$ Vs $1/T$ and ΔG^0 having been determined using equation (5), ΔS^0 may be evaluated from the ΔH^0 and ΔG^0 data.

EXPERIMENTAL

The experimental technique and method of evaluating the slopes, a_0 , a' , a'' and a_∞ have been reported in our earlier papers⁷⁻⁹. These values of the slopes have been used to compute the relaxation parameters using Higasi¹⁰ and Higasi *et al.* method.¹¹ The thermodynamical parameters reported here correspond to (τ_2) values of the relaxation data.

RESULTS

The slopes a_0 , a' , a'' and a_∞ of all the complexed species are given in Table 1. The relaxation times, distribution parameter (α) and the free energy of activation for dipolar rotational process (ΔF_c) have been reported in Table II. The thermodynamical parameters for association process and the association equilibrium constant for all the three systems have been given in Table III.

TABLE I
The values of slopes a_0 , a' , a'' and a_{00} for all three systems

Systems	Temp. (K)	a_0	a'	a''	a_{00}
Ethyl acetate + O-cresol	298	7.50	3.33	3.08	0.18
	306	5.66	2.87	2.50	0.12
	314	5.14	2.97	2.14	0.11
	322	4.05	2.50	1.70	0.10
Butyl acetate + O-cresol	298	5.14	1.97	2.23	0.07
	306	5.71	2.52	2.59	0.10
	314	3.80	1.90	1.71	0.03
	322	4.50	2.50	2.05	0.17
Benzyl acetate + O-cresol	298	5.93	2.44	2.00	0.30
	306	4.02	2.03	1.26	0.36
	314	5.61	3.08	1.80	0.31
	322	5.57	3.30	1.82	0.33

TABLE II
Relaxation times, distribution parameter and the free energy of activation

System	Temp. (K)	$\tau_{(1)}$ ps	$\tau_{(2)}$ ps	$\tau_{(0)}$ ps	τ_{OH} ps	α	(ΔF_c) Kcal/mole
Ethyl acetate + O-cresol	298	15.9	22.0	18.7	19.5	0.10	2.9
	306	14.8	18.1	16.4	16.4	0.07	2.9
	314	12.2	16.5	14.2	13.6	0.09	2.9
	322	11.5	14.8	13.1	12.4	0.08	3.0
Butyl acetate + O-cresol	298	19.0	23.0	20.9	21.9	0.06	3.0
	306	17.4	20.0	18.7	19.0	0.04	3.0
	314	14.9	18.1	16.4	16.4	0.06	3.0
	322	13.4	16.2	14.7	14.9	0.03	3.0
Benzyl acetate + O-cresol	298	15.2	28.3	20.7	24.0	0.19	3.1
	306	12.1	26.1	17.9	19.1	0.24	3.1
	314	10.5	22.9	15.5	15.0	0.22	3.1
	322	9.9	20.3	14.2	12.9	0.22	3.2

TABLE III

Equilibrium constant (K) and thermodynamic parameters of association process

System	Temp. (K)	K (lit/mole)	ΔH^0 (Kcal/mole)	ΔG^0 (Kcal/mole)	ΔS^0 (cal/mole)
Ethyl acetate + O-cresol	298	88.7	-4.2	-2.7	-5.0
	306	82.9		-2.7	-4.7
	314	69.9		-2.7	-4.8
	322	56.2		-2.6	-4.8
Butyl acetate + O-cresol	298	79.3	-5.4	-2.6	-9.3
	306	67.8		-2.6	-9.1
	314	54.2		-2.5	-9.2
	322	44.9		-2.5	-9.1
Benzyl acetate + O-cresol	298	47.3	-5.1	-2.3	-9.3
	306	34.9		-2.2	-9.5
	314	30.0		-2.1	-9.3
	322	25.7		-2.1	-9.2

DISCUSSION

The dielectric relaxation studies of acetates in dilute solutions have been made by many workers.^{9,12,13} The relaxation parameters have been interpreted in terms of the structural configuration of the molecules. It is observed (Table I) that the first two complexed species i.e.; ethyl and butyl acetate with O-Cresol, yield low value of distribution parameter (α). The system consisting of benzyl acetate and O-Cresol gives rise to comparatively high ' α ' value. This exhibits the rigid behaviour of the former two complexed systems where as the latter exhibits a flexible behaviour in dilute solution. This would indicate a weak association between the constituent molecule, thus would be expected to yield low value of equilibrium constant.

The most probable relaxation time τ_{OH} calculated by Higasi⁷ method has been found to be slightly longer than $\tau_{(0)}$, the average relaxation time, obtained by Higasi *et al.*¹¹ method. Both are in close agreement with $\tau_{(2)}$, the molecular relaxation time. This indicates that τ_{OH} represents the relaxation time of the complexed specie, resulting due to phenomenon of association. The relaxation time is found to decrease with rise in temperature as have been observed in earlier studies.

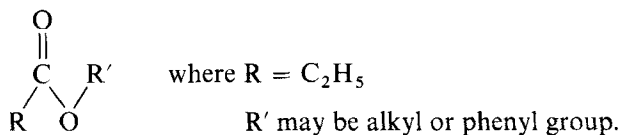
The equilibrium constant (K), for association has been found to decrease with increasing temperature. This is in agreement with the earlier results,⁵ favouring the validity of Lechatelier's principle signifying that an increase in temperature causes thermal stress. This results into an absorption of heat, which brings about the breaking of H bonds. Also, an increase of temperature

causes an increase of K.E. of the complexed specie which results into breaking of hydrogen bonds and thus, K decreases with increasing temperature.

The thermodynamical parameters for the association process reported in Table III play an important role in understanding the association mechanism. The appreciable negative values of ΔG^0 suggest that the reaction is strongly towards the product (association). The negative values of ΔH^0 and ΔS^0 indicate that the reaction is exothermic and suggests comparatively more ordered state of products than the reactants.

S. Nagakura¹⁴ has reported earlier the U.V. study of hydrogen bond formation between phenol and esters in CCl_4 . The change in enthalpy ΔH^0 for phenol + methyl acetate and phenol + ethyl acetate in carbon-tetrachloride was found to be 5.3 and 5.7 kcal/mole respectively. Our results of ΔH^0 of ethyl, butyl and benzyl acetates with O-Cresol i.e. complexed species computed using our previously proposed relation were found to be of the same order. These values were however slightly smaller than the reported literature values. It has been suggested by earlier workers^{15,16} that ΔH^0 values decrease with decreasing the acidic strength of the proton donor. The observed results of ΔH^0 of ethyl, butyl and benzyl acetates with O-Cresol which is less acidic than phenol seems to be reasonable in comparison to the acetates and phenol complexes. Sutton and his coworkers¹⁶ studied the association of trimethylamine with various proton donors. The association constant for trimethylamine with α -naphthol and β -naphthol were found to be 110 and 230 l/mole while S. Nagakura and M. Gouterman¹⁷ reported the K values for the triethylamine with α -naphthol and β -naphthol as 121 and 103 l/mole respectively. It seems from the reported literature data that the association equilibrium constant depends not only on the acidic or basic strength of the interacting components but also on their molecular structure as Sutton and his coworkers¹⁶ suggested that K and $\Delta\mu$ values do not follow the ionisation constants of the acids.

The equilibrium constant values for the first two complexed species determined under present study were larger than the values of K for the association of same base with phenol¹⁸ [ethyl acetate + phenol = (30 l/mole) and butyl acetate + phenol = (34 l/mole) at 35°C]. This anomaly may be explained by considering their specific molecular structure. The structural formula for acetate in general being;



exhibits two distinct possibilities of H-bond formation; the one formed by carbonyl oxygen and the second by alkoxy oxygen. Carbonyl oxygen being

more electronegative has stronger proton accepting power than of alkoxy oxygen. However phenol being a stronger acid may also form H-bond through alkoxy oxygen possibly of a weak strength giving rise to a low value of equilibrium constant. On the other hand, in case of complexed species of aliphatic acetates with O-Cresol, since both the proton donor (O-Cresol) and acceptor (alkoxy oxygen) possess weaker strength, a hydrogen bond formation may not occur at all. The H-bond formation occurring through the carbonyl oxygen would probably yield a higher equilibrium constant parameter K . The observed values of equilibrium constants of 88.7 l/mole and 79.3 l/mole for ethyl acetate and butyl acetate with O-Cresol complexed system at 25°C indicate that the association in the latter case is weak. This is further supported by the observed entropy ΔS° of -5.0 cal/mole and -9.30 cal/mole of the association process for ethyl and butyl acetate with O-Cresol species. Clark's *et al.*¹⁹ have also concluded in an earlier study made on the complexes of CHCl_3 with ethyl, butyl acetates and *n*-propyl formate, that higher be the entropy contribution, weaker would be the hydrogen bond.

The complexed specie consisting of benzyl acetate with O-Cresol yields an equilibrium constant of 47.3 l/mole at 298 K which is lowest in the series investigated. Also, a comparison of K of 66 l/mole of benzyl acetate and phenol complex with the former appears to be consistent with the argument that strength of $(-\text{C}=\text{O})-\text{H}-\text{O}$ bond decreases for the former case as O-Cresol would have perhaps less proton donating capability than phenol due to inductive effect of the $-\text{CH}_3$ group attached in O-Cresol molecule.

CONCLUSION

It may be concluded that the reactions taking place during association phenomenon of the system of acetates with O-Cresol in dilute solution of carbontetrachloride for the temperature range 294–318 K are of exothermic nature and are in forward direction i.e. leading to formation of more and more complex. The agreement of the reported thermodynamical parameters and of equilibrium constant K with the available literature values estimated using other methods indicate the validity of the proposed eqn. for $\text{O}-\text{H}-\text{O}$ bond complexes.

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