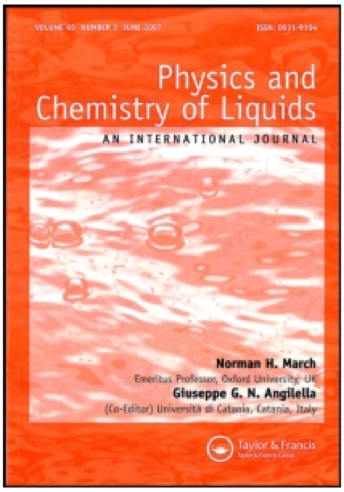

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Complex Formation and Associated Parameters in Various Non-Polar Solvents

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Complex Formation and Associated Parameters in Various Non-Polar Solvents

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A dielectric relaxation study of hydrogen bond complexes namely Benzyl acetate + Phenol and Benzaldehyde + Phenol in six non polar solvents in the temperature range 290–318 K has been made. The solvent effect on the associated parameters like K, ΔH°, ΔG° and ΔS°, obtained using dielectric relaxation data of both the complexes has also been studied. The thermodynamical parameters for both the complexes have been found in linear relationship with ϵ^{-1} of the solvents.

INTRODUCTION

The dielectric absorption study of solution of benzylacetate + phenol and benzaldehyde + phenol complexes in a number of non-polar solvents viz. *n*-heptane, cyclohexane, dioxane, carbontetrachloride, benzene and toluene is reported here. The dielectric data have been analysed to yield the values of relaxation times as well as of activation energies. The method to evaluate K from dielectric relaxation data requires the determination of constants *A* and *B*, which have already been determined and reported in our earlier papers.[1,2]

As it was realized that the solvent effects are important to study *H*-bond equilibrium, the measurements were extended to cover a number of solvents. Since all the three thermodynamic parameters ΔH°, ΔS° and ΔG° associated with complex formation depend on overall association process, solvent effects would possibly be reflected in the magnitude of the observed thermodynamic parameteric values. Hence these parameters have also been computed along with other important dielectric characteristics.

TABLE I

Slopes values of benzylacetate + phenol and benzaldehyde + phenol in various solvents

		[*A*] Benzylacetate + phenol			
Solvent	Temp. K	a_0	a'	a''	a_∞
n-Heptane	290	9.89	4.28	4.52	0.33
	299	9.58	4.88	4.31	0.33
	308	8.57	4.76	3.95	0.31
	318	7.25	4.52	3.27	0.29
Cyclohexane	290	10.33	3.86	4.62	0.35
	299	8.57	3.73	3.97	0.33
	308	8.47	4.28	3.92	0.31
	318	7.33	4.31	3.82	0.30
Dioxane	290	10.57	3.49	4.28	0.38
	299	9.89	3.65	4.38	0.38
	308	9.58	4.23	4.36	0.35
	318	8.57	4.36	4.02	0.30
Carbon tetrachloride	290	11.50	3.46	4.72	0.50
	299	11.93	4.39	5.15	0.48
	308	11.52	4.78	5.32	0.42
	318	10.70	5.38	4.96	0.40
Benzene	290	12.35	3.65	4.92	0.50
	299	11.97	4.18	5.17	0.52
	308	10.57	4.43	4.72	0.50
	318	10.38	5.18	4.74	0.47
Toluene	290	13.54	3.77	5.06	0.68
	299	12.38	4.12	5.04	0.65
	308	12.51	4.81	5.48	0.57
	318	11.09	5.10	5.08	0.60

EXPERIMENTAL DETAILS

The dielectric constant ϵ' and the dielectric loss ϵ'' have been measured in the X-band range. The static dielectric constant (ϵ_0) at 300 KHz and refractive indices using Abbe's Refractometer of all the solutions have been measured. The relaxation times have been computed using the method of Higasi[3] and Higasi *et al.*[4] Thermodynamic parameters have been calculated using Erying's theory of rate processes[5] for the molecular relaxation time.

Association parameters for benzylacetate + phenol and benzaldehyde + phenol complexes have been calculated using a previously reported relation,[1] from the known "*A*" and "*B*" values of 0.4 and 4.0 Kcal/mole; 0.2 and 3.25 Kcal/mole respectively for the specified complexes.

TABLE I (*continued*)

		[B] Benzalaldehyde + phenol			
Solvent	Temp. K	a_0	a'	a''	a^{∞}
n-Heptane	290	12.93	6.03	5.44	0.23
	299	11.57	5.97	5.16	0.21
	308	10.05	5.62	4.73	0.19
	318	9.97	6.34	4.53	0.19
Cyclohexane	290	12.05	5.27	5.01	0.30
	299	11.96	5.75	5.38	0.29
	308	11.33	6.00	5.35	0.29
	318	11.18	6.77	5.18	0.27
Dioxane	290	13.95	5.61	5.54	0.33
	299	12.75	5.61	5.55	0.29
	308	11.57	5.68	5.33	0.30
	318	10.05	5.63	4.69	0.31
Carbon tetrachloride	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
Benzene	290	15.53	5.74	6.26	0.37
	299	14.25	6.11	6.11	0.35
	308	13.95	6.47	6.53	0.28
	318	11.96	6.42	5.68	0.25
Toluene	290	16.05	5.35	6.44	0.43
	299	16,25	6.32	7.02	0.39
	308	15.53	6.93	7.09	0.37
	318	14.00	7.35	6.43	0.35

RESULTS AND DISCUSSION

The slope values a_0, a', a'' and a_{∞} have been given in Table I. Table II includes the distribution parameter "α" and the relaxation times in the temperature range 290–318 K for complexes of phenol with benzylacetate and benzaldehyde proton acceptors. The energy parameters for association equilibrium constant value have been given in Table III.

DISCUSSION

Low α values for all complexes reveal that they are of rigid nature irrespective of the solvent media. The irregular variation of "α" with temperature may

TABLE II

Relaxation time (τ in pS), distribution parameter (α) and association constant (K) in 1/mole

	[*A*] Benzylacetate + phenol					
Solvent	Temp. K	$\tau_{(1)}$	$\tau_{(2)}$	α	$\tau_{(OH)}$	K
n-Heptane	290	18.6	20.2	0.03	19.6	187.4
$\epsilon_0 = 1.910$	299	15.4	17.7	0.05	16.5	142.8
	308	14.4	15.7	0.03	14.9	110.5
	318	12.6	13.6	0.02	12.9	86.0
Cyclohexane	290	21.4	22.7	0.02	22.4	138.6
$\epsilon_0 = 2.016$	299	18.9	19.8	0.01	19.5	108.1
	308	16.0	17.4	0.03	16.7	85.5
	318	13.3	15.0	0.04	13.9	66.8
Dioxane	290	22.4	26.9	0.05	26.1	91.4
$\epsilon_0 = 2.204$	299	21.8	23.1	0.02	22.8	73.2
	308	18.3	19.9	0.03	19.3	60.6
	318	16.1	17.0	0.02	16.6	48.3
Carbontetra chloride	290	25.9	27.7	0.02	27.4	85.0
$\epsilon_0 = 2.228$	299	21.4	23.8	0.03	23.2	68.4
	308	19.8	20.6	0.01	20.3	56.0
	318	16.2	17.4	0.02	16.8	45.5
Benzene	290	25.4	28.7	0.04	28.3	77.3
$\epsilon_0 = 2.273$	299	22.9	24.6	0.02	24.2	63.6
	308	19.5	21.1	0.03	20.6	52.3
	318	16.3	17.8	0.03	17.1	43.0
Toluene	290	26.6	31.4	0.05	31.0	62.0
$\epsilon_0 = 2.379$	299	23.6	26.6	0.04	26.1	57.6
	308	21.0	22.8	0.03	22.3	43.2
	318	18.3	19.2	0.01	18.8	36.6

arise from the fact that the acetates could associate with proton donors either through alkoxy or carbonyl oxygen of which carbonyl oxygen bond would be comparatively more rigid.

The parameter $\tau_{(OH)}$ has been found to be nearly the same as $\tau_{(2)}$. This indicates that the dipolar rotation of the complexed species, as a single unit, is responsible for the relaxation process.

For both the complexes in each solvent, the relaxation time values decrease with increasing temperature. This is due to decrease in viscosity of each solvent with increasing temperature. It is worthwhile to mention here that for both complexed species the rate of variation of $\tau_{(2)}$ and $\tau_{(1)}$ with temperature is relatively similar, justifying the occurrence of a single relaxation process in each case. Apart from this trend; the dielectric absorption of these complexes in general yields relaxation time values which are closer to the sum of individual components irrespective of the solvent nature.

TABLE II (*continued*)

	[*B*] Bendaldehyde + phenol					
Solvent	Temp. K	$\tau_{(1)}$	$\tau_{(2)}$	α	$\tau_{(OH)}$	K
n-Heptane	290	15.2	20.6	0.09	18.1	49.1
$\epsilon_0 = 1.910$	299	14.6	17.6	0.06	16.0	39.5
	308	14.2	15.2	0.02	14.5	32.2
	318	11.9	13.1	0.03	12.2	26.1
Cyclohexane	290	16.4	22.0	0.08	19.8	35.5
$\epsilon_0 = 2.016$	299	16.0	18.8	0.05	17.5	29.0
	308	15.2	16.2	0.02	15.7	23.6
	318	12.9	13.8	0.00	13.3	19.3
Dioxane	290	17.0	24.5	0.11	22.0	20.8
$\epsilon_0 = 2.204$	299	16.9	20.9	0.07	19.3	16.9
	308	16.1	17.9	0.04	19.1	14.1
	318	14.3	15.3	0.02	14.7	11.6
Carbontetra chloride	290	21.5	24.9	0.04	19.0	19.0
$\epsilon_0 = 2.228$	299	19.4	21.0	0.02	16.5	16.5
	308	17.0	18.2	0.05	13.1	13.1
	318	14.0	15.5	0.02	10.9	10.9
Benzene	290	18.9	25.4	0.09	23.7	17.2
$\epsilon_0 = 2.273$	299	17.2	21.6	0.07	20.0	14.2
	308	17.1	18.6	0.03	18.0	11.2
	318	15.0	15.8	0.02	15.4	9.8
Toluene	290	21.3	26.9	0.07	25.9	12.9
$\epsilon_0 = 2.379$	299	19.2	23.0	0.06	21.8	10.5
	308	17.6	19.7	0.04	18.8	8.8
	318	14.9	16.8	0.04	15.8	7.3

On comparing the relaxation time of both the investigated complexed species, it has been found that for benzylacetate + phenol system, average relaxation time values are slightly longer. This is in accordance with the larger dimensions of the rotating units formed from the benzylacetate + phenol than benaldehyde + phenol system. The deviation of variation of relaxation parameters from usual viscosity dependence pattern for both complexed units could be accounted for by the presence of considerable influence of other factors on rotating unit of complexed species such as interaction, steric repulsion, electrostatic delocalization.

From the temperature variation of the relaxation time, an estimate of the free energy of activation for the relaxation process has been made in the usual manner. An examination of Table III shows that the free energy of activation for relaxation in complexed species increases as the temperature increases, exhibiting a behaviour similar to that of a simple polar organic

TABLE III

Thermodynamical parameters for relaxational and association process (ΔG, ΔH in Kcal/mole and ΔS in cal/mole)

	Benzyl acetate + phenol						Benzaldehyde + phenol					
Temp. K	ΔH_ϵ	ΔG_ϵ	ΔS_ϵ	ΔH°	ΔG°	ΔS°	ΔH_ϵ	ΔG_ϵ	ΔS_ϵ	ΔH°	ΔG°	ΔS°
290	2.12	2.79	2.31	5.20	3.04	7.45	2.13	2.80	2.17	4.43	2.26	7.48
299		2.81	2.31		2.97	7.46		2.81	2.14		2.20	7.46
308		2.84	2.34		2.90	7.47		2.82	2.11		2.14	7.44
318		2.87	2.36		2.83	7.45		2.84	2.11		2.08	7.32
290	2.30	2.86	1.93	4.80	2.86	6.69	2.30	2.84	1.86	4.21	2.07	7.38
299		2.88	1.94		2.80	6.69		2.85	1.84		2.01	7.36
308		2.90	1.95		2.74	6.69		2.86	1.82		1.95	7.34
318		2.93	1.98		2.67	6.70		2.87	1.79		1.88	7.33
290	2.48	2.95	1.62	4.15	2.62	5.26	2.43	2.90	1.62	3.90	1.76	7.38
299		2.97	1.64		2.57	5.28		2.91	1.61		1.69	7.39
308		2.99	1.66		2.53	5.26		2.92	1.59		1.63	7.36
318		3.01	1.67		2.40	5.28		2.94	1.60		1.56	7.37
290	2.51	2.97	1.59	4.05	2.58	5.07	2.43	2.91	1.66	3.84	1.71	7.35
299		2.99	1.61		2.53	5.08		2.92	1.64		1.68	7.22
308		3.01	1.62		2.48	5.10		2.93	1.62		1.59	7.31
318		3.03	1.64		2.43	5.09		2.95	1.64		1.52	7.30
290	2.66	2.99	1.14	3.90	2.52	4.76	2.44	2.92	1.66	3.70	1.65	7.07
299		3.01	1.17		2.48	4.75		2.93	1.64		1.59	7.06
308		3.03	1.20		2.44	4.74		2.95	1.66		1.52	7.08
318		3.04	1.20		2.39	4.75		2.96	1.64		1.45	7.08
290	2.72	3.04	1.10	3.60	2.40	4.14	2.53	2.95	1.45	3.54	1.48	7.10
299		3.06	1.14		2.36	4.15		2.97	1.47		1.49	7.12
308		3.07	1.14		2.32	4.15		2.98	1.46		1.34	7.14
318		3.09	1.16		2.29	4.12		3.00	1.46		1.26	7.17

molecule in non-polar solvents. It is also evident from the data reported that in each solvent the values of the free energy of activation for dipolar rotation are almost the same for both the complexed species. This may be attritubed to the occurrence of relatively similar types of relaxation mechanisms. However, the slightly higher value of ΔG_ϵ for the benzylacetate + phenol complex, possibly results from the larger dimension of benzylacetate molecule than benzaldehyde. Similar variations are obtained in the case of enthalpies also.

The negative values of entropy (ΔS_ϵ) for both the complexes may be explained as due to the existence of cooperative orientation of complexed species resulting from steric forces as has been observed by Branin and Smyth[6] for simple organic polar molecules in non-polar solvent. Taking into consideration the dielectric constant of the solvent media, for the present investigated complexes, the relaxation time has been found to increase with increasing dielectric constant (ϵ) of the media. This is in agreement with the classical electrostatic theory, [7–9] describing the orientational force as related inversely to ϵ of the media. The increase in the relaxation time of complexed species with ϵ of the media may be interpreted on the basis that the organic molecular complexes formed from the neutral adducts can appreciably change the polarization of the components present in the solution. It could

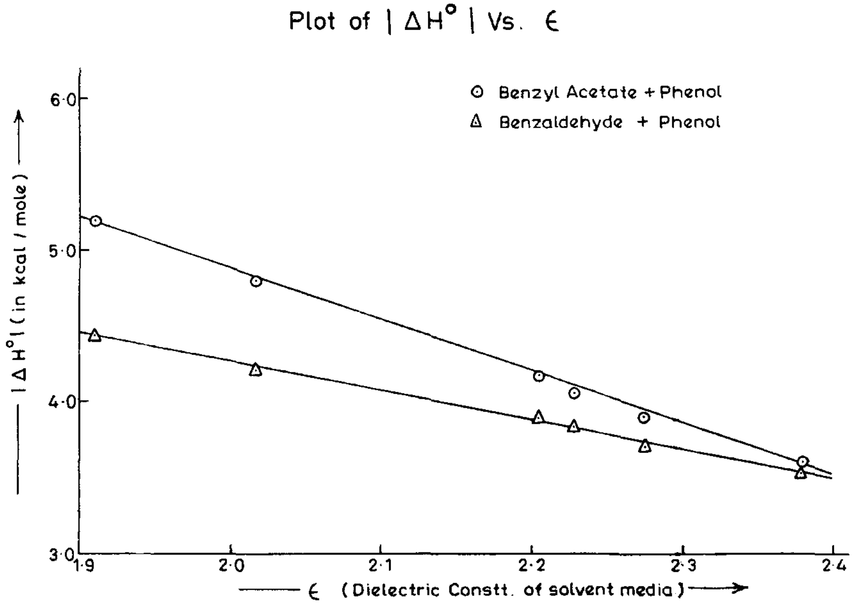


FIGURE 1

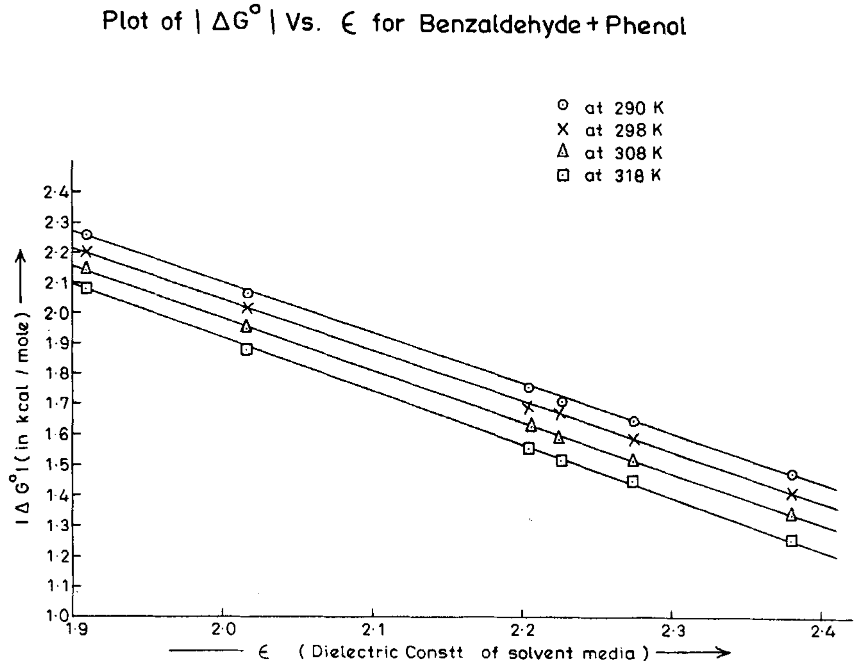


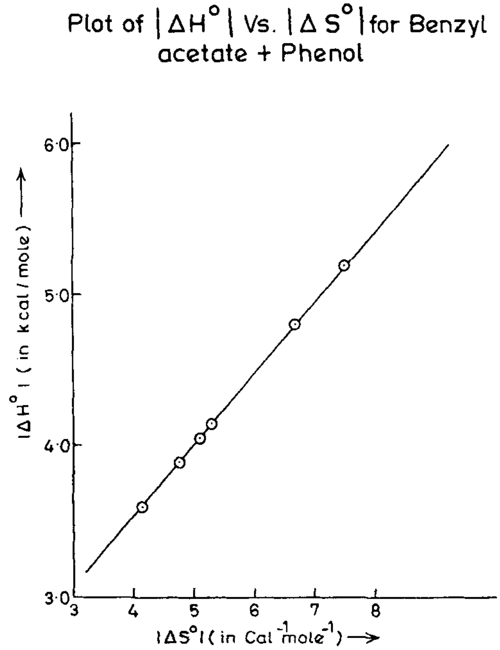
FIGURE 2

be mentioned then, that there exists relative change in the capacity of the medium to solvate different components. Hence at this stage, it could be estimated that the solvation includes the sum of non-specific interaction between the complex neighbour molecules.

Looking at the thermodynamic parameters of both complexes with respect to ϵ of the solvent media, no appreciable change in ΔG_ϵ is observed. This could be interpreted on the basis that the identical orientational processes are exhibited in different solvent media.

The association constant and thermodynamic parameters for association process of both phenol complexes with benzyl acetate and benzyldehyde have been evaluated using the temperature dependence of the relaxation time of complex species. The association equilibrium constant (K) decreases regularly on increasing the temperature from 290 to 318 K.

The negative values of ΔH°, ΔG° and ΔS° indicate that the type of reaction involved is forward and exothermic, unaffected by the change of solvent media. For the benzylacetate + phenol complexed system, since the association equilibrium constant is high, a relatively larger amount of heat would be evolved during association process than for the benzyldehyde + phenol complexed system. The reported results favour this fact as for the



Plot of |ΔH°| Vs. |ΔS°| for Benzyl acetate + Phenol

FIGURE 3

benzylacetate + phenol system, ΔH°, ranges from 5.2–3.6 Kcal/mole while for the benzaldehyde + phenol complex the ΔH° varies in the range 4.4–3.6 Kcal/mole when the solvent is varied from *n*-heptane to toluene. This larger ΔH° value for benzylacetate + phenol system is in agreement with the earlier studies[10,11] where ΔH° decreases with decreasing strength of the bond. For the phenol + benzaldehyde complex the observed low K values are supported by studies of Clark's *et al.*[12] and could be explained by the fact that the higher the entropy contribution, the weaker the *H*-bond. The larger entropy of this system accounts for its weaker character.

"K" has been found to decrease with increasing "ϵ" of the solvent medium. This may be attributed to the fact that in the media of low ϵ, higher orientational force makes approach of two opposite adducts easier to form the *H*-bond. Hence the concentration of complexed species would increase in the solution, giving rise to a higher K value and vice-versa.

The thermodynamic parameters for the association process has been found to decrease with increasing ϵ of the media. The ΔH° and ΔG° for the present complexes have been found to depend linearly on ϵ^{-1} as shown in Figures 1 and 2. This linear correlation has also been observed by some earlier workers[13,14] while studying the self-association phenomenon.

A linear relationship between the thermodynamic parameters of 1 : 1 *H*-bonded system of TEA + methylalcohol with ϵ^{-1} of the media has also been observed.[15]

For the complexes investigated here a linear relation has been found (Figure 3) between ΔS° and ΔH° agreeing in this respect also with the reported studies.[13,16]

As for computing the present data for the association process, we have used the same values of "*A*" and "*B*" (previously computed for solution in carbontetrachloride) for different solvent media; and have obtained both results and trends in agreement with basic concepts and also with those reported in literature. This indicates that the parameters, "*A*" and "*B*" may be independent of the solvent medium.

On the other hand, the two investigated complexed species having two different sets of numerical values of constant "*A*" and "*B*" show good parallelism in their behaviour. This also ensures that the parameters "*A*" and "*B*" are independent of the solvent. Hence "*A*" and "*B*" may be strictly related to the characteristic parameters, of the adducts. This could be examined further by extending such type of analysis over a number of other complexed systems.

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