Aggregation of Complexes of Some Phenols with Triethylamine in Benzene

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The practical molal osmotic coefficients and molal activity coefficients of triethylamine complexes with pentachlorophenol and 2,6-dibromo-4-nitrophenol in benzene solution were determined by vapour pressure osmometry (v.p.o.) over the concentration range 0.03—0.45 mol kg^{-1} at 27, 35, 40, and 50 °C. The non-ideal behaviour of the investigated system is interpreted in terms of an association model, which includes an extended series of multimers, and thermodynamic parameters are derived. It is shown that Beer's law does not describe these solutions.

Complexes of phenols with amine are model hydrogen-bonded systems which have been discussed in several reviews.[1–5] These demonstrate that such systems in non-polar solvents and low concentration exist in equilibrium (1). Both species may be

$$\mathrm{B}\cdots\mathrm{HA} \overset{K_{PT}}{\rightleftharpoons} \mathrm{B^{+}H}\cdots\mathrm{A^{-}} \qquad (1)$$

further solvated and can interact with an excess of acid or base. The extent and degree of interaction depend on the magnitude of the dipole moment, as well as the size and shape of the solute molecules and, additionally, on the solvent. In aprotic solvents of low permittivity solute–solvent interactions are small relative to solute–solute interactions.[1]

In this paper the non-ideal behaviour of two complexes, pentachlorophenol•triethylamine (μ 9.6 D in toluene[6] and 8.49 D in CCl_4[7]) and 2,6-dibromo-4-nitrophenol•triethylamine (μ 11.8 D in toluene[6]) in benzene solution, has been studied by vapour pressure osmometry (v.p.o.) and a step-association model applied to discuss the association process.

Experimental

Complexes were prepared by adding stoicheiometric amounts of triethylamine to pentachlorophenol or 2,6-dibromo-4-nitrophenol in acetonitrile solutions and cooling. Crystals were recrystallized from acetonitrile: pentachlorophenol•triethylamine had m.p. 69 °C (Found; C, 39.2; H, 4.4, N, 3.8. Calc. for $C_{12}H_{16}Cl_5NO$: C, 39.2; H, 4.4; N, 3.8%), 2,6-dibromo-4-nitrophenol•triethylamine had m.p. 87.5—88 °C (Found: C, 36.2; H, 4.6; N, 7.0. Calc. for $C_{12}H_{18}Br_2N_2O_3$: C, 36.2; H, 4.6; N, 7.0%).

A Knauer vapour pressure osmometer was used. The instrumental calibration procedure and the method of measurements were similar to those described previously.[8] Osmotic coefficients (Φ) were calculated from equation (2) and fitted by a

$$V = \Phi m k \qquad (2)$$

$$\Phi = 1 + \sum_{i=1}^{q=4} A_i m^i \qquad (3)$$

least-squares method to the orthogonal polynomial of form (3) where V is the measured imbalance (μV), k is the calibration constant, m is the stoicheiometric solute concentration (mol kg^{-1}), and A_i are constants.

U.v. spectra were recorded on a Zeiss–Specord M40 spectrophotometer using cells with CaF_2 windows (l 0.002 cm).

I.r. spectra were recorded on a Perkin-Elmer 580 spectrophotometer using cells with KBr windows (l 0.007 and 0.045 cm).

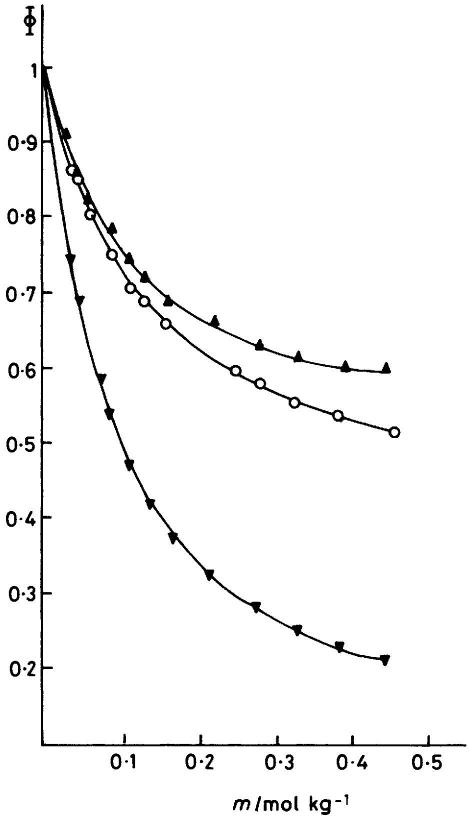

Figure 1. Concentration dependence of the practical molal osmotic coefficients for complexes of triethylamine with pentachlorophenol (○, 27 °C; ▲, 40 °C) and 2,6-dibromo-4-nitrophenol (▼, 27 °C) in benzene

Results and Discussion

In Figure 1 the practical molal osmotic coefficients of triethylaminium phenolates in benzene solutions as a function of the molal concentration are shown. The solid lines are drawn on the basis of equation (3), using the coefficients from Table 1. As with our previous treatment[8] of the experimental data, the activity coefficients of the solute, γ_2, were calculated *via* Bjerrum's relation in the form (4).

$$\ln \gamma_2 = \sum_{i=1}^{q=4} \frac{i+1}{i} A_i m^i \qquad (4)$$

For pentachlorophenol•triethylamine in CCl_4 the following values were derived: K_{PT} 2.2, μ 8.49 D.[7] A similar or even

Table 1. Values of the coefficients A_1—A_4 in equation (3)

	Pentachlorophenol•NEt$_3$				2,6-Dibromo-4-nitrophenol•NEt$_3$
	27 °C	35 °C	40 °C	50 °C	27 °C
A_1	−4.0474	−3.9259	−3.4785	−3.2541	−9.1423
A_2	18.0709	18.5526	14.2032	13.7371	52.7181
A_3	−42.7728	−47.3004	−32.4033	−34.2417	−143.7235
A_4	37.7675	45.0014	29.1577	34.3052	141.6455
10^2S_q	3.73	3.71	3.62	2.33	11.90
r^2	0.999	0.998	0.998	0.999	0.997
No. of points	12	12	12	12	12

Table 2. Values of the association constants and thermodynamic parameters for the complex of pentachlorophenol with triethylamine in benzene

T °C	K/kg mol^{-1}	$-\Delta H^\circ$/ kcal mol^{-1}	$-\Delta S^\circ$/ cal mol^{-1} K^{-1}
27	4.66 ± 0.12	2.48 ± 0.14	5.20 ± 0.45
35	4.28 ± 0.11		
40	3.95 ± 0.35		
50	3.48 ± 0.10		

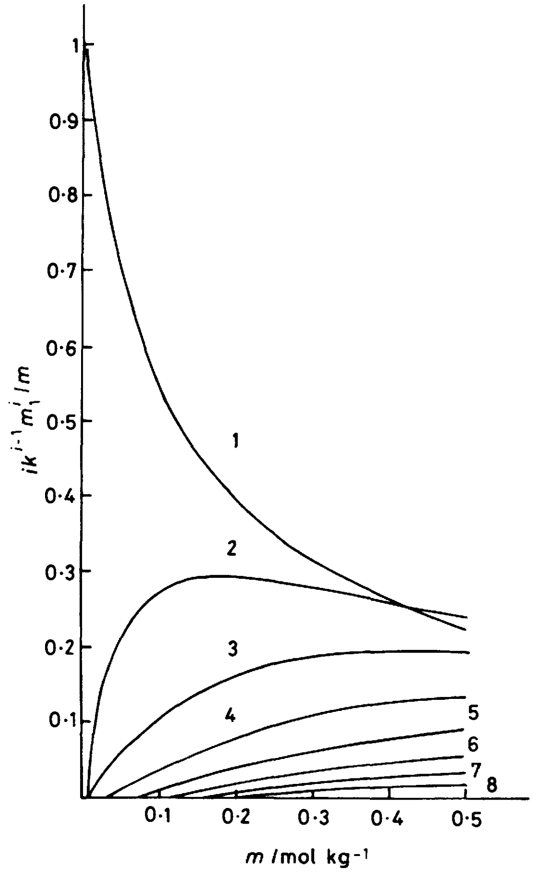

Figure 2. The distribution of dominant associated species for triethylamine–pentachlorophenol in benzene at 27 °C

Table 3. Beer's law study of triethylamine complexes with pentachlorophenol (at 328.5 nm) and 2,6-dibromo-4-nitrophenol (at 388.5 nm) in benzene

Pentachlorophenol•NEt$_3$		2,6-Dibromo-4-nitrophenol•NEt$_3$	
Concentration (mol dm^{-3})	Absorptivity (dm^3 mol^{-1} cm^{-1})	Concentration (mol dm^{-3})	Absorptivity (dm^3 mol^{-1} cm^{-1})
0.015	5 000	0.015	18 200
0.03	5 200	0.03	19 800
0.045	5 250	0.045	20 500
0.06	5 300	0.06	20 800
0.07	5 400	0.075	21 400
0.08	5 500	0.09	21 800
0.1	5 550		
0.2	5 700		

slightly larger value of K_{PT} is expected in benzene solution.[6] Since μ is 11.8 D[6] triethylamine•2,6-dibromo-4-nitrophenol, the K_{PT} value should be larger than that for triethylamine•pentachlorophenol. As Figure 1 shows, deviation from ideal behaviour increases with increasing dipole moment and K_{PT}.

Assuming that dissociation of the complexes investigated to ions in non-polar and low dielectric constant benzene is negligible, and that the extent of non-specific non-idealities due to solute–solvent interactions is equally insignificant, the deviation from ideal behaviour (Φ 1) is due to the formation of aggregates.

If the non-ideal behaviour of the investigated system is considered as a consequence of a series of association equilibria due to the dipole–dipole interactions of simple ion-pairs [relations (5) and (6) with one equilibrium constant equation (7)][8] the

$$n(B^+H\cdots A^-) \xrightleftharpoons{K_{1n}} (B^+H\cdots A^-)_n \qquad (5)$$

$$n-1(B^+H\cdots A^-) + (B^+H\cdots A^-) \xrightleftharpoons{K_{(n-1)n}} (B^+H\cdots A^-)_n \qquad (6)$$

$$K_{11} = K_{23} = \cdots = K_{(n-1)n} \equiv K \qquad (7)$$

total concentration of solute m related to the monomeric concentration is given by equation (8) where m_1 is the free

$$m = m_1 + \sum_{i=2}^{n} iK^{i-1}(m_1)^i \qquad (8)$$

monomer concentration, while the osmometric concentration Φm is given by equation (9). K is given by equation (10).

$$\Phi m = m_1 + \sum_{i=z}^{n} K^{i-1}(m_1)^i \qquad (9)$$

$$K = \frac{m - \Phi m}{(\Phi m)^2} \qquad (10)$$

The values of the equilibrium constants are given in Table 2. A set of internally consistent equilibria is obtained only for the complex with pentachlorophenol. For the second complex the resulting value depends strongly on the concentration (K 13—37 kg mol^{-1}).

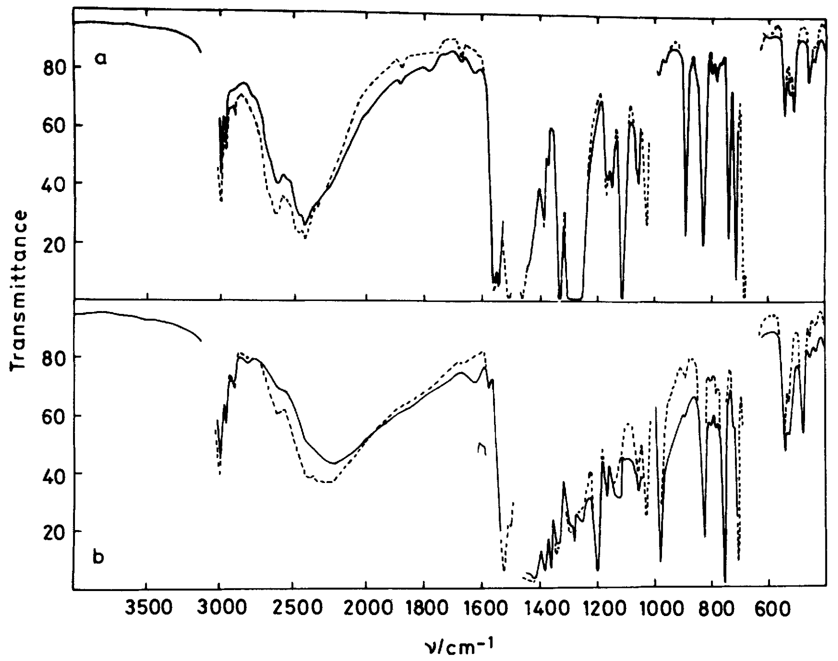

Figure 3. I.r. spectra benzene solutions of complexes of triethylamine with (a) 2,6-dibromo-4-nitrophenol and (b) pentachlorophenol: (——) 0.08M, (- - - -) 0.514M

The relative abundances of each successive aggregate can be obtained by solving the polynomials (8) and (9) with a finite number for *n*, neglecting those higher terms which contribute less to the values of *m* and Φm than the accuracy of the osmometric determination. For the investigated complex, values of *n* up to 10 satisfy this requirement.

Figure 2 presents the distribution of dominant aggregates (monomer 1, dimer 2, trimer 3 *etc.*) for the complex of triethylamine with pentachlorophenol in the concentration range studied at 27 °C.

The standard enthalpy ΔH° and entropy ΔS° for the stepwise aggregates were calculated from relation (11) and are listed in Table 2.

$$\ln K = -\Delta H^\circ/RT + \Delta S^\circ/R \qquad (11)$$

From Table 3 it appears that the value of the molar absorptivity of the complexes varies with concentration. This is certainly caused by aggregation. Similar changes of the molar absorptivity was observed for complexes of 2,4-dinitrophenol.[9]

I.r. spectra of the investigated complexes in benzene are affected by concentration. On increasing the concentration from 0.08 to 0.514M, the intensity of the broad band centred at 2 400 cm^{-1} decreases on the lower frequency side but increases on the higher frequency side (Figure 3a). The hydrogen bond in the complex of pentachlorophenol is stronger than that of 2,6-dibromo-4-nitrophenol. The broad band is centred at *ca.* 2 200 cm^{-1} and a continuous absorption appears in the 1 200—400 cm^{-1} region (Figure 3b). On increasing the concentration the absorption in the 2 000—1 600 and 1 200—400 cm^{-1} regions decreases, but that in the 2 700—2 200 cm^{-1} region increases. Changes of absorption caused by aggregation have been observed previously in the i.r. spectra of some pyridinium trifluoroacetates.[10] The observed variations in the intensity of abosrption with concentration are very similar to those predicted by *ab initio*[11] and SCF[12] calculations. Thus aggregation changes the electric field around the hydrogen bond, which causes a variation in absorption.

Acknowledgements

We acknowledge financial support from the Polish Academy of Sciences (Project MR.I.9.4.4.4.).

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Received 31*st January* 1986; *Paper* 6/213