On the Association of Phenol and 4-Chlorophenol with N,N-Dimethylmethanesulfonamide

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The association of N,N-dimethylmethanesulfonamide with phenol and 4-chlorophenol was studied by PMR spectrometry at 35 °C in carbon tetrachloride solution. The data are in accordance with a model which includes, in addition to 1:1 complexes, complexes of two phenol and one N,N-dimethylmethanesulfonamide molecule.

Introduction

The association of N,N-dimethylmethanesulfonamide (DMMSA) with phenols has been investigated by NIR spectrophotometry[1], and the densities and viscosities of binary solvent mixtures containing DMMSA have been measured[2] in our laboratory. The results indicate a weaker hydrogen bonding ability for the sulfonamide than for the corresponding carboxamide. Continuing our investigations, we have now studied the hydrogen bond acceptor properties of the compound using PMR spectrometry, which also gives information about hydrogen atoms participating in hydrogen bonds. The NIR method is based on information about the monomeric species only.

Experimental

Chemicals. N, N-Dimethylmethanesulfonamide was synthetized from methanesulfonyl chloride and dimethylamine in anhydrous ether as described earlier[2], m.p. 49.5–50.5 °C (lit.[3] m.p. 49–50 °C). Phenol, a *purum* product from E. Merck AG, Darmstadt, BRD, and 4-chlorophenol, a *praktikum* product from Fluka AG, Buchs, Switzerland, were purified by distillation from benzene solution. Carbon tetrachloride, a *Uvasol* chemical for spectroscopy from E. Merck AG, was dried and preserved above Union Carbide Molecular Sieves, Type 4A, from British Drug Houses Ltd., Poole, England.

PMR spectra were recorded on a Varian T-60 spectrometer at 35 °C. The spectrometer was calibrated by the "sideband technique" using a Krohn-Hite 4100 oscillator and an Advance TC 9 counter. The chemical shifts reported are means of the values determined from at least four spectra recorded by two successive sweeps in both direction.

Results

For the formation of the 1 : 1 complexes C_{11}

$$AH + B \rightleftharpoons C_{11} \qquad (1)$$

the equilibrium constant is

$$K_{11} = \frac{c_c}{(c_a - c_c)\,(c_b - c_c)} \qquad (2)$$

where c_c is the equilibrium concentration of the complex and c_a and c_b the initial concentrations of the proton donor and acceptor, respectively. If self-associations are negligible, the chemical shift observed is

$$\delta = \frac{c_c}{c_a}\,\delta_c + \frac{c_a - c_c}{c_a}\,\delta_a \qquad (3)$$

where δ_c and δ_a are the chemical shifts of the 1 : 1 complex and the proton donor, respectively.

When the values of the chemical shift for the OH-proton of phenol and 4-chlorophenol in carbon tetrachloride at 35 °C were plotted as a function of c_a and extrapolated to infinite dilution, we obtained for δ_a the following values: 255.3 cps for phenol and 259.3 cps for 4-chlorophenol, which are in excellent agreement with the values reported in the literature: 255.5 cps[4] for phenol and 259.9 cps[5] for 4-chlorophenol.

In the method of Higuchi[6], K_{11}, c_c and δ_c are determined by iterations from the equations

$$c_c = \frac{\delta - \delta_a}{\delta_c - \delta_a}\,c_a\,, \qquad (4)$$

$$\frac{c_b}{\delta - \delta_a} = \frac{1}{\delta_c - \delta_a}\,(c_a + c_b - c_c) + \frac{1}{K_{11}(\delta_c - \delta_a)} \qquad (5)$$

using for δ_a the value determined by extrapolation to infinite dilution. According to Gramstad and Becker[4], the self-association of the proton donor can be taken into account by using for δ_a the values measured at the actual concentrations c_a without the presence of the proton acceptor. The results calculated by these two methods are collected in Tables 1 and 2[7].

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Table 1. Chemical shifts and equilibrium constants calculated by the method of Higuchi[6] for the association of phenol (Experiments 1–6) and 4-chlorophenol (Experiments 7–11), respectively, with N,N-dimethylmethanesulfonamide in carbon tetrachloride at 35 °C .

Experiment no.	c_a mole dm^{-3}	Range of c_b mole dm^{-3}	No. of solutions	Range of δ cps	δ_a cps	K_{11} dm^3 mole^{-1}	δ_c cps
1	0.0120	0.0121–0.0883	8	269.7–318.9	255.3	11.0	388.7
2	0.0144	0.0165–0.0964	7	274.6–322.7	255.3	12.1	384.8
3	0.0191	0.0187–0.0826	11	276.7–317.0	255.3	13.4	379.4
4	0.0242	0.0272–0.0952	10	285.1–322.9	255.3	14.9	377.7
5	0.0300	0.0339–0.0917	8	291.2–324.6	255.3	16.3	377.2
6	0.0355	0.0371–0.0928	8	293.5–322.8	255.3	18.9	371.7
7	0.0120	0.0133–0.1045	8	286.0–353.7	259.3	20.2	401.7
8	0.0185	0.0197–0.1050	8	294.5–353.4	259.3	22.1	398.8
9	0.0257	0.0392–0.1005	7	316.1–351.4	259.3	24.6	396.0
10	0.0300	0.0323–0.1099	8	309.2–354.2	259.3	28.8	390.1
11	0.0360	0.0364–0.1032	7	312.7–351.9	259.3	31.1	389.7

Table 2. Chemical shifts and equilibrium constants K_{11} calculated according to Gramstad and Becker[4] as well as equilibrium constants K_{21} for the association of phenol (Experiments 1–6) and 4-chlorophenol (Experiments 7–11), respectively, with N,N-dimethylmethanesulfonamide in carbon tetrachloride at 35 °C.

Experiment no.	δ_a cps	K_{11} dm^3 mole^{-1}	δ_c cps	δ_a cps	K_{21} dm^6 mole^{-2}	δ_c cps
1	256.1	9.7	396.8	255.3	199.7	1065.8
2	256.3	10.8	391.1	255.3	175.1	1055.6
3	256.7	11.5	387.9	255.3	135.2	1049.5
4	257.2	12.7	385.1	255.3	114.7	1043.3
5	257.8	13.5	385.2	255.3	90.6	1062.4
6	258.4	14.7	381.7	255.3	79.6	1053.1
7	259.9	19.6	403.1	259.3	348.8	1123.8
8	260.2	21.1	400.5	259.3	222.1	1128.6
9	260.8	23.3	397.7	259.3	160.1	1133.7
10	261.1	26.6	392.2	259.3	142.8	1125.1
11	261.7	28.9	392.7	259.3	116.9	1133.7

For the formation of the 2 : 1 complexes C_{21}

$$2\,\mathrm{AH} + \mathrm{B} \rightleftharpoons \mathrm{C}_{21} \tag{6}$$

the equilibrium constant is

$$K_{21} = \frac{c_c}{(c_a - 2\,c_c)^2\,(c_b - c_c)} \tag{7}$$

and the chemical shift observed is

$$\delta = \frac{c_a - 2\,c_c}{c_a}\,\delta_a + \frac{c_c}{c_a}\,\delta_c\,. \tag{8}$$

Neglecting the terms containing the concentration of the complex to the second or the third power, it is easy to derive the equation

$$\frac{c_a\,c_b}{\delta - \delta_a} = \frac{1}{\delta_c - 2\,\delta_a}\,(4\,c_a\,c_b + c_a{}^2) + \frac{1}{K_{21}(\delta_c - 2\,\delta_a)} \tag{9}$$

which permits calculation of K_{21} from the values of the slope and intercept. The results are collected in Table 2.

Discussion

Using NIR spectrophotometry, the values of 11.0 cm^3 mole^{-1} and 21.4 dm^3 mole^{-1} at 35 °C have been measured for the equilibrium constant of the formation of 1 : 1 complexes for phenol and 4-chlorophenol with DMMSA at lower concentrations, respectively[1]. The values now measured at higher concentrations fall in the same range, but they increase along with the increasing proton donor concentration. This can partly be ascribed to the self-association of phenols, since associated forms can be assumed to form hydrogen bonds more readily than the monomeric species. However, although the picture of the self-association of phenols is not at all clear and different association models have been suggested, examination of the available data does not presuppose any considerable self-association. For example, for the equilibrium constant of the association to trimers the value of 2.4 dm^6 $mole^{-2}$ at 35 °C for phenol[8] and the value of 0.302 dm^6 $mole^{-2}$ at 25 °C for 4-chlorophenol[9] have been reported. The insignificance of self-association is also seen from the values in Tables 1 and 2, as the method of Gramstad and Becker does not yield more constant values of K_{11} than the method of Higuchi. Self-association of DMMSA is not apparent.

The values of K_{21} in Table 2 decrease sharply with increasing proton donor concentration. Thus our data are in accordance with the model where, in addition to 1 : 1 complexes, also 2 : 1 complexes are formed to a lesser degree. This model is analogous to that suggested for the association of phenols with sulfoxides[10]. As DMMSA is a better proton acceptor than phenol, it polarizes the phenol O-H bond more and is itself polarized in complexes. This consequently facilitates the formation of 2 : 1 complexes in the concentration range where phenol itself is not dimerized.

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