Solubility of *o*- and *p*-Chlorobenzoic Acids in Hydrotrope Solutions

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Hydrotropes at high concentrations can substantially enhance the solubilities of *o*- and *p*-chlorobenzoic acids in aqueous solutions. The solubilities of *o*- and *p*-chlorobenzoic acids are determined in aqueous solutions of sodium butyl monoglycol sulfate (NaBMGS) and sodium *p*-toluenesulfonate (Na-*p*-TS) at temperatures of 303, 313, and 323 K. *o*-Chlorobenzoic acid is solubilized to a larger extent than *p*-chlorobenzoic acid. Setschenow constants for both the acids are reported at 303, 313, and 323 K. The data are also fitted in a quadratic function of the concentration of a hydrotrope.

Introduction

Hydrotropes are surface-active and highly water soluble organic salts which can increase the solubility of sparingly soluble solutes in water by several fold (*1*). This increase in solubility in water is presumably through a self-aggregation process of hydrotrope molecules because of their amphiphilic nature and varies with the nature of the organic compounds (*1–6*). Hydrotropes have also been used to solubilize drugs and detergents and recently in heterogeneous reactions (*7–11*). Hydrotropes have been successfully used in the development of extractive separations and in distillation as extractive solvents for the separations of close boiling point mixtures (*12–15*). The use of hydrotrope solutions as solvents in industrial applications is attractive because of the lack of inflammability, high selectivity, lack of an emulsification problem as in the case of surfactant solutions, and easy recovery of solubilized material by dilution with/without solvent extraction with a polar solvent.

A number of aromatic isomers serve as raw materials/ intermediates for a wide variety of chemical and pharmaceutical products. In some cases the individual isomers are difficult to obtain in pure form, and frequently the separation involves an ortho–para pair. In order to evaluate the potential of employing hydrotrope solutions in some purification processes, the solubilities of chlorobenzoic acids were measured in hydrotrope solutions. These acids are usually obtained by oxidation of the corresponding chlorotoluenes in a mixture form. In fact this oxidation followed by separation of acids is a better method of separation than the separation of chlorotoluenes by distillation.

Experimental Section

Measurements of the solubilities of *o*- and *p*-chlorobenzoic acids were carried out at temperatures of 303, 313, and 323 K. The chlorobenzoic acids were manufactured by Aldrich Chemical Co. with a manufacturer's stated purity of 99.9%. The melting point of *o*-chlorobenzoic acid was 415 K, and that of *p*-chlorobenzoic acid was 516 K, compared to the 413–416 and 513–516 K reported values for the *ortho* and *para* isomers, respectively, in the Merck Index.

For each solubility test, about 5 g of powdered solid was placed into a stoppered glass vessel and a solution of the hydrotrope of a known concentration was added. Sodium butyl monoglycol sulfate (NaBMGS) (50% solution by weight) is marketed by Hüls, Germany. The solution has a clear yellowish appearance with no suspended particles with a

density of 1.192 × 10³ kg/m³. The solutions of different concentrations were prepared by dilution with distilled water.

Sodium *p*-toluenesulfonate (Na-*p*-TS) was prepared by neutralizing *p*-toluenesulfonic acid with sodium hydroxide. *p*-Toluenesulfonic acid obtained from Loba Chemie, Bombay, was 98% pure.

The mixture of the solid and the solution was stirred using a magnetic stirrer for 2 h in a constant-temperature bath fitted with a temperature controller which could control the temperature within ±0.1 °C. It was found from independent studies that 2 h of agitation was sufficient to reach equilibration as agitation continued for a longer time did not increase the solubility further. At the end of the necessary period, the solution was filtered from the remaining solid. The concentration of the dissolved organic acid in aqueous hydrotrope solutions was analyzed by titration using standardized NaOH solutions using phenolphthalein as an indicator. The NaOH concentration was adjusted at lower concentrations of hydrotropes so that the error in the observed solubility values was minimized (<1%). Some of the solubility experiments were conducted in duplicate or triplicate to check the reproducibility. The observed error in the reproducibility is less than 1%.

Results and Discussion

The solubility values of the chlorobenzoic acids in hydrotrope solutions are listed in Tables I–IV and are plotted in Figures 1–4. The repeated experiments are shown by filled symbols in Figures 1–4, which show the reproducibility with a maximum deviation below 1%. The solubilities of *p*- and *o*-chlorobenzoic acids in water are 0.513 × 10⁻³ and 1.35 × 10⁻² kmol/m³ at 303 K, compared to 0.435 × 10⁻³ and 1.36 × 10⁻² kmol/m³ as reported by Osol and Kilpatrick (*16*) and 0.511 × 10⁻³ and 1.34 × 10⁻² kmol/m³ as reported by Laddha and Sharma (*17*). Thus, the solubility values in water are in excellent agreement with the earlier values.

As can be determined from the examination of the values and as was anticipated from the solubilities of other isomers (*18*), *o*-chlorobenzoic acid exhibits higher solubilities than the para isomer in both the hydrotrope solutions. The solubility of the ortho isomer is almost 1 order of magnitude higher than that of *p*-chlorobenzoic acid. The dissolution, like melting, involves overcoming intermolecular forces in a crystal. *p*-Chlorobenzoic acid having a much high melting point (514.5 K) because of symmetrical structure, as compared to *o*-chlorobenzoic acid (414 K), can easily accomodate itself into a crystal lattice. On the other hand, the aggregation structure of a hydrotrope in aqueous solutions can accomodate

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Table I. Solubility (S) of p-Chlorobenzoic Acid at Various Concentrations (C) of Sodium p-Toluenesulfonate in Aqueous Solutions

C/(kmol/m³)	$10^3 S$/(kmol/m³)		
	T = 303 K	T = 313 K	T = 323 K
0.00	0.51	0.71	0.90
0.10	0.37	0.44	0.86
0.20	0.46	0.60	0.97
0.30	0.55	0.61	1.13
0.40	0.59	0.72	1.25
0.50	0.59	0.73	1.27
0.60	0.62	0.77	1.39
0.70	0.64	0.79	1.51
0.80	0.68	0.85	1.65
0.85	0.78	1.04	2.11
0.90	0.82	1.06	2.21
0.95	0.84	1.18	2.44
1.00	0.87	1.22	2.48
1.20	1.05	1.48	2.54
1.40	1.31	1.93	4.04
1.60	1.75	2.37	5.77
2.00	2.19	3.71	7.13

Table II. Solubility (S) of o-Chlorobenzoic Acid at Various Concentrations (C) of Sodium p-Toluenesulfonate in Aqueous Solutions

| C/(kmol/m³)	$10^2 S$/(kmol/m³)		
	T = 303 K	T = 313 K	T = 323 K
0.00	1.35	1.43	2.08
0.10	0.71	1.21	1.54
0.20	0.74	1.28	1.66
0.30	0.82	1.35	1.85
0.40	0.89	1.50	1.88
0.50	0.94	1.56	2.22
0.60	0.98	1.73	2.34
0.70	1.01	1.93	2.44
0.80	1.06	2.13	2.87
0.85	1.10	2.21	3.39
0.90	1.19	2.40	3.47
0.95	1.19	2.58	3.90
1.00	1.28	2.67	4.01
1.20	1.52	3.47	5.17
1.40	1.84	4.58	6.39
1.60	2.46	5.93	7.88
2.00	4.06	8.95	10.90

Table III. Solubility (S) of p-Chlorobenzoic Acid at Various Concentrations (C) of Sodium Butyl Monoglycol Sulfate in Aqueous Solutions

C/(kmol/m³)	$10^3 S$/(kmol/m³)		
	T = 303 K	T = 313 K	T = 323 K
0.00	0.51	0.71	0.90
0.10	0.81	1.18	1.73
0.20	1.43	1.20	2.31
0.30	2.04	2.48	2.67
0.40	2.44	3.02	3.47
0.50	2.85	3.45	4.24
0.60	3.26	4.11	4.62
0.70	3.46	4.75	5.59
0.80	4.03	5.52	6.37
0.82	4.32	5.84	7.12
0.85	4.59	5.96	7.31
0.90	4.88	6.49	7.90
0.95	5.40	6.92	8.44
1.00	5.71	7.56	9.24
1.20	7.53	10.36	13.68
1.30	8.95	12.42	16.19
1.60	14.65	18.12	24.29
2.00	20.98	26.21	34.10

ortho isomers because of the mobile nature of aggregates normally existing in associated solutions. It is of interest to point out that hydrotrope solutions act in a manner similar to that of organic liquid solvents in their dissolving characteristics for the o- and p-chlorobenzoic acids.

Table IV. Solubility (S) of o-Chlorobenzoic Acid at Various Concentrations (C) of Sodium Butyl Monoglycol Sulfate in Aqueous Solutions

C/(kmol/m³)	$10^2 S$/(kmol/m³)		
	T = 303 K	T = 313 K	T = 323 K
0.00	1.35	1.43	2.08
0.10	0.91	1.35	1.79
0.20	1.02	1.45	2.00
0.30	1.17	1.61	2.26
0.40	1.41	1.86	2.53
0.50	1.58	2.06	3.05
0.60	1.73	2.43	3.63
0.70	2.01	2.96	4.63
0.80	2.41	3.61	5.42
0.82	2.51	3.67	5.52
0.85	2.64	4.03	6.33
0.90	3.05	4.10	6.52
0.95	3.33	4.94	7.28
1.00	3.46	5.89	8.10
1.20	5.34	8.22	11.06
1.30	6.26	9.37	13.06
1.60	9.89	13.11	20.28
2.00	15.25	18.76	27.84
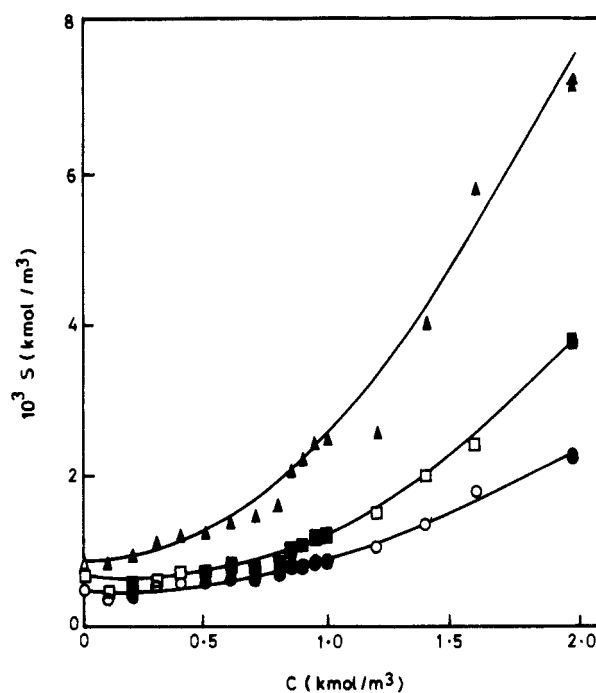
Figure 1. Solubility (S) or p-chlorobenzoic acid in various concentrations (C) of aqueous sodium p-toluenesulfonate solutions at (O) 303 K, (□) 313 K, and (Δ) 323 K.

The solubilities of o- and p-chlorobenzoic acids increase with the hydrotrope concentration and also with temperature. However, as can be seen from the data the solubilities of these acids go through a minimum; i.e., below a certain concentration, C_m, these acids are salted out of the hydrotrope solution. Thus, below C_m the solubilities of both the isomers are lower than those in pure water. The solubility data were analyzed using the equation

$$\log(S/S_m) = K_s(C_s - C_m) \qquad (1)$$

where S and S_m are the solubilities of the acid at concentrations of hydrotrope C_s and C_m, respectively. The values of K_s, i.e., the Setschenow constant, and of C_m are given in Table V. The K_s values are not significantly affected by the temperature. NaBMGS gives substantially higher values of K_s for both the acids as compared to Na-p-TS. At lower and higher concentrations, however, the exponential relation is not valid. Thus, the data have also been fitted in a quadratic equation
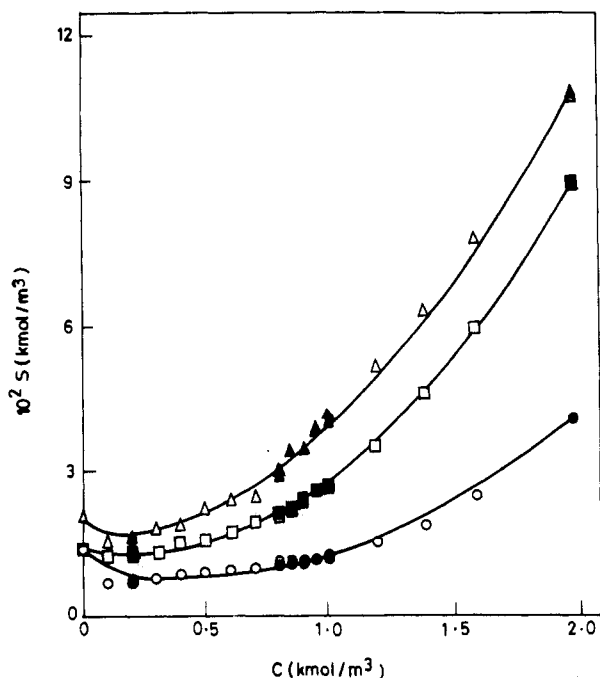
Figure 2. Solubility (S) of o-chlorobenzoic acid in various concentrations (C) of aqueous sodium p-toluenesulfonate solutions at (O) 303 K, (□) 313 K, and (△) 323 K.
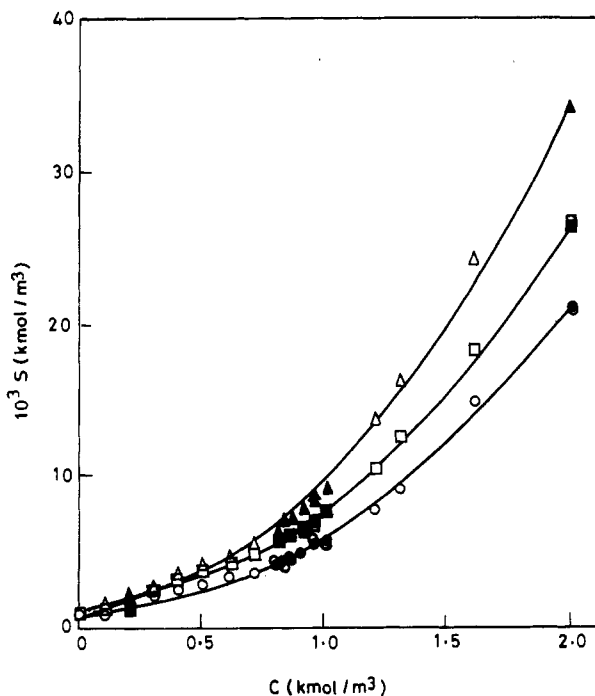

Figure 3. Solubility (S) of p-chlorobenzoic acid in various concentrations (C) of aqueous sodium butyl monoglycol sulfate solutions at (O) 303 K, (□) 313 K, and (△) 323 K.

of the form

$$S/(\text{kmol m}^{-3}) = a + bC_s + cC_s^2 \tag{2}$$

which seems to give a better fit for the solubility data than eq 1. The values of a–c are reported in Table VI along with the variance of the fit. The solid curves in Figures 1–4 are from these quadratic equations. The chlorobenzoic acids are frequently required in relatively pure form, and they most commonly must be separated from each other in a mixture not usually containing the meta isomer. These isomers can be separated by contacting the solid mixture with an aqueous alkali solution which contains alkali equivalent to neutralize
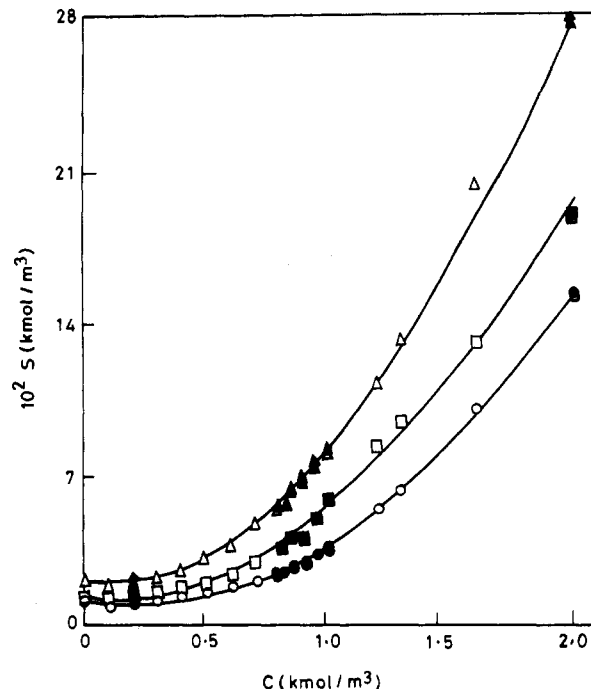

Figure 4. Solubility (S) of o-chlorobenzoic acid in various concentrations (C) of aqueous sodium butyl monoglycol sulfate solutions at (O) 303 K, (□) 313 K, and (△) 323 K.

Table V. Setschenow Constants for Chlorobenzoic Acids

T/K	o-chlorobenzoic acid		p-chlorobenzoic acid	
	C_m	K_s	C_m	K_s
Hydrotrope: Sodium p-Toluenesulfonate				
303	1.2	0.527	0.3	0.331
313	0.4	0.468	0.4	0.396
323	0.5	0.488	0.2	0.493
Hydrotrope: Sodium Butyl Monoglycol Sulfate				
303	0.4	0.670	0.0	0.994
313	0.2	0.697	0.0	0.970
323	0.3	0.764	0.0	0.964

Table VI. Correlation Constants for Quadratic Equation 2

T/K	a	b	c	variance in correlation
(i) Hydrotrope: Sodium p-Toluenesulfonate				
(a) p-Chlorobenzoic Acid				
303	1.058	−1.052	1.258	0.056
313	1.435	−1.119	2.434	0.174
323	1.646	−0.079	2.389	0.073
(b) o-Chlorobenzoic Acid				
303	0.462	−0.022	0.452	0.013
313	0.614	−0.407	0.963	0.064
323	0.912	−0.152	1.703	0.029
(ii) Hydrotrope: Sodium Butyl Monoglycol Sulfate				
(a) p-Chlorobenzoic Acid				
303	1.328	−2.308	4.685	0.128
313	0.970	−0.119	4.639	0.092
323	1.771	−0.782	7.037	0.278
(b) o-Chlorobenzoic Acid				
303	1.195	−0.415	5.163	0.018
313	0.825	1.408	5.654	0.131
323	1.680	−0.320	8.371	0.173

only the ortho isomer which is a stronger acid than the para isomer (17). The mixtures can be separated by using hydrotropic solutions as the hydrotrope solutions are highly selective to the ortho isomer. By controlled dilution the dissolved para isomer can be separated from the dissolved ortho isomer.

Conclusions

Solubility studies of *o*- and *p*-chlorobenzoic acids in aqueous hydrotropic solutions of sodium *p*-toluenesulfonate and of sodium butyl monoglycol sulfate indicate that the solubilities of both isomers increase rapidly. The enhancement in the solubility of *o*-chlorobenzoic acid at a given concentration and temperature is much more than that of *p*-chlorobenzoic acid at least by an order of magnitude. Thus, the difference in solubilities of these isomers with hydrotrope concentration and also with temperature can be exploited in the separation of chlorobenzoic acids.

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