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# Solubilities and Activity Coefficients of Chlorobenzenes and Chlorophenols in Aqueous Salt Solutions

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The solubilities and activity coefficients of six chlorinated organic compounds were determined in aqueous electrolyte solutions by UV–vis spectrophotometry at 25 °C. The salting-in and salting-out constants were determined. The systems studied were chlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene in solutions of NaCl, KCl, $Na_2CO_3$, $K_2SO_4$, and $CaCl_2$, chlorobenzene in solutions of $(C_2H_5)_4NBr$, and 2,4-dichlorophenol and 2,4,6-trichlorophenol in solutions of NaCl. The experimental values were compared with those calculated from five salt effect theories. The modified internal pressure theory gives the most satisfactory results.

## Introduction

It is well known that the solubilities of nonelectrolytes such as aromatic hydrocarbons in water are affected by the presence of electrolytes or salts. Addition of a salt usually (but not always) causes a "salting-out" effect, reducing the solubility of the organic compound and increasing its activity coefficient in water. Setschenow (*1*) proposed an empirical equation for this effect, namely

$$\log(S_0/S) = kC_S \qquad (1)$$

where $S_0$ and $S$ are the solubilities of the organic compound in pure water and the salt solution, respectively, $k$ is the salt effect constant, and $C_S$ is the salt concentration in water.

Quantifying this effect is important in several environmental situations. Organic chemicals are expected to behave differently in fresh, estuarine, and oceanic salt waters, and in extreme cases, the chemical may precipitate in salt water. The change in activity coefficient will result in a change in partitioning to air, sediments, and organisms, and it may alter toxicity, especially when toxicity is a result of water-to-lipid partitioning. Many industrial process effluents contain high concentrations of electrolytes which modify the fate and effects of organic contaminants in treatment systems and in receiving waters. An example is the effluent from pulp bleaching operations which contains a variety of chlorinated organic compounds (*2*).

Whereas there has been a considerable volume of data generated on hydrocarbon solubility in electrolyte solutions, largely as a result of concern about oil spills in the marine environment, there has been little attention to chlorinated aromatic compounds. We report here on the salt effect for selected chlorobenzenes and chlorophenols with a variety of nonelectrolytes. The aim is to enable the magnitude of the salt effect constant to be determined, or estimated, for this important class of chemicals. In addition we compare the results with predictions from five existing theories which permit estimation of the values of the salt effect constant.

**Table 1. Activity Coefficients and Salting-Out Constants *k* for Six Organic Solutes in Sodium Chloride Solutions at 298.15 K**[a]

| $C_S$/(mol·L$^{-1}$) | CB | 1,3-DCB | 1,4-DCB | 1,2,4-TCB | 2,4-DCP | 2,4,6-TCP |
|---|---|---|---|---|---|---|
| 0.0903 | | 0.0256 | | | | |
| 0.1000 | | | 0.0270 | | | |
| 0.1028 | | | | | | |
| 0.2000 | 0.0418 | | 0.0471 | 0.0547 | 0.0442 | |
| 0.2064 | | | | | | 0.0463 |
| 0.221 | | 0.0473 | | | | |
| 0.2800 | | | | 0.0710 | | |
| 0.3000 | 0.0587 | | 0.0728 | | 0.0653 | |
| 0.3987 | | | | | | 0.0953 |
| 0.4000 | 0.0779 | | 0.102 | 0.104 | 0.0905 | |
| 0.488 | | 0.1133 | | | | |
| 0.5000 | | | | | 0.111 | |
| 0.5138 | | | | | | 0.110 |
| 0.6000 | 0.122 | | | 0.153 | 0.130 | |
| 0.686 | | 0.1565 | | | | |
| 0.787 | | 0.1810 | | | | |
| 0.8000 | 0.158 | | 0.192 | | | |
| 0.8446 | | | | | | 0.192 |
| k/(L·mol$^{-1}$) | 0.198 | 0.226 | 0.240 | 0.250 | 0.218 | 0.228 |

[a] Key: CB, chlorobenzene; 1,3-DCB, 1,3-dichlorobenzene; 1,4-DCB, 1,4-dichlorobenzene; 1,2,4-TCB, 1,2,4-trichlorobenzene; 2,4-DCP, 2,4-dichlorophenol; 2,4,6-TCP, 2,4,6-trichlorophenol.

## Experimental Section

***Purification of Chemicals and Preparation of Solutions.*** Chlorobenzene, 1,2,4-trichlorobenzene, 2,4-dichlorophenol, and 2,4,6-trichlorophenol were obtained from Aldrich with a purity of 99+%. Sodium chloride and potassium sulfate were GR grade products, 1,3- and 1,4-dichlorobenzenes, sodium carbonate, calcium chloride, and potassium chloride were AR grade products which were obtained from Beijing Chemical Manufacture Co., and 98.4% pure $(C_2H_5)_4NBr$ was obtained from BDH. 1,4-Dichlorobenzene was recrystallized before use. All NaCl, KCl, and $K_2SO_4$ salts were baked before four to five salt aqueous solutions were prepared. Concentrations of $CaCl_2$ and $Na_2CO_3$ solutions were determined by density measurement, and $Et_4NBr$ was weighed directly to prepare five salt aqueous solutions. Double-distilled water was used for all experiments.

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**Table 2. Activity Coefficients and Salting-Out/In Constants $k$ for Four Organic Solvents in Various Aqueous Salt Solutions at 298.15 K**

| | | CB | | 1,3-DCB | | 1,4-DCB | | 1,2,4-TCB | |
|---|---|---|---|---|---|---|---|---|---|
| salt | $C_S$/(mol·L$^{-1}$) | log $\gamma$ | $k$/(L·mol$^{-1}$) | log $\gamma$ | $k$/(L·mol$^{-1}$) | log $\gamma$ | $k$/(L·mol$^{-1}$) | log $\gamma$ | $k$/(L·mol$^{-1}$) |
| KCl | | | 0.176 | | | | | | 0.239 |
| | 0.1567 | | | | | | | 0.0385 | |
| | 0.2000 | 0.0336 | | | | | | | |
| | 0.3000 | 0.0501 | | | | | | | |
| | 0.3914 | | | | | | | 0.0968 | |
| | 0.4000 | 0.0701 | | | | | | | |
| | 0.4893 | | | | | | | 0.118 | |
| | 0.5871 | | | | | | | 0.142 | |
| | 0.6000 | 0.107 | | | | | | | |
| | 0.8000 | 0.138 | | | | | | | |
| NaCl | | | 0.198 | | | | | | 0.250 |
| | 0.2000 | 0.0418 | | | | | | 0.0547 | |
| | 0.2800 | | | | | | | 0.0701 | |
| | 0.3000 | 0.0587 | | | | | | | |
| | 0.4000 | 0.0779 | | | | | | 0.104 | |
| | 0.6000 | 0.122 | | | | | | 0.154 | |
| | 0.8000 | 0.158 | | | | | | | |
| $K_2SO_4$ | | | 0.546 | | 0.576 | | 0.527 | | 0.623 |
| | 0.0908 | | | 0.0567 | | 0.0498 | | | |
| | 0.1362 | | | 0.0830 | | 0.0743 | | | |
| | 0.1816 | | | 0.110 | | 0.0948 | | | |
| | 0.1835 | 0.0983 | | | | | | 0.122 | |
| | 0.2725 | | | 0.163 | | 0.147 | | | |
| | 0.3059 | | | | | | | | |
| | 0.3179 | | | 0.188 | | 0.169 | | 0.185 | |
| | 0.4283 | 0.223 | | | | | | | |
| | 0.4894 | 0.266 | | | | | | 0.313 | |
| | 0.6118 | 0.332 | | | | | | 0.383 | |
| $Na_2CO_3$ | | | 0.391 | | 0.621 | | 0.588 | | |
| | 0.0830 | 0.0345 | | | | | | | |
| | 0.2085 | | | 0.131 | | | | | |
| | 0.2100 | | | | | 0.123 | | | |
| | 0.2495 | 0.0972 | | | | | | | |
| | 0.3128 | | | 0.199 | | | | | |
| | 0.3150 | | | | | 0.188 | | | |
| | 0.3327 | 0.133 | | | | | | | |
| | 0.4159 | 0.164 | | 0.266 | | | | | |
| | 0.4200 | | | | | 0.251 | | | |
| | 0.5213 | | | 0.328 | | | | | |
| | 0.6300 | | | 0.390 | | 0.375 | | | |
| | 0.8400 | | | | | 0.494 | | | |
| $CaCl_2$ | | | 0.286 | | | | | | 0.349 |
| | 0.1416 | 0.0407 | | | | | | 0.0508 | |
| | 0.2824 | 0.0972 | | | | | | 0.0959 | |
| | 0.3965 | 0.116 | | | | | | | |
| | 0.5649 | 0.162 | | | | | | 0.198 | |
| | 0.7061 | 0.203 | | | | | | 0.246 | |
| $Et_4NBr$ | | | −0.349 | | | | | | |
| | 0.2004 | −0.0715 | | | | | | | |
| | 0.4009 | −0.147 | | | | | | | |
| | 0.6013 | −0.212 | | | | | | | |
| | 0.8017 | −0.227 | | | | | | | |
| | 1.002 | −0.356 | | | | | | | |

Five different concentrations of salt solutions were prepared with double-distilled water. The optical absorbances were measured with a Shimadzu UV-120-02 and a Beckman-DU7HS spectrophotometer.

***Experimental Procedure.*** The detailed experimental procedure has been described elsewhere (*3*), so only a brief outline follows. Sufficient quantities of nonelectrolytes and water or salt solutions were sealed in ampules. They were preheated to 30–40 °C for approximately 30 min and then placed in a thermostat at 25 ± 0.001 °C. The ampules were mounted vertically on a rotary shaft and rotated for 2 h. They were then mounted horizontally on the rotary shaft and rotated for 1 h more, and finally allowed to settle in the thermostat at the desired temperature for 2 h before analysis. This procedure ensured that equilibrium was attained.

The absorption spectra of the aqueous solutions of nonelectrolytes were determined. The maximum absorption wavelengths for chlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, 2,4-dichlorophenol, and 2,4,6-trichlorophenol were 263.0, 269.5, 271.5, 226.0, 305.0, and 311.0 nm, respectively. Clear aqueous solutions of chlorobenzene, 1,3- and 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene were added to the optical cell for absorption measurements. The absorbance of each concentration was determined in triplicate, and the average value was taken.

***Data Analysis.*** From Beer's law, the absorbance of a saturated aqueous solution of nonelectolytes in pure water $A_0$ is given by $\epsilon S_0 l$ where $\epsilon$ is the optical extinction coefficient, $S_0$ is the concentration of solute, and $l$ is the path length of the optical cell. The absorbance of the saturated nonelectrolyte in a salt solution $A$ is $\epsilon Sl$. Substitution in the Setschenow expression yields

$$\log \gamma = \log[S_0/S] = \log[A_0/A] = kC_S \qquad (2)$$

where $\gamma$ is the activity coefficient of the solute referred to the

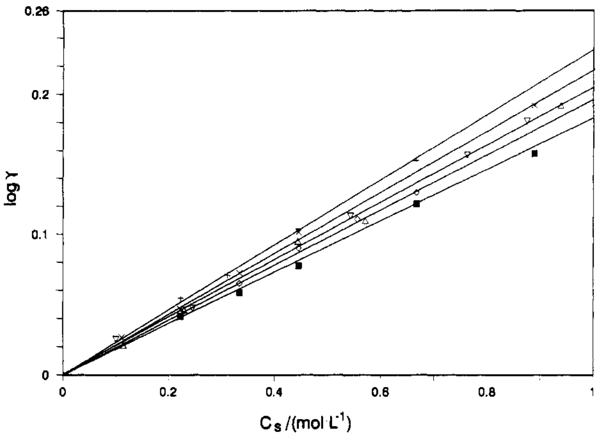

**Figure 1.** log γ versus salt concentration $C_S$ for six organic solutes in aqueous NaCl solutions at 298.15 K: (■) chlorobenzene, (▽) 1,3-dichlorobenzene, (×) 1,4-dichlorobenzene, (+) 1,2,4-trichlorobenzene, (◇) 2,4-dichlorophenol, (△) 2,4,6-trichlorophenol.

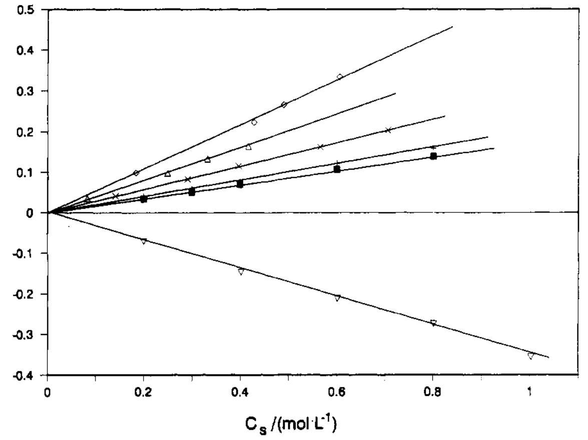

**Figure 2.** log γ versus salt concentration $C_S$ for chlorobenzene in six aqueous salt solutions at 298.15 K: (■) KCl, (+) NaCl, (◇) $K_2SO_4$, (△) $Na_2CO_3$, (×) $CaCl_2$, (▽) $(C_2H_5)_4NBr$.

solution in pure water, $k$ is the Setschenow constant, and $C_S$ is the salt concentration. For a series of experimentally determined values of $A$ for concentrations $C_S$, and from $A_0$ for pure water, the corresponding values of $\log[A_0/A]$ can be obtained. By plotting $\log[A_0/A]$ versus $C_S$, the salting constant $k$ can be calculated from the slope.

Equation 2 cannot necessarily be used to calculate the salt constant for weak acids such as the phenols because the parent and ionic forms may differ in absorbance characteristics. A modified equation is necessary if dissociation is appreciable. In this case the pH and $pK_a$ were such that dissociation was less than 1%; thus, the use of eq 2 is valid. Rigorous calculation of the activity coefficients γ including allowance for dissociation for 2,4,6-trichlorophenol showed that log γ was 0.0214 using eq 2 and 0.0213 using the rigorous equation.

## Results

Table 1 gives the activity coefficients and salting-out constants for six organic chemicals in NaCl at 25 °C. The salting-out constant of 0.240 of 1,4-dichlorobenzene agrees well with the reported value of 0.244 (*4*). Table 2 gives the activity coefficients and salting-out/in constants for five organic solutes in various aqueous salt solutions at 25 °C.

As shown in Figure 1, the empirical Setschenow equation gives a satisfactory description of the relationship between the activity coefficient of the organic solutes in NaCl solution at different salt concentrations. All displayed salting-out.

**Table 3. Comparison of Calculated and Observed Salting-Out Constants $k_s$ for Six Organic Solutes in Sodium Chloride Solutions**

| theory | CB | 1,4-DCB | 1,3-DCB | 1,2,4-TCB | 2,4-DCP | 2,4,6-TCP |
|---|---|---|---|---|---|---|
| DMT | 0.236 | 0.278 | 0.267 | 0.290 | 0.275 | 0.320 |
| CDST | 0.170 | 0.184 | 0.181 | 0.191 | 0.165 | 0.183 |
| SPT | 0.220 | 0.224 | 0.220 | 0.216 | 0.150 | 0.226 |
| IPT | 0.483 | 0.542 | 0.542 | 0.591 | 0.551 | 0.627 |
| XIPT | 0.181 | 0.197 | 0.197 | 0.212 | 0.200 | 0.222 |
| $k_s$(exptl) | 0.198 | 0.240 | 0.226 | 0.250 | 0.218 | 0.228 |

**Table 4. Comparison of the Observed and Calculated $k$ for Five Organic Solutes in Various Electrolyte Solutions at 298.15 K**

| chemical | theory and exptl | $k/(L{\cdot}mol^{-1})$ | | | | |
|---|---|---|---|---|---|---|
| | | KCl | $K_2SO_4$ | NaCl | $Na_2CO_3$ | $CaCl_2$ |
| CB | DMT | 0.192 | 0.424 | 0.236 | 0.531 | 0.757 |
| | CDST | 0.161 | 0.355 | 0.170 | 0.381 | 0.378 |
| | SPT | 0.157 | 0.607 | 0.220 | 0.542 | 0.060 |
| | IPT | 0.358 | 1.1316 | 0.483 | 1.906 | 1.327 |
| | XIPT | 0.142 | 0.596 | 0.181 | 0.806 | 0.499 |
| | exptl | 0.176 | 0.546 | 0.198 | 0.391 | 0.286 |
| 1,2-DCB | DMT | 0.200 | | 0.246 | | 0.790 |
| | CDST | 0.167 | | 0.176 | | 0.394 |
| | SPT | 0.150 | | 0.218 | | 0.035 |
| | IPT | 0.396 | | 0.535 | | 1.469 |
| | XIPT | 0.154 | | 0.196 | | 0.610 |
| | exptl | 0.207 | | 0.247 | | 0.357 |
| 1,3-DCB | DMT | 0.217 | 0.480 | 0.267 | 0.602 | 0.856 |
| | CDST | 0.172 | 0.410 | 0.181 | 0.386 | 0.407 |
| | SPT | 0.152 | 0.644 | 0.220 | 0.560 | 0.037 |
| | IPT | 0.402 | 1.473 | 0.542 | 0.140 | 1.489 |
| | XIPT | 0.156 | 0.656 | 0.197 | 0.885 | 0.547 |
| | exptl | 0.201 | 0.576 | 0.226 | 0.621 | 0.357 |
| 1,4-DCB | DMT | 0.225 | 0.479 | 0.278 | 0.622 | 0.887 |
| | CDST | 0.176 | 0.419 | 0.184 | 0.396 | 0.416 |
| | SPT | 0.156 | 0.645 | 0.224 | 0.566 | 0.044 |
| | IPT | 0.402 | 1.473 | 0.542 | 2.141 | 1.490 |
| | XIPT | 0.156 | 0.656 | 0.197 | 0.886 | 0.547 |
| | exptl | 0.192 | 0.527 | 0.240 | 0.588 | 0.344 |
| 1,2,4-TCB | DMT | 0.236 | 0.521 | 0.290 | | 0.930 |
| | CDST | 0.183 | 0.416 | 0.191 | | 0.436 |
| | SPT | 0.144 | 0.673 | 0.216 | | 0.011 |
| | IPT | 0.437 | 1.602 | 0.591 | | 1.622 |
| | XIPT | 0.167 | 0.702 | 0.212 | | 0.585 |
| | exptl | 0.239 | 0.623 | 0.250 | | 0.349 |

The salting-out sequence for chlorobenzene homologs is $k_{TCB} > k_{1,4\text{-}DCB} > k_{1,3\text{-}DCB} > k_{CB}$; for chlorophenols the sequence is $k_{TCP} > k_{DCP}$. Within a homologous series of organic solutes a larger molar volume results in a larger salting-out constant.

Figure 2 gives the relation between log γ and $C_S$ of chlorobenzene in the six salt solutions, only $Et_4NBr$ displaying salting-in. Other organic solutes gave similar results.

It is evident that for these systems (consisting of the six organic solutes and six salts) there is a consistent linear relationship between log γ and $C_S$ as expressed by the empirical Setschenow equation. Only $Et_4NBr$ showed a salting-in effect. The salting-out order with respect to the organic solutes is $K_2SO_4 > Na_2CO_3 > CaCl_2 > NaCl > KCl$, with the exception of a reversed order for $K_2SO_4$ and $Na_2CO_3$ for chlorobenzene.

## Discussion

Xie et al. (*3*) have reviewed the commonly used equations describing the salt effect including the Debye–MacAulay theory (DMT) (*5*), the Conway–Desnoyer–Smith theory (CDST) (*6*), the scaled particle theory (SPT) of Masterton and Lee (*7*), the internal pressure theory (IPT) of McDevit and Long (*8*), and the modified internal pressure theory (XIPT) of Xie et al. (*3, 9*). Tables 3–5 give the experimentally determined salting-out constants and values predicted using

**Table 5. Comparison of the Observed and Predicted Salting-Out Constants for Chlorobenzene in Aqueous Solutions of $Et_4NBr$**

| | calcd | | | | | |
|---|---|---|---|---|---|---|
| | DMT | CDST | SPT | IPT | XIPT | exptl |
| $k/(L \cdot mol^{-1})$ | 0.112 | 0.114 | 2.113 | −0.918 | −0.453 | −0.349 |

these theories for various organic solutes and electrolyte solutions.

Except for the predictions from the SPT, prediction of the salting-out sequence from these theories agreed well with experimental results. The average discrepencies between the calculated and experimental results are (DMT) 21%, (CDST) 26%, (SPT) 12%, (IPT) 33%, and (XIPT) 12%. In summary, values calculated from XIPT compared most favorably with the experimental results.

The salting-out constant for the organic solute is essential for calculating solubility in any desired salt concentration from the pure aqueous solubility. For example, for a concentration of NaCl in seawater of approximately 0.5 M, the aqueous solubility of chlorobenzene is 488 $g/m^3$, and the measured salting-out constant is 0.198. The solubility of chlorobenzene in 0.5 M NaCl solution will thus be 388 $g/m^3$ from eq 1. On the basis of the above discussion, the XPIT is recommended for estimating $k_s$ when no experimental values are available. When a number of ions are present, as in neutral water systems, knowledge of the salt effect of a single salt is insufficient; a "mixing rule" is required for estimation of the solubility. Sutton and Calder (*10*) have employed the method suggested by Gordon and Thorne (*11*) to calculate the solubility of alkanes in seawater,

$$\log S = \log S_0 - C_t \sum x_i k_i$$

where $S_0$ and $S$ are the solubilities in water and seawater, respectively, $x_i$ and $k_i$ are the mole fraction and salting-out constant of the $i$th nonelectrolyte, and $C_t$ is the total molar concentration of salt.

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