# Mutual Solubilities of Phenol, Salicylaldehyde, Phenol–Salicylaldehyde Mixture, and Water with and without the Presence of Sodium Chloride or Sodium Chloride plus Sodium Sulfate

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**The mutual solubilities of phenol, salicylaldehyde, one particular mixture of phenol–salicylaldehyde, and water with and without NaCl and NaCl plus $Na_2SO_4$ present have been determined experimentally. The interpretation of the results has been attempted by application of some existing theories. Limited success has been achieved, supporting the conclusion of many previous investigators of cautious application of theoretical tools in predicting the mutual solubilities of liquids.**

## Introduction

Synthesis of salicylaldehyde (SA) proceeds along various reaction pathways. One of them leads to a mixture of SA, phenol, and water in which NaCl and $Na_2SO_4$ are dissolved. The design requirements prompted the investigation of the solubility characteristics of this complex system. Only scarce literature data were found to exist, none of them concerning mutual solubilities of SA and water.

## Experimental Section

The mixtures were prepared by adding the organic component to a solution of NaCl or $Na_2SO_4$ in water. The specific procedure ran as follows. To 1000 g of water in which different amounts of salt (pure NaCl or a mixture of NaCl plus $Na_2SO_4$) were dissolved, 200 g of moisture-free phenol or 100 g of SA or 54.0 g of SA plus 46.0 g of phenol (close to being in equimolar quantities) were added. After the samples were vigorously shaken and mixed, they were kept at 25 ± 0.5 °C for ~6 h. The layers were separated, and in each layer the water and organic components were determined.

A gas chromatograph with the following specifications was used to analyze the organic components: a Hewlett-Packard 5750 G, UC-W 98 column, 6 ft long, $^1/_8$ in. o.d., packed with 80/100 mesh Chromosorb W, at 120 °C isothermally; the flow rate of $N_2$ as a carrier gas being 18.18 $cm^3\ min^{-1}$; the injector temperature 200 °C, the flame ionization detector at 250 °C; the $H_2$ flow rate 25 $cm^3\ min^{-1}$ and the air flow rate 500 $cm^3\ min^{-1}$; the attenuation for phenol determination $2 \times 10^2$, for SA $8 \times 10^2$. Water was analyzed on a Carle GC 8700 gas chromatograph equipped with a 6 ft × $^1/_8$ in. o.d. column filled with Poropac QS 80/100 mesh at 110 °C with helium as a carrier gas and equipped with a thermal conductivity detector. Peak areas have been determined by the Autolab System 4 Spectraphysics computing system. Linear relationships have been found between peak areas and component concentrations.

All of the chemicals used were of Pro Analysi purity grade, produced by Kemika, Zagreb, Yugoslavia.

## Results

Tables I–III summarize the results of this investigation. The graphic illustration has been presented in Figures 1–7. The data correlation has been successfully achieved through application of the well-known Setchenow (*1*, *2*, *3*) relation:

$$\log (\gamma/\gamma_0) = \log (S_0/S) = k_s C_s + k' \qquad (1)$$

where $\gamma_0$ and $\gamma$ are the activity coefficients of the solutes in water and electrolyte solution, respectively, $S_0$ and $S$ are the mole fraction solubilities of the solute in water and salt solution, respectively, $k_s$ is the Setchenow constant, and $C_s$ is the molar concentration of the salt solution.

In the case of the single-salt solution, constant $k'$ is zero, which is not the case in the mixed-electrolyte solutions. Its meaning may become obvious if a different form of the Setchenow relation is used (*4*)

$$\log (S_0/S) = h_1 I_1 + h_2 I_2 + \ldots \qquad (2)$$

where $I_k$ is the ionic strength of the solution given by

$$2I_k = \sum_i c_i z_i^2 \qquad (3)$$

As can be seen from the plots, parametric representation of the solubility in the mixed electrolyte has been used, the intercept corresponding to the ionic strength of the second electrolyte. All of the straight lines have been drawn by least squares.

The plots in Figures 1 and 2 and Table I represent the mutual solubilities of phenol and water in which NaCl and $Na_2SO_4$ are dissolved. The strong influence of the $Na_2SO_4$ concentration on the mutual solubility may be discerned. The same conclusion holds for SA–water solution in the presence of NaCl or a NaCl plus $Na_2SO_4$ mixture (Figures 3 and 4, Table II). In Figure 3 we have also drawn a line which has been obtained from extrapolated data for pure $Na_2SO_4$ solution and therefore must be used with due caution. However, it does show the more pronounced effect of $Na_2SO_4$ as compared to NaCl.

We call the reader's attention to one more fact: this difference is much more pronounced here than when dissolving phenol (aqueous NaCl solution: $k_s$(phenol) = 0.172 (*7*), $k_s$(SA) = 0.093 (this work); aqueous $Na_2SO_4$ solution: $k_s$(phenol) = 0.210 (*7*), $k_s$(SA) = 0.208 (this work, extrapolated data)).

Figures 5, 6, and 7 along with Table III show the solubility behavior of SA–PhOH mixtures in aqueous solutions of the same salts. The solubility of each organic component is, as expected, decreased, while the solubility of water in the PhOH–SA layer, as also expected, has increased compared to the case of $H_2O$ in phenol.

## Applicability of Existing Theories

The theoretical considerations have been directed along two lines: first, to predict, hopefully, the mutual solubility of pure substances; second, to predict the influence of the salts. Without going into detail, according to Hildebrand (*5*) for the case of molecules of very different sizes, eq 4 applies. (In saturated solutions of phenol or SA in water dissociation is negligible.)

$$\ln a_2 = \ln \varphi_2 + \varphi_1(1 - V_2/V_1) + V_1\varphi_1^2(\delta_1 - \delta_2)/RT \qquad (4)$$

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**Table I. Mutual Solubilities of Phenol and Aqueous NaCl plus $Na_2SO_4$ Solution**

| $C_s$, mol $L^{-1}$ | | aqueous layer[a] (phenol in water) | | | organic layer[b] (water in phenol) | | |
|---|---|---|---|---|---|---|---|
| $Na_2SO_4$ | NaCl | $10^2$ g/g aq layer | $10^3S$ | log $S_0/S$ | $10^2$ g/g org layer | $S$ | log $S_0/S$ |
| 0.4224 | 0.6222 | 3.30 | 6.329 | 0.3825 | 18.80 | 0.547 | 0.0952 |
| | 0.9167 | 3.00 | 5.699 | 0.4280 | 17.00 | 0.517 | 0.1196 |
| | 1.2009 | | | | 16.40 | 0.506 | 0.1287 |
| | 1.7402 | 2.25 | 4.293 | 0.5511 | 13.80 | 0.456 | 0.1746 |
| | 2.4839 | 1.73 | 3.234 | 0.6740 | 11.20 | 0.397 | 0.2340 |
| | | slope 0.1558 | intcpt 0.2844 | corr coeff 0.9997 | slope 0.0742 | intcpt 0.0470 | corr coeff 0.9963 |
| 0.8448 | 0.3078 | 2.40 | 5.270 | 0.4620 | 18.80 | 0.548 | 0.0947 |
| | 0.8745 | 2.10 | 3.970 | 0.5851 | 15.00 | 0.480 | 0.1520 |
| | 1.1484 | | | | 13.30 | 0.445 | 0.1847 |
| | 1.6831 | 1.84 | 3.460 | 0.6448 | | | |
| | 2.4349 | | | | 8.58 | 0.329 | 0.3155 |
| | 3.0901 | 1.24 | 1.956 | 0.8925 | 6.27 | 0.259 | 0.4197 |
| | | slope 0.1484 | intcpt 0.4251 | corr coeff 0.9899 | slope 0.1141 | intcpt 0.0540 | corr coeff 0.9960 |
| 1.2672 | 0.2950 | 1.89 | 3.710 | 0.6145 | 16.60 | 0.510 | 0.1260 |
| | 0.5685 | | | | 15.00 | 0.480 | 0.1520 |
| | 0.8334 | 1.60 | 3.000 | 0.7067 | | | |
| | 1.0943 | 1.40 | 2.610 | 0.7672 | 12.80 | 0.434 | 0.1960 |
| | 2.3228 | 0.99 | 1.831 | 0.9214 | 6.97 | 0.282 | 0.3840 |
| | | slope 0.1493 | intcpt 0.5828 | corr coeff 0.9933 | slope 0.1287 | intcpt 0.0765 | corr coeff 0.9917 |

[a] $S_0 = 1.527 \times 10^{-2}$. [b] $S_0 = 0.68107$.

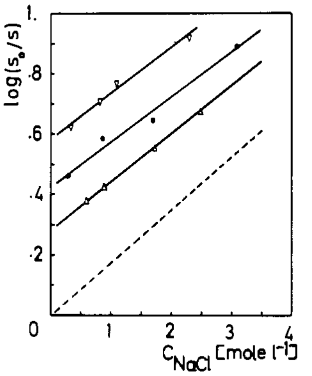

**Figure 1.** Effect of NaCl and a mixture of NaCl plus $Na_2SO_4$ on the solubility of phenol in water ($S_0 = 1.527 \times 10^{-2}$): (– – –) literature values for pure NaCl (*7*). $Na_2SO_4$ concentration (mol/1000 g of $H_2O$): (△) 0.4224; (●) 0.8448; (▽) 1.2672.

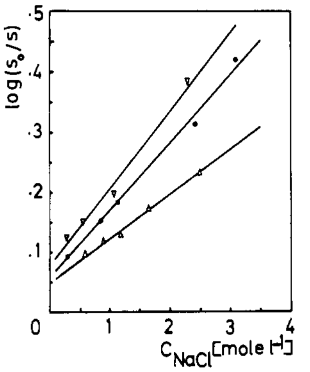

**Figure 2.** Effect of NaCl and a mixture of NaCl plus $Na_2SO_4$ on the solubility of water in phenol ($S_0 = 0.68107$). $Na_2SO_4$ concentration (mol/1000 g of $H_2O$): (△) 0.4224; (●) 0.8448; (▽) 1.2672.

Solubility parameters may be estimated from enthalpies of vaporization. When this quantity is not known, it may be estimated by various methods. A satisfactory (in numerous cases) and simple relationship is the one which utilizes the normal boiling point (eq 5). The SA solubility parameter obtained by this

$$\Delta H_{vap} - RT = \Delta E = -3542 + 23.7T_b + 0.020T_b^2 \quad (5)$$

formula is $\delta$(SA) = 10.62; for phenol, $\delta$(phenol) = 11.32.

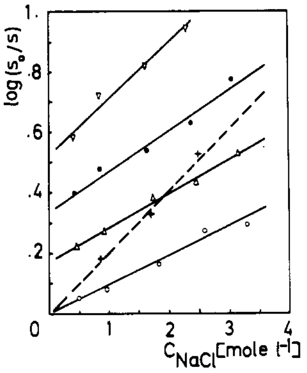

**Figure 3.** Effect of NaCl and a mixture of NaCl plus $Na_2SO_4$ on the solubility of salicylaldehyde in water ($S_0 = 6.614 \times 10^{-4}$): (– – –) extrapolated solubility for pure $Na_2SO_4$. $Na_2SO_4$ concentration (mol/1000 g of $H_2O$): (○) 0.0; (△) 0.4224; (●) 0.8448; (▽) 1.2672.

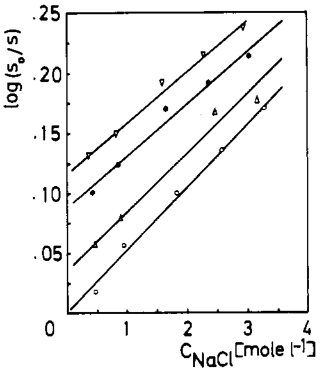

**Figure 4.** Effect of NaCl and a mixture of NaCl plus $Na_2SO_4$ on the solubility of water in salicylaldehyde ($S_0 = 5.921 \times 10^{-2}$). $Na_2SO_4$ concentration (mol/1000 g of $H_2O$): (△) 0.4224; (●) 0.8448; (▽) 1.2672.

The use of another method, which employs surface tension, by Beerbower (cited in ref *8*)

$$\delta = 3.741(\sigma / V^{1/3})^{0.5} \quad (6)$$

supposedly holding for large number of liquids, gives $\delta$(SA) = 11.16. In ref *6* a more precise determination of the solubility parameter has been discussed, giving for phenol the value 11.79 and for water 23.39. In these reports no value for $\delta$(SA) has been reported, and there are not enough data given to calculate

**Table II. Mutual Solubilities of Salicylaldehyde and Aqueous Solution of NaCl and NaCl plus $Na_2SO_4$**

| $C_s$, mol $L^{-1}$ | | aqueous layer[a] (SA in water) | | | organic layer[b] (water in SA) | | |
|---|---|---|---|---|---|---|---|
| $Na_2SO_4$ | NaCl | $10^3$g/g aq layer | $10^4S$ | log $S_0/S$ | $10^2$g/g org layer | $10^2S$ | log $S_0/S$ |
| 0 | 0.4965 | 3.87 | 5.846 | 0.0535 | 0.88 | 5.676 | 0.0184 |
| | 0.9686 | 3.58 | 5.514 | 0.0788 | 0.80 | 5.185 | 0.0576 |
| | 1.8383 | 2.84 | 4.538 | 0.1635 | 0.72 | 4.685 | 0.1017 |
| | 2.6014 | 2.08 | 3.510 | 0.2751 | 0.66 | 4.312 | 0.1377 |
| | 3.3280 | 1.97 | 3.365 | 0.2936 | 0.61 | 3.994 | 0.1710 |
| | | slope 0.0934 | intcpt 0.0003 | corr coeff 0.9891 | slope 0.0525 | intcpt 0.0002 | corr coeff 0.9968 |
| 0.4224 | 0.4744 | 2.50 | 3.965 | 0.2222 | 0.80 | 5.183 | 0.0577 |
| | 0.9086 | 2.18 | 3.514 | 0.2746 | 0.76 | 4.934 | 0.0792 |
| | 1.7357 | 1.64 | 2.736 | 0.3833 | | | |
| | 2.4601 | 1.41 | 2.426 | 0.4355 | 0.61 | 3.994 | 0.1708 |
| | 3.1591 | 1.10 | 1.952 | 0.5299 | 0.60 | 3.930 | 0.1781 |
| | | slope 0.1120 | intcpt 0.1734 | corr coeff 0.9963 | slope 0.0480 | intcpt 0.0374 | corr coeff 0.9841 |
| 0.8448 | 0.4433 | 1.60 | 2.647 | 0.3978 | 0.72 | 4.685 | 0.1017 |
| | 0.8664 | 1.30 | 2.190 | 0.4800 | 0.68 | 4.435 | 0.1255 |
| | 1.6627 | 1.10 | 1.900 | 0.5417 | 0.61 | 3.994 | 0.1708 |
| | 2.3840 | 0.85 | 1.553 | 0.6293 | 0.58 | 3.804 | 0.1923 |
| | 3.0534 | 0.60 | 1.109 | 0.7755 | 0.55 | 3.613 | 0.2146 |
| | | slope 0.1335 | intcpt 0.3403 | corr coeff 0.9843 | slope 0.0432 | intcpt 0.0833 | corr coeff 0.9897 |
| 1.2672 | 0.4174 | 1.00 | 1.726 | 0.5834 | 0.67 | 4.372 | 0.1316 |
| | 0.8347 | 0.72 | 1.267 | 0.7177 | 0.64 | 4.183 | 0.1508 |
| | 1.5955 | 0.55 | 0.998 | 0.8213 | 0.58 | 3.804 | 0.1923 |
| | 2.2866 | 0.40 | 0.746 | 0.9477 | 0.55 | 3.613 | 0.2146 |
| | 2.9609 | | | | 0.52 | 3.422 | 0.2380 |
| | | slope 0.1846 | intcpt 0.5306 | corr coeff 0.9880 | slope 0.0422 | intcpt 0.1171 | corr coeff 0.9941 |

[a] $S_0 = 6.614 \times 10^{-4}$. [b] $S_0 = 5.921 \times 10^{-2}$.

**Table III. Mutual Solubilities of Phenol plus SA and Aqueous Solution of NaCl plus $Na_2SO_4$**

| | | aqueous layer | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $C_s$, mol $L^{-1}$ | | phenol in water[a] | | | salicylaldehyde in water[b] | | | organic layer[c] (water in organic layer) | | |
| $Na_2SO_4$ | NaCl | $10^2$g/ g aq layer | $10^3S$ | log $S_0/S$ | $10^3$ g/ g aq layer | $10^4S$ | log $S_0/S$ | $10^2$ g/ g org layer | $S$ | log $S_0/S$ |
| 0.4224 | 0.4680 | 2.35 | 4.900 | 0.4936 | 1.40 | 2.260 | 0.4664 | | | |
| | 0.9159 | | | | | | | 4.90 | 0.238 | 0.0335 |
| | 1.7358 | | | | | | | 4.72 | 0.231 | 0.0465 |
| | 2.5041 | 1.33 | 2.440 | 0.7965 | 0.30 | 0.521 | 1.1045 | 4.50 | 0.222 | 0.0634 |
| | 3.1836 | 0.93 | 1.670 | 0.9611 | 0.20 | 0.390 | 1.2294 | 4.30 | 0.214 | 0.0795 |
| | | slope 0.1668 | intcpt 0.4082 | corr coeff 0.9938 | slope 0.2884 | intcpt 0.3416 | corr coeff 0.9960 | slope 0.0204 | intcpt 0.0132 | corr coeff 0.9960 |
| 0.8448 | 0.4452 | 1.90 | 4.158 | 0.5650 | 0.90 | 1.517 | 0.6395 | | | |
| | 0.8745 | 1.73 | 3.261 | 0.6706 | | | | 4.75 | 0.232 | 0.0452 |
| | 1.6627 | 1.28 | 2.361 | 0.8109 | 0.30 | 0.529 | 1.0970 | 4.50 | 0.222 | 0.0634 |
| | 2.3914 | 1.08 | 1.970 | 0.8894 | 0.20 | 0.363 | 1.2606 | 4.30 | 0.211 | 0.0795 |
| | 3.0534 | 0.76 | 1.360 | 1.0503 | | | | 4.10 | 0.206 | 0.0966 |
| | | slope 0.1756 | intcpt 0.5013 | corr coeff 0.9932 | slope 0.3250 | intcpt 0.5117 | corr coeff 0.9925 | slope 0.0243 | intcpt 0.0245 | corr coeff 0.9995 |
| 1.2672 | 0.8347 | 1.41 | 2.640 | 0.7622 | 0.30 | 0.530 | 1.0962 | 4.52 | 0.223 | 0.0618 |
| | 1.5918 | 1.13 | 2.181 | 0.8658 | | | | 4.27 | 0.213 | 0.0810 |
| | 2.2832 | 0.77 | 1.390 | 1.0408 | 0.10 | 0.188 | 1.5463 | 4.15 | 0.208 | 0.0922 |
| | 2.9167 | 0.65 | 1.091 | 1.1464 | 0.06 | 0.116 | 1.7560 | 3.95 | 0.200 | 0.1100 |
| | | slope 0.1910 | intcpt 0.5896 | corr coeff 0.9934 | slope 0.3158 | intcpt 0.8308 | corr coeff 0.9999 | slope 0.0224 | intcpt 0.0435 | corr coeff 0.9955 |

[a] $S_0 = 1.527 \times 10^{-2}$. [b] $S_0 = 6.614 \times 10^{-4}$. [c] $S_0 = 0.25717$.

this quantity by the same approach.

It is obvious that uncertainty regarding the correct value of the solubility parameter exists, diminishing confidence in the results from the very beginning. Also it is not surprising that the values obtained as a result of calculations show large discrepancies when compared with the experimental ones. When experimental values were used to back calculate the solubility parameter for water, the values in Table IV were obtained.

For the solubility of water in salicylaldehyde, very good agreement with the value of the solubility parameter reported in ref *5* was obtained. The other values are amenable to discussion, and no conclusive statement can be reached on the basis of so few experimental data.

The estimation of the salt influence may be done by application of the McDevit–Long formula (*1*, *2*, *3*)

$$k_s = V_h(V_s - V_0)/2.303\beta RT = \phi V_h$$
$$\phi = (V_s - V_0)/2.303\beta RT \qquad (7)$$

where $V_h$ is the partial molar volume of the hydrocarbon in

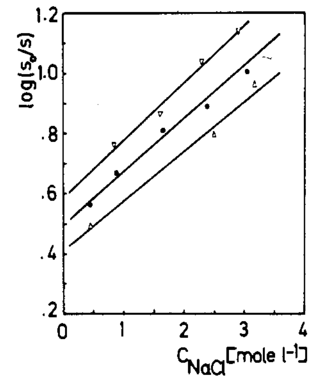

**Figure 5.** Solubility of phenol in the aqueous NaCl and NaCl plus $Na_2SO_4$ solution in the presence of salicylaldehyde ($S_0$ = 1.527 × $10^{-2}$). $Na_2SO_4$ concentration (mol/1000 g of $H_2O$): (Δ) 0.4224; (●) 0.8448; (∇) 1.2672.

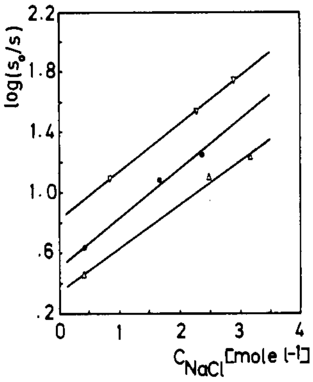

**Figure 6.** Solubility of salicylaldehyde in the aqueous NaCl and NaCl plus $Na_2SO_4$ solution in the presence of phenol ($S_0$ = 6.614 × $10^{-4}$). $Na_2SO_4$ concentration (mol/1000 g of $H_2O$): (Δ) 0.4224; (●) 0.8448; (∇) 1.2672.

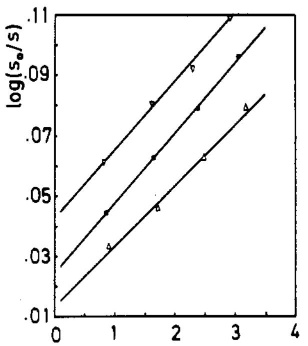

**Figure 7.** Solubility of water in a mixture of phenol plus salicylaldehyde in the presence of salts ($S_0$ = 0.25717). $Na_2SO_4$ concentration (mol/1000 g of $H_2O$): (Δ) 0.4224; (●) 0.8448; (∇) 1.2672.

solution, $V_s$ is the molar volume of the liquid salt, and $V_0$ is the partial molar volume of the salt solution, all at the system temperature ($T$), and $\beta$ is the compressibility of pure water.

This simple relationship has been used with limited success in predicting solubilities of nonelectrolytes in salt solutions. Since gross approximations in its derivation are involved, only the order of magnitude of Setchenow's constant may be obtained by its applications to the general effects such as salting in or salting out. When eq 7 has been applied to salicylaldehyde–water–salt systems, this has been confirmed since for $k_s(Na_2SO_4)$ the experimental value is somewhat smaller than $k_s$(NaCl) while these values for $Na_2SO_4$ show an even greater discrepancy, although according to eq 7 the opposite should have happened.

Table IV. Experimental and Theoretical Values for the Mutual Solubility of Phenol and Water, and Salicylaldehyde (SA) and Water (without Salt Present)

| | solute concn | | solubility parameter for water, cal/cm$^3$ | |
|---|---|---|---|---|
| solution type | mole fraction | $10^2$g/g of correspon layer | lit. value | back calculated value, $\delta$(SA) = 10.62 |
| SA in water | 6.614 × $10^{-4}$ | 0.447 | | 18.3<br>(18.8)[a] |
| water in SA | 0.1026 | 0.920 | | 21.8<br>(22.3)[a] |
| phenol in water | 0.0153 | 7.500 | 23.39 | 18.48 |
| water in phenol | 0.6811 | 29.000 | | 18.28 |

[a] $\delta$(SA) = 11.16.

We may conclude that theoretical tools currently available must be used with great caution and more as a guide where no experimental data exist.

## Acknowledgment

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## Glossary

| | |
|---|---|
| $a$ | activity |
| $C_i$, $C_s$ | salt concentration, mol L$^{-1}$ |
| $h$ | constant, L (g ion)$^{-1}$ |
| $I$ | ionic strength of the solution |
| $k_s$ | Setchenow constant, L mol$^{-1}$ |
| $R$ | gas constant |
| $S_0$, $S$ | mole fraction solubilities |
| $T$ | temperature, K |
| $V_1$, $V_2$, $V_h$ | partial molar volume of the organic solute, cm$^3$ mol$^{-1}$ |
| $V_0$ | partial molar volume of the salt solution |
| $V_s$ | molar volume of the liquid salt |
| $z_i$ | ion valency |

*Greek Letters*

| | |
|---|---|
| $\beta$ | compressibility of pure water |
| $\gamma$ | activity coefficients |
| $\delta$ | solubility parameter, cal cm$^{-3}$ |
| $\varphi$ | volume fraction |
| $\sigma$ | surface tension, dyn cm$^{-1}$ |

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