# Isopiestic Investigation of Water Activities of Aqueous $NiCl_2$ and $CuCl_2$ Solutions and the Thermodynamic Solubility Product of $NiCl_2{\cdot}6H_2O$ at 298.15 K

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Isopiestic vapor-pressure experiments have been performed for aqueous solutions of high-purity $NiCl_2$ from 1.4382 to 5.7199 mol·kg$^{-1}$ (supersaturated) at 298.15 K. The resulting osmotic coefficients were combined with published isopiestic data to yield recommended values of $a_w$, $\phi$, and $\gamma_\pm$. Similarly, the solubility of $NiCl_2{\cdot}6H_2O$(cr) was determined by this method, and combined with literature values to yield the molal thermodynamic solubility product $K_m° = 1108 \pm 19$. Isopiestic experiments were also performed for aqueous solutions of high-purity $CuCl_2$, but the isopiestic molality ratio exhibited hysteresis due to gradual loss of HCl from the $CuCl_2$ solutions, for experiments done with both degassed and air-filled chambers. The water activity of a saturated solution in equilibrium with $CuCl_2{\cdot}2H_2O$(cr) was determined to be $a_w$(satd) = 0.680 75 ± 0.000 08.

## Introduction

Rard and Platford (*1*) have given a detailed discussion of possible errors and their influence on the accuracy and precision of isopiestic measurements. They noted that, with favorable conditions and good experimental technique, the resulting osmotic coefficients $\phi$ from independent studies can agree to 0.2–0.3% or even better. Larger differences than this are, unfortunately, not uncommon. They can result from problems such as inadequate purity of the electrolytes being investigated, unreliable chemical analyses for molality, chemical reaction between the electrolyte solutions and the isopiestic sample cups, etc.

A knowledge of the thermodynamic properties of aqueous solutions of the transition-metal dichlorides is required for a variety of reasons including the economic importance of the metals and the need to develop better methods for their extraction and separation from ores. In addition, the large variation in the strength and extent of anion–cation interactions makes it more challenging to model their thermodynamic behavior than (for example) the alkaline-earth-metal dichlorides.

For these reasons, we have measured and reported isopiestic data for aqueous solutions of $MnCl_2$, $NiCl_2$, $CdCl_2$, and $ZnCl_2$ (*2–5*) from low to high molalities at 298.15 K; for the first three of these electrolytes, the measurements extend well into the supersaturated region. In those reports we critically compared our new isopiestic results to previous values.

We found that values of $\phi$ from the various isopiestic studies showed a maximum variation of about 0.5% for $MnCl_2$, although most $\phi$ values agreed to within 0.3% (*2*). Similarly, for $NiCl_2$ the various studies all agreed within 0.6%, but with better agreement over most of the molality range (*3*). Comparison of isopiestic $\phi$ values for $CdCl_2$ solutions (*4*) indicated agreement to 0.3–0.4%, with a few individual points having random deviations of up to 1%. For $ZnCl_2$ solutions the maximum discrepancy in $\phi$ was about 0.7%, with most data sets agreeing to within 0.3% (*5*). Even though these maximum discrepancies are about twice that expected for very favorable systems, the agreement is still quite reasonable, given that the degree of purity of the transition-metal dichlorides is generally not known for the earlier studies.

In the last 20 years there has been a resurgence of interest in the thermodynamic properties of aqueous $CuCl_2$, and of its mixtures with other electrolytes (*6–10*). We examined published isopiestic data for aqueous $CuCl_2$ solutions at 298.15 K (*6, 8, 11, 12*) and found that derived values of $\phi$ agree to about 0.5% at lower molalities, but these differences increase to 0.5–1.2% at higher molalities. This maximum discrepancy is about twice as great as observed for the other four transition-metal dichlorides mentioned above. Goldberg et al. (*13*) have critically compared published isopiestic $\phi$ values for aqueous $CoCl_2$ solutions and found a divergence of up to 2.3% at the highest molalities.

Because of these rather large discrepancies among the published isopiestic $\phi$ for both aqueous $CuCl_2$ and $CoCl_2$ solutions at 298.15 K, we decided to perform new isopiestic measurements. In addition we reinvestigated aqueous $NiCl_2$ solutions as a "control system", to establish how reproducible isopiestic data can be for aqueous transition-metal dichlorides. As noted in the Experimental Section, we abandoned our attempt to study aqueous $CoCl_2$ because of significant chemical contamination of our supply of "analytical reagent" $CoCl_2{\cdot}6H_2O$.

## Experimental Section

***Preparation and Analyses of Stock Solutions.*** Stock solutions were prepared of aqueous $NiCl_2$, $CuCl_2$, $CoCl_2$, NaCl, and $CaCl_2$, where the last two electrolytes were used as isopiestic reference standards. Water for these solutions was purified by ion exchange followed by distillation.

Our NaCl stock solution was prepared by mass from oven-dried Mallinckrodt AR NaCl and purified water. The molality of this solution was determined to be 1.9996 ± 0.0006 mol·kg$^{-1}$, by dehydration of samples in triplicate at 473 and 523 K. This value agrees well with the molality calculated from the masses of NaCl and water used for its preparation, 1.9991 mol·kg$^{-1}$, and the average of these two values was accepted.

Two separate concentrated stock solutions of aqueous $CaCl_2$ were prepared by reaction of Mallinckrodt primary standard $CaCO_3$ (different lots) with aqueous HCl, followed by filtration to remove excess $CaCO_3$ and other insoluble material. We recrystallized one of these batches of $CaCl_2$ before using it for

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stock solution no. 1. In contrast for stock solution no. 2, the filtered reaction mixture was adjusted to the stoichiometric pH of $CaCl_2$, as determined by potentiometric-pH titrations of samples of the unadjusted stock solution with dilute HCl.

The molalities of each $CaCl_2$ stock solution were determined by conversion of weighed samples to anhydrous $CaSO_4$, resulting from evaporation of these samples to dryness after addition of excess $H_2SO_4$. A tare crucible not containing $CaCl_2$ was treated in an identical manner, to allow a correction to be made for nonvolatile residue from the $H_2SO_4$ solution. The molality of stock solution no. 1 was determined to be 6.6076 ± 0.0040 mol·kg$^{-1}$, after firing the $CaSO_4$ at 673–773 K. Similarly, the molality of stock solution no. 2 was found to be 6.6058 ± 0.0017 mol·kg$^{-1}$ after firing the $CaSO_4$ to 673–873 K, and a second analysis at 673–923 K gave 6.6068 ± 0.0018 mol·kg$^{-1}$. These two results for stock solution no. 2 were averaged for subsequent calculations. Although reproducible stock solution molalities could be obtained from firing the $CaSO_4$ at various temperatures at or above 673 K, temperatures of about 825–925 K gave more consistent results.

We also determined the molality of $CaCl_2$ stock solution no. 2 by dehydration of samples at 473 and 498 K, but this method gave a molality about 0.1% above the values obtained by sulfate analyses. We found that the weights of $CaCl_2$ varied with the humidity of the laboratory. Thus, the dehydration results were rejected as being slightly high due to absorption of moisture.

The $CaSO_4$ from concentration analysis of stock solution no. 2 was examined for impurities by X-ray fluorescence spectroscopy and was found to contain (in mass fractions) $1 \times 10^{-4}$ Sr, $<1 \times 10^{-4}$ K, and $<1 \times 10^{-4}$ Ba, which indicates the $CaCl_2$ was fairly pure. A sample of $CaCl_2$ from evaporation of a sample of stock solution no. 1 was examined for impurities by direct current arc optical emission spectroscopy (DCA-OES) and found to contain $\sim 1 \times 10^{-3}$ Sr, $3 \times 10^{-5}$ Ba, $1 \times 10^{-4}$ Si, and $<5 \times 10^{-5}$ Na and Fe each. Fortunately, the presence of this much Sr in the $CaCl_2$ has almost no effect on its osmotic coefficients.

Concentrated stock solutions of $NiCl_2$ and $CoCl_2$ were prepared by dissolving "Baker-analyzed" $NiCl_2·6H_2O$ and $CoCl_2·6H_2O$, respectively, in purified water followed by filtration. There was very little insoluble material in the $NiCl_2$, but there was a fair amount of pink "foam" floating on top of the burgundy-wine-colored $CoCl_2$ solution, along with some higher-density light-brown material that settled to the bottom. (The density of this $CoCl_2$ stock solution was 1.386 83 g·cm$^{-3}$.) This pink foam was removed by filtration and, after washing it with water, was actually found to be a white-colored solid. Impurity analyses for a sample of the original $CoCl_2·6H_2O$ and a sample of the filtered stock solution were in complete agreement, which implies that both the white and light-brown solids were insoluble compounds of cobalt rather than some other type of impurity. The presence of these solids suggests that the $CoCl_2$ was not completely stoichiometric with regard to its chloride content. Our original sample of Baker-analyzed $CuCl_2·2H_2O$ was recrystallized once, by saturating a solution at about 325 K followed by cooling to about 278 K.

We normally analyze stock solutions of metal chlorides both by gravimetric sulfate (as described above for $CaCl_2$) and by mass titration of the chloride with aqueous $AgNO_3$, by using dichlorofluorescein as the end-point indicator. However, all three of our transition-metal dichlorides are too deeply colored to allow observation of that end-point color change. For the sulfate analyses we evaporate samples of the stock solution to dryness with excess $H_2SO_4$, followed by firing the sample above 673 K to evaporate off excess $SO_3$. Although $NiSO_4$, $CuSO_4$, and $CoSO_4$ are thermally stable at lower temperatures, we found that they underwent partial decomposition by 673 K, which makes gravimetric sulfate unsuitable for quantitative analyses. We therefore heated those sulfate samples to even higher temperatures to complete the decompositions, and weighed the samples as oxides. Analyses were always done in triplicate. Weights were converted to masses before calculating molalities.

Analysis of the $CuCl_2$ stock solution by decomposition of the sulfate indicated that stoichiometric CuO formed above 970 K. Samples heated to 973–1073 K gave consistent results. Two separate analyses gave 4.8920 ± 0.0042 and 4.8920 ± 0.0019 mol·kg$^{-1}$ for the $CuCl_2$ concentration.

We have previously shown that treatment of $NiCl_2$ solutions with $H_2SO_4$ followed by thermal decomposition above about 1073 K gave stoichiometric NiO (*3*). However, when these samples of NiO were fired to various temperatures between 1073 and 1153 K, the calculated molalities showed an average decrease of $0.010_3$% per 10 K increase in temperature. In contrast, holding the NiO samples at any fixed temperature for several days did not give rise to weight changes with time, so the NiO was not decomposing. We did observe that the top surface and bulk NiO remained gray-green-colored at all of these temperatures, but the bottom surface of the NiO in direct contact with the porcelain crucibles had turned yellow green, presumably due to a small amount of chemical reaction. We therefore restricted our calculation of the stock solution molalities to weights of NiO obtained in the temperature range of 1073–1113 K, where the likelihood of reaction should be less. Two separate analyses gave 4.8368 ± 0.0016 and 4.8373 ± 0.0011 mol·kg$^{-1}$, and their average was accepted. Because of this slight reaction during the analyses, we consider the resulting stock solution molalities to be uncertain by about 0.04%.

The following molar masses (1969 atomic masses) were used for calculation of solution molalities: 58.443 for NaCl, 110.986 for $CaCl_2$, 136.138 for $CaSO_4$, 129.616 for $NiCl_2$, 74.709 for NiO, 134.451 for $CuCl_2$, and 79.545 g·mol$^{-1}$ for CuO.

The samples of NiO, CuO, and cobalt oxides from thermal decomposition of the sulfates were analyzed for impurities by DCAOES, as was a sample of $CoCl_2·6H_2O$ taken directly from the bottle. The NiO and CuO contained the following impurities in mass fractions: $3 \times 10^{-5}$ Al, $2 \times 10^{-5}$ Ca, $1.5 \times 10^{-5}$ Si, $1 \times 10^{-5}$ Fe, $3 \times 10^{-6}$ Mg, and $\leq 1 \times 10^{-6}$ Cu in the NiO; $3 \times 10^{-5}$ Ca, $3 \times 10^{-5}$ Fe, $\leq 5 \times 10^{-6}$ Si, and $4 \times 10^{-6}$ Mg in the CuO. Thus, the purity of the $NiCl_2$ and $CuCl_2$ was about 99.99 mass % (99.98 mol %). The impurity analyses for cobalt oxides and $CoCl_2·6H_2O$ were quite consistent, and indicate the $CoCl_2$ contained about (mol %) 0.136 $NiCl_2$, 0.038 $CuCl_2$, 0.014 $FeCl_3$ and $MnCl_2$ each, about 0.01 $CaCl_2$ and $MgCl_2$ each, about 0.003 LiCl, and 0.0002 $BaCl_2$. Thus, the $CoCl_2$ contained 99.775 mol % $CoCl_2$ and 0.225 mol % impurities, with about 60% of the impurities being $NiCl_2$. We note that metallic impurities in the $CoCl_2·6H_2O$, as claimed by the manufacturer were 0.01% Ni, 0.0002% Cu, and 0.0004% Fe, presumably as percent by mass.

We abandoned our plan to perform isopiestic measurements for $CoCl_2$, in part because of the large amount of impurities present in our sample and in part because we doubted whether the $CoCl_2$ solution was stoichiometric with regard to the Co/Cl mole ratio. However, if similar amounts of impurities were present in any of the $CoCl_2$ samples used for previous isopiestic measurements, this could explain the unusually large discrepancies for $\phi$ (*13*).

***Isopiestic Measurements.*** All of the isopiestic experiments were performed at 298.15 ± 0.005 K in our stainless steel isopiestic chambers. They have been described in detail elsewhere (*14*), as has the normal operating procedure for isopiestic experiments (*1, 14, 15*). All weights of the electrolyte solutions were converted to mass.

**Table I. Isopiestic Molalities of $NiCl_2$ and $CuCl_2$ with NaCl Reference Standard, and Osmotic Coefficients of $NiCl_2$ at 298.15 ± 0.005 K**

| [NaCl]/ (mol·kg$^{-1}$) | [$NiCl_2$]/ (mol·kg$^{-1}$) | [$CuCl_2$]$^a$/ (mol·kg$^{-1}$) | $\phi(NiCl_2)$ | equilibration time$^b$/days |
|---|---|---|---|---|
| | | Series 1, Degassed Chamber | | |
| 5.1399 | 2.5185 | 3.5302 | 1.6346 | 19 |
| 5.1842 | 2.5351 | 3.5726 | 1.6426 | 10 |
| 5.2422 | 2.5585 | 3.6236 | 1.6520 | 11 |
| 4.8913 | 2.4145 | | 1.5965 | 10 |
| 4.9637 | 2.4442 | | 1.6080 | 12 |
| | | Series 2, Air-Filled Chamber | | |
| 4.9975 | 2.4575 | 3.4147 | 1.6138 | 20 |
| 5.3053 | 2.5855 | 3.6743 | 1.6612 | 17 + 31 = 48 |
| 5.5136 | 2.6716 | 3.8493<br>3.8300$^c$ | 1.6932 | 22 |
| 4.8690 | 2.4045 | 3.3403<br>3.3284$^c$ | 1.5935 | 23 + 29 = 52 |
| 4.8953 | 2.4155 | 3.3643<br>3.3550$^c$<br>3.3466$^d$ | 1.5975 | 42 |
| | | Series 2, Degassed Chamber$^e$ | | |
| 4.9618 | 2.4433 | | 1.6078 | 25 |
| 4.4696 | 2.2381 | | 1.5308 | 17 |
| 4.0833 | 2.0775 | | 1.4686 | 17 |
| 3.4894 | 1.8247 | | 1.3741 | 22 |
| 3.1791 | 1.6916 | | 1.3235 | 21 |
| 2.6078 | 1.4382 | | 1.2317 | 12$^f$ |

[a] These molalities of $CuCl_2$ were calculated by assuming all weight changes were due to loss or gain of water. Because of loss of HCl during the equilibrations, these values are not accurate. [b] For some of the equilibrations done with an air-filled chamber, the initial equilibration period was inadequate and it was necessary to requilibrate the samples. In those cases both equilibration times are listed. [c] After the previous equilibration, this fresh sample was added to the chamber and used for these experiments. [d] Another fresh sample added after the previous equilibration. [e] Same samples of NaCl and $NiCl_2$ as for the experiments done with the air-filled chamber (series 2). [f] Partway through this equilibration the refrigerator/circulator malfunctioned, and the temperature of the "constant-temperature" bath rose several degrees above 298 K. The listed equilibration time is the time after proper temperature control was reestablished.

There is one feature of our isopiestic chambers that was not made clear in the detailed drawing (*14*): the alignment of the copper temperature-equilibration block in the chamber. The bottom of each chamber contains two narrow railroad-track-type extensions of stainless steel to raise the copper block up from the bottom of the chamber, and each side wall of the chamber contains two stainless steel studs to keep the copper block from moving about as the chamber is rocked back-and-forth. Only 12% of the total surfaces of the sides and bottom of the copper block are thus in direct thermal contact with the bottom and sides of the isopiestic chamber. Limiting their thermal contact is desirable, in order to "buffer" out temperature fluctuations in the constant-temperature water bath.

Tables I and II contain all of the isopiestic equilibrium molalities. Each of the four main series of measurements involves sequential equilibrations of the same sets of solution samples, although in several cases fresh samples were added part way through to check the reproducibility of the experimental measurements. Separate samples of stock solutions were weighed out for each different series of measurements, except for a pair of samples of $CaCl_2$ stock solution no. 1 that were reused because we ran out of that solution.

Equilibrium molalities in these tables are nearly always the average of two values for duplicate samples. However, in one case for $NiCl_2$ only a single sample was involved, because of crystallization in the other sample cup. The uncertainties of the reported molalities are less than 0.1%, with the majority of molalities for duplicate samples agreeing to better than 0.05%.

Experimental measurements for $NiCl_2$ solutions extend to the highest supersaturated molalities that could be achieved without the occurrence of spontaneous crystallization. Two attempted experiments for $NiCl_2$ molalities above 5.72 mol·kg$^{-1}$ resulted in crystallization in one or both sample cups (water liberated from the crystallizing sample is absorbed by the other samples, thus diluting them slightly). This upper limit agrees with our earlier observation that $NiCl_2$ solutions were unstable with regard to crystallization above 5.7 mol·kg$^{-1}$ (*3*), although in that study we did manage to reach a molality of 6.1364 mol·kg$^{-1}$.

We generally combine and sort isopiestic molalities from different series of isopiestic experiments into some regular order with increasing or decreasing molalities when we publish isopiestic data. However, here we give the results for each series separately and give them in the order that the experiments were actually performed within that series. This is done because of difficulties with the experiments for $CuCl_2$ solutions, which we describe in the following paragraphs. Some experiments were done with increasing the molalities above the previous equilibration values (achieved by adding an extra sample cup to the chamber that contained a few drops of concentrated $H_2SO_4$ to absorb water vapor), and some with decreasing the molalities (done by adding one or more drops of water to the isopiestic cups).

Our first isopiestic experiments were the series 3 experiments using samples of $CaCl_2$ stock solution no. 1 as isopiestic reference standard. Derived values of $\phi$ for $NiCl_2$ from these experiments were in very good agreement with our previous measurements (*3*). However, the initial experiments for $CuCl_2$ gave values of $\phi$ that were significantly higher than those from previous isopiestic studies (*6, 8, 11, 12*), about 1–1.5% higher, but as we continued to reequilibrate these samples the $\phi$ values approached those from the other studies and ultimately dropped below them. A careful examination of the isopiestic cups (tantalum metal) indicated that they were not being corroded by the $CuCl_2$ solutions, nor were any precipitates present, nor did the solutions appear to be turbid.

We note that the molalities of the duplicate samples used in these equilibrations always agreed to within a few hundredths of a percent, which is remarkably good agreement at such high molalities. This agreement seemed to imply that the chemical integrity of the $CuCl_2$ samples had not been compromised, or that if chemical changes had occurred, they were affecting both samples by exactly the same amount.

We then performed solubility measurements for aqueous $CuCl_2$. Solubility experiments with equilibrations of 14, 16, 17, and 20 days gave essentially equal activities of water, because the $CaCl_2$ reference standard molalities were equal within the scatter of the data. Although these water activities were constant, the molality of $CuCl_2$ in the isopiestic cups continued to increase as the samples were reequilibrated (apparent $\phi$ were decreasing). This information, together with the drift in $\phi$ noted above, definitely indicates the $CuCl_2$-to-$CaCl_2$ isopiestic molality ratio was exhibiting hysteresis. In contrast, the $NiCl_2$-to-$CaCl_2$ molality ratio depended only on molality and not on time, and was quite reproducible. While the $CuCl_2$ solubility experiments were in progress, we began the series 1 experiments in which $NiCl_2$ and $CuCl_2$ solutions were equilibrated against a NaCl reference standard. We found a similar drift in the $CuCl_2$-to-NaCl isopiestic molality ratio as samples were reequilibrated, whereas the $NiCl_2$-to-NaCl molality ratio was quite reproducible. Thus $NiCl_2$, $CaCl_2$, and NaCl solutions were not affected by the irreversible changes in the $CuCl_2$ solutions.

**Table II. Isopiestic Molalities of $NiCl_2$ and $CuCl_2$ with $CaCl_2$ Reference Standards, and Osmotic Coefficients of $NiCl_2$ at 298.15 ● 0.005 K**

| $[CaCl_2]^a$/ (mol·kg$^{-1}$) | $[CaCl_2]^b$/ (mol·kg$^{-1}$) | $[NiCl_2]^c$/ (mol·kg$^{-1}$) | $[NiCl_2]^d$/ (mol·kg$^{-1}$) | $[CuCl_2]^e$/ (mol·kg$^{-1}$) | $\phi$-($NiCl_2$)$^f$ | $[CaCl_2]^a$/ (mol·kg$^{-1}$) | $[CaCl_2]^b$/ (mol·kg$^{-1}$) | $[NiCl_2]^c$/ (mol·kg$^{-1}$) | $[NiCl_2]^d$/ (mol·kg$^{-1}$) | $[CuCl_2]^e$/ (mol·kg$^{-1}$) | $\phi$-($NiCl_2$)$^f$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Series 3, Degassed Chamber | | | | | | | | | | | |
| 2.7115 | | 2.6556 | | 3.7826 | 1.6858 | 3.3502 | | 3.3453 | | 5.2949 | 1.9146 |
| 2.7433 | | 2.6877 | | 3.8492 | 1.6982 | 3.1527 | | 3.1249 | | 4.8406 | 1.8466 |
| 2.7929 | | 2.7393 | | 3.9569 | 1.7167 | 2.8883 | | 2.8409 | | 4.2583 | 1.7510 |
| 2.8477 | | 2.7955 | | 4.0706 | 1.7377 | 3.7979 | | 3.8656 | | | 2.0605 |
| 2.9168 | | 2.8701 | | 4.2276 | 1.7621 | 3.8203 | | 3.8933 | | | 2.0670 |
| 2.9863 | | 2.9434 | | 4.3777 | 1.7879 | 3.8555 | | 3.9366 | 3.9371 | | 2.0772 |
| 3.0602 | | 3.0239 | | 4.5483 | 1.8139 | 3.8942 | | 3.9815 | 3.9805 | | 2.0905 |
| 3.1299 | | 3.0986 | | 4.7017 | 1.8394 | 3.9698 | | 4.0765 | 4.0759 | | 2.1116 |
| 3.1936 | | 3.1678 | | 4.8461 | 1.8622 | 4.0627 | | 4.1920 | 4.1914 | | 2.1385 |
| 3.2666 | | 3.2499 | | 5.0197 | 1.8869 | 4.2140 | | 4.3859 | 4.3846 | | 2.1796 |
| 3.3416 | | 3.3322 | | 5.1898 | 1.9136 | 4.3288 | | 4.5329 | 4.5320 | | 2.2106 |
| 3.5519 | | 3.5737 | | 5.7146$^g$ | 1.9832 | 3.2756 | 3.2764 | | 3.2600 | | 1.8904 |
| 3.5595 | | 3.5845 | | 5.7512$^h$ | 1.9845 | 3.4595 | 3.4609 | | 3.4675 | | 1.9532 |
| 3.5600 | | 3.5844 | | 5.7659$^i$ | 1.9851 | 3.6857 | 3.6857 | | 3.7299 | | 2.0265 |
| 3.5394 | | 3.5589 | | 5.7199$^j$ | 1.9792 | 3.8722 | 3.8722 | | 3.9536 | | 2.0842 |
| 3.5612 | | 3.5858 | | 5.7814$^k$ | 1.9855 | 4.0936 | 4.0942 | | 4.2307 | | 2.1474 |
| 3.5598 | | 3.5833 | | 5.7861$^l$ | 1.9855 | 4.3378 | 4.3381 | | 4.5446 | | 2.2129 |
| Series 4, Degassed Chamber | | | | | | | | | | | |
| | 4.4645 | 4.7089 | | | 2.2459 | 3.8947 | 3.8956 | 3.9819 | | | 2.0909 |
| | 4.5625 | 4.8405 | | | 2.2693 | 4.1289 | 4.1309 | 4.2759 | | | 2.1576 |
| | 4.7220 | 5.0589 | | | 2.3051 | 4.4564 | 4.4577 | 4.7016 | | | 2.2429 |
| | 4.7932 | 5.1578 | | | 2.3203 | 4.5698 | 4.5718 | 4.8560 | | | 2.2693 |
| | 4.8924 | 5.2944 | | | 2.3417 | 4.5789 | 4.5801 | 4.8659$^o$ | | | 2.2722 |
| | 4.9655 | 5.4004 | | | 2.3550 | 4.5973 | 4.5995 | 4.8939$^p$ | | | 2.2754 |
| | 5.0811 | 5.5666 | | | 2.3762 | 4.6162 | 4.6168 | 4.9159$^q$ | | | 2.2808 |
| | 5.1928 | 5.7199 | | | 2.3993 | 4.6086 | 4.6082 | 4.9058$^r$ | | | 2.2785 |
| | 5.1430 | 5.6497$^m$ | | | 2.3899 | 4.7871 | 4.7880 | 5.1527 | | | 2.3179 |
| 3.7412$^n$ | 3.7425 | 3.7976 | | | 2.0436 | | | | | | |
| Series 5, Air-Filled Chamber | | | | | | | | | | | |
| 3.5594$^s$ | 3.5604$^s$ | | | | | | | | | | |

[a] These molalities are for $CaCl_2$ stock solution no. 1. [b] These molalities are for (pH-adjusted) $CaCl_2$ stock solution no. 2. [c] These molalities are for the initial samples of $NiCl_2$. [d] These molalities are for fresh samples of $NiCl_2$ added later in series 3 experiments. [e] These molalities of $CuCl_2$ were calculated by assuming all weight changes were due to loss or gain of water. Because of loss of HCl during the equilibrations, these values are not accurate. [f] For experiments with two pairs of samples of $NiCl_2$, their average molality was used for calculation of $\phi$. For experiments with samples of both $CaCl_2$ stock solutions, values of $\phi$ for $NiCl_2$ were calculated from each $CaCl_2$ molality pair and then averaged. [g] Solubility determination with 12-day equilibration. [h] Solubility determination with 14-day equilibration. [i] Solubility determination with 16-day equilibration. [j] Solubility determination with 12-day equilibration. [k] Solubility determination with 17-day equilibration. [l] Solubility determination with 20-day equilibration. [m] Single sample owing to crystallization in the other sample cup. [n] These are the same $CaCl_2$ stock no. 1 samples used in the series 3 experiments. [o] Solubility determination with 7-day equilibration. [p] Solubility determination with 17-day equilibration. [q] Solubility determination with 7-day equilibration; temperature control was lost earlier during this equilibration and the temperature rose to about 305 K. The 7 days refer to the equilibration after temperature control was reestablished at 298.15 K. This value was not included in the least-squares analysis with eq 7. [r] Solubility determination with 28-day equilibration. [s] Solubility determination for $CuCl_2$ with 41-day equilibration in an air-filled chamber with a reservoir of saturated solution and crystals. No molality is given for $CuCl_2$ because of crystallization in the sample cups. Same samples of $CaCl_2$ as in series 4 experiments.

We suspected that these problems were due to loss of HCl and consequently due to hydrolysis of the aqueous $CuCl_2$, but the lack of turbidity or a precipitate was puzzling. The outer walls of our isopiestic chambers are made of stainless steel, which is readily attacked by HCl. A careful examination of the chamber lids showed a thin film of corrosion products was present right above each sample cup containing $CuCl_2$, with a "tail" extending toward the needle valve used to evacuate air from that chamber. This film was easily wiped off with a paper towel, and gave a dark-brown smear. It was undoubtably iron oxide. Small amounts of hydrogen gas should have been produced by reaction of HCl with the steel, but it would not affect the isopiestic experiments. Even a single isopiestic equilibration involving $CuCl_2$ solutions was found to cause enough corrosion to give a visible smear on a white paper towel. No corrosion was detected above sample cups containing $NiCl_2$, $CaCl_2$, or NaCl, nor was it detected in any other part of the chamber.

After the series 3 experiments involving $CuCl_2$ solutions were completed, we examined those samples. The $CuCl_2$ solutions were still clear, and exhibited no turbidity, nor had they any precipitate. However, when they were diluted with water, they rapidly became turbid and then started precipitating. Obviously, these $CuCl_2$ solutions had become extensively hydrolyzed, but apparently the chloride concentrations were high enough to suppress precipitation of copper hydroxide or hydroxide chloride.

When samples of $NiCl_2$ were equilibrated against samples of $CaCl_2$ or NaCl isopiestic reference standards, a number of experiments were first done while increasing the molalities and then were followed by additional equilibrations while diluting the samples. At any particular molality, the $NiCl_2$-to-NaCl and $NiCl_2$-to-$CaCl_2$ isopiestic molality ratios were reproducible within 0.05%, no matter whether samples of $CuCl_2$ were present or not. This reproducibility seems to imply that the molalities and water activities were unaffected by the possible presence of HCl in the vapor phase, and thus other solutions were not absorbing it to any significant degree. However, an alternative possibility exists: that the $NiCl_2$, $CaCl_2$, and NaCl solutions were all absorbing about the same amounts of HCl, and that its effects cancel out when molality ratios are calculated. We checked for this possibility by the following procedure.

After the equilibrations involving $CuCl_2$, $NiCl_2$, and $CaCl_2$ were completed for the series 3 measurements, the $CuCl_2$ samples were discarded and additional experiments performed with these same samples of $NiCl_2$ and $CaCl_2$. In addition, two "fresh" samples of the $NiCl_2$ stock solution were equilibrated against the "earlier" samples of $NiCl_2$ and the $CaCl_2$. For all six equilibrations the molalities of the fresh samples and earlier samples of $NiCl_2$ agreed to 0.015–0.03% which is excellent agreement. We did not have any $CaCl_2$ stock solution no. 1 left to allow the same type of check to be made for the reference standard, so instead we added fresh samples of $CaCl_2$ stock no. 2. Six equilibrations were performed, and the molalities of earlier samples of $CaCl_2$ stock solution no. 1 and fresh samples of stock solution no. 2 agreed to 0.00–0.04%, which is well within the uncertainty limits for the stock solution analyses. These experiments indicate that water activities of $NiCl_2$ and $CaCl_2$ were not changed by having been equilibrated with $CuCl_2$ samples, and if any HCl had been absorbed by the $NiCl_2$ or $CaCl_2$, the amounts were too small to affect the isopiestic measurements.

We have already described the pattern of corrosion on the chamber lid above the samples of $CuCl_2$. One possible interpretation of that pattern is that essentially all of the HCl loss occurred as air was being evacuated from the chamber. If so, then it could be possible to avoid this problem and perform meaningful experiments for $CuCl_2$ solutions simply by performing the isopiestic experiments with an air-filled isopiestic chamber, rather than by degassing the chamber.

Most isopiestic experiments are performed with partial or fairly complete removal of air from the chamber, because equilibrium is reached much more rapidly under those conditions than when air is present. As discussed by Rard and Platford (*1*) in their review paper, isopiestic experiments are sometimes performed in air-filled chambers, but vapor-phase stirring is usually employed to compensate for lower rates of diffusion of water vapor. However, our chambers do not contain vapor stirrers. In addition, there is only 2 cm of "head room" between the tops of the isopiestic cups and the lid of the isopiestic chamber, which is hardly adequate for the addition of such a device.

We compensated for this lower rate of diffusion in the vapor phase for experiments in air-filled chambers by allowing longer periods of time for the solutions to reach isopiestic equilibrium. We performed some check experiments for $CuCl_2$ and $NiCl_2$ solutions with NaCl as the reference standard, by equilibrating samples both in a degassed chamber (series 1 experiments) and in an air-filled chamber (series 2 experiments) over approximately the same molality range. The $CuCl_2$ molalities were varied between about 3.3 and 3.8 $mol \cdot kg^{-1}$, and those of $NiCl_2$ between about 2.4 and 2.7 $mol \cdot kg^{-1}$.

We found that when air was evacuated from a chamber, equilibration periods of 10–12 days gave highly reproducible results with good agreement of molalities for duplicate samples of the same electrolyte. It is likely that slightly shorter equilibration periods would have been adequate. In contrast, when similar experiments were done in an air-filled chamber with 17–23-day equilibrations, two of the four experiments gave discrepant molalities and were thus unsuccessful, and the samples had to be reequilibrated. Although two other experiments were successful with those equilibration times (molalities of duplicate samples agreed to ±0.1% or better), the average imprecision was significantly larger than for experiments with a degassed chamber. A subsequent experiment with a 42-day equilibration gave quite precise agreement between molalities of duplicate samples. From the results of these experiments we conclude that to achieve isopiestic data of comparable quality in an air-filled chamber without vapor stirring will require equilibration periods about 3 or 4 times as long as experiments done in a degassed chamber.

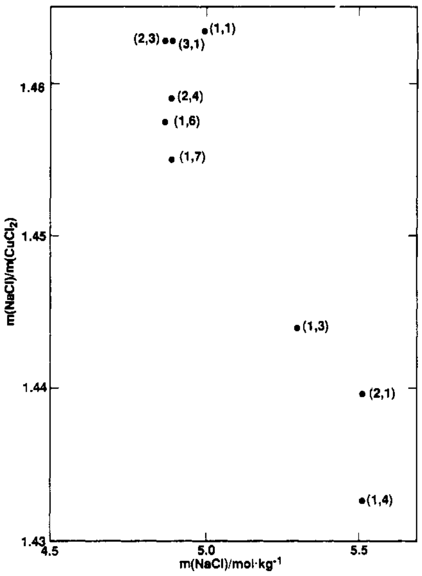

**Figure 1.** Isopiestic molality ratio of NaCl to $CuCl_2$ for experiments performed in an air-filled isopiestic chamber. Of each pair of indices, the first represents the sample number: 1 denotes the initial pair of samples, 2 denotes the first fresh sample, and 3 denotes the second fresh sample. The second index indicates the *n*th time that the sample was equilibrated; some attempted equilibrations were not successful and are not plotted. This downward drift in the molality ratio is due to progressive hydrolysis of the $CuCl_2$.

Unfortunately, isopiestic molality ratios for $CuCl_2$ relative to the other electrolytes still showed a drift as samples were reequilibrated, in a manner quite similar to the earlier experiments done in the degassed chambers. The presence of a film of corrosion product was again found above the sample cups that contained $CuCl_2$, but not elsewhere, and this film was similar in appearance to that resulting from experiments done with the degassed chambers. It is thus clear that the loss of HCl and the resulting hydrolysis of $CuCl_2$ solutions occurred no matter whether air was present or whether the chamber had been degassed.

We did one further type of experiment to confirm that hydrolysis was occurring in the air-filled chamber. After the initial pair of $CuCl_2$ samples had been used for several equilibrations, a fresh sample of $CuCl_2$ was added and used for several additional equilibrations, and finally a second fresh sample was added for the last equilibration. The original pair of $CuCl_2$ samples gave apparent molalities at equilibrium (calculated by treating all changes in mass as being solely due to loss or gain of $H_2O$) that were 0.01–0.02 $mol \cdot kg^{-1}$ higher than the first fresh sample, which in turn was about 0.01 $mol \cdot kg^{-1}$ above that of the second fresh sample. The direction of this shift is in the direction expected from increasing hydrolysis.

Figure 1 is a plot of the isopiestic ratio *m*(NaCl) divided by *m*($CuCl_2$) for a pair of solutions in isopiestic equilibrium, plotted against *m*(NaCl), for series 2 experiments done in the air-filled chamber. Next to each point is a pair of numbers in parentheses. The first index of each pair is the sample number; 1 denotes the initial pair of $CuCl_2$ solutions added to the chamber, 2 denotes the first fresh sample, and 3 denotes the second fresh sample. The second index number indicates the total number of times that sample had been equilibrated with samples of NaCl and $NiCl_2$, up to and including the experiment under consideration. Initial experiments for each sample, i.e., experiments (1,1), (2,1), and (3,1) fall on a curve that is distinctly higher than results for subsequent equilibrations with those samples. The downward drift in the isopiestic molality ratio is especially obvious for the results of any particular equilibration, for which $m$(NaCl) is constant. For example, points (3,1), (2,4), and (1,7) denote the last experiment done with the air-filled chamber. The progressive nature of this hydrolysis of aqueous $CuCl_2$ solutions is clearly established.

Although HCl was continuously being lost from the $CuCl_2$ solutions during isopiestic equilibrations, it reacted with the stainless steel lid of the chamber, which therefore acted as a "trap" for the HCl and removed it from the vapor phase before it could diffuse far enough to contaminate other samples. However, we note that most isopiestic apparatus are constructed out of glass vacuum desiccators. Thus, they would not act as a chemical trap for the HCl, which would then be transferred to the other solutions. That would then make the molalities and $\phi$ of both $CuCl_2$ and isopiestic reference standards be in error but in opposite directions. Undoubtably, the fairly large discrepancies between $\phi$ for different isopiestic studies (*6, 8, 11, 12*) are largely due to this HCl transfer.

Experiments were also performed in which solubility and water activity were determined simultaneously, both for $NiCl_2$ and for $CuCl_2$ solutions. For those experiments a reservoir cup was added to the chamber, which contained a sample of saturated solution and crystals of one of the electrolytes being studied. Crystals were obtained by concentrating samples of the stock solutions in a desiccator.

Crystals of $CuCl_2 \cdot nH_2O$ were aged at room temperature for several months before the solubility experiments were started, to allow for crystal growth. The observed solubilities (series 3 experiments with degassed chamber; series 5 with air-filled chamber) increased as the samples were reequilibrated, which is expected because of the progressive hydrolysis. However, the molality of the isopiestic reference standard $CaCl_2$, and thus the water activity of the saturated $CuCl_2$, was constant with time for equilibrations of 14–20 days for the degassed chamber and 41 days for the air-filled chamber. This indicates that the water activity at saturation was not affected by changing amounts of hydrolysis in the $CuCl_2$ solutions, but was controlled by the thermodynamically stable hydrate $CuCl_2 \cdot 2H_2O$(cr) in equilibrium with these solutions. Thus, this $a_w$ value should also be the correct value for a saturated solution of stoichiometric $CuCl_2$. Minor variations in the reference standard molalities for 12-day solubility equilibrations imply the initial solid phase was not the pure dihydrate, but that by day 14 it had become pure $CuCl_2 \cdot 2H_2O$(cr).

We had previously performed solubility experiments for $NiCl_2 \cdot nH_2O$(cr) (*3*), and observed that the solubility varied with time. Apparently when the crystals were being grown, the enthalpy of precipitation was large enough to bring the sample above the hexahydrate to tetrahydrate transition temperature which is about 302 K. Conversion of the mixtures of hydrates to the pure hexahydrate was obviously quite slow at 298.15 K.

We also grew our crystals of $NiCl_2 \cdot nH_2O$(cr) by concentrating a sample of stock solution in a desiccator, which was the method used earlier (*3*). In an attempt to convert these crystals to pure hexahydrate (the reported thermodynamically stable phase at 298.15 K and lower temperatures), we then placed the crystals plus saturated solution in a refrigerator at 276–277 K and aged them. Samples of $NiCl_2 \cdot nH_2O$(cr) were thus aged for 110–149 days prior to using them for solubility experiments. Unfortunately, even after lengthy aging, samples were apparently two-phase, with a few larger dark-green clear crystals and a lot of small light-green opaque crystals. The light-green crystals were selected for solubility experiments, but apparently were neither the hexahydrate nor tetrahydrate because the measured solubility varied with time and this variation was in the opposite direction than found earlier (*3*). However, when the two sets of solubilities were extrapolated to infinite time (see below), they gave results that agreed to 0.074%. The limiting values should be the solubility of pure $NiCl_2 \cdot 6H_2O$(cr). At the end of the longest solubility experiment, 28 days, most of the solid phase consisted of a few quite large dark-green clear crystals, with a much smaller amount of the light-green crystals.

During one of our solubility experiments, the refrigerator/circulator that provides cooling water to our constant-temperature bath failed, and instead warmed the bath to about 305 K, which is above the hexahydrate to tetrahydrate transition temperature. We replaced the defective unit and rapidly cooled the temperature bath back to 298.15 K. The solubility of $NiCl_2 \cdot nH_2O$ determined after this event was higher than obtained in the other experiments, and was reasonably close to the value obtained by extrapolating the other solubilities to infinite time. This agreement suggests that a rapid temperature change speeds up conversion of other hydrates to the hexahydrate.

## Calculation of Osmotic Coefficients

Osmotic coefficients of aqueous $NiCl_2$ solutions were calculated from the fundamental equation for isopiestic equilibrium:

$$\phi = \frac{\nu^* m^* \phi^*}{\nu m} \tag{1}$$

where $m$ is the molality of $NiCl_2$, $m^*$ is the molality of the reference standard in isopiestic equilibrium with that solution, $\phi^*$ is the osmotic coefficient of the isopiestic reference standard, and $\nu$ and $\nu^*$ are the stoichiometric ionization numbers of $NiCl_2$ and reference standard, respectively ($\nu^* = 2$ for NaCl; $\nu = \nu^* = 3$ for $NiCl_2$ and $CaCl_2$).

Values of $\phi^*$ for $CaCl_2$ were taken from Rard et al. (*16*) and for NaCl from Hamer and Wu (*17*). A small correction was applied to those $\phi^*$ values for NaCl because Hamer and Wu neglected the nonideal behavior of water vapor.

Tables I and II contain the derived values of $\phi$ for aqueous $NiCl_2$ solutions. Values of $\phi$ were not reported for aqueous $CuCl_2$ solutions, because the variable and unknown amounts of hydrolysis make the results unreliable.

Published isopiestic molalities for aqueous $NiCl_2$ solutions (*8, 11, 18, 19*) were recalculated to these same isopiestic reference standards, to allow a more meaningful comparison with our new values for $\phi$. Values of $\phi$ reported by Rard (*3*) are already based upon these standards.

## Osmotic and Activity Coefficients for $NiCl_2$

A preliminary assessment was made of the quality and consistency of various sets of isopiestic values of $\phi$ for $NiCl_2$ by use of a direct plot of $\phi$ against $m$. This plot indicated that the results given in Tables I and II, those of Rard (*3*), and recalculated results from Robinson and Stokes (*11*) and from Robinson (as tabulated by Stokes (*18*) in his Appendix) are in fairly good agreement. Values of $\phi$ from the investigation of Shul'ts et al. (*19*) are fairly consistent with these other four studies, but exhibit several times more scatter.

Filippov et al. (*8*) reported seven values of $\phi$ for $NiCl_2$. Their values at the three lower molalities agree well with those from other studies (*3, 11, 18, 19*), but their $\phi$ are rather scattered above 2 $mol \cdot kg^{-1}$. Isopiestic reference standard molalities were not reported by them at the highest $NiCl_2$ molalities so their $\phi$ could not be recalculated, but LiCl was probably used as a reference standard.

Rard (*3*) considered published direct vapor-pressure measurements, freezing-point depression, and emf values for

**Table III. Coefficients and Powers for Equations 2 and 3 for $NiCl_2$ at 298.15 K[a]**

| $i$ | $r_i$ | $A_i$[b] | $\sigma(A_i)/A_i$[c] |
|---|---|---|---|
| 1 | 1.0 | 5.129 26 | 0.015 |
| 2 | 1.5 | −10.987 33 | 0.043 |
| 3 | 2.0 | 15.808 946 | 0.073 |
| 4 | 2.5 | −14.659 18 | 0.100 |
| 5 | 3.0 | 8.808 026 | 0.121 |
| 6 | 3.5 | −3.284 447 | 0.134 |
| 7 | 4.0 | 0.682 633 2 | 0.143 |
| 8 | 4.5 | −0.059 993 72 | 0.150 |

[a] Standard deviation of fit $\sigma(\phi) = 0.002\,50$. [b] These parameters are based upon 151 values of $\phi$ from isopiestic measurements and 10 estimated values at low molalities. [c] Ratio of standard error of coefficient to that coefficient.

aqueous $NiCl_2$ solutions, and concluded that none of them yielded reliable osmotic or activity coefficients. We thus do not consider them here. He also gave a table of estimated $\phi$ at 0.01 $mol \cdot kg^{-1}$ intervals from 0.01 to 0.10 $mol \cdot kg^{-1}$, which were derived by extrapolation of available values of $\phi(NiCl_2) - \phi(CaCl_2)$ to low molalities. These estimated $\phi$ of $NiCl_2$ are useful for constraining least-squares representations of $\phi$ at molalities below those available from isopiestic experiments.

On the basis of the above considerations, for least-squares fits equal weight was given to each experimental value in Tables I and II, to values from the more reliable isopiestic studies (*3, 11, 18*), and to the estimated dilute solution values (*3*). Zero weight was given to values from other studies because they are of lower precision or are inaccurate.

The more reliable values of $\phi$ (preceding paragraph) for aqueous $NiCl_2$ at 298.15 K were represented by least-squares equations of the form

$$\phi = 1 - (A/3)m^{1/2} + \sum_i A_i m^{r_i} \qquad (2)$$

where $A = (0.51082)(\ln 10)(2)(3^{1/2}) = 4.0744\ mol^{-1/2} \cdot kg^{1/2}$ is the Debye–Hückel limiting slope for aqueous 2–1 electrolytes at 298.15 K. The corresponding form of this equation for mean molal activity coefficients is

$$\ln \gamma_{\pm} = -Am^{1/2} + \sum_i A_i \left(\frac{r_i + 1}{r_i}\right) m^{r_i} \qquad (3)$$

Various least-squares fits were performed using terms in $m$, $m^{1/2}$, $m^{1/4}$, and $m^{1/8}$, and both sequential and nonsequential series were examined. Series with six or fewer parameters were unable to represent the experimental values of $\phi$ within experimental error, as were some of the seven- and eight-parameter fits.

Several of the seven- and eight-parameter series gave accurate representations of the experimental data, with $\sigma(\phi) = 0.00250$–$0.00256$. Most of those fits had some or most coefficients with fairly large standard errors, and were consequently rejected. One of the eight-parameter fits, a sequential series in $m^{1/2}$ beginning with $m^1$, had both the lowest value of $\sigma(\phi)$ and the smallest percentage errors for the least-squares parameters $A_i$, and it was selected as the "best fit" for $\phi$. Values of $A_i$ and $\sigma(A_i)/A_i$ for this fit are given in Table III, and were used to generate the recommended smoothed values of $\phi$, $a_w$, and $\gamma_{\pm}$ given in Table IV.

Figure 2 illustrates the differences (residuals) between the experimental values of $\phi$ and values calculated from eq 2 using the coefficients in Table III, as a function of the square root of molality. Most experimental values of $\phi$ fall within ±0.2% of the least-squares equation: all of our new experimental data and all but four of our earlier $\phi$ points (*3*) fall within these uncertainty limits. Most of the $\phi$ values of Robinson and Stokes (*11*) and Robinson (*18*) also fall within these uncertainty limits, but several of their $\phi$ values are 0.3–0.5% above the least-squares curve.

The $NiCl_2$ stock solution for our earlier experiments was prepared from Mallinckrodt AR $NiCl_2 \cdot 6H_2O$ (*3*) and in the present study was prepared from Baker-analyzed material. Two separate sources of $NiCl_2$ were deliberately chosen as part of our test of the reproducibility of isopiestic measurements. Values of $\phi$ for $NiCl_2$ from Table I and from our earlier experiments (*3*), with NaCl as reference standard, agree to within 0.1%, which is excellent agreement. Values of $\phi$ from Table II and our earlier values, both with $CaCl_2$ as reference standard, are in quite good agreement, with the Table II values being slightly higher.

A smooth curve drawn through our newer values and one through our previous values (*3*) agree to about 0.15–0.2%, although some individual data points differ by as much as 0.3–0.35%. However, these differences of 0.3–0.35% in $\phi$ correspond to differences of only 0.1–0.2% in the $NiCl_2$-to-$CaCl_2$ isopiestic molality ratio (the primary experimental quantity), which is within the expected experimental error. Smoothed values of $\phi$ in Table IV should be reliable to about 0.2% relative to the isopiestic standards.

Values of $\phi$ for aqueous solutions of $NiCl_2$ were also represented by Pitzer's equation:

$$\phi = 1 + 2f^{\phi} + (4/3)mB^{\phi} + (2^{5/2}/3)m^2 C^{\phi} \qquad (4)$$

where

$$f^{\phi} = -A^{\phi} I^{1/2}/(1 + bI^{1/2}) \qquad (5)$$

is a Debye–Hückel term (*20*). Following Pitzer, we accept $A^{\phi} = 0.3915\ mol^{-1/2} \cdot kg^{1/2}$ at 298.15 K and $b = 1.2\ mol^{-1/2} \cdot kg^{1/2}$. The ionic strength $I$ is on the molal scale. This $B^{\phi}$ term in eq 4 has an ionic strength dependence:

$$B^{\phi} = \beta^{(0)} + \beta^{(1)} \exp\{-\alpha I^{1/2}\} \qquad (6)$$

The quantity $\alpha$ is usually assigned a value of 2.0 $mol^{-1/2} \cdot kg^{1/2}$, except for 2–2 electrolytes.

When eq 4 was used to represent $\phi$ of $NiCl_2$ over the entire molality range, the least-squares fit was quite poor with $\sigma(\phi) = 0.0150$ and a maximum deviation of 0.0312. The quality of the fit was improved by using larger values for $\alpha$, and $\alpha = 3.0\ mol^{-1/2} \cdot kg^{1/2}$ was about optimum. Using this value gave $\sigma(\phi) = 0.0111$, but large cyclic systematic deviations still occurred from the experimental $\phi$.

Dramatic but gradual improvements occurred as the molality range being fit was reduced, as indicated by smaller $\sigma(\phi)$ and smaller systematic deviations, and the optimum value of $\alpha$ approached 2.0 $mol^{-1/2} \cdot kg^{1/2}$ as recommended by Pitzer (*20*). Restricting the fits to molalities of 3 $mol \cdot kg^{-1}$ and lower gave reasonably good fits with $\sigma(\phi) = 0.002\,89$ for an optimum value of $\alpha$ of 2.25 $mol^{-1/2} \cdot kg^{1/2}$, and $\sigma(\phi) = 0.003\,12$ for the traditional value of $\alpha = 2.0\ mol^{-1/2} \cdot kg^{1/2}$. We chose this latter fit to maintain consistency with the majority of Pitzer's parameters (*20*). The resulting parameters are $(4/3)\beta^{(0)} = 0.475\,22 \pm 0.001\,41\ mol^{-1} \cdot kg$, $(4/3)\beta^{(1)} = 1.9647 \pm 0.0271\ mol^{-1} \cdot kg$, and $(2^{5/2}/3)C^{\phi} = -0.012\,977 \pm 0.000\,529\ mol^{-2} \cdot kg^2$.

## Activity Data for $CuCl_2$ Solutions

In the part of the Experimental Section on isopiestic measurements, we observed that all of our isopiestic experiments for aqueous $CuCl_2$ solutions yielded inaccurate results because of hydrolysis as HCl was lost during the isopiestic equilibrations. Similar difficulties undoutably occurred in the other isopiestic studies (*6, 8, 11, 12*). Thus, none of these isopiestic results for aqueous $CuCl_2$ solutions are trustworthy. There is a small amount of other types of activity data for $CuCl_2$ solutions, which we now discuss.

**Table IV. Osmotic Coefficients, Water Activities, and Activity Coefficients of Aqueous $NiCl_2$ Solutions at 298.15 K**[a]

| $m/(\mathrm{mol \cdot kg^{-1}})$ | $\phi$ | $a_w$ | $\gamma_\pm$ | $m/(\mathrm{mol \cdot kg^{-1}})$ | $\phi$ | $a_w$ | $\gamma_\pm$ |
|---|---|---|---|---|---|---|---|
| 0.1 | 0.8556 | 0.995 387 | 0.5174 | 3.0 | 1.8048 | 0.7463 | 1.651 |
| 0.2 | 0.8656 | 0.990 687 | 0.4739 | 3.2 | 1.8700 | 0.7237 | 1.860 |
| 0.3 | 0.8842 | 0.985 77 | 0.4587 | 3.4 | 1.9316 | 0.7012 | 2.089 |
| 0.4 | 0.9064 | 0.980 60 | 0.4550 | 3.5 | 1.9610 | 0.6901 | 2.211 |
| 0.5 | 0.9312 | 0.975 15 | 0.4580 | 3.6 | 1.9894 | 0.6790 | 2.338 |
| 0.6 | 0.9580 | 0.969 41 | 0.4656 | 3.8 | 2.0433 | 0.6573 | 2.607 |
| 0.7 | 0.9864 | 0.963 37 | 0.4770 | 4.0 | 2.0933 | 0.6360 | 2.895 |
| 0.8 | 1.0163 | 0.957 01 | 0.4915 | 4.2 | 2.1396 | 0.6153 | 3.202 |
| 0.9 | 1.0475 | 0.950 32 | 0.5090 | 4.4 | 2.1823 | 0.5951 | 3.527 |
| 1.0 | 1.0798 | 0.943 31 | 0.5292 | 4.5 | 2.2024 | 0.5853 | 3.697 |
| 1.2 | 1.1473 | 0.928 29 | 0.5779 | 4.6 | 2.2218 | 0.5756 | 3.871 |
| 1.4 | 1.2180 | 0.911 96 | 0.6378 | 4.8 | 2.2584 | 0.5566 | 4.232 |
| 1.5 | 1.2543 | 0.903 31 | 0.6722 | 4.9155[b] | 2.2783 | 0.5459 | 4.450 |
| 1.6 | 1.2911 | 0.894 4 | 0.7098 | 5.0 | 2.2923 | 0.5382 | 4.612 |
| 1.8 | 1.3659 | 0.875 6 | 0.7950 | 5.2 | 2.3238 | 0.5204 | 5.011 |
| 2.0 | 1.4415 | 0.855 7 | 0.8946 | 5.4 | 2.3531 | 0.5032 | 5.427 |
| 2.2 | 1.5171 | 0.835 0 | 1.010 | 5.5 | 2.3669 | 0.4948 | 5.642 |
| 2.4 | 1.5919 | 0.813 4 | 1.142 | 5.6 | 2.3802 | 0.4866 | 5.860 |
| 2.5 | 1.6288 | 0.802 5 | 1.215 | 5.8 | 2.4049 | 0.4705 | 6.308 |
| 2.6 | 1.6653 | 0.791 4 | 1.292 | 6.0 | 2.4269 | 0.4552 | 6.765 |
| 2.8 | 1.7364 | 0.768 9 | 1.462 | 6.1364 | 2.4399 | 0.4452 | 7.078 |

[a] Values of $\phi$, $a_w$, and $\gamma_\pm$ were calculated by using the least-squares parameters in Table III. [b] Saturated solution in equilibrium with $NiCl_2 \cdot 6H_2O(cr)$.

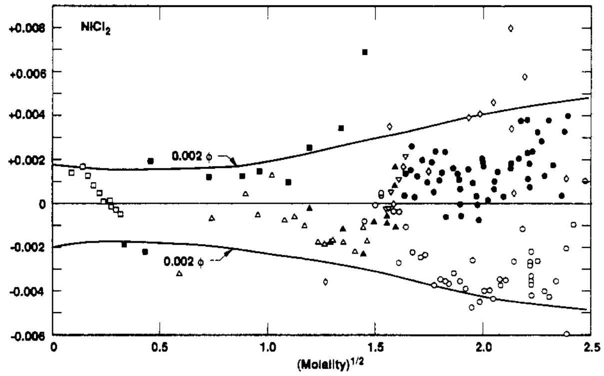

**Figure 2.** Differences between experimental osmotic coefficients and least-squares values from eq 2 with Table III coefficients: (○) Rard (*3*), $CaCl_2$ standard; (△) Rard (*3*), NaCl standard; (■) Robinson and Stokes (*11*), KCl standard; (◇) Robinson (*18*), $CaCl_2$ standard; (●) this research, $CaCl_2$ standard; (▲) this research, NaCl standard with degassed chamber; (▽) this research, NaCl standard with air-filled chamber; (□) estimated dilute solution values from Rard (*3*).

Ellis et al. (*7*) did a detailed emf study of aqueous $CuCl_2$ at 298.15 K from 0.2005 to 5.794 mol·kg$^{-1}$, by using $Cl_2$ electrodes and concentration cells with transport. Reference solution molalities of 0.1, 0.5, and 1.0 mol·kg$^{-1}$ were used for those experiments. They also reported numerous values of the cation transference number as determined by the moving boundary method. Unfortunately, the emf results do not extend to low enough molalities to allow calculation of activity coefficients.

Lilich and Sapozhnikova (*21*) performed emf measurements of the activities of HCl in $CuCl_2$–HCl–$H_2O$ at 298 K by using Ag–AgCl, glass, and $Cl_2$ electrodes. They did one series of experiments for solutions without added HCl, with 1.509–5.410 mol·kg$^{-1}$ $CuCl_2$. It is not entirely clear what potential they measured, but it may simply be the potential due to the small amounts of HCl present in $CuCl_2$ solutions at their "natural" pH.

Huang and Pan (*22*) performed freezing temperature depression measurements for aqueous $CuCl_2$ solutions from 0.0025 to 0.0980 mol·kg$^{-1}$, from which they derived values of the osmotic coefficients at the freezing temperatures of the solutions $\phi(T)$. Conversion of these values to $\phi$ at 298.15 K requires both enthalpies of solution and heat capacities. All but one of the heat capacity values of Vasilev et al. (*23*) are at molalities considerably above those for the freezing temperature experiments. Goldberg (*24*) was unable to find adequate thermodynamic data for the temperature corrections and instead made approximate conversion of the $\phi(T)$ to 298.15 K by using thermal data for $Cu(ClO_4)_2$. The reliability of these approximate corrections is questionable.

It is obvious that more extensive emf measurements are needed for aqueous $CuCl_2$ solutions to provide unambiguous thermodynamic activities.

We noted in the Experimental Section that the isopiestic molalities of $CaCl_2$ reference standards equilibrated against saturated $CuCl_2$ solutions, in the presence of a reservoir cup containing solution and crystals, were essentially constant for equilibration times of 14 days and longer. These $CaCl_2$ molalities did not depend on whether the chamber was degassed or air filled, or how many times the $CuCl_2$ solutions were reequilibrated. This implies that the water activity of the saturated solution is independent of hydrolysis in the solution, and is controlled solely by the thermodynamically stable solid phase of $CuCl_2 \cdot 2H_2O(cr)$. Water activities were calculated from these $CaCl_2$ molalities and are plotted in Figure 3.

Values of $a_w$ for experiments with the degassed chamber (14–20-day equilibrations) and for the air-filled chamber (41-day equilibration) are quite concordant, and yield a water activity of $a_w = 0.680\,75 \pm 0.000\,08$ for a saturated $CuCl_2$ solution in equilibrium with $CuCl_2 \cdot 2H_2O(cr)$. This uncertainty limit is statistical only, and does not include the uncertainty in $\phi^*$ of $CaCl_2$ (*16*).

### Solubility and Solubility Product for $NiCl_2 \cdot 6H_2O(cr)$

Figure 4 is a plot of the new solubilities of aqueous $NiCl_2$ at 298.15 K as a function of $1/t$; our earlier determinations (*3*) are also included. Each of these two separate sets of solubility determinations gives a linear plot and yields a similar intercept at "infinite time", but their slopes have opposite signs. Agreement between the intercepts of these two curves implies that solubilities for mixed hydrates of $NiCl_2$ ultimately reach a common value, which then corresponds to the solubility for pure $NiCl_2 \cdot 6H_2O(cr)$.

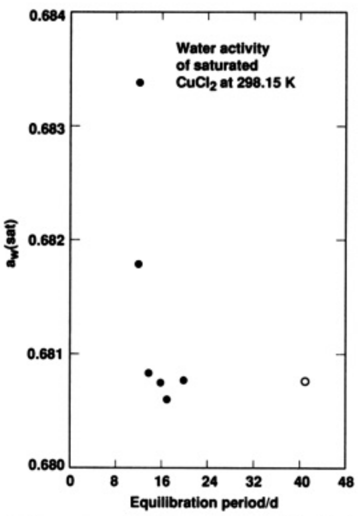

**Figure 3.** Activity of water for saturated solutions of $CuCl_2$ at 298.15 K in equilibrium with solid $CuCl_2 \cdot 2H_2O$(cr): (●) experiments in degassed chamber; (○) experiment in air-filled chamber.

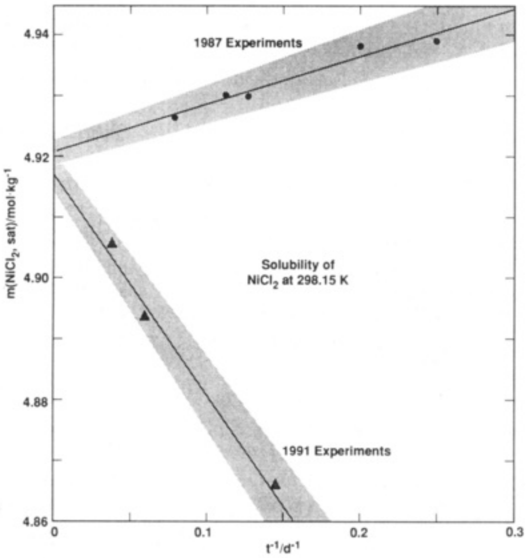

**Figure 4.** Solubilities of $NiCl_2$ solutions as a function of $t^{-1}$. The 1987 experiments are from Rard (*3*). Least-squares curves are indicated, as are the 1 $\sigma$ uncertainty limits.

The three molal solubilities for $NiCl_2$ from Table II follow the least-squares equation

$$m(t) = (4.9171_7 \pm 0.0029_3) - (0.3618_8 \pm 0.0320_2)/t \quad (7)$$

where $t$ is the equilibration time in days, and the correlation coefficient is −0.9961. Solubilities from our study reported in 1987 (*3*) follow the least-squares equation

$$m(t) = (4.9208_4 \pm 0.0018_9) + (0.0792_9 \pm 0.0114_2)/t \quad (8)$$

with a correlation coefficient of 0.9712. These listed uncertainty limits for the coefficients are standard errors (standard deviations), and are solely due to the imprecision of the isopiestic solubility experiments. Those uncertainties do not include the ~0.04% uncertainty from the stock solution molality analyses. Including that uncertainty then yields solubilities for $NiCl_2 \cdot 6H_2O$(cr) of 4.9172 ± 0.0049 and 4.9208 ± 0.0039 mol·kg$^{-1}$, respectively. This agreement is excellent.

Table V gives a comparison of our solubility values to published solubilities for aqueous $NiCl_2$ at 298.15 K (*8*, *25*–*34*), all of which are purportedly for the solid-phase $NiCl_2 \cdot 6H_2O$(cr). Published solubility values were converted to the same molar mass that was used in our study if sufficient information was given to permit this. The reported solubilities vary from 4.438 to 5.060 mol·kg$^{-1}$, which is a considerable difference. The value of 4.438 mol·kg$^{-1}$ from Kim et al. (*32*) is anomalously low, but the other ones also show a fair amount of variation. Clearly the equilibrium periods used to achieve saturation were inadequate for most of those studies, and the solid phases were probably mixtures of hydrates rather than pure $NiCl_2 \cdot 6H_2O$(cr).

**Table V. Solubilities $S$ of $NiCl_2 \cdot 6H_2O$(cr) at 298.15 K**

| $S$/(mol·kg$^{-1}$) | equilibration time | researchers | year | ref |
|---|---|---|---|---|
| 4.9112 ± 0.0032[a] | 10–24 days | Pearce and Eckstrom | 1937 | 25 |
| 5.054 | uk[b] | Linke | 1958, 1965 | 26 |
| 4.908 | uk | | | 26 |
| 5.058 | uk | | | 26 |
| 5.060[c] | 20 h | Oikova | 1979 | 27 |
| 5.060[c] | uk | Ojkova and Makarow | 1979 | 28 |
| 5.058[d] | uk | Petrov and Shevchuk | 1979, 1980 | 29–31 |
| 4.438 | uk | Kim et al. | 1983 | 32 |
| 4.91 | 6 h | Filippov et al. | 1985 | 33 |
| 4.89 | 6–8 h | Filippov et al. | 1986 | 8 |
| 4.933 | 2 days | Lileev et al. | 1989 | 34 |
| 4.9208 ± 0.0039[e] | 4–13 days | Rard | 1987 | 3 |
| 4.9172 ± 0.0049[e] | 7–28 days | this study | | |

[a] Average of four reported solubilities. [b] uk denotes unknown; equilibration periods were not given. [c] The same value was given in both studies and probably represents a single determination. Oikova and Ojkova are just variant spellings of the same name. [d] Different equilibration times are given in the three papers for ternary solution solubility experiments. It was not clear if any of those times apply to the binary solution $NiCl_2$–$H_2O$(cr). [e] Statistical uncertainty plus assumed 0.04% uncertainty for stock solution molality. Solubilities were extrapolated to infinite time as described in the text.

The only other solubility study in which the equilibrium period was varied to check whether true equilibrium was present was that of Pearce and Eckstrom (*25*). They removed their first samples for analysis after 10 days, and removed additional samples three other times over the next 2 weeks. The solubilities did not vary with the equilibrium time, which implies that their initial solid phase was pure or nearly pure $NiCl_2 \cdot 6H_2O$(cr). Our derived solubility from that study is 4.9112 ± 0.0032 mol·kg$^{-1}$ ($\sigma_{n-1}$ standard deviation), which is in reasonably good agreement with our values. This is the only value from the other studies in which we have confidence. Our recommended solubility for $NiCl_2 \cdot 6H_2O$(cr) is the statistically weighted average of this value with the two values obtained from extrapolation of our solubilities to infinite time: 4.9155 ± 0.0022 mol·kg$^{-1}$.

By using this recommended solubility and the activity values in Table IV, we calculate the thermodynamic solubility product:

$$\begin{aligned} K_m{}^\circ &= 4(m/m^\circ)^3 \gamma_\pm{}^3 a_w{}^6 \\ &= 4(4.9155)^3(4.450)^3(0.5459)^6 \\ &= 1108 \qquad (9) \end{aligned}$$

Here $m^\circ = 1$ mol·kg$^{-1}$ is included to make $K_m{}^\circ$ dimensionless, and $m$, $a_w$, and $\gamma_\pm$ all pertain to the saturated solution.

By using the standard methods for propagation of error, we obtain

$$\delta K_m{}^\circ = ((\delta K_m{}^\circ)^2)^{1/2} = K_m{}^\circ\{9(\delta m/m)^2 + 9(\delta\gamma_\pm/\gamma_\pm)^2 + 36(\delta a_w/a_w)^2\}^{1/2} \quad (10)$$

At this stage we do not know the uncertainty in $a_w$, but we have already concluded that $\phi$ is uncertain by about 0.2%.

The relationship between $a_w$ and $\phi$ for aqueous $NiCl_2$ is

$$\ln a_w = -3M_w\phi m/1000 \qquad (11)$$

where $M_w = 18.0153$ g·mol$^{-1}$ is the molar mass of water. The error in $a_w$ is then given by

$$(\delta a_w/a_w)^2 = (9M_w^2/10^6)\{m^2(\delta\phi)^2 + \phi^2(\delta m)^2\} \qquad (12)$$

assuming that the uncertainty in the molar mass of water is negligible compared to other uncertainties. Inserting this equation into eq 10 gives

$$\delta K_m^\circ = K_m^\circ\{9(\delta m/m)^2 + 9(\delta\gamma_\pm/\gamma_\pm)^2 + (324M_w^2/10^6)\{m^2(\delta\phi)^2 + \phi^2(\delta m)^2\}\}^{1/2} \qquad (13)$$

We have already concluded that $m = 4.9155$ mol·kg$^{-1}$ and $\delta m = 0.0022$ mol·kg$^{-1}$. From Table IV, $\gamma_\pm = 4.450$, $\phi = 2.2783$, and $a_w = 0.5459$. An uncertainty of 0.2% of $\phi$ is thus $\delta\phi = 0.0045_6$. The uncertainty in $\gamma_\pm$ is conservatively estimated to be about 0.5% (about 0.2% from the precision of the isopiestic experiments, and about 0.3% from the extrapolation of $\phi$ to infinite dilution). Using these uncertainties gives $\delta K_m^\circ = 18.6$ for the estimated standard deviation, and thus $K_m^\circ = 1108 \pm 19$.

The dissolution reaction to form a saturated solution is

$$NiCl_2{\cdot}6H_2O(cr) \rightleftarrows Ni^{2+}(soln) + 2Cl^-(soln) + 6H_2O(soln) \qquad (14)$$

for which the Gibbs energy change is

$$\Delta_{soln}G_m^\circ = -RT\ln K_m^\circ = -17.38 \pm 0.04 \text{ kJ·mol}^{-1} \qquad (15)$$

Since there is no value of $\Delta_f G_m^\circ(Ni^{2+},aq,298.15K)$ in the CODATA tables, we do not report a value for $\Delta_f G_m^\circ(NiCl_2{\cdot}6H_2O,cr,298.15K)$ at this time.

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## Glossary

| | |
|---|---|
| $a_w$ | activity of water in solution |
| $A$ | Debye–Hückel constant for 2–1 electrolytes (it includes the product of the valence of the ions and the ionic strength-to-molality conversion factor) |
| $A_i$ | least-squares coefficients for eqs 2 and 3 |
| $A^\phi$ | Debye–Hückel constant (1–1 charge type) for $\phi$ in Pitzer's equations |
| $G_m^\circ$ | standard state molar Gibbs energy |
| $K_m^\circ$ | thermodynamic solubility product, molal scale |
| $m$ | molality of solute |
| $m^\circ$ | unit molality |
| $M_w$ | molar mass of $H_2O$ |
| $r_i$ | powers of molality of eqs 2 and 3 |
| $\beta^{(0)},\beta^{(1)},C^\phi,\alpha$ | parameters for Pitzer's equations |
| $\gamma_\pm$ | mean molal activity coefficient |
| $\nu$ | ionization number for complete dissociation of solute |
| $\sigma(\phi)$ | standard deviation of fitting equation for $\phi$ |
| $\phi$ | molal (practical) osmotic coefficient |
| * | denotes an isopiestic reference standard (NaCl or $CaCl_2$) |

## Literature Cited

(1) Rard, J. A.; Platford, R. F. Experimental Methods: Isopiestic. In *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC Press: Boca Raton, FL, 1991; Chapter 5.

(2) Rard, J. A. *J. Chem. Eng. Data* **1984**, *29*, 443–450.

(3) Rard, J. A. *J. Chem. Eng. Data* **1987**, *32*, 334–341.

(4) Rard, J. A.; Miller, D. G. *J. Solution Chem.* **1985**, *14*, 271–299.

(5) Rard, J. A.; Miller, D. G. *J. Chem. Thermodyn.* **1989**, *21*, 463–482.

(6) Downes, C. J.; Pitzer, K. S. *J. Solution Chem.* **1976**, *5*, 389–398.

(7) Ellis, R. N.; Stokes, R. H.; Wright, A. C.; Spiro, M. *Aust. J. Chem.* **1983**, *36*, 1913–1921.

(8) Filippov, V. K.; Charykov, N. A.; Fedorov, Yu. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1986**, *31*, 1071–1074.

(9) Furst, W.; Hachimi, S.; Renon, H. *J. Solution Chem.* **1988**, *17*, 953–965.

(10) Haung, H.-H. *J. Solution Chem.* **1989**, *18*, 1069–1084.

(11) Robinson, R. A.; Stokes, R. H. *Trans. Faraday Soc.* **1940**, *36*, 1137–1138.

(12) Brown, J. B. *Trans. Roy. Soc. N. Z.* **1948**, *77*, 19–23.

(13) Goldberg, R. N.; Nuttall, R. L.; Staples, B. R. *J. Phys. Chem. Ref. Data* **1979**, *8*, 923–1003.

(14) Rard, J. A. *J. Solution Chem.* **1985**, *14*, 457–471.

(15) Spedding, F. H.; Weber, H. O.; Saeger, V. W.; Petheram, H. H.; Rard, J. A.; Habenschuss, A. *J. Chem. Eng. Data* **1976**, *21*, 341–360.

(16) Rard, J. A.; Habenschuss, A.; Spedding, F. H. *J. Chem. Eng. Data* **1977**, *22*, 180–186.

(17) Hamer, W. J.; Wu, Y.-C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047–1099.

(18) Stokes, R. H. *Trans. Faraday Soc.* **1948**, *44*, 295–307.

(19) Shul'ts, M. M.; Makarov, L. L.; Yu-jêng, S. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1962**, *36*, 1181–1183.

(20) Pitzer, K. S. Ion Interaction Approach: Theory and Data Correlation. In *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC Press: Boca Raton, FL, 1991; Chapter 3.

(21) Lilich, L. S.; Sapozhnikova, O. V. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1964**, *9*, 1198–1200.

(22) Huang, J.-T.; Pan, K. *J. Chin. Chem. Soc.* (*Taipei*) **1966**, *13*, 64–76.

(23) Vasilev, V. A.; Karapet'yants, M. Kh.; Sanaev, E. S.; Novikov, S. N. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1974**, *48*, 1398–1399.

(24) Goldberg, R. N. *J. Phys. Chem. Ref. Data* **1979**, *8*, 1005–1050.

(25) Pearce, J. N.; Eckstrom, H. C. *J. Phys. Chem.* **1937**, *41*, 563–565.

(26) Linke, W. F. *Solubilities Inorganic and Metal-Organic Compounds*; American Chemical Society: Washington, DC, 1958; Vol. I, pp 725, 812, 1016; 1965; Vol. II, p 1208.

(27) Oikova, T. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1979**, *24*, 122–124.

(28) Ojkova, T.; Makarow, L. L. *Z. Phys. Chem.* (*Leipzig*) **1979**, *260*, 609–615.

(29) Petrov, G. V.; Shevchuk, V. G. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1979**, *24*, 935–936.

(30) Petrov, G. V.; Shevchuk, V. G. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1979**, *24*, 1274–1276.

(31) Petrov, G. V.; Shevchuk, V. G. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1980**, *25*, 1715–1716.

(32) Kim, T. P.; Imanakunov, B. I.; Kazybaev, S. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1983**, *28*, 596–598.

(33) Filippov, V. K.; Charykov, N. A.; Solechnik, N. D. *J. Appl. Chem. USSR* (*Engl. Transl.*) **1985**, *58*, 1811–1814.

(34) Lileev, A. S.; Tepavicharova, S.; Lyashchenko, A. K.; Balarev, Kh. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1989**, *34*, 281–284.

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