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Densities and Apparent Molal Volumes of Aqueous Nickel Chloride at 25 °C

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Densities of aqueous $NiCl_2$ solutions were measured from 0.04 to 4.98 mol (kg of H_2O)$^{-1}$ at 25.00 °C, using very high purity $NiCl_2$. Each density was measured in duplicate with 31-cm^3 single-stem pycnometers. These experimental densities are critically compared to published literature data, and least-squares equations were used to represent the higher quality data.

Introduction

Density data for aqueous electrolyte solutions are required for a number of applications including conversion of mass concentrations to volumetric concentrations, for making buoyancy corrections when weighing samples, for converting mean molal activity coefficients to mean molar values, and for calculation of partial molal volumes. These partial molal volumes are related to the pressure derivatives of solute and solvent chemical potentials (*1*). In addition, volumetric data provide information about ion-solvent and ion-ion interactons.

We have been characterizing various aqueous electrolytes at 25.00 °C in terms of their osmotic and activity coefficients, their mutual diffusion coefficients, and their densities and apparent molal volumes. We have reported such data for alkali-metal and alkaline-earth-metal chlorides (*2-5*), and have recently extended these measurements to include the transition-metal chlorides $MnCl_2$, $CdCl_2$, and $ZnCl_2$ (*6-9*). We investigated $MnCl_2$ because it appears to be a fairly strong electrolyte, $CdCl_2$ because it is a highly self-complexed electrolyte, and $ZnCl_2$ because it is intermediate in behavior.

Of the transition-metal aquo ions, Ni^{2+} is the most extensively studied by spectroscopic and diffraction methods. There is nearly universal agreement that $Ni(H_2O)_6{}^{2+}$ is the dominant species in aqueous solutions of $NiCl_2$ and $Ni(ClO_4)_2$ (*10*). However, Weingärtner et al. (*11*) summarized various types of evidence that 1 mol (kg of H_2O)$^{-1}$ $NiCl_2$ solutions contain 5-15% inner-sphere monochloro complex. Thermodynamic and transport data for $NiCl_2$ solutions are therefore important, since it is one of the few electrolytes whose aqueous solution coordination is fairly well understood.

Density data for aqueous $NiCl_2$ solutions at 25 °C have been reported by a number of workers (*12-17*). The results of Karapet'yants et al. (*12*) are seriously discrepant from all the other studies, up to 3% high at 4.08 mol (kg of H_2O)$^{-1}$, and can be rejected as highly inaccurate. The other data (*13-17*) agree with each other much better, but still show differences several times greater than expected from the usual stock solution concentration errors. We, therefore, reinvestigated $NiCl_2$ densities from 0.04 to 4.98 mol (kg of H_2O)$^{-1}$ and report these results here. We are also remeasuring osmotic/activity coefficients (*18*) and diffusion coefficients (*19*) for aqueous $NiCl_2$.

Experimental Section

All of our $NiCl_2$ densities were measured in duplicate at 25.00 ± 0.005 °C (IPTS-68) with two matched 30.87-cm^3 single-stem pycnometers. These pycnometers were wiped with 95% ethanol about 0.5 h before weighing. All weights were corrected to vacuum. $NiCl_2$ solution densities are uncertain by (2-3) × 10^{-5} g cm^{-3}.

Pycnometer volumes are known to (3-4) × 10^{-4} cm^3, and were obtained by calibrating 7-9 times using purified water. Our water was purified first by ion exchange and then by distillation. The density of water at 25.00 °C, 0.997 045 g cm^{-3}, was taken from Kell (*20*).

Our aqueous $NiCl_2$ stock solution was prepared by dissolving and filtering Mallinckrodt analytical reagent $NiCl_2{\cdot}6H_2O$. Lower concentrations were obtained by mass dilution; higher concentrations were obtained by gently warming samples to drive off water.

Direct current arc optical emission spectroscopic analysis of this $NiCl_2{\cdot}6H_2O$ for impurities indicated the presence of 10 ppm Sr, ≤5 ppm Si, and ≤1 ppm Ca by weight. The anticipated main impurity, Co, was actually below its 10 ppm detection limit.

We have analyzed the concentrations of several other transition-metal chloride solutions both by mass titration with $AgNO_3$ (dichlorofluorescein end-point indicator), and by conversion to the anhydrous sulfate by addition of excess H_2SO_4 followed by evaporation and drying at 400-500 °C (*6-9*). However, the green color of $NiCl_2$ solutions makes it rather difficult to detect the yellow to pink dichlorofluorescein end-point color change. An attempt to convert samples of $NiCl_2$ to anhydrous $NiSO_4$ at 500 °C gave results that were initially about 1.5% high, but which became low after a few days and showed a steady weight decrease with time. This apparently indicates that partial formation of nickel polysulfate occurs initially, and that this nickel sulfate/polysulfate is thermodynamically unstable in air at 500 °C and gradually decomposes to NiO. Thus, neither of these methods is satisfactory for quantitative analysis.

We then attempted to obtain the stock solution concentration by dehydration of acidified samples in air at 200 °C. The "$NiCl_2$" sample changed color with time from orange-yellow to brownish yellow, and sample weights decreased with time. Clearly the $NiCl_2$ was being slowly converted to NiO. At higher temperatures most of the material was converted to NiO, but some chloride still seemed to remain so this method is unsatisfactory. An additional attempt to get NiO by precipitation of $NiCl_2$ solutions with aqueous ammonia followed by thermal decomposition had similar problems. $Ni_2O_3{\cdot}nH_2O$ formation was not a problem since it decomposes to NiO at 400 °C (*21*).

The method finally chosen for concentration analysis is as follows. Weighed $NiCl_2$ stock solution samples were evaporated to dryness with excess H_2SO_4; this eliminates the chloride ions and gives bright yellow nickel sulfate/polysulfate. This was then decomposed in air to form NiO at 800 °C. After about 5 days at 800 °C the decomposition was complete, and sample weights were constant after that. The NiO was greenish gray ash colored.

The $NiCl_2$ stock solution concentration was thus determined to be 3.9221 ± 0.0012 mol (kg of H_2O)$^{-1}$ using triplicate samples. Assumed molecular masses are 129.616 g mol^{-1} for $NiCl_2$ and 74.709 g mol^{-1} for NiO.

X-ray fluorescence spectroscopic analysis of NiO prepared in this manner showed it contained <0.015% Cl and ≤0.02% S. These impurity amounts are too low to affect the calculated stock concentration, so thermal decomposition of nickel sul-

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Table I. Densities and Apparent Molal Volumes of Aqueous $NiCl_2$ at 25.00 °C

m, mol (kg of $H_2O)^{-1}$	c, mol dm^{-3}	d, g cm^{-3}	ϕ_v, cm^3 mol^{-1}
0.039987	0.039856	1.001 893	8.00
0.089987	0.089654	1.007 912	8.43
0.15996	0.15926	1.016 247	9.07
0.24988	0.24853	1.026 805	9.90
0.35986	0.35745	1.039 66	10.43
0.48997	0.48590	1.054 66	11.07
0.64587	0.63914	1.072 42	11.72
0.81012	0.79975	1.090 87	12.34
0.99961	0.98393	1.111 84	12.99
1.2097	1.1866	1.134 71	13.64
1.4398	1.4066	1.159 30	14.31
1.6661	1.6209	1.183 01	14.93
1.9994	1.9329	1.217 28	15.72
2.0001	1.9336	1.217 34	15.73
2.3331	2.2404	1.250 67	16.46
2.6652	2.5418	1.283 14	17.11
3.0008	2.8414	1.315 19	17.70
3.3082	3.1117	1.343 93	18.19
3.6128	3.3756	1.371 87	18.63
3.9221	3.6394	1.399 64	19.05
4.2549	3.9187	1.428 90	19.47
4.4271	4.0613	1.443 80	19.67
4.9832	4.5133	1.490 71	20.30

fate/polysulfate to NiO is suitable for quantitative analysis for Ni.

Results and Discussion

Table I contains the experimental density data for aqueous $NiCl_2$ at 25 °C. Although the highest concentration of 4.9832 mol (kg of $H_2O)^{-1}$ is slightly above the solubility (*18*) of 4.9208 ± 0.0028 mol (kg of $H_2O)^{-1}$, no crystallization occurred during the density measurements. Quantities tabulated in Table I are the molality m in mol (kg of $H_2O)^{-1}$, the molarity c in mol dm^{-3}, the density d in g cm^{-3}, and the apparent molal volume ϕ_v of $NiCl_2$ in cm^3 mol^{-1}. These apparent molal volumes were calculated by using the equation

$$\phi_v = \frac{10^3(d^0 - d)}{md^0d} + \frac{M_2}{d} \qquad (1)$$

where M_2 is the molecular weight of $NiCl_2$ and d^0 = 0.997 045 g cm^{-3} is the density of pure water.

These density data were represented by the least-squares equations

$$d = d^0 + \sum_{i=2}^{n} B_i X^{i/2} \qquad (2)$$

where X denotes m or c. Table II contains the least-squares values of B_i and the standard deviations σ of eq 2. The values of σ were 1.1×10^{-5} g cm^{-3} (maximum deviation of 2.1×10^{-5} g cm^{-3}) for the molarity fit and $\sigma = 1.4 \times 10^{-5}$ g cm^{-3} (maximum deviation 2.8×10^{-5} g cm^{-3}) for the molality fit; they are well within our claimed precision of $(2-3) \times 10^{-5}$ g cm^{-3}.

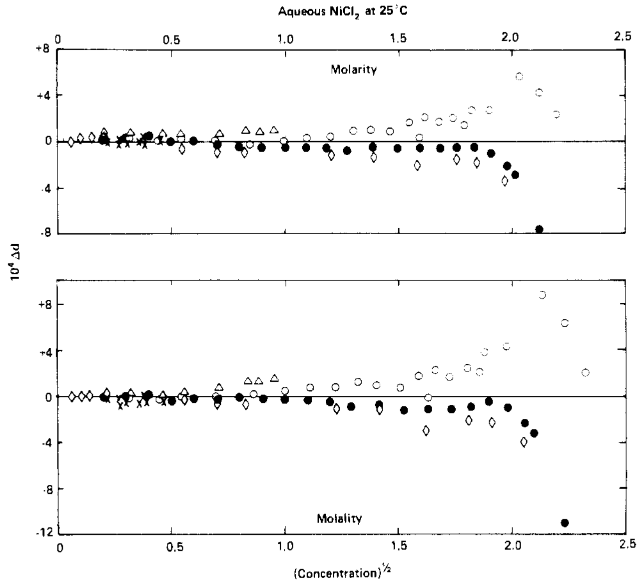

Figure 1. Differences between experimental densities and least-squares equations for $NiCl_2$ solutions in g cm^{-3} × 10^4: (●) this research; (×) Spitzer et al. (*14*); (◇) Stokes et al. (*15*); (△) Lo Surdo and Millero (*16*); (○) Perron et al. (*17*). Top curve is for molarity fit; bottom curve is for molality fit.

Published density data for $NiCl_2$ solutions cover the concentration ranges 0.0200–4.081 (*12*), 0.0999–4.9111 (*13*), 0.044 88–0.2015 (*14*), 0.003 66–4.210 (*15*), 0.040 99–0.91782 (*16*), and 0.095 54–5.384 mol (kg of $H_2O)^{-1}$ (*17*). The data of Karapet'yants et al. (*12*) are considerably higher than all of the other studies so they were rejected. Pearce and Eckstrom's values (*13*) are somewhat low, up to (4–5) × 10^{-4} g cm^{-3} at high concentrations. This set of data (*13*) was also rejected, even though it is low only by about the same amount that the better quality data sets differ. The reason it was rejected was because their densities (*13*) show a significantly different variation with concentration than the three other high concentration data sets (this work and ref *15* and *17*). Also, the points of Stokes et al. (*15*) at 0.082 80, 0.104 03, and 0.116 70 mol (kg of $H_2O)^{-1}$ are inconsistent with their own data at other concentrations, so these three points were also rejected.

The least-squares parameters for eq 2 were then redetermined by giving equal weight to our data and to the more reliable published data (*14*–*17*). Table II contains these new B_i values, and Figure 1 shows the differences between the experimental data and the least-squares equations for both molality and molarity fits.

Our density data agree best with that of Stokes et al. (*15*), but their results are slightly lower. The data of Lo Surdo and Millero (*16*) agree with ours up to 0.16 mol (kg of $H_2O)^{-1}$, but theirs are higher than ours at higher concentrations. Perron et al. (*17*) agree with our densities up to about 0.5 mol (kg of $H_2O)^{-1}$, but their data are intermediate between ours and those of Lo Surdo and Millero (*16*) at higher concentrations. Data from Spitzer et al. (*14*) tend to be slightly low. It should be noted that our data fall between results from the other two

Table II. Coefficients for $NiCl_2$ Density Polynomials

B_i	molarity[a]	molality[a]	molarity[b]	molality[b]
B_2	0.123963	0.123283	0.121639	0.122701
B_3	−0.0120816	−0.0105978	−0.00203718	−0.00671096
B_4	0.0122930	0.00894802	−0.00399048	0.000614096
B_5	−0.0117619	−0.0103255	0.00106881	−0.00231334
B_6	0.00496078	0.00411775		0.000573561
B_7	−0.000755002	−0.000587033		
max concn	4.5133	4.9832	4.8382	5.384
σ	0.000011	0.000014	0.000170	0.000236

[a] Data from Table I only. [b] Data from Table I and ref *14–17*.

studies (*15*, *17*) that were based on use of high-purity $NiCl_2$.

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Glossary

d	density of solution, g cm^{-3}
d^0	density of pure water, g cm^{-3}
m	molal concentration of solute, mol (kg of $H_2O)^{-1}$
c	molar concentration of solute, mol dm^{-3}
ϕ_V	apparent molal volume of solute, cm^3 mol^{-1}
M_2	molecular weight of solute, g mol^{-1}
B_i	least-squares coefficients for eq 2
X	denotes m or c in eq 2
σ	standard deviation of eq 2

Registry No. $NiCl_2$, 7718-54-9.

Literature Cited

(1) Millero, F. J. In "Activity Coefficients in Electrolyte Solutions"; Pytkowicz, R. M., Ed.; CRC Press: Boca Raton, FL, 1979; Vol. II, Chapter 2.
(2) Rard, J. A.; Miller, D. G. *J. Chem. Eng. Data* **1980**, *25*, 211–215; **1981**, *26*, 38–43; **1982**, *27*, 169–173.
(3) Rard, J. A.; Miller, D. G. *J. Solution Chem.* **1979**, *8*, 701–716, 755–766; **1983**, *12*, 413–425.
(4) Rard, J. A.; Miller, D. G. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 887–896.
(5) Miller, D. G.; Rard, J. A.; Eppstein, L. B.; Albright, J. G. *J. Phys. Chem.* **1984**, *88*, 5739–5748.
(6) Rard, J. A. *J. Chem. Eng. Data* **1984**, *29*, 443–450.
(7) Rard, J. A.; Miller, D. G. *J. Chem. Eng. Data* **1984**, *29*, 151–156.
(8) Rard, J. A.; Miller, D. G. *J. Solution Chem.* **1985**, *14*, 271–299.
(9) Rard, J. A.; Miller, D. G. *Z. Phys. Chem. N. F.* **1984**, *142*, 141–155.
(10) Hunt, J. P.; Friedman, H. L. In "Progress in Inorganic Chemistry"; Lippard, S. J., Ed.; Wiley Interscience: New York, 1983; Vol. 30.
(11) Weingärtner, H.; Müller, C.; Hertz, H. G. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 2712–2734.
(12) Karapet'yants, M. Kh.; Vasilëv, V. A.; Sanaev, E. S. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1977**, *51*, 1281–1283.
(13) Pearce, J. N.; Eckstrom, H. C. *J. Phys. Chem.* **1937**, *41*, 563–565.
(14) Spitzer, J. J.; Singh, P. P.; McCurdy, K. G.; Hepler, L. G. *J. Solution Chem.* **1978**, *7*, 81–86.
(15) Stokes, R. H.; Phang, S.; Mills, R. *J. Solution Chem.* **1979**, *8*, 489–500.
(16) Lo Surdo, A.; Millero, F. J. *J. Phys. Chem.* **1980**, *84*, 710–715.
(17) Perron, G.; Roux, A.; Desnoyers, J. E. *Can. J. Chem.* **1981**, *59*, 3049–3054.
(18) Rard, J. A., unpublished data.
(19) Rard, J. A.; Miller, D. G., unpublished data.
(20) Kell, G. S. *J. Chem. Eng. Data* **1975**, *20*, 97–105.
(21) Richardson, J. T. *J. Phys. Chem.* **1963**, *67*, 1377–1378.

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Thermodynamics of Binary Mixtures Containing Cyclic Alkanones. 1. Excess Enthalpies of Cyclopentanone and Cyclohexanone + *n*-Alkanes, + Cyclohexane, + Benzene, and + Tetrachloromethane

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A Tian-Calvet type calorimeter has been used to determine molar excess enthalpies, H^E, as a function of concentration at atmospheric pressure and 298.15 K for some binary liquid mixtures containing cycloalkanones (cyclopentanone and cyclohexanone) with *n*-alkanes, $CH_3-(CH_2)_{m-2}-CH_3$ (m = 6, 7, 12, 16), cyclohexane, C_6H_{12}, benzene, C_6H_6, and tetrachloromethane, CCl_4. The experimental H^E results are interpreted in terms of molecular interactions and the Patterson effect.

Introduction

This work is part of a systematic study of the thermodynamic properties of organic mixtures, T.O.M. Project (*1–8*), with the purpose of characterizing the type and magnitude of molecular interaction in the binary liquid mixtures and to improve the group contribution models currently used to predict thermodynamic properties (*1*, *8*).

Moreover, the study of mixtures containing cycloalkanones offers an opportunity to test the applicability of the energy interchange parameters determined from mixtures of *n*-alkanones (*9–11*).

Furthermore, there are many intriguing problems related to binary liquid mixtures containing *n*-alkanes (*12–15*). For example, mixtures of *n*-alkanes with spherical nonpolar molecules, such as cyclohexane (*16*), have been discussed by Patterson (*12*) in terms of destruction of partial order assumed to exist in pure liquid *n*-alkanes of sufficient chain length. Such an effect will manifest itself by a positive contribution to the excess enthalpy, H^E. In view of this, cycloalkanones + *n*-alkane mixtures were regarded as interesting in that by formally replacing $-CH_2-$ groups of cycloalkanes by the $-CO-$ group, the influence exerted by group dipole moments and shape upon the thermodynamic excess functions can be further investigated.

No experimental excess Gibbs free energy or excess enthalpy data could be found in the literature for these mixtures. In order to characterize the behavior of the "cycloalkanone" group with respect to the main functional groups of organic chemistry, it was decided to measure excess enthalpies in a systematic way for mixtures of cyclopentanone and cyclohexanone with *n*-alkanes of general formula

$$CH_3-(CH_2)_{m-2}-CH_3 \qquad (m = 6, 7, 12, 16)$$

and with cyclohexane, benzene, and tetrachloromethane.