Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous $NiCl_2$, $Pr(NO_3)_3$, and $Lu(NO_3)_3$ and Solubility of $NiCl_2$ at 25 °C

Joseph A. Rard

Lawrence Livermore National Laboratory, University of California, Livermore, California 94550

Osmotic coefficients of aqueous $NiCl_2$ and $Pr(NO_3)_3$ have been measured at 25 °C from 0.299 76 to 6.1364 and from 0.493 86 to 7.6610 mol·kg^{-1}, respectively, by using the isopiestic method. These data extend well into the supersaturated concentration region. Previous isopiestic data for $NiCl_2$ are in fair to good agreement with the present results. However, some of the earlier osmotic coefficients for $Pr(NO_3)_3$ are too high by 0.3–1.3%, apparently due to a stock solution concentration error, and have been normalized to the present results. A few osmotic coefficients were also measured for concentrated $Lu(NO_3)_3$ solutions from 4.1935 to 7.5961 mol·kg^{-1}; these osmotic coefficients agree to 0.1–0.3% with previous data. The solubility of a solid phase, probably metastable $Lu(NO_3)_3 \cdot 6H_2O(cr)$, was determined to be ≥ 7.596 mol·kg^{-1}. The solubility of $NiCl_2$ was found to vary slowly with time, apparently due to the proximity of 25 °C to the tetrahydrate to hexahydrate transition temperature. Extrapolation to infinite equilibration time gave the solubility of $NiCl_2 \cdot 6H_2O(cr)$ to be 4.9208 ± 0.0028 mol·kg^{-1}.

Introduction

Osmotic/activity coefficient and solubility data are essential for calculation of Gibbs energies of dilution and of dissolution of salts, and for chemical speciation and reaction thermodynamics calculations. Thus, they are required for a detailed thermodynamic analysis of electrolyte solutions and hydrated salts in equilibrium with their saturated solutions.

Various properties of aqueous $NiCl_2$ solutions have been studied in recent years by different workers (*1-6*), mainly because it is one of the few transition-metal halides whose aqueous solution coordination has been well characterized. X-ray diffraction, neutron diffraction, and NMR measurements indicate that $Ni(H_2O)_6^{2+}$ is the dominant cationic species in $NiCl_2$ solutions up to high concentrations (*7*), although Weingärtner et al. (*8*) have discussed evidence that 1 mol·dm^{-3} $NiCl_2$ solutions contain 5–15% inner-sphere $NiCl(H_2O)_5^+$.

Activity data are available for aqueous $NiCl_2$ solutions at 25 °C. Robinson and Stokes (*9*) reported isopiestic data for 10 concentrations from 0.1188 to 2.123 mol·kg^{-1} using a KCl standard, and Robinson (cited in Stokes' appendix (*10*)) used the same method but a $CaCl_2$ standard for 13 points from 1.634 to 5.714 mol·kg^{-1}. Shul'ts et al. (*11*) reported isopiestic data with various standards from 1.0521 to 4.9203 mol·kg^{-1}; although these data are in general agreement with the other two studies (*9*, *10*), they have about a factor of 10 more scatter. Pearce and Eckstrom (*12*) reported direct vapor pressure measurements from 0.1 to 4.91 mol·kg^{-1}; osmotic coefficients calculated from these data are much lower than the isopiestic results by 0.03–0.13 up to 4.0 mol·kg^{-1}, but are too high by 0.11 at 4.91 mol·kg^{-1}. Although the direct vapor pressure study seems to contain the major error, none of the isopiestic studies provides sufficient details to judge their accuracy.

Goldberg et al. (*13*) and Timmermans (*14*) cite early freezing point depression data and vapor pressure data for $NiCl_2$ solutions at other temperatures. Several of these studies are of low precision, and Goldberg et al.'s analysis (*13*) indicates that the remaining sets are also inaccurate. Consequently, they will not be considered further. Holmes and Mesmer (*15*) have reported apparently accurate isopiestic data at 382.96 and 413.36 K. Unfortunately, available enthalpy and heat capacity data are not extensive enough to relate their values to the lower temperature data.

Hass and Jellinek (*16*) reported emf data for $NiCl_2$ solutions from 0.032 to 3.021 mol·dm^{-3} at 25 °C; unfortunately, they used a cell with liquid junction so the emf results cannot be rigorously analyzed. Phang (*2*) reported emf data for cells with transport from 0.1266 to 4.283 mol·dm^{-3}. Stokes et al. (*3*) have reported cation transference numbers for 0.0529–3.921 mol·dm^{-3} $NiCl_2$ which can be used in principle to obtain activities from these data. Above 0.9792 mol·dm^{-3} only four transference numbers were reported, and this is insufficient for accurate analysis of the emf data at high concentrations. Although, the transference numbers are fairly well characterized from 0.0529 to 0.9792 mol·kg^{-1}, the calculated osmotic coefficients are highly sensitive to errors in both emf and transference numbers.

Of all these $NiCl_2$ activity studies reported at 25 °C, only two seem to provide reliable data (*9*, *10*), and none alone covers the entire concentration range. Thus, we decided to reinvestigate $NiCl_2$ by the isopiestic method over a wider concentration range and report these results here. We have also redetermined the solubility of $NiCl_2$ by the same method, since published values show a fair amount of variation. Reported solubilities cluster either around 4.91 mol·kg^{-1} (*12*, *17*) or 5.06 mol·kg^{-1} (*18-20*).

Much less activity data are available for aqueous $Pr(NO_3)_3$ solutions. Freezing point depression data (*21*) are available from 0.0158 to 0.1267 mol·L^{-1}, and enthalpy of dilution (*22*) and heat capacity data (*23*) are available to convert them to osmotic coefficients at 25 °C. Unfortunately, these freezing point measurements were done before ion-exchange or liquid–liquid extraction methods were available to separate rare earths from each other. Thus, the $Pr(NO_3)_3$ used in the freezing point study probably was not very pure so the derived osmotic coefficients are questionable (and scattered). Rard et al. (*24*) reported isopiestic data for four $Pr(NO_3)_3$ concentrations from 0.804 67 to 1.1084 mol·kg^{-1}, and later (*25*) gave data from 0.125 53 to 6.2861 mol·kg^{-1}.

We recently reported solubility measurements for $Pr(NO_3)_3 \cdot 6H_2O(cr)$ at 25.00 °C using the isopiestic method (*26*). Whereas the experimental solubility agreed well with previous data, the calculated osmotic coefficient disagreed with previous isopiestic data (*25*) in this concentration region.

There are 14 rare earth nitrates with isopiestic data at 25 °C (*24*, *25*, *27-29*) from low concentrations to saturation or supersaturation. For several of these salts, the solution preparations, analyses, and isopiestic measurements were done at Ames Laboratory (*24*); for several others all of this was done

0021-9568/87/1732-0334$01.50/0

at Lawrence Livermore National Laboratory (*28*). However, for six rare earth nitrates, the solutions were prepared and analyzed at Ames Laboratory and then shipped to LLNL for isopiestic measurements (*25*, *27*, *29*).

Of these six salts (*25*, *27*), the $Nd(NO_3)_3$, $Dy(NO_3)_3$, $Ho(NO_3)_3$, and $Lu(NO_3)_3$ stock solutions were reanalyzed for concentration at LLNL by the gravimetric sulfate method (*29*). For $Nd(NO_3)_3$, $Ho(NO_3)_3$, and $Lu(NO_3)_3$, the new analyses agreed well with the values reported by Ames Laboratory, but for $Dy(NO_3)_3$ the reanalysis gave higher results. This indicates that some evaporation of solvent occurred from $Dy(NO_3)_3$ during the handling or shipping of this stock solution to LLNL. Unfortunately, all of each of the $La(NO_3)_3$ and $Pr(NO_3)_3$ stock solutions supplied to us were required for the isopiestic measurements, so none were left for reanalysis of concentrations.

The osmotic coefficient for saturated $Pr(NO_3)_3$ (*26*), measured with a new stock solution, was lower than values obtained earlier (*25*). This implies that the actual concentration of the first stock solution supplied by Ames Laboratory was higher than reported by them. It thus appears likely that some evaporation of solvent occurred during the handling or shipping of this stock solution of LLNL, similar to what occurred for $Dy(NO_3)_3$. In addition, this same type of problem occurred for one other salt, $La(NO_3)_3$. We have discussed this problem in greater detail elsewhere (*29*) and have redetermined and reported new isopiestic data for $La(NO_3)_3$ at 25 °C (*29*).

In view of the above considerations, we have now redetermined the osmotic coefficients of $Pr(NO_3)_3$ to high concentrations by using the isopiestic method. Since $Pr(NO_3)_3$ solutions readily supersaturate, we have extended these isopiestic measurements to even higher concentrations than reported previously (*25*).

The recent IUPAC review of aqueous rare earth nitrate solubilities (*30*) showed little data for $Lu(NO_3)_3$, with the recommended solubility at 25 °C being based on isothermal saturation measurements at Ames Laboratory. Since there is a change in the stable solid phase around 25 °C from the hexahydrate to the pentahydrate near the end of the rare earth series, and because of uncertainty in the degree of hydration for several of the heavier rare earth nitrate crystals, another determination of the solubility of $Lu(NO_3)_3$ was desirable. We, therefore, attempted to determine the solubility of $Lu(NO_3)_3\cdot 5H_2O$(cr) by using the isopiestic method. This attempt was unsuccessful, but it did yield a lower bound for the solubility of a different solid phase which was probably the metastable hexahydrate.

Experimental Section

All of the isopiestic experiments were performed at 25.00 ± 0.005 °C (IPTS-68) with the same stainless steel isopiestic chambers used for our previous measurements (*24–29*). Their design and operation have been described in detail elsewhere (*26*). Isopiestic equilibration times were generally 4-6 days above 2.5 mol·kg^{-1}, but they were slowly increased with decreasing concentration and were about one month at the lowest concentrations. All sample weights were converted to masses by using available density data. Water used for sample preparations and dilutions was purified by deionization followed by distillation.

Our $NiCl_2$ stock solution was prepared by dissolving Mallinckrodt AR $NiCl_2\cdot 6H_2O$ in water followed by filtration. The purity of this material was checked by direct current arc optical emission spectroscopy (DCAOES); impurities found were 10 ppm Sr, ≤5 ppm Si, and ≤1 ppm Ca by weight. Cobalt was below its 10 ppm detection limit.

The concentration of this $NiCl_2$ stock solution was determined as follows. Weighed samples of stock solution were evaporated to dryness with excess H_2SO_4 (this eliminates chloride ions), and the resulting sulfate/oxysulfate was then thermally decomposed in air at 800 °C to form stoichiometric NiO (*6*). The stock solution concentration was thus determined to be 3.9221 ± 0.0012 mol·kg^{-1}. Here and elsewhere, the uncertainty limits are estimated standard deviations. Assumed molecular masses are 129.616 g·mol^{-1} for $NiCl_2$ and 74.709 for NiO. This is the same stock solution that was used for our density measurements (*6*).

The $Pr(NO_3)_3$ and $Lu(NO_3)_3$ stock solutions were prepared at Ames Laboratory by reacting ion-exchange-purified rare earth oxides with AR HNO_3. These stock solutions were adjusted to their equivalence pH values with dilute HNO_3; these equivalence pH values were determined by potentiometric pH titration of unadjusted stock samples with the same dilute HNO_3. These stock solutions were then bottled and shipped to LLNL for the isopiestic measurements.

Prior to its shipment to LLNL, the $Lu(NO_3)_3$ stock solution was analyzed for concentration at Ames Laboratory by using mass titration with EDTA (xylenol orange indicator, sodium acetate/acetic acid buffer) and by the gravimetric sulfate method. Their average analysis result was 0.374 18 mol·kg^{-1}. Reanalysis at LLNL by the gravimetric sulfate method, after decomposing nitrate ions to avoid coprecipitation (*29*), gave 0.374 23 ± 0.000 08 mol·kg^{-1} which is excellent agreement. Assumed molecular masses are 360.985 g·mol^{-1} for $Lu(NO_3)_3$ and 638.112 for $Lu_2(SO_4)_3$. An overall concentration uncertainty of 0.05% will be assumed in subsequent calculations. Samples of this stock solution were concentrated in a desiccator before the isopiestic solubility measurements were started. (The concentration of this stock solution was lower than desired, since the relatively low mass fraction of water in concentrated solutions will cause the uncertainty in the molalities to increase to about 0.15% at saturation.)

The $Lu_2(SO_4)_3$ produced during the sulfate analysis was examined for impurities by using DCAOES. Impurities found, in ppm by weight, are 5 ppm Fe, 4 ppm each Ca and Al, 1 ppm Ba, and ≤1 ppm each Mg, Si, Cu, and Sr. Other rare earths were below their 1–100 ppm detection limits.

A new $Pr(NO_3)_3$ solution was supplied to us by Ames Laboratory, and it was used by us to prepare both high and low concentration stock solutions. Gravimetric sulfate analyses (*29*) gave 4.8400 ± 0.0024 and 0.745 94 ± 0.000 24 mol·kg^{-1}, respectively, for their concentrations. Assumed molecular masses are 326.922 g·mol^{-1} for $Pr(NO_3)_3$ and 569.988 for $Pr_2(SO_4)_3$. The more concentrated stock solution was the same one used for solubility determinations (*26*). Samples of the higher concentration stock solution were equilibrated against a $CaCl_2$ reference standard, and samples of the low concentration stock solution were equilibrated mainly against NaCl but with a few equilibrations against $CaCl_2$. By using two separately analyzed stock solutions, we can check the reproducibility of isopiestic data for $Pr(NO_3)_3$.

A sample of our $Pr(NO_3)_3$ solution was dried and thermally decomposed to the black oxide $PrO_{1.5+n}$ at 800 °C and then examined for impurities. DCAOES gave ≤10 ppm Ca and ≤5 ppm Fe by weight. Other rare earths were below their 1–100 ppm detection limits. No impurities could be detected in the $PrO_{1.5+n}$ by using X-ray fluorescence spectroscopy.

The NaCl reference stock solution was prepared by weight from oven-dried Mallinckrodt AR NaCl and purified water; its calculated concentration was 1.9991 mol·kg^{-1}. A check on this concentration was made by dehydration of triplicate samples at 200 and 250°C. The resulting concentration of 1.9996 ± 0.0006 mol·kg^{-1} agreed with the direct weighing value. The $CaCl_2$ reference stock solution was prepared by reacting $CaCO_3$ with HCl, and its concentration of 6.6264 mol·kg^{-1} was obtained by dehydration and by gravimetric sulfate analyses. Detailed analyses results are given elsewhere (*31*). Assumed molecular

Table I. Isopiestic Molalities of $NiCl_2$ and $Pr(NO_3)_3$ with NaCl or $CaCl_2$ Reference Solutions at 25 °C

[reference], mol·kg^{-1}	[$NiCl_2$], mol·kg^{-1}	[$Pr(NO_3)_3$], mol·kg^{-1}	$\Phi(NiCl_2)$	$\Phi(Pr(NO_3)_3)$	[reference], mol·kg^{-1}	[$NiCl_2$], mol·kg^{-1}	[$Pr(NO_3)_3$], mol·kg^{-1}	$\Phi(NiCl_2)$	$\Phi(Pr(NO_3)_3)$
NaCl Reference									
0.43090	0.29976		0.8813		2.7886	1.5202	1.4852	1.2602	0.9674
0.83552	0.54839	0.49386	0.9435	0.7857	2.9869	1.6078	1.5802	1.2923	0.9862
1.3133	0.81291	0.75196	1.0209	0.8277	3.2397	1.7177	1.7003	1.3335	1.0103
1.5235	0.92261	0.86071	1.0544	0.8476	3.5142	1.8358	1.8301	1.3778	1.0365
1.7709	1.0451	0.98489	1.0962	0.8724	3.8357	1.9729	1.9827	1.4292	1.0666
2.0430	1.1780	1.1222	1.1391	0.8968	4.1280	2.0952	2.1203	1.4765	1.0943
2.2222	1.2621	1.2102	1.1686	0.9140	4.2691	2.1550	2.1860	1.4985	1.1079
2.4807	1.3813	1.3362	1.2105	0.9385					
$CaCl_2$ Reference									
2.1568	2.0949	2.1219	1.4767	1.0935	4.5599	4.8487		2.2632	
2.3071	2.2441	2.2891	1.5337	1.1276	4.5849		5.0783		1.6362
2.4037	2.3408	2.3988	1.5703	1.1493	4.6183	4.9265^c		2.2775	
2.4136	2.3506	2.4103	1.5742	1.1514	4.6191	4.9299^d		2.2766	
2.5620	2.5022	2.5816	1.6295	1.1845	4.6199	4.9302^e		2.2771	
2.6554	2.6005	2.6900	1.6629	1.2057	4.6267	4.9389^f		2.2789	
2.6755	2.6190	2.7130	1.6719	1.2105	4.6277	4.9392^g		2.2797	
2.7441	2.6909	2.7929	1.6970	1.2263	4.6709		5.1879		1.6543
2.7927		2.8508		1.2370	4.7184	5.0634		2.3000	
2.8486	2.8016	2.9106	1.7348	1.2524	4.7688		5.3168		1.6733
2.9624	2.9225	3.0454	1.7764	1.2785	4.8200^a		5.3832^h		1.6835
3.0462	3.0124	3.1462	1.8067	1.2974	4.8274	5.2168		2.3224	
3.0717^a		3.1854		1.2997	4.8538		5.4252		1.6907
3.1432	3.1192	3.2642	1.8405	1.3190	4.8965		5.4743		1.7010
3.1782^a		3.3141		1.3240	4.9212	5.3484	5.5115	2.3416	1.7042
3.2306		3.3777		1.3360	4.9472		5.5425		1.7101
3.2443	3.2301	3.3865	1.8763	1.3422	4.9495		5.5470		1.7101
3.2710^a		3.4260		1.3455	5.0159	5.4809	5.6334	2.3608	1.7227
3.3522	3.3509	3.5182	1.9133	1.3668	5.0682		5.7013		1.7326
3.3684	3.3693		1.9188		5.0915^a		5.7279^h		1.7380
3.4585	3.4711	3.6491	1.9495	1.3908	5.1371		5.7914		1.7452
3.5551	3.5829	3.7685	1.9812	1.4127	5.1484	5.6671	5.8013	2.3868	1.7487
3.6612	3.7076	3.9017	2.0151	1.4361	5.1644^a	5.6974^i		2.3866	
3.7252	3.7847		2.0347		5.1913		5.8508		1.7584
3.7496	3.8113	4.0100	2.0437	1.4568	5.2630		5.9418		1.7719
3.8325	3.9137	4.1173	2.0678	1.4741	5.2890	5.8684	5.9763	2.4119	1.7762
3.9264	4.0280	4.2350	2.0961	1.4953	5.3595		6.0625		1.7901
3.9899	4.1068	4.3153	2.1146	1.5093	5.4699		6.1953		1.8118
4.0754	4.2146	4.4249	2.1386	1.5277	5.4728^a	6.1364		2.4410	
4.1463	4.3035		2.1588		5.5041^a		6.2420^h		1.8167
4.1577	4.3185	4.5293	2.1617	1.5458	5.6203		6.3828		1.8381
4.2464	4.4325	4.6430	2.1855	1.5648	5.8182		6.6185		1.8735
4.3633	4.5842	4.7910	2.2163	1.5905	5.8538		6.6561		1.8808
4.4751	4.7306	4.9332	2.2449	1.6145	5.9546		6.7772		1.8971
4.5099	4.7788	4.9776	2.2526	1.6220	6.1256		6.9705		1.9260
4.5314		5.0089		1.6253	6.2803		7.1398		1.9514
4.5324		5.0107		1.6253	6.4444		7.3137		1.9775
4.5404		5.0251^b		1.6256	6.5043^a		7.3698		1.9884
4.5406		5.0251^b		1.6258	6.6062		7.4794		2.0023
4.5440		5.0270^b		1.6273	6.7883		7.6610		2.0285

[a] Quadruplicate $CaCl_2$ samples were used for these determinations. [b] Solubility determinations. These three points were taken from ref *26* and are for $Pr(NO_3)_3{\cdot}6H_2O$. [c] Fifth solubility attempt, 13-day equilibration. [d] Third solubility attempt, 9-day equilibration. [e] Second solubility attempt, 8-day equilibration [f] Fourth solubility attempt, 5-day equilibration. [g] First solubility attempt, 4-day equilibration. [h] These three points and the NaCl reference solution points for $Pr(NO_3)_3$ were based on the 0.745 94 mol·kg^{-1} stock solution; all other $CaCl_2$ reference solution points were based on the 4.8400 mol·kg^{-1} $Pr(NO_3)_3$ stock solution. [i] Single sample since the other one crystallized.

masses are 58.443 g·mol^{-1} for NaCl, 110.986 for $CaCl_2$, and 136.138 for $CaSO_4$.

Tables I and II contain the experimental isopiestic equilibrium molalities; these concentrations are reliable to ±0.096% or better (except that 0.493 86 mol·kg^{-1} $Pr(NO_3)_3$ is uncertain by ±0.137% and 0.430 90 mol·kg^{-1} NaCl is uncertain by ±0.121%), with the majority being uncertain by less than 0.05%. Reported molalities are the average of duplicate determinations, except that triplicate or quadruplicate samples of $CaCl_2$ were used in several experiments.

Experimental data for $NiCl_2$ extend 1.216 mol·kg^{-1} above saturation, and for $Pr(NO_3)_3$ they extend 2.635 mol·kg^{-1} above saturation. None of these salts show much tendency to spontaneously crystallize at these levels of supersaturation. No crystallization occurred in the any of the supersaturated $Pr(NO_3)_3$ or $Lu(NO_3)_3$ solution runs, but two of the four attempts to measure data for $NiCl_2$ above 5.7 mol·kg^{-1} resulted in one or both samples going dry.

Table II. Isopiestic Molalities of $Lu(NO_3)_3$ with $CaCl_2$ Reference Solutions at 25 °C

[$CaCl_2$] mol·kg^{-1}	[$Lu(NO_3)_3$], mol·kg^{-1}	$\Phi(Lu(NO_3)_3)$
4.6102^a	4.1935	2.0005
5.1647^a	4.8317	2.1109
5.8002^a	5.5654	2.2171
6.5043^a	6.3338	2.3137
7.4660^a	7.2863	2.4034
7.5790^a	7.3899	2.4117
7.8126^b	7.5961	2.4290

[a] Quadruplicate $CaCl_2$ samples were used for these determinations. [b] Triplicate $CaCl_2$ samples were used for this determination.

Crystals of $NiCl_2 \cdot nH_2O$ and $Lu(NO_3)_3 \cdot nH_2O$ were prepared by concentrating samples of their corresponding stock solutions in a desiccator at room temperature until crystallization occurred. An extra isopiestic cup containing saturated solution and crystals was added to the isopiestic chamber for solubility determinations; see ref *26* for details.

The apparent solubility of $NiCl_2 \cdot nH_2O$ showed a slow decrease with the length of the isopiestic equilibration. Obviously, a slow transformation was occurring in the solid phase. Five solubility experiments were performed with different equilibration periods. The solubility seemed to be approaching a constant value asymptotically with increasing equilibration time. A least-squares analysis of the molal solubility data gave

$$m_s(t) = 4.92084 + 0.07929/t \qquad (1)$$

where t is in days and the correlation coefficient is 0.971. The intercept at infinite time, 4.9208 ± 0.0016 $mol \cdot kg^{-1}$, was interpreted as the true solubility of the thermodynamically stable hydrate at 25 °C. This uncertainty limit is statistical only.

After the solubility determinations had been completed, the saturated solution was decanted from the crystals; these crystals were then dried in a desiccator to eliminate solution absorbed on their surfaces. The amount of $NiCl_2$ in these crystals was determined by the same method used to analyze the $NiCl_2$ stock solution. Their degree of hydration was obtained by difference.

$NiCl_2 \cdot 6H_2O(cr)$ was found to be the equilibrium hydrate for the $NiCl_2$–H_2O system at 25 °C, but the precision of our hydrate analysis was not great enough to tell whether a few percent of lower or higher hydrate was still present after the final 13-day equilibration.

Three attempts were made to determine the solubility of $Lu(NO_3)_3 \cdot nH_2O$ at 25 °C. In each case, all of the crystals initially in the reservoir cup dissolved during the equilibration due to water gained from the isopiestic samples, and the $Lu(NO_3)_3$ and $CaCl_2$ solutions became more concentrated. Obviously, a more soluble higher temperature hydrate was initially present, but it dissolved before it could transform into thermodynamically stable $Lu(NO_3)_3 \cdot 5H_2O(cr)$. The analysis of rare earth nitrate solubilities by Siekierski et al. (*30*) indicates that this higher temperature form probably was the hexahydrate, and they estimated its solubility to be 7.60 ± 0.10 $mol \cdot kg^{-1}$. Our highest concentration equilibration in Table II provides a lower bound of ≥ 7.596 $mol \cdot kg^{-1}$ for the solubility, which is consistent with their estimate.

The three highest $Lu(NO_3)_3$ concentrations in Table II are an extension of our previous isopiestic data by 0.416 $mol \cdot kg^{-1}$ further into the supersaturated concentration region. Several lower concentration points were also measured in order to overlap with previous isopiestic data (*27*); the agreement is good (0.1–0.3%) in the overlap region.

Calculation of Osmotic and Activity Coefficients

Osmotic coefficients, Φ, of our solutions were calculated by using the equation for isopiestic equilibrium

$$\Phi = \frac{\nu^* m^* \Phi^*}{\nu m} \qquad (2)$$

where m is the molality of the solution of interest, ν is the number of ions formed by the dissociation of one molecule of solute, and the corresponding quantities for the NaCl or $CaCl_2$ reference standards are denoted with asterisks. Reference solution osmotic coefficients were taken from published critical reviews for NaCl (*32*) and $CaCl_2$ (*33*). Tables I and II contain the isopiestic equilibrium molalities and Φ values for $NiCl_2$, $Pr(NO_3)_3$, and $Lu(NO_3)_3$.

Our experimental osmotic coefficients and other available activity data were represented by least-squares equations of the type

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

where A is the Debye–Hückel slope (4.0744 for 2–1 electrolytes and 8.6430 for 3–1 electrolytes). Details are given in following sections. Mean molal activity coefficients $\gamma_\pm$ can be calculated from these least-squares parameters by using

$$\ln \gamma_\pm = -Am^{1/2} + \sum_i A_i \left(\frac{r_i + 1}{r_i}\right) m^{r_i} \qquad (4)$$

These osmotic coefficients were also represented by Pitzer's equations (*34*) using $A^\phi = 0.3920$ at 25 °C. Following Pitzer, for $Pr(NO_3)_3$ we set $3\beta^{(1)}/2 = 7.700$ and restricted the fits to ≤ 1.5 $mol \cdot kg^{-1}$, and for $NiCl_2$ fits were restricted to ≤ 2.5 $mol \cdot kg^{-1}$. Higher concentration data were not included since they caused excessive cycling of fits of Pitzer's equations about the experimental data.

Solubility Data

Our experimental solubility (from Table I) is 4.9208 ± 0.0028 $mol \cdot kg^{-1}$ for $NiCl_2 \cdot 6H_2O(cr)$, and, as noted above, it was obtained by extrapolation to infinite time of apparent solubilities. This listed uncertainty limit includes both the uncertainty from the isopiestic equilibrations and the analytical uncertainty in the stock solution concentration. The slow but significant variation of solubility with equilibration period indicates that some kind of slow transformation is occurring in the solid phase.

Solubility data cited in Linke (*18*) indicate that $NiCl_2 \cdot 6H_2O(cr)$ is the stable solid phase from around −30 to about +29 °C; $NiCl_4 \cdot 4H_2O(cr)$ is then stable from about 29 to 45 °C. These data indicate that the solubility of metastable $NiCl_2 \cdot 4H_2O(cr)$ is about 0.27 $mol \cdot kg^{-1}$ above that of the thermodynamically stable $NiCl_2 \cdot 6H_2O(cr)$ at 25 °C. The slow decrease of solubility with equilibration time is consistent with an assumption that our initial solid was a mixed phase containing both hexahydrate and tetrahydrate and that it slowly transformed to nearly pure $NiCl_2 \cdot 6H_2O(cr)$ at longer equilibration times.

As noted in the Introduction, two other studies (*12*, *17*) report about 4.91 $mol \cdot kg^{-1}$ for the solubility of $NiCl_2 \cdot 6H_2O(cr)$; this is about 0.22% below our value and thus in good agreement. Other reported solubilities of about 5.06 $mol \cdot kg^{-1}$ (*18–20*) probably refer to mixed hydrate solid phases and not pure hexahydrate.

Activity Results for Aqueous $NiCl_2$

Table I contains our new isopiestic data for aqueous $NiCl_2$ in the concentration range of 0.299 76–6.1364 $mol \cdot kg^{-1}$. Osmotic coefficients from previous data (*9–11*) were recalculated from their isopiestic molalities by using eq 2 and current values for osmotic coefficients of the NaCl, KCl, and $CaCl_2$ isopiestic reference standards (*32*, *33*).

Recalculated osmotic coefficients of Robinson and Stokes (*9*) are in excellent agreement with ours, within 0.2% up to 1.443 $mol \cdot kg^{-1}$, but they are 0.3–0.4% higher between 1.831 and 2.213 $mol \cdot kg^{-1}$. Robinson's data (*10*) are in good agreement with our results (within 0.1–0.3%) up to about 3.5 $mol \cdot kg^{-1}$, are then 0.4–0.6% higher than our values up to 4.926 $mol \cdot kg^{-1}$, but are within 0.1% of us at their highest concentration of 5.715 $mol \cdot kg^{-1}$. Unfortunately, no experimental details were given in that study (*10*), so the purity of his $NiCl_2$ and his experimental error is thus uncertain.

Recalculated isopiestic data of Shul'ts et al. (*11*) are in general agreement with our isopiestic data and the other studies (*9*, *10*), but a few of their points deviate by up to 2.0%. The larger deviations are due to scatter in their measurements (*11*) and are not systematic in nature. As mentioned in the Introduction, Pearce and Eckstrom's vapor pressures (*12*) are

Table III. Estimated Osmotic Coefficients of Aqueous $NiCl_2$ Solutions at Low Concentrations and 25 °C[a]

m, mol·kg^{-1}	$\Phi(NiCl_2)$	m, mol·kg^{-1}	$\Phi(NiCl_2)$
0.01	0.9077	0.06	0.8596
0.02	0.8869	0.07	0.8577
0.03	0.8752	0.08	0.8563
0.04	0.8678	0.09	0.8556
0.05	0.8630	0.10	0.8553

[a] These estimates were based on extrapolation of the difference in Φ between $NiCl_2$ at $CaCl_2$ at lower molalities. The estimated $NiCl_2$ Φ values are uncertain by 0.001–0.002.

considerably in error and give very low osmotic coefficients over most of the concentration range.

In view of the above considerations, in our subsequent calculations we gave unit weights to our $NiCl_2$ data, to those of Robinson and Stokes (*9*), and to those of Robinson (*10*). Zero weight was given to other isopiestic and to vapor pressure data because of scatter (*11*) or gross deviations from other data sets (*12*).

In addition, there is a set of emf data for cells with transference (*2*) and cation transference numbers (*3*) t_+ which can be used to analyze these data. These data were reported as functions of molarity, and we converted them to molalities using their reported densities (*2*, *3*).

The osmotic coefficients can be calculated from emf data for cells with transference that have electrodes reversible to the anion by using the following expression (*35*)

$$m\Phi - m'\Phi' = -(\nu_+ z_+ F/\nu RT)\int_{m'}^{m}(m/t_+)\,d\epsilon_t \qquad (5)$$

where ϵ_t is the potential in volts, R is the universal gas constant, T is the temperature in K, F, is Faraday's constant, ν_+ is the number of cations in one molecule of solute, and z_+ is the signed valence of the cation. For $NiCl_2$ at 25 °C, $\nu_+ z_+ F/\nu RT$ = 25.9478 (abs V)$^{-1}$. The reference molality m' was included since the available emf values do not extend to low enough concentrations to do the integral from zero molality.

Values of Φ were calculated from the emf data at the experimental molalities of the emf study. These derived Φ values were found to be very sensitive to the chosen reference molality m' in eq 5. In addition, reasonable Φ values were only obtained close to m', with results discrepant by up to several percent at higher and lower concentrations. Thus, these emf based results were not included in subsequent fits of activity data by least-squares equations, but the emf values will be used by us elsewhere (*36*) when testing the Onsager reciprocal relations for $NiCl_2$.

There are no Φ values below 0.1188 mol·kg^{-1}, and this is inadequate to constrain fits to eq 3 at low concentrations. We, therefore, used an extension (*37*) of the Åkerlöf-Thomas approach (*38*) to estimate low concentration Φ points for $NiCl_2$.

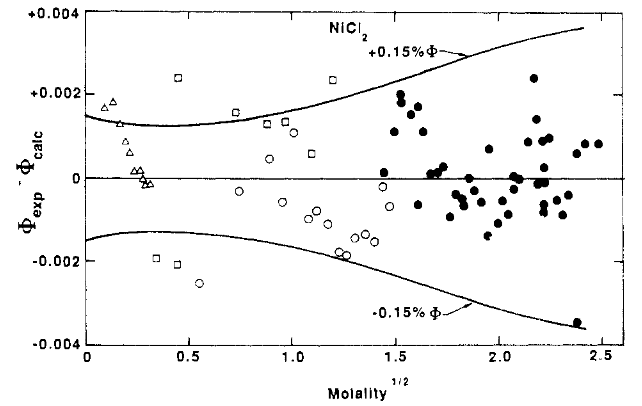

Figure 1. Differences between experimental osmotic coefficients and the least-squares eq 3 for $NiCl_2$: (○) this research, NaCl standard; (●) this research, $CaCl_2$ standard; (□) isopiestic data of Robinson and Stokes (*9*); (△) estimated values based on $CaCl_2$, from Table III.

The difference between osmotic coefficients for two strong electrolytes of the same valence type at low and moderate concentrations is given by

$$\Delta\Phi = Em + \text{higher order terms} \qquad (6)$$

where Debye-Hückel limiting law terms cancel, and E is an empirical constant. Differences for $NiCl_2$ were taken relative to $CaCl_2$, since activity data for that salt are well characterized (*33*). A plot of $\Delta\Phi$ vs. m was found to be nearly linear up to 1.5 mol·kg^{-1}. This graph and $CaCl_2$ Φ values (*33*) were in turn used to estimate $NiCl_2$ Φ points from 0.01 to 0.10 mol·kg^{-1} at 0.01 mol·kg^{-1} intervals. These estimated Φ points were also given unit weight in least-squares fits to available activity data, and they are reported in Table III.

When all of the above $NiCl_2$ osmotic coefficients were included in the least-squares fits to 3, a small amount of cycling was present in the residuals and the standard errors of the least-squares coefficients were large (several coefficients errors were in the 20–30% range). When these least-squares fits were repeated using only our data, that of Robinson and Stokes (*9*) with ≤1.443 mol·kg^{-1}, and our estimated dilute solution values, then the standard deviations for the better quality fits decreased by about 50% and coefficient errors were reduced to a few percent. There is some justification for preferring the latter fits, given the lack of experimental details in the earlier studies as mentioned above.

Tables IV and V contain the least-squares parameters for eq 3 and Pitzer's equation. Figure 1 shows the differences between the various Φ values and eq 3, and Table VI contains calculated values of Φ, a_1, and $\gamma_\pm$ from this equation. This plot and calculated results in Table VI were based on fits to our Table I data, data of Robinson and Stokes (*9*) with ≤1.443 mol·kg^{-1}, and estimated dilute solution values. However,

Table IV. Coefficients and Powers for $NiCl_2$, $Pr(NO_3)_3$, and $Lu(NO_3)_3$ Polynomials

	$NiCl_2$[a]		$NiCl_2$[b]		$Pr(NO_3)_3$[c]		$Lu(NO_3)_3$[d]	
i	r_i	A_i	r_i	A_i	r_i	A_i	r_i	A_i
1	1.0	5.142 397	1.0	5.103 469	1.00	24.218 23	0.75	−3.629 009
2	1.5	−11.061 56	1.5	−10.763 85	1.25	−55.592 40	1.00	49.174 60
3	2.0	15.943 52	2.0	15.099 06	1.50	58.437 13	1.25	−119.444 7
4	2.5	−14.749 69	2.5	−13.550 52	1.75	−32.484 99	1.50	140.442 0
5	3.0	8.808 882	3.0	7.864 715	2.00	9.229 725	1.75	−88.547 73
6	3.5	−3.257 907	3.5	−2.838 641	2.25	−1.052 995	2.00	28.724 94
7	4.0	0.671 0291	4.0	0.572 6719			2.25	−3.772 575
8	4.5	−0.058 43132	4.5	−0.048 95091				
$\sigma(\Phi)$		0.001 26		0.002 68		0.001 44		0.001 90

[a] Based on our data, Robinson and Stokes (*9*) up to 1.443 mol·kg^{-1}, and estimated dilute solution data. These parameters apply to 6.1364 mol·kg^{-1}, and were used to compute the results in Table VI. [b] Based on our data, Robinson and Stokes (*9*), Robinson (*10*), and estimated dilute solution data. These parameters apply to 6.1364 mol·kg^{-1}. [c] These parameters apply to 7.6610 mol·kg^{-1}. [d] These parameters apply to 7.5961 mol·kg^{-1}.

Table V. Parameters for Pitzer's Equations at 25 °C

parameter	$NiCl_2$[a]	parameter	$Pr(NO_3)_3$[b]
$(4/3)\beta^{(0)}$	0.46655	$(3/2)\beta^{(0)}$	0.7245
$(4/3)\beta^{(1)}$	2.0400	$(3/2)\beta^{(1)}$	7.700[c]
$(2^{5/2}/3)C^{\phi}$	−0.008881	$(3^{3/2}/2)C^{\phi}$	−0.1734
$\sigma(\Phi)$	0.0020	$\sigma(\Phi)$	0.0049

[a] Fit based on data up to 2.5 mol·kg^{-1}. [b] Fit based on data up to 1.5 mol·kg^{-1}. [c] Fixed at this value.

least-squares parameters are given in Table IV both for this case and for the case where all the data in ref *9* and *10* were included. Maximum differences between Φ values calculated with the two sets of coefficients in Table IV are 0.0021, which is fairly good agreement.

Activity Results for Aqueous $Pr(NO_3)_3$ and $Lu(NO_3)_3$

Table I contains our new isopiestic molalities and osmotic coefficients for $Pr(NO_3)_3$ with NaCl and $CaCl_2$ as isopiestic reference standards. The two highest concentration Φ points based on the NaCl standard overlap with the lowest concentration data from the $CaCl_2$ standard and agree within 0.1%. Solutions of $ZnCl_2$ and $NiCl_2$ were also equilibrated with $Pr(NO_3)_3$ and reference standards in this concentration region; they also agreed within 0.1% when the standards were changed. This $ZnCl_2$ data will be published separately (*36*), since self-complexing makes the data analysis more complicated.

Our isopiestic data for $Pr(NO_3)_3$ involve two separate stock solutions, a low concentration one for equilibrations with the NaCl standard and a higher concentration one used with the $CaCl_2$ standard. For both $NiCl_2$ and $ZnCl_2$, only single stock solutions were used, and osmotic coefficients agreed well in the overlap region when standards were changed. Since data from our two separate $Pr(NO_3)_3$ stock solutions with two separate standards agree as well as for the single $ZnCl_2$ and $NiCl_2$ stock solutions with different standards, this indicates that our two $Pr(NO_3)_3$ stock solutions are highly consistent with each other. In addition, samples of the lower concentration $Pr(NO_3)_3$ stock solution were concentrated in a desiccator and then equilibrated with the $CaCl_2$ standard at high concentrations. These three Φ points agree completely with Φ points measured by using the concentrated $Pr(NO_3)_3$ stock solution. Similarly, the four points for $Pr(NO_3)_3$, measured with a KCl standard at Ames Laboratory (*24*), agree within 0.25% of our present data. The excellent agreement between these various studies indicates the essential correctness and reproducibility of our $Pr(NO_3)_3$ osmotic coefficients.

It is also possible to recalculate our earlier isopiestic study (*25*) which used KCl and $CaCl_2$ reference solutions. We concluded in the Introduction that the concentration of the $Pr(NO_3)_3$ stock solution, which was supplied by Ames Laboratory for that study, was higher than reported by them owing to some evaporation of solvent during handling or shipping of it to LLNL.

$CaCl_2$ was used as the isopiestic reference standard in the earlier study (*25*) with nominal $Pr(NO_3)_3$ concentrations of 1.1629–6.2861 mol·kg^{-1}, and samples from the very same $CaCl_2$ stock solution were used as standards in our present study for $Pr(NO_3)_3$ concentrations of 2.1219–7.6610 mol·kg^{-1}. Thus, our new values for the $Pr(NO_3)_3$ to $CaCl_2$ isopiestic molality ratio $R^* = m/m^*$ can be used to adjust the earlier $Pr(NO_3)_3$ molalities by using their $CaCl_2$ reference molalities (*25*).

A large expanded scale plot of R^* was made by using all of the $CaCl_2$ standard data in Table I for concentrations that overlap with the earlier study (*25*). Seven approximately equally spaced $CaCl_2$ concentrations were chosen from the earlier study, from 2.5367 to 5.5888 mol·kg^{-1} $CaCl_2$, and their corresponding R^* values were graphically interpolated from our data and were then used to calculate what their $Pr(NO_3)_3$ molality should have been for that particular equilibration. From these adjusted $Pr(NO_3)_3$ molalities, the final weights of the duplicate $Pr(NO_3)_3$ samples for that equilibration, and the initial weights of stock solution added to the isopiestic cups, we back-calcu-

Table VI. Osmotic Coefficients, Water Activities, and Activity Coefficients of $NiCl_2$, $Pr(NO_3)_3$, and $Lu(NO_3)_3$ at Even Molalities

m, mol·kg^{-1}	Φ	a_1	$\gamma_\pm$	m, mol·kg^{-1}	Φ	a_1	$\gamma_\pm$	m, mol·kg^{-1}	Φ	a_1	$\gamma_\pm$
					$NiCl_2$						
0.1	0.8556	0.995386	0.5176	1.0	1.0801	0.94330	0.5294	3.5	1.9579	0.6905	2.202
0.2	0.8655	0.990689	0.4740	1.2	1.1477	0.92827	0.5782	4.0	2.0900	0.6365	2.882
0.3	0.8839	0.98577	0.4587	1.4	1.2183	0.91194	0.6381	4.5	2.1991	0.5858	3.678
0.4	0.9062	0.98060	0.4549	1.5	1.2546	0.90329	0.6725	5.0	2.2889	0.5387	4.587
0.5	0.9310	0.97516	0.4579	1.6	1.2913	0.8943	0.7101	5.5	2.3639	0.4953	5.611
0.6	0.9579	0.96942	0.4656	1.8	1.3657	0.8756	0.7950	6.0	2.4260	0.4553	6.742
0.7	0.9864	0.96337	0.4770	2.0	1.4409	0.8558	0.8943	6.1364	2.4402	0.4452	7.062
0.8	1.0164	0.95700	0.4916	2.5	1.6272	0.8026	1.213				
0.9	1.0477	0.95031	0.5091	3.0	1.8023	0.7466	1.646				
					$Pr(NO_3)_3$						
0.1	0.7412	0.994673	0.2968	1.2	0.9113	0.92423	0.2051	4.5	1.5402	0.6069	0.4787
0.2	0.7446	0.98933	0.2489	1.4	0.9499	0.90862	0.2109	5.0	1.6236	0.5571	0.5532
0.3	0.7569	0.98377	0.2277	1.5	0.9696	0.90050	0.2145	5.5	1.7038	0.5090	0.6385
0.4	0.7715	0.97801	0.2159	1.6	0.9894	0.8922	0.2185	6.0	1.7814	0.4629	0.7361
0.5	0.7871	0.97204	0.2087	1.8	1.0293	0.8750	0.2277	6.5	1.8571	0.4190	0.8477
0.6	0.8034	0.96586	0.2044	2.0	1.0695	0.8572	0.2382	7.0	1.9314	0.3775	0.9757
0.7	0.8202	0.95947	0.2019	2.5	1.1696	0.8100	0.2703	7.5	2.0051	0.3384	1.123
0.8	0.8376	0.95286	0.2008	3.0	1.2676	0.7603	0.3102	7.6610	2.0287	0.3263	1.175
0.9	0.8555	0.94603	0.2007	3.5	1.3623	0.7092	0.3579				
1.0	0.8737	0.93898	0.2015	4.0	1.4532	0.6578	0.4139				
					$Lu(NO_3)_3$						
0.1	0.7768	0.994418	0.3114	1.2	1.1413	0.90602	0.3306	4.5	2.0519	0.5141	1.714
0.2	0.7989	0.98855	0.2744	1.4	1.2158	0.8846	0.3661	5.0	2.1331	0.4637	2.086
0.3	0.8265	0.98229	0.2613	1.5	1.2526	0.8734	0.3860	5.5	2.2047	0.4174	2.505
0.4	0.8565	0.97561	0.2572	1.6	1.2890	0.8619	0.4074	6.0	2.2682	0.3751	2.973
0.5	0.8885	0.96849	0.2581	1.8	1.3602	0.8383	0.4545	6.5	2.3249	0.3366	3.490
0.6	0.9221	0.96092	0.2623	2.0	1.4290	0.8139	0.5075	7.0	2.3755	0.3017	4.058
0.7	0.9570	0.95288	0.2691	2.5	1.5885	0.7511	0.6666	7.5	2.4207	0.2703	4.676
0.8	0.9928	0.94437	0.2780	3.0	1.7293	0.6881	0.8652	7.5961	2.4288	0.2646	4.800
0.9	1.0294	0.93542	0.2887	3.5	1.8522	0.6268	1.105				
1.0	1.0665	0.92602	0.3011	4.0	1.9590	0.5686	1.388				

Table VII. Isopiestic Molalities from Rard, Miller, and Spedding (*25*) Normalized to Table I Data

[reference], mol·kg^{-1}	[Pr(NO$_3$)$_3$], mol·kg^{-1}	Φ(Pr(NO$_3$)$_3$)	[reference], mol·kg^{-1}	[Pr(NO$_3$)$_3$], mol·kg^{-1}	Φ(Pr(NO$_3$)$_3$)	[reference], mol·kg^{-1}	[Pr(NO$_3$)$_3$], mol·kg^{-1}	Φ(Pr(NO$_3$)$_3$)
KCl Reference								
0.20504	0.12586	0.7429	0.81030	0.46655	0.7788	1.7837	0.93798	0.8626
0.21249	0.13067	0.7410	1.0147	0.57177	0.7963	1.9755	1.0243	0.8783
0.50176	0.29871	0.7552	1.1959	0.66223	0.8116	2.2806	1.1579	0.9033
0.67018	0.39138	0.7682	1.3538	0.73888	0.8251	2.3641	1.1924	0.9112
0.68341	0.39842	0.7694	1.5736	0.84235	0.8441			
CaCl$_2$ Reference								
1.2564	1.1669	0.9041	2.8198	2.8795	1.2446	4.1572	4.5274	1.5461
1.2733	1.1835	0.9077	2.8982	2.9741	1.2617	4.2724	4.6718	1.5719
1.2947	1.2059	0.9113	2.9329	3.0138	1.2703	4.3374	4.7581	1.5848
1.3186	1.2312	0.9151	2.9706	3.0597	1.2785	4.3962	4.8334	1.5974
1.4587	1.3724	0.9446	3.0413	3.1451	1.2943	4.5083	4.9747	1.6219
1.5903	1.5099	0.9711	3.1164	3.2309	1.3133	4.5367	5.0095	1.6284
1.6822	1.6087	0.9891	3.1885	3.3202	1.3289	4.6688	5.1766	1.6566
1.7515	1.6808	1.0047	3.2634	3.4131	1.3452	4.7452	5.2772	1.6715
1.8250	1.7597	1.0203	3.3399	3.5053	1.3631	4.8233	5.3755	1.6879
1.9094	1.8509	1.0386	3.4201	3.6040	1.3813	4.9152	5.4929	1.7064
1.9724	1.9188	1.0527	3.5365	3.7468	1.4080	5.0238	5.6246	1.7300[a]
2.0519	2.0053	1.0705	3.5962	3.8236	1.4205	5.0703	5.6843	1.7390[a]
2.1395	2.1015	1.0902	3.6563	3.9017	1.4328	5.1577	5.8037	1.7533
2.2266	2.1975	1.1102	3.7271	3.9904	1.4486	5.2457	5.9114	1.7712
2.2962	2.2793	1.1240	3.7693	4.0375	1.4602	5.3125	5.9954	1.7837
2.3751	2.3686	1.1417	3.8288	4.1137	1.4729	5.3978	6.1017	1.7997
2.4518	2.4553	1.1594	3.8359	4.1223	1.4746	5.4884	6.2172	1.8154
2.5367	2.5524	1.1788	3.9218	4.2296	1.4941	5.5404	6.2761	1.8264
2.6053	2.6319	1.1943	4.0050	4.3362	1.5120	5.5888	6.3345	1.8353
2.7061	2.7466	1.2184	4.0743	4.4240	1.5273			

[a] These two points were given zero weight in the least-squares fits.

lated both what the correct number of moles of Pr(NO$_3$)$_3$ and the weight fraction of water were for each sample in the earlier study. The average of the back-calculated Pr(NO$_3$)$_3$ stock solution concentration from all seven duplicate samples was then used to recalculate the Pr(NO$_3$)$_3$ molalities from the earlier study (*25*). More details of this calculation procedure are given elsewhere (*29*).

Table VII contains the normalized isopiestic data from the earlier study (*25*). Molality changes for Pr(NO$_3$)$_3$ range from 0.77% at their highest concentration to 0.26% at their lowest concentration. This variation with concentration is due to the change in molality with the weight fraction of water present.

The uncertainty of the normalized Pr(NO$_3$)$_3$ molalities in Table VII, due to the normalization only, ranges from 0.25% at 6.3345 mol·kg^{-1} to 0.11% at 1.1669 mol·kg^{-1}. Thus, the total uncertainty in the normalized Φ values of Table VII is about twice as large as for the data of Table I at higher concentrations, but their relative uncertainty is only about $1^1/_2$ times at lower concentrations.

The combined isopiestic data extend from 0.125 86 to 7.6610 mol·kg^{-1}, but values at much lower concentrations are required to properly constrain Φ when doing least-squares fits to the data. Consequently, we used values of Φ for rare earth nitrates at 0.0050, 0.0010, 0.0015, and 0.0020 mol·kg^{-1} that were estimated (*24*) by using ion size parameters from electrical conductance data.

The various osmotic coefficient data for Pr(NO$_3$)$_3$ solutions were then represented by eq 3 up to 7.6610 mol·kg^{-1} and also by Pitzer's equation (*34*) up to 1.5 mol·kg^{-1}. In these least-squares calculations, unit weights were given to our data of Table I, to the four points given earlier (*24*), and to the estimated low concentration points (*24*). The normalized data of Table VII were given weights of 0.5 except for two somewhat high points that were weighted zero. Table IV and V give the least-squares parameters and standard deviations $\sigma(\Phi)$ for these two types of equations, and Table VI gives smoothed values of Φ, a_1, and $\gamma_\pm$ for Pr(NO$_3$)$_3$.

Figure 2 shows the difference between the various Φ values and eq 3 for Pr(NO$_3$)$_3$, using the least-squares parameters in Table IV. Our new data obtained by using NaCl and CaCl$_2$ solutions as standards are obviously in excellent agreement, as are the four KCl standard points from Ames Laboratory (*24*). Similarly, the normalized data of Rard et al. (*25*), Table VII, from 0.125 86 to 5.0095 mol·kg^{-1} are in good agreement with our data; all of their points in this concentration range are within 0.3% of ours and most are within 0.2%. Their normalized data from 5.1766 to 6.3345 mol·kg^{-1} are systematically higher than ours by 0.2–0.3%. Since the uncertainty of their normalized Φ values is about twice that of ours in this concentration region, the agreement is good.

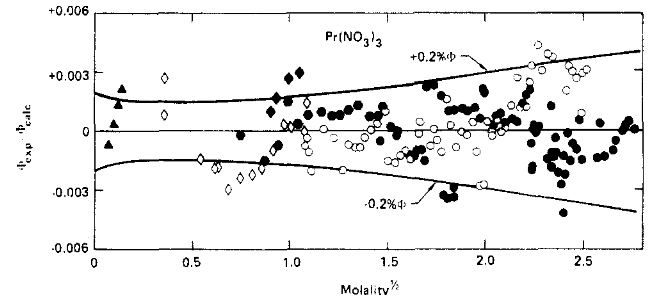

Figure 2. Differences between experimental osmotic coefficients and the least-squares eq 3 for Pr(NO$_3$)$_3$: (●) this research, NaCl standard; (●) this research, CaCl$_2$ standard; corrected data of Rard et al. (*25*) from Table VII: (◇) KCl standard and (○) CaCl$_2$ standard; (♦) KCl standard data of Rard et al. (*24*); (▲) estimated dilute solution values from electrical conductances (*24*).

Figure 3 shows the difference between the experimental Φ results and eq 3 for Lu(NO$_3$)$_3$ by using the least-squares parameters of Table IV. Our new data are in good agreement with earlier results (*27*) but are 0.1–0.3% higher. Pitzer equation parameters were not revised for this salt since they are based on lower concentrations than were studied here.

Some insights about ionic association can be obtained from the isopiestic data. The data in Table I indicate that the equlibrium molalities for Pr(NO$_3$)$_3$ are comparable to those of CaCl$_2$ and NiCl$_2$ up to about 5 mol·kg^{-1} and are close to NiCl$_2$ up to 6.1 mol·kg^{-1}. Since CaCl$_2$ and NiCl$_2$ are considered to

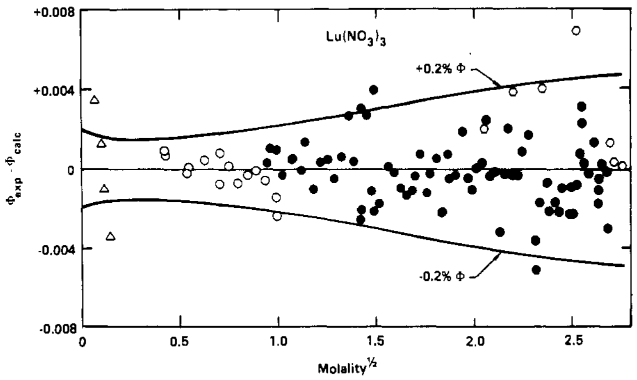

Figure 3. Differences between experimental osmotic coefficients and the least-squares eq 3 for $Lu(NO_3)_3$: (○) this research, $CaCl_2$ standard; data of Rard and Spedding (*27*): (O) KCl standard and (●) $CaCl_2$ standard; (△) estimated values from electrical conductances (*24*).

be fairly strong electrolytes, this implies that $Pr(NO_3)_3$ is behaving rather like a 2–1 electrolyte in this concentration region. $Lu(NO_3)_3$ behaves likewise but is slightly less associated (*39*). A similar comparison indicates that the $MnCl_2$ to $CaCl_2$ molality ratio (*37*) is much higher than the $NiCl_2$ to $CaCl_2$ molality ratio (Table I) at high concentrations, 1.4 vs. 1.1. This suggests that ionic association also becomes important for concentrated $MnCl_2$ solutions. Thus, $MnCl_2$, unlike $NiCl_2$, may not be as strong an electrolyte at high concentrations as is usually assumed.

Acknowledgment

We thank Donald G. Miller for assistance with calculations and for helpful suggestions, and Sue Frumenti and Denise VanderBeek for the word processing/typing of the manuscript.

Glossary

m	molal concentration of solute, mol·kg^{-1}
m_s	molal solubility, mol·kg^{-1}
t	time, days
Φ	molal (practical) osmotic coefficient
ν	number of ions formed by the complete dissociation of one molecule of solute
A	Debye–Hückel constant at 25 °C
A_i	least-squares coefficients of eq 3 and 4
r_i	powers of eq 3 and 4
$\gamma_\pm$	mean molal activity coefficient of solute
a_1	activity of water in solution
A^ϕ	Debye–Hückel constant (1–1 charge type) for Pitzer's equations
$\beta^{(0)}$, $\beta^{(1)}$, C^ϕ	parameters for Pitzer's equations
t_+	cation transference number of solute
ϵ_t	emf of concentration cell with transport, V
$\sigma(\Phi)$	standard deviation of fitting equations for Φ
z	valence of an ion
$+$	symbols subscripted $+$ refer to the cation
E	parameter in the extended Åkerlöf–Thomas equation
R^*	isopiestic molality ratio of $Pr(NO_3)_3$ to $CaCl_2$
F	Faraday's constant

Registry No. $NiCl_2$, 7718-54-9; $Pr(NO_3)_3$, 10361-80-5; $Lu(NO_3)_3$, 10099-67-9.

Literature Cited

(1) Spitzer, J. J.; Singh, P. P.; McCurdy, K. G.; Hepler, L. G. *J. Solution Chem.* **1978**, *7*, 81–86.
(2) Phang, S. *Aust. J. Chem.* **1979**, *32*, 1149–1153.
(3) Stokes, R. H.; Phang, S.; Mills, R. *J. Solution Chem.* **1979**, *8*, 489–500.
(4) Lo Surdo, A.; Millero, F. J. *J. Phys. Chem.* **1980**, *84*, 710–715.
(5) Perron, G.; Roux, A.; Desnoyers, J. E. *Can. J. Chem.* **1981**, *59*, 3049–3054.
(6) Rard, J. A. *J. Chem. Eng. Data* **1986**, *31*, 183–185.
(7) Hunt, J. P.; Friedman, H. L. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley Interscience: New York, 1983; Vol. 30.
(8) Weingärtner, H.; Müller, C.; Hertz, H. G. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 2712–2734.
(9) Robinson, R. A.; Stokes, R. H. *Trans. Faraday Soc.* **1940**, *36*, 1137–1138.
(10) Stokes, R. H. *Trans. Faraday Soc.* **1948**, *44*, 295–307.
(11) Shul'ts, M. M.; Makarov, L. L.; Yu-jêng, Su. *Russ. J. Phys. Chem.* (*Engl. Trans.*) **1962**, *36*, 1181–1183.
(12) Pearce, J. N.; Eckstrom, H. C. *J. Phys. Chem.* **1937**, *41*, 563–565.
(13) Goldberg, R. N.; Nuttall, R. L.; Staples, B. R. *J. Phys. Chem. Ref. Data* **1979**, *8*, 923–1003.
(14) Timmermans, J. *The Physico-chemical Constants of Binary Systems in Concentrated Solutions*; Interscience: London, 1960; Vol. 3.
(15) Holmes, H. F.; Mesmer, R. E. *J. Chem. Thermodyn.* **1981**, *13*, 131–137.
(16) Hass, K.; Jellinek, K. *Z. Phys. Chem.* (*Leipzig*) **1932**, *162A*, 153–173.
(17) Linke, W. F. *Solubilities Inorganic and Metal-Organic Compounds*; American Chemical Society: Washington, DC, 1958; Vol. I, p 812.
(18) Linke, W. F. *Solubilities Inorganic and Metal-Organic Compounds*; American Chemical Society: Washington, DC, 1958; Vol. I, p 725; 1965, Vol. II, p 1208.
(19) Ojkova, T.; Makarow, L. L. *Z. Phys. Chem.* (*Leipzig*) **1979**, *260*, 609–615.
(20) Petrov. G. V.; Shevchuk, V. G. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1980**, *25*, 1715–1716.
(21) Jones, H. C.; Getman, F. H. *Z. Phys. Chem.* **1903**, *46*, 244–286.
(22) Spedding, F. H.; Derer, J. L.; Mohs, M. A.; Rard, J. A. *J. Chem. Eng. Data* **1976**, *21*, 474–488.
(23) Spedding, F. H.; Baker, J. L.; Walters, J. P. *J. Chem. Eng. Data* **1979**, *24*, 298–305.
(24) Rard, J. A.; Shiers, L. E.; Heiser, D. J.; Spedding, F. H. *J. Chem. Eng. Data* **1977**, *22*, 337–347.
(25) Rard, J. A.; Miller, D. G.; Spedding, F. H. *J. Chem. Eng. Data* **1979**, *24*, 348–354.
(26) Rard, J. A. *J. Solution Chem.* **1985**, *14*, 457–471.
(27) Rard, J. A.; Spedding, F. H. *J. Chem. Eng. Data* **1981**, *26*, 391–395.
(28) Rard, J. A.; Spedding, F. H. *J. Chem Eng. Data* **1982**, *27*, 454–461.
(29) Rard, J. A. *J. Chem. Eng. Data* **1987**, *32*, 92–98.
(30) Siekierski, S.; Mioduski, T.; Salomon, M. *Solubility Data Series Volume 13. Scandium, Yttrium, Lanthanum and Lanthanide Nitrates*; Pergamon: Oxford, U.K., 1983.
(31) Rard, J. A.; Miller, D. G. *J. Chem. Eng. Data* **1981**, *26*, 38–43.
(32) Hamer, W. J.; Wu, Y.-C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047–1099.
(33) Rard, J. A.; Habenschuss, A.; Spedding, F. H. *J. Chem. Eng. Data* **1977**, *22*, 180–186.
(34) Pitzer, K. S. *In Activity Coefficients in Electrolyte Solutions*; Pytkowicz, R. M., Ed.; CRC Press: Boca Raton, FL, 1979; Vol. 1, Chapter 7.
(35) Rard, J. A.; Miller, D. G. *J. Solution Chem.* **1985**, *14*, 271–299.
(36) Rard, J. A.; Miller, D. G., unpublished data, this laboratory.
(37) Rard, J. A. *J. Chem. Eng. Data* **1984**, *29*, 443–450.
(38) Åkerlöf, G.; Thomas, H. C. *J. Am. Chem. Soc.* **1934**, *56*, 593–601.
(39) Rard, J. A.; Spedding, F. H. *J. Phys. Chem.* **1975**, *79*, 257–262.

Received for review October 27, 1986; Accepted April 24, 1987. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.