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Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25 °C. 1. The Rare Earth Chlorides

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The osmotic coefficients of the aqueous trichlorides of La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y have been determined from 0.1 *m* to saturation at 25 °C. Semiempirical least-squares equations were obtained for the osmotic coefficients as a function of molality and these equations were used to calculate water activities and mean molal activity coefficients. The water activities of the light rare earth chlorides at constant molalities are higher than for the heavy rare earths, while the mean molal activity coefficients are larger for the heavy rare earths than for the light ones. The above effects are discussed in terms of changes in the cationic radii and hydration of the rare earth ions.

Attempts to explain irregularities in the thermodynamic (*3, 10, 17, 20, 24, 25*) and transport (*23, 26*) properties of aqueous rare earth electrolyte solutions have given rise to a model in which the light and heavy rare earth cations have different inner sphere hydration numbers, with the rare earths from Nd to Tb being mixtures of the two different coordinated forms. Transport properties (*23, 26*) depend mainly on overall hydration and indicate that an overall hydration increase occurs from La to Lu. The inner sphere hydration change is not seen directly in the rare earth chlorides but is reflected in the overall hydration trend. Water activities and electrolyte activity coefficients were determined since they are of fundamental importance in studying the thermodynamic behavior of these systems. In addition, the water activities are intimately related to solvation in aqueous solutions so isopiestic measurements are also of value for studying changes in hydration across the rare earth series.

Activity coefficient measurements on the rare earth chlorides have been reported by Robinson (*14*), Mason (*7, 8*), and Mason and Ernst (*9*). However, these measurements were for less than half of the rare earths and extend only to 2.0 *m*. In this study, isopiestic measurements have been performed from 0.1 *m* to saturation on 14 of the rare earth chlorides, including YCl_3. A number of the the first and second derivative properties of the activities are available including the partial molal volumes (*24*), expansibilities (*2, 3*), heats of dilution (*1, 11*), and heat capacities (*25*).

Experimental Section

Apparatus and Experimental Procedure. The isopiestic apparatus employed in this research consisted of three rectangular stainless steel equilibration chambers, each containing a copper block. Each of these copper blocks had eight recesses (gold plated to reduce corrosion) in which the sample cups were firmly positioned. The cups were constructed of tantalum or of heavily gold-plated silver. A piece of platinum gauze was added to each cup to assist in the equilibration process. The equilibration chambers were slowly evacuated at the beginning of each isopiestic run. The temperature bath was controlled at 25.00 ± 0.01 °C and contained a rocking device for the chambers. The chambers were made large enough to act as thermal buffers; consequently thermal fluctuations within the chambers were much smaller than in the temperature bath. The experimental apparatus and procedure are described in more detail elsewhere (*12, 15*).

The isopiestic equilibrium molalities were calculated from the weight of analyzed stock solution added to each cup and the weight of solution present in these cups at the end of each equilibration period. Two samples of each solution were run and the average equilibrium molalities were used in all calculations. Each cup was covered with a tight fitting plastic cap when removed from the equilibration chambers for weighing. All weights were corrected to vacuum. Vacuum corrections for the rare earth chloride solutions were made using the density data of

Spedding and co-workers (*24*) and the density data for KCl and $CaCl_2$ were taken from the International Critical Tables.

The samples in each chamber were assumed to have reached isopiestic equilibrium when the concentrations of two samples of each salt solution were found to agree to within ±0.1% of their average molality for concentrations above 0.5 *m* and to within 0.15% for the more dilute solutions. However, in many cases the equilibrations were done to better than ±0.05% above 0.3 *m*. Conductivity water was added to the various cups in such a manner that isopiestic equilibrium was approached from both directions for each salt concentration. Equilibration periods ranged from 2 to 4 days for the more concentrated solutions and from 2 weeks to 1 month for the dilute solutions. Extra cups containing both solution and crystals were added to the chamber when the saturated solutions were being studied. Duplicate samples were equilibrated in the chambers for at least 1 week before saturated solution weighings were started and measurements were made at 3- or 4-day intervals for about 2 weeks.

Preparation of Solutions. Solutions of the stoichiometric salts of the rare earth chlorides were prepared by the method of Spedding, Pikal, and Ayers (*20*). When these solutions are brought to their equivalence points, chemical analyses indicate that the ratio of rare earth ion to chloride ion is one to three. These solutions were analyzed for the chloride ion by the standard gravimetric method and for the rare earth ion by oxalate or sulfate methods (*20*).

The KCl used in preparing the isopiestic standards was twice recrystallized reagent grade KCl which had been fused under nitrogen. The standard KCl solutions were prepared from weighed amounts of this anhydrous KCl and conductivity water. The $CaCl_2$, used in the preparation of the other set of standards, was prepared by the method of Stokes (*28*). The $CaCl_2$ standard solutions were analyzed by the standard gravimetric chloride and sulfate methods. The anion and cation analyses gave results that agreed to within ±0.05% of the average for both $CaCl_2$ and rare earth chloride stock solutions. The conductivity water used in the solution preparation and dilution processes was distilled from a $KOH-KMnO_4$ solution.

Calculations and Errors

The molal osmotic coefficient of an electrolyte solution, ϕ, is defined by the equation

$$\phi = -(1000 \ln a_1)/(\nu m M_1) \quad (1)$$

where a_1 is the activity of the solvent, ν is the total number of ions formed by the complete dissociation of one molecule of the solute, m is the molality of the solute, and $M_1 = 18.0154$ g/mol is the molecular weight of water. If this solution is in equilibrium with a reference standard solution having a known osmotic coefficient, then

$$\phi = (\nu^* \phi^* m^*)/(\nu m) \quad (2)$$

where the asterisk refers to the standard solution. The resulting osmotic coefficients can then be used in the calculation of the mean molal activity coefficients of the electrolyte being studied. Application of the Gibbs–Duhem equation gives

$$\ln \gamma_\pm = \int_1^\phi d\phi - \int_0^m (1-\phi)/m \, dm \quad (3)$$

These integrations are most conveniently performed using analytic representations for the osmotic coefficients.

Values for the osmotic coefficients of the KCl solutions were taken from Hamer and Wu (*4*) and were corrected for the nonideal behavior of the solvent vapor, proportional to the amount of vapor pressure data used (*13*). Literature values for the osmotic coefficients of $CaCl_2$ and H_2SO_4 measured isopiestically against KCl and NaCl were recalculated using Hamer and Wu's equations corrected for the nonideal behavior of the solvent vapor. Vapor pressure measurements for $CaCl_2$ and H_2SO_4 were corrected for the nonideal behavior of the solvent vapor and converted to presently accepted values for the vapor pressure of water. The new values for the osmotic coefficients of H_2SO_4 (*13*) were used to calculate additional osmotic coefficients for $CaCl_2$ from available isopiestic ratio data. The resulting values were fitted to

$$\phi = 1 - (A/B^3 m)((1 + B\sqrt{m}) - 1/(1 + B\sqrt{m}) - 2 \ln (1 + B\sqrt{m})) + \sum_i A_i m^{r_i} \quad (4)$$

where $A = 4.0743$, $B = 3.470$, $r_1 = 0.750$, $r_2 = 0.875$, $r_3 = 1.000$, $r_4 = 1.125$, $r_5 = 7$, $r_6 = 8$, $r_7 = 10$, $A_1 = -1.763\,151\,4$, $A_2 = 5.174\,772\,7$, $A_3 = -5.714\,201\,5$, $A_4 = 2.467\,735\,4$, $A_5 = -3.876\,519\,2 \times 10^{-6}$, $A_6 = 5.045\,287\,8 \times 10^{-7}$, and $A_7 = -1.421\,369\,5 \times 10^{-9}$. This equation was used to calculate the rare earth chloride osmotic coefficients for solutions in equilibrium with $CaCl_2$. The analysis of the $CaCl_2$ osmotic coefficient data will be the subject of a forthcoming paper.

The isopiestic data for the rare earth chloride solutions do not quite extend to the minima in the osmotic coefficient vs. *m* curves. Since eq 3 involves integrals of ϕ from infinite dilution to the concentration of interest, it is important that an analytic expression for ϕ be reliable at low concentrations. Consequently, the data reported here are insufficient to guarantee that mean molal activity coefficients would be as accurate as desired when calculated from eq 3, since the integrals would be uncertain below 0.1 *m*. Fortunately, experimental emf measurements are available for the rare earth chlorides from about 0.001 to 0.02–0.04 *m* (*16, 18, 19, 21, 22, 27*) and activity coefficients calculated from these data can be used to yield low concentration osmotic coefficients by use of

$$\phi = 1 + 1/m \int_0^m m \, d \ln\gamma_\pm \quad (5)$$

Heiser's $LaCl_3$ data (*5*) and Mason's YCl_3 data (*7*) are in good agreement with the data reported here, so their data were recalculated to conform to the same isopiestic standards used here and were included in the least-squares analysis.

Spedding et al. (*16, 18, 19, 21, 22, 27*) report mean molar activity coefficients as a function of the molarity whereas mean molal activity coefficients as a function of the molality are desirable for performing the integration in eq 5. These emf data were measured using concentration cells with transference so activity coefficients relative to a reference concentration were obtained. They obtained absolute values for the activity coefficients assuming that the Debye–Huckel equation was obeyed for each salt up to 0.02–0.04 *m*. However, examination of these data indicated that small systematic deviations occurred when their data were assumed to obey the Debye–Huckel equation with an ion-size parameter. It appeared that adding a term linear in *m* to the Debye–Huckel equation would give a slightly better fit for each salt. Consequently, it was decided to recalculate their data and to cast them into a form consistent with the data reported here.

Spedding et al. data (*18, 19, 21, 22, 27*) were updated for changes in the fundamental constants in recent years. Relative mean molal activity coefficients were then obtained from their emf data using the equation

$$\ln (\gamma_\pm/\gamma_\pm') = \ln (m'/m) - 3F/4RT(E/t_+' + \int_0^E (1/t_+ - 1/t_+') \, dE) \quad (6)$$

where $3F/4RT = 3(96\,487.0)/4(8.3143)(298.15) = 29.192$ (abs V)$^{-1}$, F is Faraday's constant, E is the observed emf in absolute volts, m is the molality of the solution being studied, and t_+ is the cation transference number of this solution. The primed symbols refer to the solution used as a reference solution for all of the measurements for that salt in the concentration cells. In some cases the experimental emf's were not listed in Spedding et al. papers and in most cases only molar concentrations were reported. The remaining emf and molality data were obtained from the theses and original laboratory notebooks upon which these papers were based. The resulting values of m, t_+, E, and $\gamma_\pm/\gamma_\pm'$ are listed in Table I (see paragraph at end of paper regarding supplementary material). It was necessary to make these recalculations in terms of m and $\gamma_\pm$ in order to calculate the osmotic coefficients by eq 5.

Since the mean molal activity coefficients do not follow the Debye–Huckel equation quite up to 0.02–0.04 m, a linear term was added to the equation such that

$$\ln \gamma_\pm = \ln (\gamma_\pm/\gamma_\pm') + \ln \gamma_\pm' = -A\sqrt{m}/(1 + B\sqrt{m}) + Dm \qquad (7)$$

where $A = (0.5108)(3)(\sqrt{6})(2.302\,585) = 8.6430$, $B = (0.3287)(\sqrt{6})\mathring{a} = 0.80515\mathring{a}$ and $\mathring{a}$ is the Debye–Huckel ion-size parameter in ångstroms. This equation can be rearranged to give

$$\ln (\gamma_\pm/\gamma_\pm') + Am^{1/2} + \ln \gamma_\pm' - Dm = -B(-Dm^{3/2} + m^{1/2}(\ln (\gamma_\pm/\gamma_\pm') + \ln \gamma_\pm')) \qquad (8)$$

where $\gamma_\pm/\gamma_\pm'$, A, and m are known. Optimum values for $\gamma_\pm'$, B, and D were obtained by use of a nonlinear least-squares method. Values for $\gamma_\pm'$ and B were also obtained at $D = 0$. The final values for these parameters are listed in Table II. The inclusion of the linear term in the Debye–Huckel equation resulted in changes in $\gamma_\pm$ of less than 0.6% in all cases. Tb, Dy, and Lu are not listed in Tables I and II since the scatter in their data is too large to warrent applying this procedure. In addition, no emf data were available for Y. It should be noted that D is always negative and is smallest for Eu but becomes larger for the light and heavy rare earths.

In Figure 1 the differences between the experimental and calculated values of the relative activity coefficients are shown, for La, as a function of the square root of the molality. These deviations are shown for $D = 0$ and for the best value of D. It should be noted that adding a linear term to the Debye–Huckel equation appears adequate to represent rare earth chloride activity coefficients up to 0.02–0.04 m.

Substitution of eq 7 into eq 5 and integrating gives

$$\phi = 1 - (A/B^3m)((1 + B\sqrt{m}) - 1/(1 + B\sqrt{m}) - 2 \ln (1 + B\sqrt{m})) + (D/2)m \qquad (9)$$

Values of ϕ were calculated at 0.005 m intervals up to, and including, the highest concentration for each salt using the values of $\mathring{a}$ and D from Table II. Values for the osmotic coefficients of Tb, Dy, and Lu were obtained by interpolation of the data for the adjacent rare earths. Dilute osmotic coefficients for Y were obtained assuming that it fell between Er and Tm (as it does at higher concentrations). These dilute ϕ values, the experimental isopiestic molalities, and the rare earth chloride osmotic coefficients are listed in Table III. Except for the $ErCl_3$ set 1 solutions, the highest concentration reported for each salt is the saturated solution. Although the values of $\mathring{a}$ and D are quite different for the two sets of Yb dilute emf data, the calculated osmotic coefficients are in good agreement, so their averages are listed in Table III and were used in subsequent calculations.

All the osmotic coefficients for each rare earth chloride in Table III were then fitted to equations of the form

$$\phi = 1 - (A/3)\sqrt{m} + \sum_i A_i m^{r_i} \qquad (10)$$

using unit weights. The r_i's were not required to form a consecutive sequence of powers. Originally the osmotic coefficients for several salts were fitted to equations of the form of eq 9 with additional terms, but it was found that the additional terms alternated in sign and were large relative to the ion-size term. Consequently, only the Debye–Huckel limiting law was retained and eq 10 used instead. Substitution of eq 10 into eq 3 and integrating yields

$$\ln \gamma_\pm = -A\sqrt{m} + \sum_i A_i((r_i + 1)/r_i)m^{r_i} \qquad (11)$$

It was found that good fits could be obtained for the rare earth chlorides using seven terms in the series with the first four terms fixed at $r_1 = 0.75$, $r_2 = 0.875$, $r_3 = 1$, and $r_4 = 1.125$ while the other terms were allowed to vary up to m^{12} in increments of $m^{1/2}$ (a similar series was found to work best for H_2SO_4). These parameters and powers are listed in Table IV. There were other series that would have done almost as well as the ones used here, but the ones reported were chosen because they required the smallest number of terms and had the most powers in common. The differences between the experimental and calculated osmotic coefficients, $\Delta\phi$, are listed in Table III. For most of the salts the dilute points generated from the emf data connected up well with the experimental isopiestic data. For Ho, Tm, and Lu the deviations from the fits indicated that slight mismatches occur in the data so activity coefficients for these salts will be known less accurately. The standard deviations of eq 10 ranged from 0.0012 to 0.0023 for the various rare earth chlorides and these values are also listed in Table IV. Table V contains values of ϕ, a_1, and $\gamma_\pm$ at various even molalities.

Table II. Rare Earth Chloride Debye–Huckel Equation Parameters

Salt	$\mathring{a}$[a]	D[a]	$\gamma_\pm'$[a]	$\mathring{a}$[b]	$\gamma_\pm'$[b]	m[c]
La[d]	6.662	−1.60	0.4346	5.798	0.4320	0.031 19
Ce[d]	6.213	−0.70	0.4098	5.830	0.4089	0.040 09
Pr[d]	6.175	−0.85	0.4284	5.731	0.4271	0.032 35
Nd[e]	6.087	−1.05	0.4201	5.573	0.4189	0.033 52
Sm[d]	5.950	−0.55	0.4119	5.659	0.4110	0.037 46
Eu[d]	5.696	−0.15	0.4156	5.616	0.4153	0.035 32
Gd[f]	6.044	−0.70	0.4183	5.679	0.4172	0.035 15
Ho[e]	6.446	−0.75	0.4314	6.032	0.4302	0.034 23
Er[e]	6.520	−1.00	0.4235	5.982	0.4221	0.036 40
Tm[e]	6.649	−1.65	0.4731	5.895	0.4714	0.021 78
Yb[d]	6.021	−0.50	0.4076	5.748	0.4068	0.040 17
Yb[e]	6.800	−1.65	0.4276	5.903	0.4254	0.034 17

[a] These parameters are obtained by optimizing D. [b] These parameters are obtained for $D = 0$. [c] Highest concentrations to which eq 7 and 9 apply. [d] Data of Spedding, Porter, and Wright (*22*). [e] Data of Spedding and Dye (*18*). [f] Data of Spedding and Yaffe (*27*).

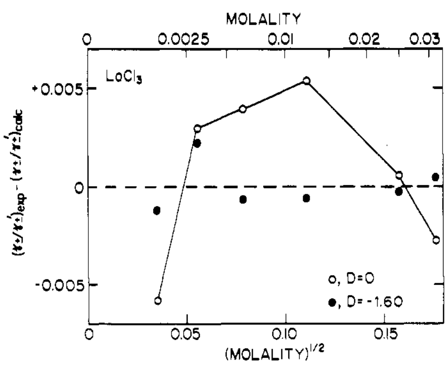

Figure 1. Differences between experimental and calculated relative mean molal activity coefficients of $LaCl_3$ at 25 °C. Deviations at $D = 0$ (eq 7) and for the optimized D are shown.

Table III. Isopiestic Molalities and Osmotic Coefficients of Some Rare Earth Chlorides

m, $ReCl_3$	m, standard	ϕ, $ReCl_3$	$10^3\Delta\phi$
	$LaCl_3$ (from emf)		
0.005 00	—	0.8712	0.0
0.010 00	—	0.8428	1.1
0.015 00	—	0.8257	1.4
0.020 00	—	0.8134	0.9
0.025 00	—	0.8037	−0.1
0.030 00	—	0.7957	−1.7
0.031 19	—	0.7939	−2.1
	$LaCl_3$ vs. KCl		
0.113 13	0.192 61	0.7773[a]	0.2
0.116 04	0.196 00	0.7709[a,b]	−6.5
0.175 65	0.304 85	0.7857[a]	−3.2
0.184 33	0.322 91	0.7923[a]	1.2
0.188 12	0.329 65	0.7923[a]	0.2
0.199 30	0.351 26	0.7961[a]	1.0
0.231 23	0.414 90	0.8086[a]	4.3
0.258 47	0.467 37	0.8136[a]	0.8
0.276 99	0.502 45	0.8156[a]	−3.3
0.303 16	0.559 29	0.8286[a]	0.8
0.435 13	0.850 66	0.8766[a]	−1.0
0.448 67	0.882 98	0.8825[a]	−0.6
0.517 22	1.051 4	0.9124[a]	0.4
0.559 68	1.159 4	0.9307[a]	0.1
0.632 00	1.351 4	0.9629[a]	−0.6
0.637 66	1.368 6	0.9667[a]	0.6
0.695 50	1.531 4	0.9942	0.6
0.713 92	1.581 4	1.0010[a]	−1.5
0.802 28	1.850 1	1.0475[a]	0.9
0.835 81	1.954 2	1.0643	0.6
0.938 55	2.288 2	1.1184	0.4
1.018 8	2.558 4	1.1598[a]	−1.9
1.109 5	2.881 3	1.2100[a]	−2.5
1.125 6	2.944 3	1.2210	−0.7
1.177 2	3.140 6	1.2524	1.2
1.269 0	3.495 0	1.3067	2.1
1.279 9	3.538 8	1.3136	2.5
1.395 9	4.006 6	1.3839	3.9
1.540 6	4.620 2	1.4750[b]	7.6
	$LaCl_3$ vs. $CaCl_2$		
1.1256	1.5206	1.2209	−0.8
1.1772	1.5958	1.2507	−0.5
1.2468	1.6974	1.2915	−0.2
1.2690	1.7294	1.3041	−0.6
1.2799	1.7462	1.3115	0.5
1.3959	1.9152	1.3804	0.4
1.5214	2.0956	1.4538	−2.0
1.5406	2.1264	1.4686	1.2
1.6441	2.2734	1.5285	−1.9
1.7322	2.4010	1.5830	−1.3
1.9190	2.6668	1.6958	−2.5
2.0211	2.8138	1.7604	0.4
2.0664	2.8760	1.7861	−1.1
2.0934	2.9152	1.8038	0.4
2.2167	3.0864	1.8768	0.4
2.3060	3.2102	1.9299	1.6
2.3380	3.2526	1.9470	0.3
2.5290	3.5112	2.0557	1.6
2.5963	3.6000	2.0918	1.1
2.7043	3.7410	2.1484	0.3
2.7852	3.8456	2.1898	0.0
2.7854	3.8442	2.1882	−1.7
3.0128	4.1329	2.2989	−2.5
3.1284	4.2798	2.3548	0.2
3.2115	4.3830	2.3922	0.7
3.2817	4.4667	2.4203	−1.5
3.3346	4.5339	2.4452	1.1
3.4561	4.6816	2.4953	1.7
3.4725	4.7000	2.5005	0.4
3.6286	4.8859	2.5595	−1.2
3.6339	4.8924	2.5617	−1.1
3.6818	4.9541	2.5835	2.7
3.7690	5.0538	2.6113	−2.0
3.8196	5.1172	2.6320	−0.1
3.8672	5.1742	2.6489	−0.8
3.8944	5.2098	2.6610	1.3
	$PrCl_3$ (from emf)		
0.005 00	—	0.8691	−0.8
0.010 00	—	0.8404	0.1
0.015 00	—	0.8236	0.6
0.020 00	—	0.8120	0.6
0.025 00	—	0.8033	0.3
0.030 00	—	0.7963	−0.3
0.032 35	—	0.7934	−0.7
	$PrCl_3$ vs. KCl		
0.115 80	0.197 40	0.7779	−1.2
0.137 40	0.237 20	0.7850	2.2
0.277 17	0.506 27	0.8212	−2.0
0.379 35	0.729 20	0.8621	1.4
0.433 17	0.852 14	0.8821	0.1
0.465 21	0.925 81	0.8925	−2.7
0.467 23	0.930 41	0.8931	−2.9
0.598 19	1.269 1	0.9543	1.0
0.630 19	1.355 3	0.9685	0.5
0.665 89	1.455 3	0.9856	0.9
0.692 97	1.533 3	0.9991	1.4
0.693 57	1.536 7	1.0005	2.5
0.700 63	1.556 0	1.0032	1.8
0.706 25	1.572 8	1.0063	2.2
0.726 39	1.629 7	1.0148	0.8
0.727 20	1.632 1	1.0152	0.9
0.860 85	2.040 9	1.0813	−0.7
0.864 87	2.060 3	1.0869	2.9
0.974 92	2.417 8	1.1413	−1.6
0.994 68	2.489 1	1.1537	0.0
1.057 4	2.706 4	1.1868	−1.7
1.062 3	2.724 9	1.1900	−1.3
1.065 3	2.736 1	1.1919	−1.1
1.189 5	3.196 9	1.2637	−0.5
1.194 1	3.217 9	1.2679	1.0
1.201 5	3.251 5	1.2745	3.3
1.296 9	3.617 1	1.3283	0.5
1.409 5	4.083 5	1.4003	4.3
1.466 3	4.321 1	1.4353	4.4
1.476 5	4.363 7	1.4414	4.2
1.476 8	4.365 3	1.4417	4.4
	$PrCl_3$ vs. $CaCl_2$		
0.379 35	0.479 77	0.8626	2.0
0.433 17	0.549 99	0.8811	−0.9
0.598 19	0.775 44	0.9539	0.7
0.630 19	0.817 90	0.9661	−1.9
0.665 89	0.869 48	0.9856	0.9
0.692 97	0.906 21	0.9971	−0.6
0.693 57	0.908 33	0.9991	1.1
0.700 63	0.917 44	1.0014	0.1
0.706 25	0.925 97	1.0051	0.9
0.726 39	0.952 07	1.0120	−2.0
0.727 20	0.953 10	1.0122	−2.1
1.057 4	1.425 2	1.1864	−2.1
1.062 3	1.431 8	1.1891	−2.2
1.065 3	1.436 8	1.1910	−2.0
1.097 7	1.482 4	1.2077	−3.6
1.189 5	1.617 9	1.2625	−1.7
1.194 1	1.625 3	1.2660	−0.9
1.296 9	1.774 7	1.3257	−2.1

Table III. Continued

m, $ReCl_3$	m, standard	ϕ, $ReCl_3$	$10^3\Delta\phi$
1.303 3	1.784 3	1.3297	−1.8
1.409 5	1.941 1	1.3952	−0.7
1.476 5	2.040 2	1.4372	0.0
1.479 6	2.044 7	1.4391	0.0
1.707 3	2.378 4	1.5819	−0.1
1.794 8	2.506 5	1.6379	0.3
1.800 3	2.514 3	1.6411	0.1
1.821 4	2.544 2	1.6537	−0.8
1.942 1	2.719 4	1.7307	−0.8
1.949 3	2.727 4	1.7327	−3.3
2.039 6	2.862 1	1.7949	1.4
2.145 5	3.009 7	1.8577	−2.9
2.231 1	3.130 7	1.9106	−3.8
2.236 3	3.140 1	1.9160	−1.7
2.349 4	3.299 9	1.9865	−1.5
2.381 1	3.345 1	2.0068	−0.7
2.393 3	3.363 2	2.0153	0.3
2.412 1	3.389 9	2.0273	0.8
2.433 7	3.419 6	2.0400	0.3
2.510 6	3.527 3	2.0874	1.2
2.564 1	3.600 5	2.1186	0.5
2.613 4	3.668 5	2.1480	0.7
2.658 0	3.730 7	2.1752	2.0
2.667 0	3.742 8	2.1803	1.8
2.675 3	3.753 6	2.1846	1.2
2.718 8	3.812 4	2.2093	0.9
2.742 5	3.844 7	2.2230	1.1
2.824 8	3.954 6	2.2682	0.0
2.835 1	3.968 9	2.2744	0.5
2.908 1	4.066 5	2.3145	0.5
2.920 5	4.082 3	2.3205	−0.2
3.002 7	4.191 0	2.3642	−0.3
3.026 0	4.222 0	2.3767	0.0
3.110 9	4.332 2	2.4194	−1.1
3.119 4	4.341 9	2.4223	−2.5
3.225 5	4.482 5	2.4778	0.3
3.241 3	4.502 6	2.4851	0.0
3.307 7	4.588 2	2.5170	0.1
3.331 2	4.616 9	2.5267	−1.3
3.404 9	4.711 9	2.5614	−0.5
3.434 9	4.751 2	2.5760	0.5
3.566 7	4.918 5	2.6340	0.4
3.587 1	4.943 1	2.6416	−0.7
3.762 3	5.167 0	2.7163	1.0
3.777 3	5.186 9	2.7232	1.7
3.896 9	5.336 2	2.7683	−1.4
	$NdCl_3$ (from emf)		
0.005 00	—	0.8679	1.5
0.010 00	—	0.8382	1.7
0.015 00	—	0.8207	1.2
0.020 00	—	0.8083	0.4
0.025 00	—	0.7989	−0.9
0.030 00	—	0.7913	−2.4
0.033 52	—	0.7866	−3.6
	$NdCl_3$ vs. KCl		
0.107 20	0.182 76	0.7792	1.6
0.120 34	0.206 04	0.7807	1.2
0.174 20	0.305 33	0.7935	2.1
0.238 73	0.429 47	0.8103	0.1
0.291 28	0.536 89	0.8282	0.5
0.389 29	0.748 56	0.8623	−1.3
0.437 89	0.860 88	0.8816	−1.3
0.487 13	0.979 20	0.9018	−1.4
0.693 74	1.531 4	0.9967	−0.3
0.833 17	1.954 2	1.0677	0.3
0.849 39	2.004 4	1.0754	−0.5
0.935 42	2.288 2	1.1221	0.0

m, $ReCl_3$	m, standard	ϕ, $ReCl_3$	$10^3\Delta\phi$
0.987 40	2.468 2	1.1518	1.0
1.120 5	2.944 3	1.2265	−0.4
1.171 6	3.140 6	1.2584	1.3
1.262 6	3.495 0	1.3133	1.7
1.273 4	3.538 8	1.3203	2.1
1.387 5	4.006 6	1.3922	3.7
1.530 0	4.620 2	1.4852[b]	6.8
	$NdCl_3$ vs. $CaCl_2$		
1.1205	1.5206	1.2264	−0.5
1.1716	1.5958	1.2567	−0.4
1.2626	1.7294	1.3107	−1.0
1.2734	1.7462	1.3182	0.0
1.3875	1.9152	1.3888	0.2
1.5106	2.0956	1.4642	−1.9
1.5300	2.1264	1.4787	0.4
1.6309	2.2734	1.5409	−2.1
1.7171	2.4010	1.5969	−1.8
1.8980	2.6668	1.7145	−1.9
1.9974	2.8138	1.7813	0.0
2.0408	2.8760	1.8085	−0.9
2.0670	2.9152	1.8268	0.3
2.2303	3.1501	1.9317	−0.4
2.2712	3.2102	1.9595	1.2
2.3748	3.3570	2.0245	0.4
2.5459	3.5977	2.1308	−0.1
2.5472	3.6000	2.1321	0.4
2.7218	3.8442	2.2394	2.0
2.7237	3.8456	2.2392	0.8
2.7842	3.9278	2.2738	−0.3
2.8919	4.0740	2.3351	−1.3
3.0418	4.2798	2.4218	1.7
3.0588	4.3003	2.4287	−0.7
3.1194	4.3830	2.4629	0.8
3.2564	4.5632	2.5323	−1.5
3.3438	4.6816	2.5791	1.2
3.3599	4.7000	2.5843	−1.6
3.5003	4.8859	2.6533	−0.5
3.5060	4.8924	2.6551	−1.4
3.6288	5.0538	2.7122	−1.2
3.6637	5.1016	2.7298	0.6
3.7180	5.1742	2.7552	1.7
3.7833	5.2607	2.7843	2.1
3.8583	5.3567	2.8139	−0.7
3.9031	5.4180	2.8346	0.8
3.9286	5.4503	2.8440	−0.7
3.9307	5.4530	2.8448	−0.8
	$SmCl_3$ (from emf)		
0.005 00	—	0.8679	0.7
0.010 00	—	0.8389	0.9
0.015 00	—	0.8221	0.8
0.020 00	—	0.8107	0.5
0.025 00	—	0.8022	0.0
0.030 00	—	0.7956	−0.7
0.035 00	—	0.7902	−1.6
0.037 46	—	0.7879	−2.1
	$SmCl_3$ vs. KCl		
0.106 86	0.182 76	0.7817	0.9
0.120 04	0.206 04	0.7826	−0.1
0.145 78	0.253 59	0.7900	2.2
0.237 81	0.429 47	0.8134	−0.4
0.290 02	0.536 89	0.8318	0.3
0.386 68	0.748 56	0.8681	0.2
0.435 34	0.860 88	0.8867	−1.1
0.483 91	0.979 20	0.9078	−0.7
0.604 40	1.294 2	0.9635	0.4
0.688 54	1.531 4	1.0043	0.4
0.767 02	1.763 6	1.0426	−1.2
0.827 30	1.954 2	1.0753	−0.2

Table III. Continued

m, $ReCl_3$	m, standard	ϕ, $ReCl_3$	$10^3\Delta\phi$
0.843 12	2.004 4	1.0834	−0.5
0.933 76	2.307 3	1.1340	0.5
0.980 04	2.468 2	1.1605	0.9
1.104 6	2.914 1	1.2304	−1.3
1.223 4	3.375 7	1.3044	1.4
1.299 4	3.678 8	1.3509	1.1
1.392 8	4.068 6	1.4112	3.0
	$SmCl_3$ vs. $CaCl_2$		
1.2312	1.6974	1.3078	0.0
1.4996	2.0956	1.4749	−1.4
1.6191	2.2734	1.5521	−1.4
1.7048	2.4010	1.6084	−1.1
1.8844	2.6668	1.7269	−0.9
1.9843	2.8138	1.7930	−0.7
2.0267	2.8760	1.8211	−0.5
2.0534	2.9152	1.8389	−0.3
2.1708	3.0864	1.9164	0.3
2.2566	3.2102	1.9722	0.3
2.2851	3.2526	1.9921	1.8
2.4678	3.5112	2.1067	0.0
2.5308	3.6000	2.1459	0.0
2.5478	3.6241	2.1567	0.2
2.6298	3.7410	2.2093	2.6
2.7058	3.8442	2.2526	0.2
2.7080	3.8456	2.2522	−1.5
2.9185	4.1329	2.3732	−2.3
3.0250	4.2798	2.4353	0.9
3.1027	4.3830	2.4761	0.1
3.1669	4.4667	2.5080	−1.7
3.3250	4.6792	2.5913	1.6
3.3712	4.7389	2.6129	0.4
3.4587	4.8530	2.6541	−0.7
3.5438	4.9667	2.6958	0.6
3.6414	5.0952	2.7407	−0.5
	$EuCl_3$ (from emf)		
0.005 00	—	0.8667	0.5
0.010 00	—	0.8374	0.4
0.015 00	—	0.8207	0.4
0.020 00	—	0.8096	0.3
0.025 00	—	0.8015	0.0
0.030 00	—	0.7954	−0.3
0.035 00	—	0.7906	−0.8
0.035 32	—	0.7903	−0.8
	$EuCl_3$ vs. KCl		
0.165 25	0.290 47	0.7964	1.0
0.233 03	0.422 17	0.8162	−0.1
0.263 49	0.483 79	0.8258	−1.0
0.350 65	0.671 71	0.8594	−0.2
0.374 97	0.727 66	0.8703	1.0
0.417 31	0.824 50	0.8859	−0.9
0.447 01	0.897 69	0.9006	1.1
0.458 93	0.925 25	0.9042	−0.4
0.465 44	0.942 67	0.9084	0.9
0.514 80	1.067 3	0.9306	1.1
0.516 73	1.072 3	0.9315	1.1
0.530 77	1.106 9	0.9364	−0.4
0.538 41	1.127 9	0.9408	0.5
0.628 86	1.373 3	0.9837	0.1
0.642 63	1.412 1	0.9903	0.0
0.720 13	1.639 5	1.0299	0.3
0.745 37	1.714 5	1.0420	−0.8
0.822 67	1.958 9	1.0840	−0.1
0.830 43	1.983 5	1.0880	−0.4
0.910 87	2.251 3	1.1328	−0.3
0.934 53	2.334 7	1.1473	0.8
0.999 37	2.558 5	1.1824	−1.5
1.014 4	2.620 3	1.1950	2.3
1.092 5	2.901 7	1.2383	−0.9
1.122 6	3.020 6	1.2587	1.3
1.206 9	3.345 0	1.3090	−0.2
1.209 9	3.355 9	1.3104	−0.6
1.268 3	3.592 7	1.3480	0.5
1.276 7	3.626 4	1.3531	0.3
1.345 3	3.911 6	1.3976	1.2
1.353 9	3.948 3	1.4034	1.5
1.423 4	4.246 0	1.4493	2.6
1.435 8	4.300 7	1.4579	3.2
1.523 1	4.689 3	1.5176	5.9
1.530 2	4.719 5	1.5218	5.4
	$EuCl_3$ vs. $CaCl_2$		
0.417 31	0.534 86	0.8861	−0.7
0.458 93	0.591 87	0.9045	−0.2
0.530 77	0.690 71	0.9363	−0.5
0.538 41	0.702 22	0.9413	0.9
0.628 86	0.828 21	0.9830	−0.5
0.642 63	0.847 61	0.9897	−0.7
0.720 21	0.958 68	1.0296	−0.1
0.745 37	0.993 95	1.0415	−1.3
0.822 67	1.106 7	1.0840	−0.2
0.830 43	1.117 5	1.0876	−0.8
0.910 87	1.235 6	1.1328	−0.2
0.934 53	1.270 7	1.1467	0.2
0.999 37	1.365 7	1.1832	−0.7
1.014 4	1.388 9	1.1931	0.4
1.092 5	1.504 4	1.2389	−0.3
1.122 6	1.550 5	1.2585	1.1
1.199 5	1.662 9	1.3028	−1.8
1.206 9	1.675 7	1.3093	0.1
1.209 9	1.680 0	1.3110	−0.1
1.235 7	1.717 4	1.3256	−1.5
1.268 3	1.767 9	1.3479	0.3
1.276 7	1.780 5	1.3532	0.3
1.282 0	1.786 2	1.3540	−2.2
1.332 3	1.861 7	1.3859	−2.3
1.345 3	1.883 5	1.3967	0.3
1.353 9	1.897 3	1.4032	1.2
1.377 1	1.929 1	1.4147	−2.2
1.423 4	2.001 1	1.4472	0.5
1.425 1	2.001 5	1.4459	−1.9
1.435 8	2.020 1	1.4556	0.9
1.470 4	2.069 5	1.4753	−2.0
1.523 1	2.151 5	1.5129	1.1
1.530 2	2.161 6	1.5169	0.5
1.537 2	2.170 0	1.5192	−1.8
1.575 1	2.226 5	1.5437	−2.2
1.643 9	2.329 9	1.5896	−1.9
1.674 3	2.375 7	1.6101	−1.6
1.743 5	2.479 3	1.6564	−1.4
1.789 5	2.548 1	1.6874	−1.2
1.863 9	2.658 9	1.7373	−1.0
1.891 9	2.700 5	1.7562	−0.9
1.978 7	2.828 8	1.8142	−0.9
2.008 9	2.873 6	1.8347	−0.5
2.085 4	2.986 5	1.8863	0.2
2.132 9	3.055 9	1.9177	0.2
2.219 7	3.181 9	1.9747	0.0
2.267 9	3.251 8	2.0064	0.2
2.358 1	3.382 1	2.0654	0.8
2.393 3	3.432 1	2.0876	0.4
2.472 0	3.543 9	2.1374	0.2
2.513 2	3.602 1	2.1632	0.0
2.585 5	3.704 7	2.2089	0.8
2.611 8	3.741 0	2.2245	0.2
2.689 7	3.849 9	2.2720	0.4

Table III. Continued

m, $ReCl_3$	m, standard	ϕ, $ReCl_3$	$10^3\Delta\phi$
2.716 9	3.887 1	2.2877	−0.1
2.796 1	3.996 1	2.3341	−0.6
2.826 2	4.037 9	2.3521	−0.2
2.904 1	4.144 3	2.3966	−0.3
2.997 3	4.271 1	2.4490	−0.1
3.105 4	4.416 9	2.5077	0.1
3.145 3	4.470 0	2.5285	−0.2
3.211 7	4.558 5	2.5629	−0.4
3.237 5	4.593 2	2.5765	0.0
3.345 9	4.736 5	2.6303	−0.7
3.373 2	4.774 1	2.6452	0.6
3.407 1	4.819 6	2.6623	1.1
3.431 8	4.851 3	2.6733	0.1
3.449 9	4.875 1	2.6818	−0.2
3.499 4	4.940 8	2.7056	−0.3
3.517 3	4.964 8	2.7144	−0.1
3.583 9	5.054 0	2.7464	0.0
	$GdCl_3$ (from emf)		
0.005 00	—	0.8684	1.9
0.010 00	—	0.8394	1.8
0.015 00	—	0.8226	1.4
0.020 00	—	0.8110	0.7
0.025 00	—	0.8024	−0.3
0.030 00	—	0.7955	−1.5
0.035 00	—	0.7899	−2.9
0.035 15	—	0.7898	−2.9
	$GdCl_3$ vs. KCl		
0.106 32	0.182 76	0.7856	1.4
0.119 44	0.206 04	0.7865	0.1
0.145 13	0.253 59	0.7936	1.5
0.172 58	0.305 33	0.8009	1.6
0.236 25	0.429 47	0.8188	−0.6
0.287 79	0.536 89	0.8382	0.4
0.431 48	0.860 88	0.8947	−1.6
0.597 30	1.294 2	0.9749	1.0
0.680 14	1.531 4	1.0167	0.5
0.758 01	1.763 6	1.0550	−2.8
0.831 91	2.004 4	1.0980	−0.7
0.920 22	2.307 3	1.1507	1.2
0.966 12	2.468 2	1.1772	0.7
1.088 2	2.914 1	1.2489	−1.7
1.204 7	3.375 7	1.3246	0.9
1.279 2	3.678 8	1.3722	0.6
1.371 0	4.068 6	1.4336	2.0
1.427 2	4.315 2	1.4723	3.5
1.524 0	4.752 0	1.5402	6.6
	$GdCl_3$ vs. $CaCl_2$		
1.4272	2.0222	1.4668	−2.1
1.5240	2.1694	1.5317	−1.8
1.5508	2.2066	1.5459	−5.7
1.6416	2.3485	1.6122	−0.9
1.7385	2.4948	1.6781	−1.0
1.8151	2.6099	1.7302	−1.3
1.9183	2.7661	1.8025	0.3
2.0070	2.8984	1.8632	0.4
2.1498	3.1098	1.9603	0.4
2.1778	3.1501	1.9782	−0.5
2.2474	3.2526	2.0255	0.0
2.3188	3.3570	2.0734	0.3
2.4859	3.5977	2.1823	−0.2
2.5856	3.7410	2.2470	0.9
2.7176	3.9278	2.3296	1.3
2.8124	4.0574	2.3838	−1.7
2.8226	4.0740	2.3924	0.8
2.9872	4.3003	2.4870	−0.2
3.0349	4.3646	2.5127	−1.1
3.1799	4.5632	2.5932	0.4
3.1921	4.5788	2.5988	−0.5
3.2655	4.6792	2.6386	0.8
3.3106	4.7389	2.6607	−0.3
3.3943	4.8530	2.7045	1.0
3.4799	4.9667	2.7453	−0.8
3.5898	5.1172	2.8005	0.1
	$TbCl_3$ (from emf)		
0.005 00	—	0.8702	0.2
0.010 00	—	0.8406	−1.1
0.015 00	—	0.8265	1.1
0.020 00	—	0.8156	1.0
0.025 00	—	0.8075	0.6
0.030 00	—	0.8005	−0.6
	$TbCl_3$ vs. KCl		
0.134 65	0.233 33	0.7882	−3.2
0.272 43	0.506 27	0.8355	1.8
0.454 62	0.925 81	0.9133	3.7
0.498 43	1.033 0	0.9301	0.0
0.745 27	1.732 9	1.0537	−4.5
0.837 59	2.040 9	1.1113	0.4
0.841 95	2.060 3	1.1165	3.1
0.874 31	2.160 3	1.1300	−2.4
0.909 90	2.292 5	1.1559	2.3
0.921 33	2.324 9	1.1586	−1.9
0.922 08	2.329 4	1.1600	−0.9
1.056 5	2.820 9	1.2420	−1.8
1.061 1	2.839 3	1.2453	−1.4
1.089 3	2.951 1	1.2648	0.3
1.099 1	2.986 6	1.2699	−0.9
1.186 7	3.334 5	1.3267	−0.6
1.188 4	3.340 5	1.3274	−1.0
1.290 2	3.766 1	1.3967	1.0
1.473 9	4.578 2	1.5256	5.6
1.480 1	4.607 2	1.5303	6.0
	$TbCl_3$ vs. $CaCl_2$		
1.0565	1.4735	1.2442	0.4
1.0611	1.4809	1.2475	0.8
1.1867	1.6716	1.3269	−0.5
1.1884	1.6741	1.3279	−0.6
1.2902	1.8315	1.3965	0.9
1.4370	2.0543	1.4925	−2.3
1.4739	2.1141	1.5212	1.2
1.4801	2.1231	1.5249	0.6
1.5134	2.1719	1.5452	−2.0
1.6474	2.3784	1.6394	−0.9
1.7470	2.5311	1.7097	−0.4
1.7533	2.5442	1.7179	3.5
1.8715	2.7194	1.7960	−1.6
1.8785	2.7274	1.7980	−4.5
1.9595	2.8537	1.8591	−0.4
1.9651	2.8621	1.8630	−0.5
2.0639	3.0097	1.9311	−1.7
2.1453	3.1307	1.9871	−2.6
2.2441	3.2797	2.0578	−0.4
2.3067	3.3739	2.1026	1.4
2.3177	3.3899	2.1098	1.1
2.4111	3.5273	2.1735	1.4
2.4255	3.5465	2.1812	−0.6
2.5082	3.6685	2.2381	1.2
2.5251	3.6919	2.2480	0.0
2.6303	3.8447	2.3178	1.3
2.7177	3.9689	2.3727	0.6
2.7867	4.0665	2.4153	0.4
2.7983	4.0823	2.4219	−0.2
2.8757	4.1910	2.4686	−0.2
2.8978	4.2220	2.4819	−0.1
2.9774	4.3322	2.5279	−0.7

Table III. Continued

m, $ReCl_3$	m, standard	ϕ, $ReCl_3$	$10^3\Delta\phi$
2.9852	4.3419	2.5312	−1.8
3.0857	4.4825	2.5900	0.3
3.1006	4.5026	2.5979	−0.1
3.1629	4.5882	2.6322	0.4
3.1846	4.6169	2.6430	−0.5
3.2541	4.7119	2.6801	0.0
3.4057	4.9185	2.7585	1.0
3.4245	4.9431	2.7670	0.1
3.5733	5.1462	2.8405	−0.4
	$DyCl_3$ (from emf)		
0.005 00	—	0.8714	−1.2
0.010 00	—	0.8435	−0.8
0.015 00	—	0.8284	0.4
0.020 00	—	0.8176	0.6
0.025 00	—	0.8102	1.1
0.030 00	—	0.8028	−0.3
	$DyCl_3$ vs. KCl		
0.106 05	0.182 76	0.7876	0.3
0.118 92	0.206 04	0.7900	0.6
0.144 90	0.253 59	0.7948	0.0
0.172 54	0.305 33	0.8011	−1.1
0.235 34	0.429 47	0.8220	−0.4
0.381 51	0.748 56	0.8799	−0.5
0.476 09	0.979 20	0.9227	−0.5
0.592 84	1.294 2	0.9823	1.6
0.675 23	1.531 4	1.0241	0.2
0.750 24	1.763 6	1.0659	0.8
0.825 54	2.004 4	1.1065	−1.5
0.912 86	2.307 3	1.1600	0.4
0.957 64	2.468 2	1.1876	0.8
1.078 1	2.914 1	1.2606	−1.6
1.193 0	3.375 7	1.3376	0.6
1.266 1	3.678 8	1.3864	0.6
1.356 1	4.068 6	1.4494	2.3
1.411 9	4.315 2	1.4883	2.7
1.507 0	4.752 0	1.5576	5.4
	$DyCl_3$ vs. $CaCl_2$		
1.4119	2.0222	1.4827	−2.9
1.5070	2.1694	1.5490	−3.2
1.5322	2.2066	1.5647	−5.2
1.6208	2.3485	1.6328	−0.1
1.7163	2.4948	1.6998	−1.6
1.7906	2.6099	1.7539	−1.1
1.8918	2.7661	1.8277	−0.4
1.9769	2.8984	1.8915	1.8
2.1008	3.0864	1.9803	1.3
2.1156	3.1098	1.9920	2.4
2.1446	3.1501	2.0089	−1.5
2.2818	3.3570	2.1071	−0.7
2.3840	3.5112	2.1807	1.6
2.4438	3.5977	2.2199	−0.5
2.6312	3.8713	2.3453	−1.1
2.6693	3.9278	2.3717	0.3
2.7592	4.0574	2.4298	0.4
2.7706	4.0740	2.4373	0.7
2.9300	4.3003	2.5355	−0.1
2.9765	4.3646	2.5620	−1.5
3.1164	4.5632	2.6461	0.8
3.1292	4.5788	2.6510	−1.5
3.2003	4.6792	2.6923	−0.2
3.2020	4.6816	2.6933	−0.2
3.2434	4.7389	2.7159	−0.5
3.3247	4.8530	2.7611	0.7
3.4074	4.9667	2.8038	−0.2
3.4975	5.0952	2.8534	3.0
3.5562	5.1742	2.8805	0.4
3.6196	5.2607	2.9102	−1.5
3.6302	5.2766	2.9165	−0.6
	$HoCl_3$ (from emf)		
0.005 00	—	0.8716	−2.3
0.010 00	—	0.8444	−0.7
0.015 00	—	0.8287	0.4
0.020 00	—	0.8180	1.0
0.025 00	—	0.8101	1.2
0.030 00	—	0.8038	0.9
0.034 23	—	0.7994	0.4
	$HoCl_3$ vs. KCl		
0.134 05	0.233 33	0.7917	−2.7
0.271 67	0.506 27	0.8378	−2.7
0.370 13	0.729 20	0.8835	2.4
0.422 15	0.852 14	0.9051	0.9
0.453 07	0.925 81	0.9165	−1.9
0.454 85	0.930 41	0.9174	−1.8
0.580 77	1.269 1	0.9829	2.6
0.612 67	1.355 3	0.9962	−0.5
0.671 00	1.528 4	1.0285	1.1
0.679 89	1.556 0	1.0338	1.7
0.685 57	1.572 8	1.0366	1.4
0.704 68	1.629 7	1.0460	0.4
0.708 81	1.643 3	1.0489	1.0
0.833 67	2.045 1	1.1189	0.5
0.838 05	2.060 3	1.1217	0.7
0.905 03	2.292 5	1.1621	1.4
0.989 38	2.597 7	1.2139	1.5
1.024 5	2.722 3	1.2327	−1.8
1.024 6	2.724 9	1.2338	−0.7
1.027 3	2.736 1	1.2360	−0.2
1.146 9	3.196 9	1.3107	−2.7
1.150 7	3.217 9	1.3157	−0.1
1.158 9	3.251 5	1.3214	0.1
1.247 7	3.617 1	1.3806	0.0
1.253 8	3.640 1	1.3836	−1.1
1.353 1	4.083 5	1.4586	5.7
1.370 4	4.150 3	1.4669	2.0
1.407 4	4.321 1	1.4954	4.7
1.417 1	4.363 7	1.5019	4.3
1.417 4	4.365 3	1.5022	4.4
1.419 7	4.379 3	1.5052	5.9
	$HoCl_3$ vs. $CaCl_2$		
0.370 13	0.479 77	0.8841	3.0
0.422 15	0.549 99	0.9041	−0.1
0.580 77	0.775 44	0.9826	2.2
0.612 67	0.817 90	0.9937	−3.0
0.645 47	0.869 48	1.0168	3.0
0.671 00	0.903 73	1.0262	−1.2
0.679 89	0.917 44	1.0320	−0.2
0.685 57	0.925 97	1.0354	0.1
0.704 68	0.952 07	1.0431	−2.5
1.020 9	1.425 2	1.2288	−3.4
1.023 1	1.429 1	1.2309	−2.7
1.024 5	1.431 8	1.2324	−2.0
1.058 5	1.482 4	1.2524	−3.7
1.060 1	1.487 7	1.2568	−0.3
1.146 9	1.617 9	1.3094	−4.0
1.150 7	1.625 3	1.3137	−2.2
1.247 7	1.774 7	1.3779	−2.7
1.253 8	1.784 3	1.3822	−2.5
1.353 1	1.941 1	1.4534	0.5
1.370 4	1.967 4	1.4647	−0.2
1.407 4	2.025 1	1.4907	0.0
1.419 7	2.044 7	1.4998	0.5
1.425 7	2.054 3	1.5043	0.8
1.633 6	2.378 4	1.6532	1.1

Table III. Continued

m, $ReCl_3$	m, standard	ϕ, $ReCl_3$	$10^3\Delta\phi$
1.645 9	2.397 2	1.6618	0.8
1.731 4	2.531 1	1.7251	1.9
1.857 1	2.719 4	1.8099	−5.3
1.864 1	2.727 4	1.8119[b]	−8.4
2.045 9	3.009 7	1.9481	−5.6
2.124 5	3.130 7	2.0065	−4.7
2.221 0	3.279 7	2.0792	−2.3
2.281 9	3.373 9	2.1254	−0.2
2.292 3	3.389 9	2.1332	0.2
2.383 2	3.527 3	2.1989	0.7
2.397 1	3.546 5	2.2070	−1.1
2.477 3	3.668 5	2.2660	1.1
2.493 6	3.691 9	2.2764	0.1
2.595 3	3.844 7	2.3490	1.9
2.683 0	3.975 0	2.4099	2.7
2.745 9	4.066 5	2.4512	1.7
2.756 9	4.082 3	2.4582	1.4
2.831 3	4.191 0	2.5073	1.3
2.852 6	4.222 0	2.5212	1.2
2.929 1	4.332 2	2.5695	0.1
2.936 4	4.341 9	2.5733	−0.9
3.032 7	4.482 5	2.6353	0.5
3.046 9	4.502 6	2.6437	0.1
3.106 5	4.588 2	2.6800	−0.2
3.127 3	4.616 9	2.6914	−1.4
3.193 5	4.711 9	2.7310	−1.4
3.220 5	4.751 2	2.7475	−0.8
3.355 7	4.943 1	2.8237	−2.0
3.370 8	4.957 7	2.8254[b]	−8.8
3.511 3	5.167 0	2.9105	0.3
3.524 7	5.186 9	2.9184	1.1
3.698 7	5.433 7	3.0056	0.4
	$ErCl_3$ (from emf)		
0.005 00	—	0.8716	−0.1
0.010 00	—	0.8440	0.9
0.015 00	—	0.8280	1.2
0.020 00	—	0.8169	1.1
0.025 00	—	0.8084	0.5
0.030 00	—	0.8016	−0.4
0.035 00	—	0.7960	−1.7
0.036 40	—	0.7945	−2.1
	$ErCl_3$, Set 1 vs. KCl		
0.164 33	0.290 47	0.8009	0.1
0.231 38	0.422 17	0.8220	−0.3
0.261 41	0.483 79	0.8324	−0.8
0.347 41	0.671 71	0.8674	−0.1
0.371 47	0.727 66	0.8785	0.8
0.412 94	0.824 50	0.8953	−0.7
0.442 29	0.897 69	0.9102	0.8
0.453 74	0.925 25	0.9145	−0.1
0.460 35	0.942 67	0.9185	0.7
0.508 73	1.067 3	0.9417	0.9
0.510 53	1.072 3	0.9428	1.1
0.524 27	1.106 9	0.9480	−0.4
0.531 28	1.127 9	0.9535	1.6
0.620 19	1.373 3	0.9974	0.2
0.633 57	1.412 1	1.0045	0.2
0.709 33	1.639 5	1.0456	0.3
0.733 81	1.714 5	1.0584	−0.5
0.809 32	1.958 9	1.1019	−0.2
0.816 65	1.983 5	1.1063	−0.1
0.895 17	2.251 3	1.1526	−0.5
0.917 93	2.334 7	1.1681	1.1
0.981 15	2.558 5	1.2044	−1.7
0.995 77	2.620 3	1.2174	2.1
1.071 5	2.901 7	1.2625	−1.2
1.100 4	3.020 6	1.2841	1.6
1.182 3	3.345 0	1.3362	−0.5

m, $ReCl_3$	m, standard	ϕ, $ReCl_3$	$10^3\Delta\phi$
1.185 2	3.355 9	1.3377	−0.9
1.241 7	3.592 7	1.3769	0.0
1.249 7	3.626 4	1.3824	0.1
1.315 9	3.911 6	1.4288	1.0
1.324 1	3.948 3	1.4350	1.4
1.391 3	4.246 0	1.4828	2.1
1.403 3	4.300 7	1.4917	2.6
1.487 1	4.689 3	1.5544	5.6
1.493 9	4.719 5	1.5588	5.1
	$ErCl_3$, Set 1 vs. $CaCl_2$		
0.412 94	0.534 86	0.8954	−0.5
0.453 74	0.591 87	0.9148	0.2
0.524 27	0.690 71	0.9479	−0.5
0.531 28	0.702 22	0.9539	2.0
0.620 19	0.828 21	0.9968	−0.5
0.633 57	0.847 61	1.0039	−0.4
0.733 81	0.993 95	1.0579	−1.0
0.809 32	1.106 7	1.1018	−0.3
0.816 65	1.117 5	1.1059	−0.5
0.895 17	1.235 6	1.1527	−0.4
0.917 93	1.270 7	1.1674	0.4
0.981 15	1.365 7	1.2052	−0.9
0.995 77	1.388 9	1.2155	0.2
1.071 5	1.504 4	1.2632	−0.5
1.100 4	1.550 5	1.2839	1.4
1.174 6	1.662 9	1.3304	−1.2
1.182 3	1.675 7	1.3366	−0.2
1.185 2	1.680 0	1.3383	−0.4
1.209 5	1.717 4	1.3543	−0.7
1.241 7	1.767 9	1.3767	−0.1
1.249 7	1.780 5	1.3824	0.1
1.255 1	1.786 2	1.3830	−3.0
1.302 9	1.861 7	1.4171	−1.7
1.315 9	1.883 5	1.4279	0.0
1.324 1	1.897 3	1.4348	1.2
1.346 4	1.929 1	1.4469	−2.2
1.391 3	2.001 1	1.4806	0.0
1.394 7	2.001 5	1.4774	−5.6
1.403 3	2.020 1	1.4894	0.3
1.436 1	2.069 5	1.5105	−1.8
1.487 1	2.151 5	1.5495	0.7
1.493 9	2.161 6	1.5538	0.1
1.500 3	2.170 0	1.5566	−1.7
1.536 7	2.226 5	1.5823	−2.2
1.602 4	2.329 9	1.6307	−1.5
1.632 7	2.375 8	1.6512	−3.2
1.697 7	2.479 3	1.7011	−1.1
1.741 5	2.548 1	1.7339	−0.7
1.812 5	2.658 9	1.7866	−0.7
1.839 0	2.700 5	1.8067	−0.3
1.921 3	2.828 8	1.8684	0.0
1.950 6	2.873 6	1.8895	−0.8
2.022 9	2.986 5	1.9445	0.1
2.067 9	3.055 9	1.9780	−0.1
2.149 5	3.181 9	2.0391	0.2
2.194 9	3.251 8	2.0731	0.3
2.279 3	3.382 1	2.1368	1.5
2.312 5	3.432 1	2.1606	0.7
2.386 3	3.543 9	2.2142	0.2
2.424 9	3.602 1	2.2420	−0.2
2.492 7	3.704 7	2.2912	−0.1
2.516 7	3.741 0	2.3085	0.1
2.589 7	3.849 9	2.3597	−0.8
2.614 1	3.887 1	2.3777	−0.1
2.687 5	3.996 1	2.4284	−0.8
2.715 8	4.037 9	2.4477	−1.2
2.787 3	4.144 3	2.4970	−0.9
2.873 3	4.271 1	2.5547	−1.2

Table III. Continued

m, $ReCl_3$	m, standard	ϕ, $ReCl_3$	$10^3\Delta\phi$
2.973 2	4.416 9	2.6193	−2.2
3.009 1	4.470 0	2.6430	−1.7
3.069 7	4.558 5	2.6815	−1.8
3.093 5	4.593 2	2.6964	−1.8
3.192 1	4.736 5	2.7571	−2.2
3.217 5	4.774 1	2.7732	−1.5
3.248 3	4.819 6	2.7924	−0.8
3.270 5	4.851 3	2.8051	−1.4
3.286 1	4.875 1	2.8155	−0.2
3.331 0	4.940 8	2.8424	0.2
3.347 7	4.964 8	2.8519	−0.1
	$ErCl_3$, Set 2 vs. KCl		
0.123 06	0.211 49	0.7832	−7.4
0.127 34	0.223 73	0.7998	8.3
0.598 47	1.311 2	0.9860	0.1
0.599 92	1.315 2	0.9867	0.0
0.776 54	1.852 0	1.0833	0.2
0.784 41	1.875 1	1.0864	−1.3
0.790 69	1.896 7	1.0906	−0.7
0.798 42	1.923 9	1.0962	0.4
1.406 7	4.325 2	1.4977	6.2
1.416 2	4.365 6	1.5036	5.3
1.436 6	4.451 1	1.5154	2.7
	$ErCl_3$, Set 2 vs. $CaCl_2$		
0.784 41	1.0684	1.0859	−1.8
0.790 69	1.0777	1.0895	−1.8
0.798 42	1.0903	1.0953	−0.4
1.539 1	2.2326	1.5867	0.4
1.559 5	2.2668	1.6040	3.0
1.561 0	2.2723	1.6087	6.5
1.716 8	2.5065	1.7123	−4.0
1.721 9	2.5143	1.7159	−4.2
1.727 4	2.5228	1.7198	−4.3
1.733 4	2.5323	1.7244	−4.2
2.176 5	3.2247	2.0607	1.6
2.257 7	3.3451	2.1165	−2.9
2.302 8	3.4136	2.1494	−3.3
2.303 9	3.4196	2.1549	1.4
2.406 4	3.5756	2.2302	1.5
2.423 0	3.6005	2.2420	1.2
2.509 0	3.7307	2.3044	1.5
2.516 7	3.7428	2.3105	2.0
2.523 9	3.7530	2.3150	1.3
2.563 4	3.8124	2.3432	1.3
2.652 8	3.9501	2.4104	5.4
2.875 8	4.2714	2.5527	−4.7
2.904 6	4.3144	2.5725	−4.1
2.965 6	4.4073	2.6159	−0.6
3.032 6	4.5068	2.6605	0.8
3.036 2	4.5110	2.6617	−0.3
3.040 0	4.5190	2.6667	2.2
3.046 5	4.5290	2.6713	2.7
3.058 2	4.5464	2.6791	3.0
3.071 2	4.5653	2.6872	2.9
3.137 6	4.6616	2.7281	2.4
3.138 3	4.6624	2.7283	2.1
3.139 1	4.6632	2.7284	1.8
3.649 5	5.4098	3.0240	1.8
3.651 7	5.4247	3.0360[b]	12.5
3.773 5	5.5952	3.0906	0.2
3.784 0	5.6098	3.0951	−1.1
	$TmCl_3$ (from emf)		
0.005 00	—	0.8710	−1.5
0.010 00	—	0.8424	0.1
0.015 00	—	0.8251	0.7
0.020 00	—	0.8127	0.4
0.021 78	—	0.8089	0.1
	$TmCl_3$ vs. KCl		
0.124 85	0.218 51	0.7971[b]	14.6
0.154 17	0.271 85	0.7998[b]	9.6
0.238 95	0.435 71	0.8212	1.0
0.349 21	0.674 53	0.8665	−0.2
0.350 70	0.677 83	0.8670	−0.4
0.426 67	0.857 49	0.9012	−1.2
0.433 63	0.874 21	0.9040	−1.6
0.497 35	1.036 5	0.9353	−1.3
0.511 37	1.072 7	0.9417	−1.8
0.560 63	1.206 3	0.9671	−1.2
0.624 81	1.394 3	1.0055	3.7
0.665 73	1.512 6	1.0256	1.9
0.734 69	1.729 5	1.0667	5.0
0.784 87	1.887 7	1.0933	3.1
0.826 66	2.021 9	1.1150	0.6
0.866 41	2.153 1	1.1363	−1.6
0.906 98	2.296 5	1.1617	−0.6
0.962 07	2.493 5	1.1951	−1.0
0.973 03	2.534 9	1.2025	−0.4
1.062 9	2.872 4	1.2589	−1.0
1.065 4	2.883 9	1.2613	−0.2
1.075 7	2.919 5	1.2660	−2.2
1.161 9	3.265 5	1.3242	−0.7
1.169 3	3.295 5	1.3291	−0.7
1.254 9	3.653 2	1.3880	0.2
1.262 5	3.685 1	1.3931	0.0
1.368 8	4.151 2	1.4690	1.8
1.380 8	4.205 1	1.4777	2.1
1.480 6	4.666 0	1.5523	5.1
1.483 6	4.678 9	1.5541	4.8
	$TmCl_3$ vs. $CaCl_2$		
1.0629	1.4924	1.2591	−0.8
1.0757	1.5114	1.2666	−1.6
1.1619	1.6449	1.3238	−1.0
1.1693	1.6565	1.3289	−0.9
1.2549	1.7897	1.3872	−0.6
1.2625	1.8013	1.3922	−0.8
1.3688	1.9675	1.4665	−0.6
1.3808	1.9863	1.4750	−0.6
1.4317	2.0661	1.5113	−0.6
1.4806	2.1429	1.5466	−0.5
1.4836	2.1473	1.5484	−0.9
1.5158	2.1982	1.5722	−0.5
1.5716	2.2857	1.6128	−0.8
1.6536	2.4149	1.6737	−0.5
1.6985	2.4855	1.7072	−0.4
1.7922	2.6327	1.7776	−0.4
1.8554	2.7317	1.8252	−0.5
1.8701	2.7545	1.8361	−0.8
1.9387	2.8619	1.8881	−0.7
1.9551	2.8875	1.9005	−0.8
2.0203	2.9898	1.9507	−0.1
2.0355	3.0131	1.9618	−0.5
2.1055	3.1223	2.0153	−0.1
2.1269	3.1555	2.0315	−0.1
2.2275	3.3111	2.1076	−0.1
2.2533	3.3511	2.1272	0.2
2.3453	3.4923	2.1959	0.1
2.3553	3.5079	2.2037	0.4
2.4445	3.6445	2.2701	0.8
2.4466	3.6475	2.2714	0.6
2.5555	3.8129	2.3510	0.6
2.5573	3.8161	2.3528	1.2
2.6041	3.8855	2.3851	−0.3
2.6476	3.9536	2.4189	2.4
2.6516	3.9581	2.4201	0.8
2.6559	3.9635	2.4220	−0.4

Table III. Continued

m, $ReCl_3$	m, standard	ϕ, $ReCl_3$	$10^3\Delta\phi$
2.6995	4.0289	2.4528	−0.5
2.7441	4.0957	2.4840	−0.6
2.8443	4.2459	2.5539	−0.1
2.8944	4.3177	2.5850	−3.2
2.9884	4.4603	2.6511	−0.1
3.0303	4.5222	2.6785	−0.4
3.1092	4.6393	2.7301	−0.3
3.1728	4.7336	2.7709	−0.2
3.2221	4.8065	2.8019	−0.4
3.3687	5.0253	2.8935	0.4
3.3982	5.0689	2.9111	0.0
3.5741	5.3347	3.0170	0.9
3.5892	5.3572	3.0254	0.5
3.7182	5.5548	3.0999	−0.3
3.7281	5.5714	3.1067	0.8
3.8481	5.7607	3.1758	0.5
3.8647	5.7889	3.1867	1.8
3.8814	5.8103	3.1916	−3.0
	$YbCl_3$ (from emf)		
0.005 00	—	0.8704	0.1
0.010 00	—	0.8422	1.3
0.015 00	—	0.8255	1.8
0.020 00	—	0.8139	1.7
0.025 00	—	0.8050	1.1
0.030 00	—	0.7978	0.0
0.035 00	—	0.7918	−1.4
0.040 00	—	0.7865	−3.0
0.040 17	—	0.7864	−3.1
	$YbCl_3$ vs. KCl		
0.126 45	0.218 51	0.7870	−0.2
0.154 35	0.271 85	0.7989	4.5
0.238 22	0.435 71	0.8237	0.8
0.349 10	0.674 53	0.8668	−1.1
0.350 55	0.677 83	0.8674	−1.1
0.426 69	0.857 49	0.9011	−1.5
0.433 35	0.874 21	0.9046	−1.1
0.497 11	1.036 5	0.9357	−0.2
0.511 13	1.072 7	0.9421	−0.7
0.561 15	1.206 3	0.9662	−1.5
0.625 37	1.394 3	1.0046	3.6
0.666 29	1.512 6	1.0248	1.9
0.785 61	1.887 7	1.0923	2.8
0.827 38	2.021 9	1.1141	0.3
0.867 01	2.153 1	1.1355	−1.7
0.907 45	2.296 5	1.1611	−0.6
0.915 72	2.324 9	1.1657	−1.1
0.916 54	2.329 4	1.1670	−0.2
0.962 61	2.493 5	1.1944	−1.4
0.973 64	2.534 9	1.2017	−0.9
1.049 8	2.820 9	1.2499	−1.2
1.054 2	2.839 3	1.2535	−0.5
1.066 5	2.883 9	1.2600	−1.9
1.178 5	3.334 5	1.3359	−0.3
1.180 1	3.340 5	1.3367	−0.6
1.280 5	3.766 1	1.4072	1.0
1.284 3	3.782 9	1.4101	1.2
1.461 0	4.578 2	1.5391	4.4
1.467 3	4.607 2	1.5436	4.4
	$YbCl_3$ vs. $CaCl_2$		
1.0498	1.4735	1.2521	1.0
1.0542	1.4809	1.2557	1.7
1.1785	1.6716	1.3361	−0.1
1.1801	1.6741	1.3372	−0.1
1.2805	1.8315	1.4070	0.9
1.2843	1.8363	1.4084	−0.5
1.4303	2.0661	1.5128	0.4
1.4610	2.1141	1.5347	0.0
1.4673	2.1231	1.5382	−1.0
1.5145	2.1982	1.5735	−0.1
1.5702	2.2857	1.6142	−0.5
1.6518	2.4149	1.6755	0.1
1.6969	2.4855	1.7088	−0.4
1.7883	2.6284	1.7767	−1.7
1.7904	2.6327	1.7794	−0.6
1.8048	2.6548	1.7897	−1.2
1.8535	2.7317	1.8271	−0.9
1.8635	2.7465	1.8337	−1.9
1.8677	2.7545	1.8384	−0.3
1.8829	2.7771	1.8486	−1.8
1.9360	2.8619	1.8908	−0.2
1.9526	2.8875	1.9030	−0.6
1.9703	2.9147	1.9159	−1.2
2.0011	2.9629	1.9395	−1.2
2.0175	2.9898	1.9534	0.1
2.0325	3.0131	1.9647	0.0
2.1025	3.1223	2.0182	−0.1
2.1236	3.1555	2.0347	0.3
2.2237	3.3111	2.1112	0.5
2.2495	3.3511	2.1308	0.6
2.3409	3.4923	2.2000	0.7
2.3507	3.5079	2.2080	1.3
2.4398	3.6445	2.2745	1.1
2.4419	3.6475	2.2758	0.8
2.5503	3.8129	2.3558	0.7
2.5521	3.8161	2.3576	1.2
2.5721	3.8442	2.3697	−1.3
2.5989	3.8855	2.3899	−0.7
2.6073	3.8985	2.3962	−0.4
2.6423	3.9536	2.4238	1.8
2.6458	3.9581	2.4254	0.9
2.6505	3.9635	2.4270	−0.9
2.6838	4.0289	2.4671[b]	15.3
2.7233	4.0743	2.4800	−0.1
2.7375	4.0957	2.4900	−0.2
2.7514	4.1170	2.5002	0.2
2.8373	4.2459	2.5602	−0.3
2.8851	4.3177	2.5934	−0.2
2.8991	4.3395	2.6039	0.6
2.9200	4.3715	2.6189	1.3
2.9801	4.4603	2.6585	−0.1
3.0217	4.5222	2.6862	−0.5
3.0994	4.6393	2.7387	0.3
3.1629	4.7336	2.7796	−0.6
3.2118	4.8065	2.8109	−1.0
3.3569	5.0253	2.9037	−0.8
3.3857	5.0689	2.9218	−0.8
3.5588	5.3347	3.0299	0.2
3.5735	5.3572	3.0387	0.0
3.7003	5.5548	3.1148	−0.7
3.7101	5.5714	3.1217	0.3
3.8285	5.7607	3.1921	0.0
3.8447	5.7889	3.2033	1.6
3.9260	5.9216	3.2504	0.9
3.9291	5.9261	3.2517	0.3
4.0018	6.0455	3.2921	−1.6
	$LuCl_3$ (from emf)		
0.005 00	—	0.8705	−0.3
0.010 00	—	0.8412	−0.4
0.015 00	—	0.8253	0.5
0.020 00	—	0.8125	−1.0
0.025 00	—	0.8045	−0.9
0.030 00	—	0.7985	−1.0
	$LuCl_3$ vs. KCl		
0.125 07	0.218 51	0.7957	6.2
0.154 42	0.271 85	0.7985	1.4

Table III. Continued

m, $ReCl_3$	m, standard	ϕ, $ReCl_3$	$10^3\Delta\phi$
0.238 18	0.435 71	0.8238	−1.3
0.349 14	0.674 53	0.8667	−2.9
0.350 49	0.677 83	0.8675	−2.6
0.426 43	0.857 49	0.9017	−1.9
0.433 37	0.874 21	0.9046	−2.2
0.496 76	1.036 5	0.9364	−0.1
0.510 99	1.072 7	0.9424	−1.0
0.561 23	1.206 3	0.9661	−2.0
0.625 32	1.394 3	1.0047	3.7
0.666 21	1.512 6	1.0249	2.2
0.735 29	1.729 5	1.0658	5.4
0.786 09	1.887 7	1.0916	2.4
0.827 40	2.021 9	1.1140	0.9
0.867 13	2.153 1	1.1353	−1.3
0.907 59	2.296 5	1.1609	−0.2
0.962 67	2.493 5	1.1943	−0.7
0.973 49	2.534 9	1.2019	0.1
1.063 2	2.872 7	1.2586	−0.4
1.066 3	2.883 9	1.2603	−0.8
1.075 9	2.919 5	1.2657	−1.6
1.161 8	3.265 5	1.3243	0.0
1.169 3	3.295 5	1.3291	−0.2
1.254 7	3.653 2	1.3882	0.5
1.262 4	3.685 1	1.3932	0.1
1.368 5	4.151 2	1.4693	1.6
1.380 3	4.205 1	1.4782	2.1
1.480 0	4.666 0	1.5529	4.7
1.482 9	4.678 9	1.5548	4.5
	$LuCl_3$ vs. $CaCl_2$		
1.0632	1.4924	1.2587	−0.4
1.0759	1.5114	1.2663	−1.0
1.1618	1.6449	1.3240	−0.3
1.1693	1.6565	1.3289	−0.4
1.2547	1.7897	1.3875	−0.3
1.2624	1.8013	1.3923	−0.8
1.3685	1.9675	1.4668	−0.9
1.3803	1.9863	1.4756	−0.6
1.4310	2.0661	1.5121	−0.5
1.4800	2.1429	1.5472	−1.0
1.4829	2.1473	1.5492	−1.2
1.5150	2.1982	1.5730	−0.9
1.5705	2.2857	1.6139	−0.9
1.6523	2.4149	1.6750	−0.9
1.6971	2.4855	1.7086	−1.0
1.7906	2.6327	1.7792	−1.3
1.8535	2.7317	1.8271	−1.3
1.8680	2.7545	1.8381	−1.3
1.9361	2.8619	1.8907	−0.9
1.9524	2.8875	1.9032	−0.9
2.0173	2.9898	1.9536	−0.2
2.0327	3.0131	1.9645	−1.1
2.1022	3.1223	2.0185	−0.4
2.1235	3.1555	2.0348	−0.4
2.2234	3.3111	2.1114	0.0
2.2493	3.3511	2.1310	−0.2
2.3403	3.4923	2.2006	0.5
2.3503	3.5079	2.2084	0.7
2.4385	3.6445	2.2757	1.8
2.4408	3.6475	2.2768	1.2
2.5485	3.8129	2.3574	2.0
2.5503	3.8161	2.3592	2.5
2.5983	3.8855	2.3904	−1.6
2.6398	3.9536	2.4261	3.9
2.6437	3.9581	2.4274	2.3
2.6495	3.9635	2.4279	−1.4
2.6929	4.0289	2.4588	−1.8
2.7367	4.0957	2.4908	−1.3
2.8359	4.2459	2.5615	−0.9
2.8837	4.3177	2.5946	−1.2
2.9783	4.4603	2.6601	−1.0
3.0194	4.5222	2.6882	−1.0
3.0963	4.6393	2.7414	0.4
3.1589	4.7336	2.7831	0.3
3.2075	4.8065	2.8146	−0.1
3.3517	5.0253	2.9082	−0.1
3.3805	5.0689	2.9263	−0.5
3.5519	5.3347	3.0358	0.8
3.5671	5.3572	3.0441	−0.4
3.6927	5.5548	3.1213	−1.3
3.7023	5.5714	3.1283	−0.1
3.8063	5.7414	3.1936	1.1
3.8187	5.7607	3.2002	0.1
3.8354	5.7889	3.2111	0.7
3.9149	5.9216	3.2596	0.4
3.9178	5.9261	3.2610	0.1
3.9902	6.0493	3.3048	−0.6
4.0015	6.0699	3.3126	0.2
4.1239	6.2867	3.3871	−0.4
	YCl_3 (from emf)		
0.005 00	—	0.8710	−1.8
0.010 00	—	0.8425	−1.5
0.015 00	—	0.8277	0.6
0.020 00	—	0.8170	1.2
0.025 00	—	0.8093	1.8
0.030 00	—	0.8019	0.6
	YCl_3 vs. KCl		
0.071 00	0.1237	0.8028[b,c]	19.7
0.114 8	0.1974	0.7847[c]	−1.3
0.134 7	0.2312	0.7809[b,c]	−9.2
0.136 6	0.2372	0.7896[c]	−0.9
0.195 7	0.3494	0.8065[c]	−1.4
0.226 6	0.4118	0.8190[c]	0.2
0.316 5	0.6055	0.8588[c]	3.9
0.356 7	0.6927	0.8711[c]	−1.4
0.471 5	0.9721	0.9249[c]	−1.5
0.544 9	1.1667	0.9620[c]	−1.3
0.595 06	1.3112	0.9917	2.2
0.596 41	1.3152	0.9925	2.4
0.633 7	1.4169	1.0078[c]	−2.3
0.761 7	1.8067	1.0764[c]	−5.0
0.772 23	1.8520	1.0894	1.8
0.779 67	1.8751	1.0930	1.1
0.786 06	1.8967	1.0971	1.5
0.793 82	1.9239	1.1025	2.5
0.911 4	2.3147	1.1658[c]	−4.4
0.960 15	2.4891	1.1952	−5.0
1.033 7	2.7652	1.2424[c]	−4.0
1.124 0	3.1241	1.3041[c]	−0.6
1.305 1	3.8920	1.4326[c]	6.4
1.406 1	4.3252	1.4984	2.2
1.415 8	4.3656	1.5040	1.0
1.416 4	4.3663	1.5036[c]	0.2
1.435 3	4.4511	1.5168	0.1
1.459 3	4.5676	1.5368	3.1
1.511 8	4.8040	1.5723[c]	1.3
	YCl_3 vs. $CaCl_2$		
0.772 13	1.0588	1.0904	2.9
0.779 67	1.0684	1.0925	0.7
0.786 06	1.0777	1.0959	0.3
0.793 82	1.0903	1.1017	1.6
1.559 9	2.2668	1.6036	−1.9
1.561 6	2.2723	1.6080	1.3
1.714 1	2.5065	1.7150	−2.8
1.719 1	2.5143	1.7186	−2.8

Table III. Continued

m, $ReCl_3$	m, standard	ϕ, $ReCl_3$	$10^3\Delta\phi$	m, $ReCl_3$	m, standard	ϕ, $ReCl_3$	$10^3\Delta\phi$
1.724 4	2.5228	1.7228	−2.5	3.026 6	4.5068	2.6658	0.0
1.730 4	2.5323	1.7274	−2.3	3.029 0	4.5101	2.6671	−0.3
2.120 5	3.1401	2.0207	0.4	3.034 4	4.5190	2.6716	0.7
2.224 3	3.2999	2.0982	0.5	3.041 2	4.5290	2.6760	0.7
2.265 0	3.3632	2.1295	1.4	3.053 1	4.5464	2.6835	0.5
2.297 2	3.4136	2.1546	2.6	3.065 8	4.5653	2.6919	0.6
2.587 7	3.8826	2.3970[b]	32.7	3.131 0	4.6616	2.7339	0.8
2.869 0	4.2714	2.5588	−2.1	3.132 0	4.6624	2.7338	0.2
2.897 9	4.3144	2.5784	−2.0	3.132 9	4.6632	2.7338	−0.4
2.959 6	4.4073	2.6212	−0.5	3.947 8	5.8941	3.2091	0.0

[a] Data of Heiser (*5*); [b] Entry not used in the least-squares fits. [c] Data of Mason (*7*).

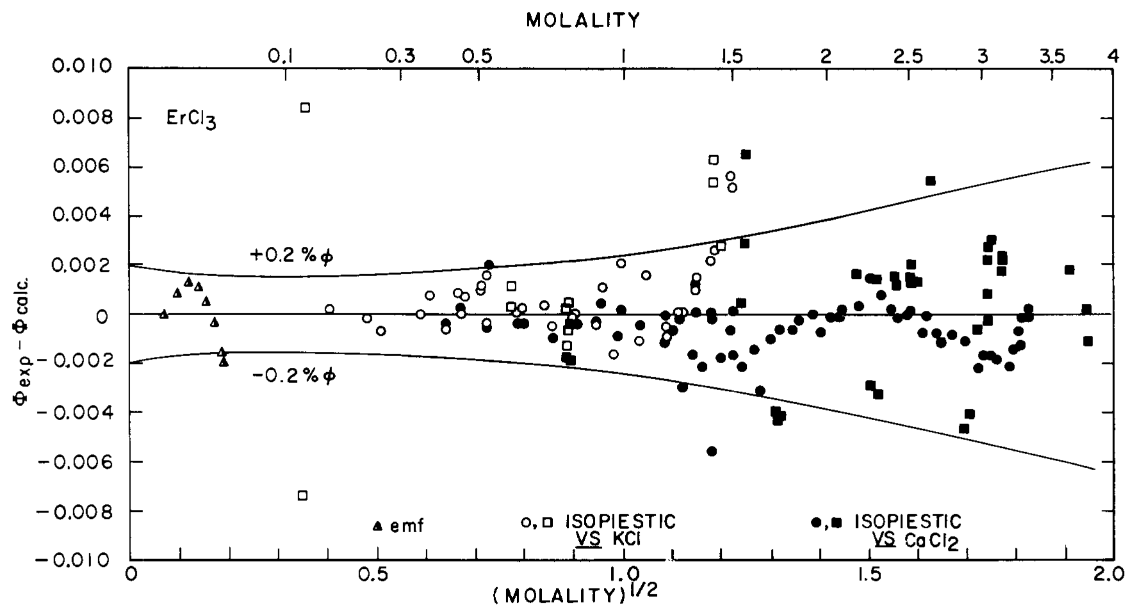

Figure 2. Differences between experimental and calculated osmotic coefficients of $ErCl_3$ at 25 °C. Circles represent set 1 while squares represent set 2.

As mentioned above, the concentration uncertainties of the stock solutions are 0.05% (which decreases to about 0.02% for the most dilute rare earth chloride solutions) and the isopiestic equilibrations were made to at least 0.1% above 0.5 m and to 0.15% below this concentration. The above uncertainties limit the ultimate precision to which the data reported here can be used to yield osmotic and activity coefficients. Assuming the maximum errors above for both rare earth chloride and standard solutions, rare earth chloride osmotic coefficients resulting from these data would be uncertain to 0.3% above 0.5 m and 0.34% below this concentration with the probable errors about two-thirds of these values. The scatter for $ErCl_3$ set 2 and YCl_3 is somewhat larger than this, about 0.5% at high concentrations.

In obtaining smoothed osmotic coefficients and activity coefficients, consideration must also be made of the reliability of the fits and of the dilute solution emf data since they influence these fits. Inspection of these emf data with regard to scatter and series trends indicates that dilute solution osmotic coefficients calculated from them are reliable to about 0.5%. However, their uncertainties have little effect on the results above 0.1 m so the uncertainties from the fits are about 0.1–0.2% for the osmotic coefficients and 0.3–0.4% for the activity coefficients. Including the concentration uncertainties, this indicates that our smoothed osmotic coefficients should be known to about 0.4–0.5% and the activity coefficients to about 0.6–0.7%. The exceptions are Ho, Tm, and Yb since, as mentioned previously, they do not connect up as well with the dilute solution emf data. For these salts the osmotic coefficients are uncertain to about 0.7% below 0.5 m and 0.5% above this concentration. The activity coefficients are uncertain to about 1.0% above 0.1 m for these three salts. Also, ϕ and $\gamma_\pm$ for YCl_3 are known only to about 1.0% due to the larger scatter. Since there is a gap in the YCl_3 data between 3.13 and 3.95 m (saturated solution), the errors in these properties may be larger above 3.1 m for this salt.

To test the reproducibility of the experimental procedure two separate KCl, $CaCl_2$, and $ErCl_3$ solutions were prepared and analyzed by different workers. Isopiestic measurements were then performed using these different solutions. In Figure 2 the differences between the experimental and calculated osmotic coefficients of $ErCl_3$ for these two sets of data are shown as a function of the square root of the molality. The two sets of data agree within the error limits quoted above. The emf based osmotic coefficients appear to deviate in a smooth fashion since the original emf data were smoothed in the process of calculating the ϕ's. Figure 3 is a similar plot for $EuCl_3$. This plot and similar ones for the other rare earth chlorides indicate that discrepancies exist between the osmotic coefficients of the standards KCl and $CaCl_2$ in the overlap region.

The osmotic coefficients of Robinson (*14*), Mason (*7, 8*), and Mason and Ernst (*9*) agree with those reported here within 0.4–0.7% for La, Pr, and Nd and about 1.1% for Sm and Eu.

Table IV. Parameters for Equations 10 and 11

i	r_i	A_i	r_i	A_i
		$LaCl_3$		$PrCl_3$
1	0.75	−7.399 06	0.75	−8.927 51
2	0.875	47.172 41	0.875	53.157 73
3	1	−61.405 60	1	−69.632 31
4	1.125	24.708 09	1.125	28.830 48
5	3	−0.046 135	1.5	−0.362 784
6	4	2.632 1 × 10^{-3}	3	−2.800 4 × 10^{-2}
7	9	3.405 1 × 10^{-7}	9	4.016 2 × 10^{-7}
S.D.		0.001 6		0.001 7
		$NdCl_3$		$SmCl_3$
1	0.75	−12.002 70	0.75	−13.102 58
2	0.875	63.657 55	0.875	69.304 94
3	1	−81.106 48	1	−90.219 68
4	1.125	32.595 60	1.125	37.396 27
5	2.5	−0.109 547	2	−0.326 974
6	3	4.488 9 × 10^{-3}	7	−1.434 3 × 10^{-4}
7	9.5	1.155 0 × 10^{-7}	7.5	6.705 4 × 10^{-5}
S.D.		0.001 4		0.001 2
		$EuCl_3$		$GdCl_3$
1	0.75	−13.713 50	0.75	−14.653 42
2	0.875	71.128 79	0.875	75.426 52
3	1	−91.876 66	1	−98.221 74
4	1.125	37.825 99	1.125	40.910 88
5	2	−0.294 883	2	−0.384 440
6	3.5	−4.433 7 × 10^{-3}	8	−3.147 2 × 10^{-5}
7	12	7.118 1 × 10^{-9}	8.5	1.537 9 × 10^{-5}
S.D.		0.001 3		0.001 9
		$TbCl_3$		$DyCl_3$
1	0.75	−12.159 28	0.75	−10.343 98
2	0.875	67.023 53	0.875	61.969 94
3	1	−88.738 20	1	−85.959 32
4	1.125	37.320 34	1.125	38.868 95
5	2	−0.356 873	1.5	−1.438 954
6	7.5	−1.349 7 × 10^{-5}	5	−4.503 6 × 10^{-3}
7	11.5	4.559 0 × 10^{-8}	5.5	1.828 3 × 10^{-3}
S.D.		0.001 9		0.001 7
		$HoCl_3$		$ErCl_3$
1	0.75	−4.962 48	0.75	−9.598 87
2	0.875	37.404 59	0.875	56.733 58
3	1	−47.749 62	1	−74.847 03
4	1.125	18.210 42	1.125	31.017 66
5	2	0.275 104	2	−0.203 421
6	3	−8.366 5 × 10^{-2}	4	−2.956 9 × 10^{-3}
7	4	5.679 7 × 10^{-3}	10	1.487 2 × 10^{-7}
S.D.		0.002 3		0.002 2
		$TmCl_3$		$YbCl_3$
1	0.75	−3.705 01	0.75	−7.824 86
2	0.875	31.976 34	0.875	48.116 53
3	1	−40.914 89	1	−61.726 08
4	1.125	15.669 00	1.125	24.549 08
5	2.5	0.100 555	3.5	−0.014 418
6	4	−3.809 9 × 10^{-2}	8.5	3.551 9 × 10^{-6}
7	4.5	1.291 0 × 10^{-2}	12	−8.874 0 × 10^{-9}
S.D.		0.001 5		0.001 4
		$LuCl_3$		YCl_3
1	0.75	−8.138 50	0.75	−8.597 86
2	0.875	49.562 05	0.875	54.552 08
3	1	−63.707 13	1	−75.578 79
4	1.125	25.398 94	1.125	33.943 37
5	3.5	−0.015 859	1.5	−1.211 852
6	7.5	1.855 8 × 10^{-5}	5.5	−1.042 9 × 10^{-3}
7	10	−1.732 5 × 10^{-7}	6.5	1.845 5 × 10^{-4}
S.D.		0.001 7		0.002 3

Table V. Osmotic Coefficients, Water Activities, and Activity Coefficients at Even Molalities

m	ϕ	a_1	$\gamma_\pm$
		$LaCl_3$	
0.1	0.7760	0.994 42	0.3312
0.2	0.7953	0.988 60	0.2905
0.3	0.8267	0.982 29	0.2775
0.4	0.8637	0.975 41	0.2753
0.5	0.9046	0.967 93	0.2794
0.6	0.9487	0.959 81	0.2881
0.7	0.9958	0.951 01	0.3006
0.8	1.0454	0.941 5	0.3168
0.9	1.0974	0.931 3	0.3364
1.0	1.1514	0.920 4	0.3598
1.2	1.2644	0.896 4	0.4182
1.4	1.3825	0.869 8	0.4945
1.6	1.5035	0.840 8	0.5921
1.8	1.6257	0.809 9	0.7150
2.0	1.7473	0.777 4	0.8679
2.2	1.8666	0.743 8	1.056
2.4	1.9821	0.709 8	1.284
2.6	2.0927	0.675 6	1.559
2.8	2.1973	0.641 9	1.884
3.0	2.2953	0.608 8	2.265
3.2	2.3865	0.576 8	2.705
3.4	2.4710	0.545 9	3.210
3.6	2.5498	0.516 1	3.786
3.8	2.6248	0.487 4	4.447
3.8944	2.6597	0.474 1	4.794
		$PrCl_3$	
0.1	0.7773	0.994 41	0.3298
0.2	0.7985	0.988 56	0.2902
0.3	0.8311	0.982 19	0.2780
0.4	0.8687	0.975 27	0.2763
0.5	0.9099	0.967 75	0.2809
0.6	0.9541	0.959 59	0.2899
0.7	1.0011	0.950 76	0.3028
0.8	1.0506	0.941 2	0.3192
0.9	1.1026	0.931 0	0.3392
1.0	1.1566	0.920 0	0.3630
1.2	1.2704	0.896 0	0.4227
1.4	1.3901	0.869 1	0.5012
1.6	1.5142	0.839 8	0.6026
1.8	1.6409	0.808 3	0.7319
2.0	1.7683	0.775 0	0.8954
2.2	1.8949	0.740 5	1.100
2.4	2.0191	0.705 3	1.354
2.6	2.1393	0.669 8	1.664
2.8	2.2544	0.634 5	2.040
3.0	2.3631	0.600 0	2.489
3.2	2.4650	0.566 4	3.020
3.4	2.5597	0.534 1	3.639
3.6	2.6478	0.503 1	4.355
3.8	2.7307	0.473 4	5.184
3.8969	2.7697	0.459 4	5.633
		$NdCl_3$	
0.1	0.7767	0.994 42	0.3238
0.2	0.7985	0.988 56	0.2850
0.3	0.8307	0.982 20	0.2729
0.4	0.8678	0.975 30	0.2711
0.5	0.9086	0.967 79	0.2753
0.6	0.9528	0.959 64	0.2841
0.7	1.0001	0.950 80	0.2968
0.8	1.0502	0.941 3	0.3130
0.9	1.1029	0.931 0	0.3329
1.0	1.1579	0.919 9	0.3566
1.2	1.2740	0.895 7	0.4164
1.4	1.3963	0.868 6	0.4954
1.6	1.5232	0.838 9	0.5978
1.8	1.6526	0.807 1	0.7291
2.0	1.7829	0.773 4	0.8958
2.2	1.9126	0.738 4	1.105
2.4	2.0401	0.702 7	1.367
2.6	2.1640	0.666 7	1.690
2.8	2.2834	0.630 8	2.085
3.0	2.3971	0.595 6	2.563
3.2	2.5047	0.561 3	3.134
3.4	2.6056	0.528 1	3.809
3.6	2.7003	0.496 3	4.602
3.8	2.7895	0.465 9	5.529
3.9307	2.8456	0.446 6	6.220
		$SmCl_3$	
0.1	0.7800	0.994 39	0.3271
0.2	0.8021	0.988 51	0.2888
0.3	0.8351	0.982 11	0.2771
0.4	0.8733	0.975 14	0.2760
0.5	0.9155	0.967 55	0.2811
0.6	0.9610	0.959 30	0.2909
0.7	1.0096	0.950 35	0.3046
0.8	1.0610	0.940 7	0.3221
0.9	1.1148	0.930 2	0.3435
1.0	1.1709	0.919 1	0.3688
1.2	1.2888	0.894 5	0.4325
1.4	1.4128	0.867 2	0.5166
1.6	1.5411	0.837 2	0.6258
1.8	1.6721	0.805 0	0.7661
2.0	1.8040	0.771 0	0.9447
2.2	1.9352	0.735 8	1.170
2.4	2.0639	0.699 8	1.452
2.6	2.1885	0.663 6	1.799
2.8	2.3078	0.627 7	2.224
3.0	2.4207	0.592 5	2.735
3.2	2.5268	0.558 4	3.345
3.4	2.6265	0.525 4	4.066
3.6	2.7217	0.493 6	4.922
3.6414	2.7411	0.487 1	5.119
		$EuCl_3$	
0.1	0.7814	0.994 38	0.3264
0.2	0.8056	0.988 46	0.2892
0.3	0.8401	0.982 00	0.2784
0.4	0.8795	0.974 97	0.2780
0.5	0.9228	0.967 30	0.2839
0.6	0.9695	0.958 95	0.2946
0.7	1.0193	0.949 88	0.3093
0.8	1.0718	0.940 1	0.3279
0.9	1.1269	0.929 5	0.3505
1.0	1.1843	0.918 2	0.3774
1.2	1.3049	0.893 3	0.4449
1.4	1.4316	0.865 5	0.5344
1.6	1.5624	0.835 1	0.6507
1.8	1.6956	0.802 6	0.8004
2.0	1.8293	0.768 3	0.9913
2.2	1.9618	0.732 7	1.232
2.4	2.0915	0.696 5	1.534
2.6	2.2170	0.660 1	1.908
2.8	2.3370	0.624 0	2.364
3.0	2.4505	0.588 7	2.916
3.2	2.5572	0.554 5	3.575
3.4	2.6577	0.521 4	4.357
3.5839	2.7464	0.492 0	5.208
		$GdCl_3$	
0.1	0.7833	0.994 37	0.3279
0.2	0.8075	0.988 43	0.2909
0.3	0.8424	0.981 95	0.2804
0.4	0.8827	0.974 88	0.2805
0.5	0.9272	0.967 14	0.2871
0.6	0.9753	0.958 71	0.2985

Table V. Continued

m	ϕ	a_1	$\gamma_\pm$
0.7	1.0266	0.949 53	0.3142
0.8	1.0809	0.939 6	0.3341
0.9	1.1377	0.928 9	0.3582
1.0	1.1968	0.917 4	0.3867
1.2	1.3208	0.892 1	0.4587
1.4	1.4508	0.863 8	0.5542
1.6	1.5848	0.833 0	0.6789
1.8	1.7212	0.799 9	0.8401
2.0	1.8580	0.765 1	1.047
2.2	1.9937	0.729 0	1.309
2.4	2.1267	0.692 3	1.640
2.6	2.2553	0.655 4	2.052
2.8	2.3781	0.618 9	2.558
3.0	2.4943	0.583 2	3.172
3.2	2.6035	0.548 6	3.910
3.4	2.7063	0.515 3	4.790
3.5898	2.8004	0.484 6	5.789
		$TbCl_3$	
0.1	0.7857	0.994 35	0.3353
0.2	0.8089	0.988 41	0.2976
0.3	0.8440	0.981 92	0.2870
0.4	0.8852	0.974 81	0.2876
0.5	0.9309	0.967 02	0.2948
0.6	0.9804	0.958 50	0.3072
0.7	1.0333	0.949 21	0.3242
0.8	1.0892	0.939 1	0.3456
0.9	1.1477	0.928 3	0.3716
1.0	1.2085	0.916 6	0.4023
1.2	1.3360	0.890 9	0.4801
1.4	1.4695	0.862 2	0.5836
1.6	1.6072	0.830 8	0.7195
1.8	1.7473	0.797 2	0.8962
2.0	1.8880	0.761 8	1.124
2.2	2.0277	0.725 1	1.416
2.4	2.1646	0.687 7	1.787
2.6	2.2969	0.650 3	2.250
2.8	2.4231	0.613 3	2.824
3.0	2.5415	0.577 3	3.521
3.2	2.6517	0.542 5	4.358
3.4	2.7546	0.509 2	5.356
3.5733	2.8409	0.481 2	6.384
		$DyCl_3$	
0.1	0.7866	0.994 35	0.3399
0.2	0.8105	0.988 39	0.3021
0.3	0.8466	0.981 87	0.2920
0.4	0.8885	0.974 72	0.2929
0.5	0.9346	0.966 89	0.3007
0.6	0.9843	0.958 33	0.3137
0.7	1.0373	0.949 02	0.3312
0.8	1.0932	0.938 9	0.3533
0.9	1.1519	0.928 0	0.3800
1.0	1.2130	0.916 3	0.4118
1.2	1.3416	0.890 5	0.4924
1.4	1.4773	0.861 5	0.6005
1.6	1.6181	0.829 8	0.7435
1.8	1.7618	0.795 7	0.9309
2.0	1.9064	0.759 8	1.174
2.2	2.0498	0.722 5	1.488
2.4	2.1902	0.684 7	1.887
2.6	2.3258	0.646 8	2.390
2.8	2.4552	0.609 3	3.016
3.0	2.5775	0.572 8	3.784
3.2	2.6924	0.537 5	4.717
3.4	2.8001	0.503 6	5.840
3.6	2.9020	0.471 0	7.188
3.6302	2.9170	0.466 2	7.414

m	ϕ	a_1	$\gamma_\pm$
		$HoCl_3$	
0.1	0.7878	0.994 34	0.3430
0.2	0.8142	0.988 33	0.3061
0.3	0.8518	0.981 75	0.2968
0.4	0.8942	0.974 55	0.2985
0.5	0.9405	0.966 68	0.3068
0.6	0.9902	0.958 09	0.3203
0.7	1.0430	0.948 75	0.3385
0.8	1.0990	0.938 6	0.3614
0.9	1.1577	0.927 7	0.3890
1.0	1.2190	0.915 9	0.4219
1.2	1.3486	0.889 9	0.5055
1.4	1.4855	0.860 8	0.6180
1.6	1.6278	0.828 9	0.7673
1.8	1.7733	0.794 5	0.9636
2.0	1.9201	0.758 3	1.220
2.2	2.0663	0.720 7	1.552
2.4	2.2102	0.682 3	1.979
2.6	2.3504	0.643 8	2.522
2.8	2.4855	0.605 6	3.206
3.0	2.6144	0.568 2	4.059
3.2	2.7363	0.532 1	5.109
3.4	2.8503	0.497 4	6.384
3.6	2.9561	0.464 5	7.912
3.6987	3.0052	0.448 9	8.767
		$ErCl_3$	
0.1	0.7868	0.994 35	0.3386
0.2	0.8116	0.988 37	0.3013
0.3	0.8481	0.981 83	0.2915
0.4	0.8902	0.974 67	0.2927
0.5	0.9366	0.966 82	0.3006
0.6	0.9867	0.958 23	0.3138
0.7	1.0402	0.948 88	0.3317
0.8	1.0967	0.938 7	0.3541
0.9	1.1560	0.927 8	0.3814
1.0	1.2180	0.916 0	0.4138
1.2	1.3486	0.889 9	0.4963
1.4	1.4868	0.860 7	0.6075
1.6	1.6305	0.828 6	0.7555
1.8	1.7780	0.794 0	0.9511
2.0	1.9273	0.757 5	1.208
2.2	2.0766	0.719 5	1.543
2.4	2.2240	0.680 7	1.976
2.6	2.3678	0.641 7	2.531
2.8	2.5065	0.603 1	3.234
3.0	2.6388	0.565 3	4.114
3.2	2.7640	0.528 7	5.204
3.4	2.8823	0.493 5	6.542
3.6	2.9949	0.459 8	8.180
3.7840	3.0962	0.429 9	10.02
		$TmCl_3$	
0.1	0.7780	0.994 41	0.3342
0.2	0.8054	0.988 46	0.2966
0.3	0.8452	0.981 89	0.2873
0.4	0.8899	0.974 68	0.2890
0.5	0.9378	0.966 77	0.2974
0.6	0.9887	0.958 15	0.3108
0.7	1.0424	0.948 77	0.3287
0.8	1.0989	0.938 6	0.3510
0.9	1.1581	0.927 6	0.3781
1.0	1.2198	0.915 9	0.4102
1.2	1.3504	0.889 8	0.4921
1.4	1.4893	0.860 5	0.6030
1.6	1.6345	0.828 2	0.7513
1.8	1.7839	0.793 4	0.9482
2.0	1.9354	0.756 6	1.208

Table V. Continued

m	ϕ	a_1	$\gamma_\pm$
2.2	2.0869	0.718 3	1.547
2.4	2.2365	0.679 2	1.988
2.6	2.3824	0.639 9	2.555
2.8	2.5235	0.601 0	3.276
3.0	2.6589	0.562 8	4.186
3.2	2.7884	0.525 7	5.325
3.4	2.9121	0.489 9	6.742
3.6	3.0313	0.455 5	8.501
3.8	3.1475	0.422 4	10.69
3.8814	3.1946	0.409 2	11.73
	$YbCl_3$		
0.1	0.7822	0.994 38	0.3334
0.2	0.8090	0.988 41	0.2966
0.3	0.8472	0.981 85	0.2872
0.4	0.8904	0.974 66	0.2886
0.5	0.9374	0.966 79	0.2967
0.6	0.9877	0.958 19	0.3098
0.7	1.0412	0.948 83	0.3275
0.8	1.0977	0.938 7	0.3498
0.9	1.1572	0.927 7	0.3767
1.0	1.2193	0.915 9	0.4089
1.2	1.3508	0.889 8	0.4910
1.4	1.4906	0.860 4	0.6023
1.6	1.6368	0.828 0	0.7514
1.8	1.7872	0.793 1	0.9495
2.0	1.9399	0.756 1	1.211
2.2	2.0926	0.717 7	1.555
2.4	2.2437	0.678 4	2.001
2.6	2.3913	0.638 9	2.578
2.8	2.5344	0.599 7	3.314
3.0	2.6720	0.561 2	4.248
3.2	2.8043	0.523 8	5.425
3.4	2.9316	0.487 6	6.900
3.6	3.0549	0.452 7	8.747
3.8	3.1751	0.419 2	11.06
4.0	3.2926	0.387 1	13.95
4.0018	3.2937	0.386 8	13.98
	$LuCl_3$		
0.1	0.7848	0.994 36	0.3358
0.2	0.8115	0.988 37	0.2992
0.3	0.8491	0.981 81	0.2898
0.4	0.8917	0.974 62	0.2912
0.5	0.9380	0.966 77	0.2992
0.6	0.9879	0.958 19	0.3123
0.7	1.0410	0.948 84	0.3301
0.8	1.0972	0.938 7	0.3524
0.9	1.1565	0.927 7	0.3795
1.0	1.2185	0.915 9	0.4118
1.2	1.3501	0.889 8	0.4944
1.4	1.4903	0.860 4	0.6066
1.6	1.6368	0.828 0	0.7571
1.8	1.7876	0.793 0	0.9571
2.0	1.9406	0.756 0	1.221
2.2	2.0936	0.717 5	1.568
2.4	2.2450	0.678 2	2.020
2.6	2.3932	0.638 7	2.603
2.8	2.5371	0.599 3	3.351
3.0	2.6760	0.560 7	4.301
3.2	2.8099	0.523 1	5.502
3.4	2.9392	0.486 7	7.016
3.6	3.0650	0.451 5	8.921
3.8	3.1886	0.417 6	11.33
4.0	3.3114	0.385 0	14.37
4.1239	3.3875	0.365 4	16.66
		YCl_3	
0.1	0.7838	0.994 37	0.3383
0.2	0.8094	0.988 40	0.3007
0.3	0.8479	0.981 84	0.2913
0.4	0.8922	0.974 61	0.2932
0.5	0.9405	0.966 68	0.3020
0.6	0.9921	0.958 01	0.3159
0.7	1.0465	0.948 58	0.3346
0.8	1.1037	0.938 4	0.3578
0.9	1.1632	0.927 3	0.3857
1.0	1.2251	0.915 5	0.4188
1.2	1.3550	0.889 4	0.5025
1.4	1.4919	0.860 3	0.6149
1.6	1.6345	0.828 2	0.7643
1.8	1.7811	0.793 7	0.9617
2.0	1.9301	0.757 2	1.221
2.2	2.0796	0.719 1	1.561
2.4	2.2279	0.680 2	2.001
2.6	2.3731	0.641 1	2.568
2.8	2.5137	0.602 2	3.289
3.0	2.6484	0.564 1	4.197
3.2	2.7764	0.527 2	5.327
3.4	2.8978	0.491 6	6.723
3.6	3.0136	0.457 6	8.441
3.8	3.1260	0.424 9	10.56
3.9478	3.2092	0.401 3	12.47

Some of these differences may arise from Mason's method of solution preparation (anhydrous salt added to water) which has been shown to result in the formation of small amounts of basic species in solution (*20*). Their largest source of error, however, is probably the purity of their rare earths since rare earth samples generally contained considerable amounts of other rare earths before ion-exchange separation methods were perfected. In spite of this, all of their data agree with ours to within 2.2 times our experimental error.

When comparing water activities and osmotic and activity coefficients for the various rare earth chlorides, the above sources of error are the major ones that need to be considered. When comparing the results of this study to data obtained using different experimental methods, the uncertainty in the isopiestic standards' osmotic coefficients also needs to be considered. Examination of Hamer and Wu's results (*4*) and comparison to similar reviews indicate the osmotic coefficients of KCl are known to about 0.1–0.2% at all concentrations. Our examination of the $CaCl_2$ osmotic coefficients indicates that they are uncertain to 0.3–0.4% below 2.5 m and may have larger errors above this concentration. Examination of deviation plots for the various rare earth chlorides (see Figures 2 and 3) indicates that mismatches occur when the isopiestic standards were changed from KCl to $CaCl_2$. If more reliable $CaCl_2$ osmotic coefficient data were to become available, their use should result in the reduction of the standard deviations for eq 10 by 10–40% for the salts reported here.

Results

Figure 4 is a plot of the mean molal activity coefficients of La, Tb, and Lu chlorides as a function of the molality. The activity coefficients start out at a value of one at infinite dilution and decrease to values of 0.27–0.29 by 0.3–0.4 m. After going through a flat minimum, the activity coefficients begin to increase and reach values of 4.8–16.7 by saturation. Figure 5 is a similar plot for the osmotic coefficients. The osmotic coefficients decrease from one at infinite dilution, reach a minimum value of 0.7–0.8 by 0.1 m, and then increase to values of 2.6–3.4 by

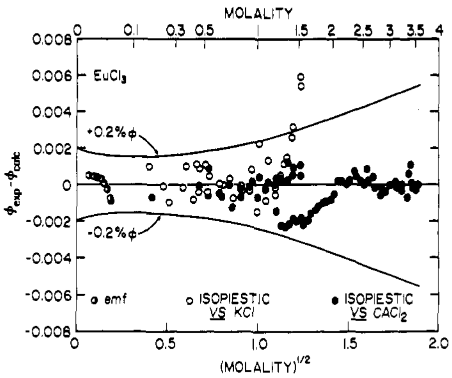

Figure 3. Differences between experimental and calculated osmotic coefficients of $EuCl_3$ at 25 °C.

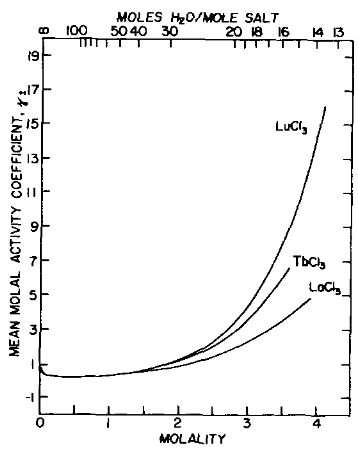

Figure 4. Mean molal activity coefficients of $LaCl_3$, $TbCl_3$, and $LuCl_3$ solutions at 25 °C.

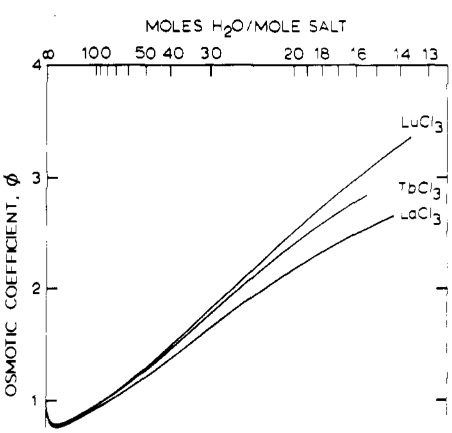

Figure 5. Osmotic coefficients of $LaCl_3$, $TbCl_3$, and $LuCl_3$ solutions at 25 °C.

saturation. In Figure 6 the water activities of the same three rare earth chlorides are shown as a function of the molality. The water activities decrease regularly from their values of one at infinite dilution to values of 0.37–0.49 by saturation. This decrease is more rapid above 1–1.5 *m* than it is at lower concentrations. The shapes of these curves are typical for strong electrolytes.

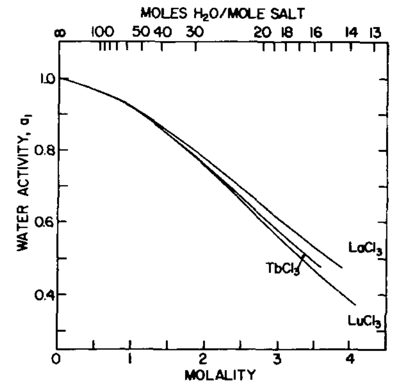

Figure 6. Water activities of $LaCl_3$, $TbCl_3$, and $LuCl_3$ solutions at 25 °C.

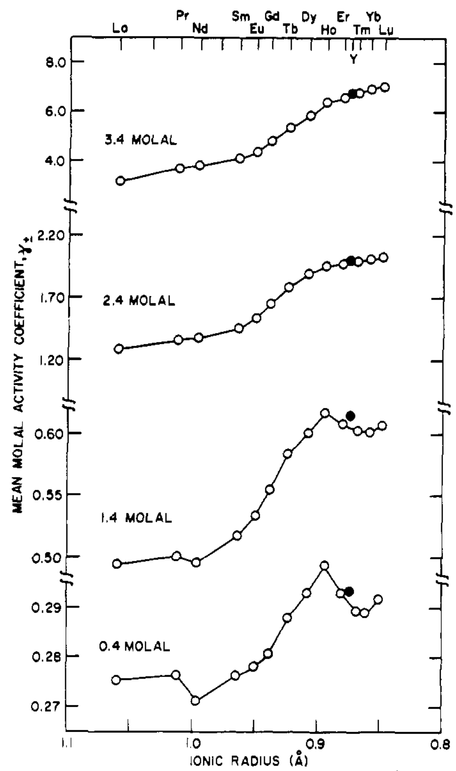

Figure 7. Mean molal activity coefficients of rare earth chloride solutions at constant molalities.

The initial decreases in $\gamma_\pm$, ϕ, and a_1 can be qualitatively accounted for in terms of the electrostatic interactions present in these solutions (Debye–Huckel theory) and the formation of small amounts of ion-pairs. At higher concentrations of rare earth chloride large amounts of water become tied up by the ions and by solvent separated ion-pairs resulting in an increase in $\gamma_\pm$ and a decrease in a_1 for each of the salts.

Because of limitations on the size of graphs allowed here, it would be of little advantage to plot results for more rare earth chlorides in Figures 4–6. Consequently, in order to illustrate the small but real differences between the various rare earth chlorides, constant molality plots of $\gamma_\pm$, ϕ, and a_1 are given vs. the ionic radii of Templeton and Dauben (*29*) in Figures 7–9 at 0.4, 1.4, 2.4, and 3.4 *m*. The radius of yttrium was taken from Zachariasen (*30*). According to Hinchey and Cobble (*6*), Zachariasen's radius for yttrium is consistent with Templeton and Dauben's values for the other rare earths. It is known that the position of yttrium in the rare earth series changes with the property since it has one less completed electron shell than the

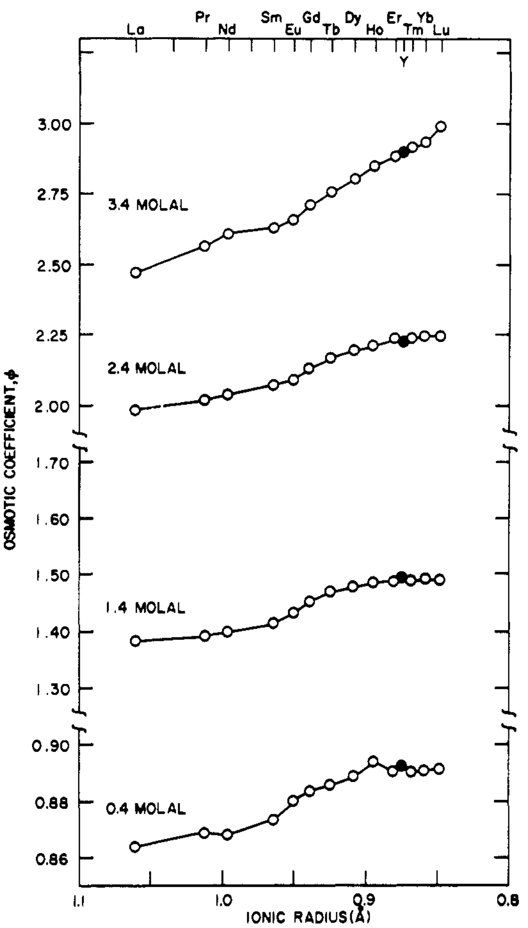

Figure 8. Osmotic coefficients of rare earth chloride solutions at constant molalities.

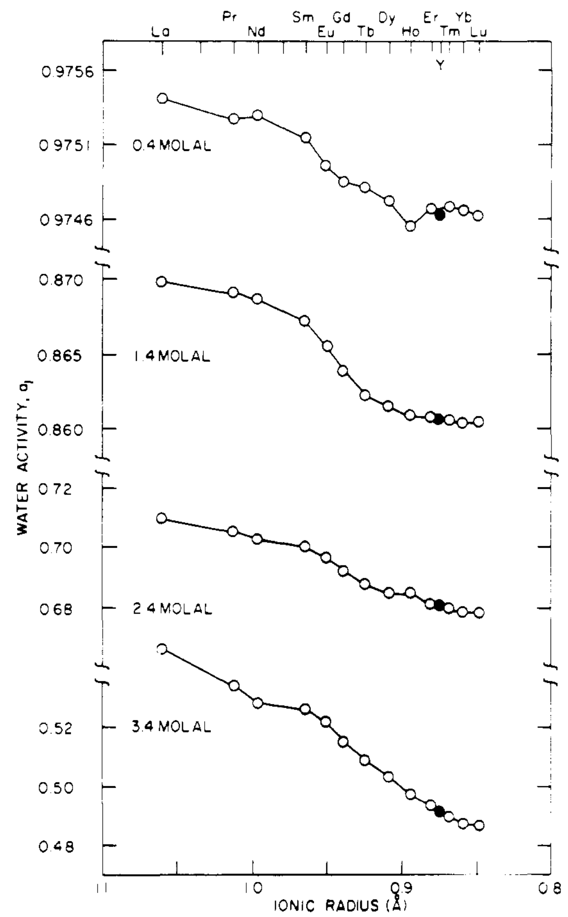

Figure 9. Water activities of rare earth chloride solutions at constant molalities.

lanthanides. For volume properties it falls between Tb and Dy (*24*).

Series plots for $\gamma_\pm$ at various concentrations are shown in Figure 7. It should be noted that these curves are S shaped with some modification occurring with increasing concentration. The jagged appearance of the curve at 0.4 *m* is mainly due to the uncertainties in the dilute osmotic coefficients obtained from emf measurements. In Figures 8 and 9 similar plots are shown for ϕ and a_1. These curves are also S shaped at low and moderate concentrations. At high concentrations the shapes become modified with a_1 decreasing from La to Nd and for Sm to Lu. In addition, the water activities of Sm through Lu are displaced relative to the light rare earth chlorides. A related effect is observed for the osmotic coefficients, and the relative viscosities (*26*) also show changes of the same type.

As the lanthanide contraction occurs, the radius of the trivalent cation decreases and its surface charge density increases across the rare earth series. The net result is an increase in the total number of waters associated with the cation across the rare earth series, giving rise to the increasing viscosities (*26*), the decreasing electrical conductances (*23*), and the decreasing water activities. From consideration of partial molal volume data (*20*), it has been suggested that a decrease in the inner sphere hydration number begins to occur when a critical radius size is reached at Nd and this hydration change is complete by Tb. The displacement of the trend in a_1 for the light rare earths from the trend in a_1 for the heavy rare earths indicates that the total hydration is greater for the rare earths with the lower inner sphere hydration number than for those with the higher inner sphere hydration number. In the electrical conductance paper (*23*) it was concluded that the effect of ion-pair formation appears to be about the same for all of the rare earth chlorides. The same appears to be true for the water activities and the activity coefficients although some of the high concentration changes in series trends may be influenced by differences in the amount of complex formation for the various rare earth chlorides.

The water activities at low and moderate concentrations form S shaped curves across the rare earth series and so must the partial molal free energies of water in these solutions. However, the relative partial molal enthalpies (*1, 11*) and the partial molal volumes of water (*24*) show distinct breaks at Nd and Tb at low and moderate concentrations. These breaks imply that although the free energy of water in these solutions depends mainly on the total hydration of the cation, its temperature and pressure derivatives are more sensitive to changes in the inner hydration sphere. Similar considerations hold for the partial molal properties of the solute although changes in the standard states of the rare earth ions also need to be taken into account for the free energies and enthalpies. The excess free energies and entropies for these solutions will be discussed in a separate paper, after the enthalpies of dilution of these solutions have been reported.

Acknowledgments

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Supplementary Material Available: Table I (12 pages). Ordering information is given on any current masthead page.

Three-Phase Solid–Liquid–Vapor Equilibria of Binary-*n*-Alkane Systems (Ethane–*n*-Octane, Ethane–*n*-Decane, Ethane–*n*-Dodecane)

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Pressure–temperature profiles along with liquid compositions and molar volumes are presented for three *n*-alkane solutes with ethane as a common solvent. The data were taken employing cryoscopic techniques over a liquid compositional range from solute-rich solutions to very dilute solute solutions. The liquid compositional data when represented as logarithm of composition vs. T_{FUS}/T (where T_{FUS} = freezing temperature of each pure solute) are smooth curves which become quite linear in the dilute solute range. The standard deviations of the liquid composition data are 0.67% for *n*-octane, 0.84% for *n*-decane, and 2.04% for *n*-dodecane.

Solid solubility data of hydrocarbon components in low molecular weight solvents are relatively rare compared to the amount of data available on the vapor–liquid behavior of such systems. Solid solubility data are quite important for use in the design of liquefaction, vaporization, and transport systems for liquefied natural gas (LNG) and liquefied petroleum gas (LPG). Kurata (*5*) has reviewed and summarized most of the experimental data on solid solubility of hydrocarbons in liquefied methane. The best recent data on the solid solubility of hydrocarbons in methane are those of Kuebler and McKinley (*2, 3*). Luks et al. (*7*) have developed procedures for predicting solid solubility in multicomponent systems based upon experimental data on all of the constitutive binary systems. Additional experimental data on solid solubility of hydrocarbon components including alkane, naphthene, and aromatic substances in methane, ethane, and propane are necessary. Such data will be used in the design of a variety of cryogenic processes, including the design of the recently proposed slurry pipe lines to transport both LNG and crude oil simultaneously.

Experimental Section

The apparatus was identical with that reported by Lee and Kohn (*6*) which was used in other solid phase studies (*1, 4*). The equilibrium cell was immersed in a bath contained in a 4.0-l. cylindrical Dewar flask which was concentrically mounted inside an 8 in. o.d. cylindrical battery jar. The bottom of the air space between the Dewar flask and the battery jar contained about 100 g of 13A molecular sieves. This prevented the condensation of water on the Dewar flask. At temperatures higher than 156 K the bath liquid was absolute ethyl alcohol. Mixtures of absolute alcohol and *n*-propyl alcohol were found suitable at temperatures down to 140 K. Bath temperatures down to 188 K were achieved by use of a "CRYOCOOL-100" cascade refrigerator whose cooling coil was immersed in the working bath. At temperatures below 188 K liquid nitrogen was metered to a copper coil inside the working bath. Temperatures of the bath were controlled using a Model 94 Bayley Precision temperature controller which generally could achieve temperature control to ±0.05 °C. Temperatures were taken on a platinum resistance thermometer which had a calibration correct at least to ±0.03 °C. Pressures were taken on Heise bourdon tube gauges which were set against a dead weight gauge. The pressure gauges were accurate to about ±0.07 atm. Volumes of the liquid phase inside the cell were taken relative to calibration marks on the outside of the cell. The volume calibration was correct to at least ±0.2% when filled to about 10 ml.

Pure solute liquid was charged to a clean empty equilibrium cell. The mass of the liquid was determined by weighing techniques to at least ±0.2 mg. The cell was chilled to 0 °C and the air was flushed from it by repeated charging to 7 or 8 atm with ethane gas. The cell was then immersed in the Dewar flask and ethane added from a reservoir at constant pressure and temperature by use of mercury displacement pump. The reservoir