  Bull. Chem. Soc. Jpn., 59, 2973—2978 (1986)

Solubilities and Free Energies of Transfer for Lanthanoid Iodates in Dimethyl Sulfoxide-Water Mixtures

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(Received February 14, 1986)

The solubilities of lanthanoid iodates in dimethyl sulfoxide (DMSO)-water mixtures at 25 °C were measured. Thirteen lanthanoid iodate dihydrates $Ln(IO_3)_3 \cdot 2H_2O$ (Ln=Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) were used. From the measured solubilities, the Gibbs free energies of the transfer of the iodates from water into aqueous DMSO solutions were calculated. The tetrad effect behavior reported by Peppard et al. was observed in both the variation with the lanthanoid atomic number of the solubility data and that with the atomic number of the free energies of transfer. The tetrad effect behavior seems to depend on a change in the solvation of the lanthanoid ions in variation with the crystal radii of the trivalent lanthanoid ions. In each system the logarithm of the solubility of the iodates decreases almost linearly with the reciprocal of the dielectric constant of the mixtures, as is expected from the Born equation or its modification when dealing with mixtures with narrow dielectric constant, ranging between 78.5 and 78.0.

As is well-known, variations in the thermodynamic data regarding lanthanoid(III) ions in aqueous solutions show no simple correlation with the crystal radii of the trivalent cations. A plot of the thermodynamic data as a function of the radius often exhibits a break somewhere in the middle of the lanthanoid series. For example, a plot of the stability constants of many lanthanoid complex systems against the lanthanoid atomic number shows a gadolinium break.[1,2] Peppard et al.[3] have reported that in certain liquid-liquid extraction systems the behavior of lanthanoid(III) ions has been interpreted in terms of four tetrads, rather than in terms of two octads. The tetrad effect proposed by Peppard et al. has been theoretically studied by Nugent.[4] He stated that the effect originates mainly from the quantum mechanical interelectronic repulsion energy of the q electrons in a $4f^q$ electron configuration.

Siekierski and Salomon[5,6] have studied the thermodynamic behavior of the solubility phenomena using recently published critically evaluated solubility and activity data of lanthanoid nitrates. They stated that the variations of the thermodynamic and congruent melting points as a function of atomic number can be interpreted mainly in terms of changes in the inner-sphere coordination number for both solid hexahydrates and aquo ions. Bertha and Choppin[7] have measured the heats of solution and the solubilities of the lanthanoid iodates in water at 25 °C and from these data the thermodynamic parameters of hydration were calculated. They proposed that the variations of the entropies of hydration across the lanthanoid series support the suggestion of a change in the hydration number of the lanthanoid ions somewhere in the middle of the series.

The lanthanoid iodates were chosen for this study of the solubility phenomena for several reasons. For all of the lanthanoid iodates except lanthanum and promethium salts their dihydrates could be prepared. Their relative insolubility allowed an easy determination of the solubility product values. They exhibited desirable precipitation characteristics with no evidence of colloidal suspension.

The solubility data of lanthanoid iodates in water at 25 °C except those of cerium, promethium and lutetium iodates have been reported by Firsching and Paul.[8] Bertha and Choppin[7] have also measured the solubilities of the iodates in water at 25 °C except that of promethium iodate. However, the solubilities of lanthanoid iodates in a variety of binary solvent mixtures have not yet been studied systematically. Monk[9,10] measured the solubilities of lanthanum iodate only in various solvent mixtures, and discussed the relation between the solubility of the iodates and the dielectric constant of aqueous solvent mixtures. Miyamoto, Shimura, and Sasaki[11] have reported the solubilities of lanthanoid iodates except lanthanum and promethium iodates in aqueous methanol media and in aqueous ethanol media. They also pointed out that the neodymium and erbium breaks appeared in addition to the gadolinium break in these systems.

In this study, the solubilities of thirteen iodates of the lanthanoid series in dimethyl sulfoxide (DMSO)-water mixed solvents were measured. From the solubility data, the Gibbs free energies of transfer from water into aqueous DMSO solutions were calculated. The dependence of the solubility of the lanthanoid iodates in aqueous aprotic solvent mixtures on the crystal radii of trivalent lanthanoid ions and on the lanthanoid atomic number was studied, and the dependence of the free energies of transfer on those was also considered.

Experimental

Preparation of Lanthanoid Iodates. The lanthanoid iodates were prepared by a dropwise addition of both the acidic solutions of lanthanoid nitrates and the aqueous potassium iodate solution. The agreement between the chemically found and the theoretically calculated values for dihydrate salts was within ±0.5 %. The results of chemical analyses of the prepared iodates were supported by thermal analyses.

Preparation details and analytical methods of the iodates

Table 1. Solubility of Lanthanoid Iodates in Dimethyl Sulfoxide-Water Mixtures at 25 °C

DMSO mass%	DMSO mol%	Dielectric constant	Solubility / 10^3 mol dm^{-3}			
			$Ce(IO_3)_3$	$Pr(IO_3)_3$	$Nd(IO_3)_3$	$Sm(IO_3)_3$
0(This work)		78.54[a]	1.963±0.001	1.098±0.001	1.044±0.001	0.771±0.002
0(Ref. 11)		78.40[b]	1.96	1.12	1.03	0.82
5.03	1.21	78.31[a]	1.495±0.003	0.881±0.006	0.855±0.001	0.631±0.001
10.03	2.51	78.07[a]	1.261±0.002	0.733±0.003	0.693±0.001	0.518±0.001
20.09	5.48	77.42[a]	0.905±0.001	0.493±0.001	0.476±0.001	0.359±0.001
40.03	13.34	76.01[a]	0.428±0.001	0.226±0.008	0.209±0.001	$0.164\pm0.000_3$
			$Eu(IO_3)_3$	$Gd(IO_3)_3$	$Tb(IO_3)_3$	
0(This work)		78.54[a]	0.782±0.003	0.893±0.002	0.933±0.001	
0(Ref. 11)		78.40[b]	0.79	0.88	0.93	
5.03	1.21	78.31[a]	0.647±0.003	0.747±0.002	0.776±0.001	
10.03	2.51	78.07[a]	$0.534\pm0.000_2$	$0.614\pm0.000_4$	0.627±0.001	
20.09	5.48	77.42[a]	$0.369\pm0.000_2$	$0.422\pm0.000_4$	0.427±0.001	
40.03	13.34	76.01[a]	0.166±0.001	$0.185\pm0.000_3$	0.177±0.001	
			$Dy(IO_3)_3$	$Ho(IO_3)_3$	$Er(IO_3)_3$	
0(This work)		78.54[a]	1.010±0.001	1.162±0.001	$1.379\pm0.000_1$	
0(Ref. 11)		78.40[b]	1.02	1.16	1.36	
5.03	1.21	78.31[a]	0.836±0.004	0.965±0.003	1.120±0.001	
10.03	2.51	78.07[a]	0.687±0.001	0.786±0.001	0.904±0.001	
20.09	5.48	77.42[a]	0.453±0.001	$0.505\pm0.000_3$	$0.573\pm0.000_2$	
40.03	13.34	76.01[a]	$0.181\pm0.000_3$	$0.193\pm0.000_0$	0.208±0.002	
			$Tm(IO_3)_3$	$Yb(IO_3)_3$	$Lu(IO_3)_3$	
0(This work)		78.54[a]	1.467±0.001	1.620±0.003	2.036±0.005	
0(Ref. 11)		78.40[b]	1.47	1.63	2.04	
5.03	1.21	78.31[a]	$1.217\pm0.000_2$	1.343±0.001	1.629±0.001	
10.03	2.51	78.07[a]	$0.978\pm0.000_2$	1.085±0.001	1.304±0.004	
20.09	5.48	77.42[a]	$0.616\pm0.000_1$	0.662±0.001	$0.794\pm0.000_3$	
40.03	13.34	76.01[a]	$0.214\pm0.000_1$	0.227±0.001	$0.258\pm0.000_1$	

a) Data for pure water and for DMSO-water mixture from Ref. 12. b) Data for pure water from Ref. 13.

were previously reported.[11]

Preparation of Binary Aqueous Solvent Mixtures. Guaranteed grade DMSO was purchased from Wako Chemicals Co., and was distilled under reduced pressure three times. Redistilled water with a specific conductivity of 0.98±0.05 $\mu S\,cm^{-1}$ was used. The binary solvent mixtures by weight were made from the purified DMSO and the redistilled water.

Solubility Measurements. The supersaturation method was used. The purified lanthanoid iodates and DMSO-water mixtures were placed into glass-stoppered bottles, which were slowly rotated in a thermostat at 27 °C for about 12 h. The temperature was lowered to 25.00±0.05 °C and the bottles were continuously rotated for 48 h, after which no further change was observed within the relative average deviation of 0.3%. The solubilities of the iodates were determined in water and in 40 mass percent DMSO solvent mixtures.

After settling in a thermostat at 25 °C for about one hour, the solutions were filtered through a vaccum-jacketed sintered-glass filter. The filtrates were kept in the thermostat at 25 °C for about one hour. Aliquots were diluted with redistilled water for adjusting to a suitable concentration for titration. Aqueous potassium iodide and hydrochloric acid were added and the liberated iodine was titrated with a sodium thiosulfate solution that had been standardized with potassium iodate using a starch indicator. In cases where the solubility was small, aliquots of the saturated solution were added to a known amount of potassium iodate and the mixtures were back-titrated with a standardized thiosulfate solution. All solubility measurements were performed in duplicate.

Results and Discussion

Solubilities of Lanthanoid Iodates in DMSO–Water Solvent Mixtures. The observed solubilities of lanthanoid iodate dihydrates $Ln(IO_3)_3\cdot 2H_2O$ (Ln=Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) in DMSO-water mixtures at 25 °C are given in Table 1 along with the standard deviations of each solubility determination. The dielectric constants of DMSO-water mixtures[12] and of water[13] are also listed in Table 1.

The solubility determination of lanthanum iodate in the mixtures was not performed since the iodate dihydrate crystals could not be prepared. The solubility of promethium iodate is also missing from the table since a starting material such as promethium oxide or nitrate for the preparation of promethium iodate could not be purchased.

The solubilities of lanthanoid iodates in water at 25 °C have been reported by Firsching and Paul,[8] and Bertha and Choppin.[7] Miyamoto, Shimura, and Sasaki[11] measured the solubilities of the iodates in water at 25 °C and have reported the recommended values of the iodate solubilities in water at 25 °C by applying the evaluation guidelines[14] of the IUPAC Solubility Data Project. Our results regarding the solubility determination of the iodates are in good agreement with the recommended values.

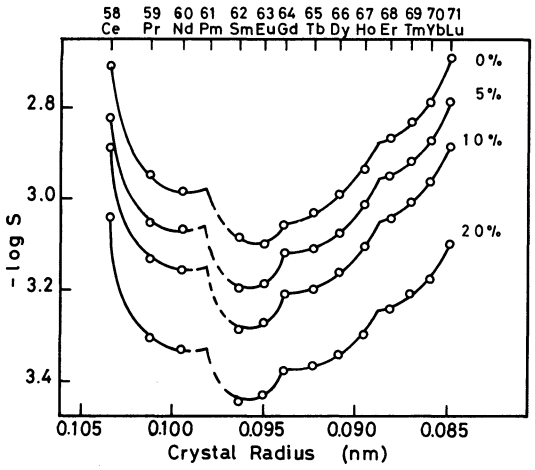

Fig. 1. Dependence of the logarithm of the solubility on the crystal radii (nm) of lanthanoid ions(III).

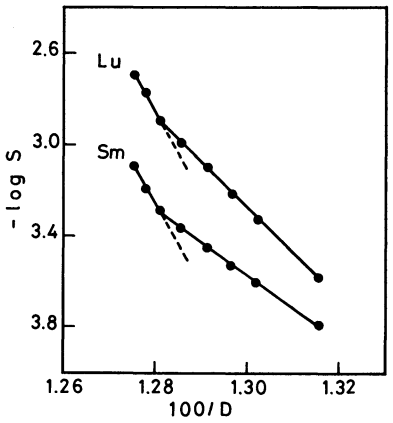

Fig. 2. Dependence of the logarithm of the solubility of samarium and lutetium iodates on the reciprocal of the dielectric constant of DMSO-water mixtures.

In this study, the DMSO concentrations of the solvent mixtures were in the range from 0 to 40 mass percent. At concentrations above 40 mass percent, the solubility could not be determined by an iodometric titration because the end point of the titration was not clear.

The relation between the logarithm of the solubility of lanthanoid iodates in DMSO-water mixtures and the lanthanoid atomic number is shown in Fig. 1., which also shows the dependence of the solubility of the iodates on the crystal radii of the trivalent lanthanoid ions. Recently, the ionic radii of many cations in aqueous solutions containing trivalent lanthanoid ions were theoretically determined by Marcus,[15] but the data of some cations in a series of trivalent lanthanoid ions are lacking. Therefore, the crystal radii of trivalent lanthanoid ions reported by Templeton and Dauben[16] were adopted.

In Fig. 1, although the points corresponding to lanthanum and promethium are lacking, it can be seen that the solubility curves pass through a minimum at atomic number 62 (samarium). By analyzing the solubility curves in further detail, the points on a plot of the logarithm of the solubility of lanthanoid iodates in DMSO-water mixtures vs. atomic number may be grouped, through the use of four smooth curves without inflections, into four tetrads with the gadolinium point being common to the second and third tetrads and the extended smooth curves intersecting, additionally, in the 60—61 and 67—68 atomic number regions.

As is well known, a plot of the stability constants of many lanthanoid complex systems[1,2] against the lanthanoid atomic number shows a gadolinium break. Peppard et al.[3] have reported that in certain liquid-liquid extraction systems the behavior of trivalent lanthanoid ions can be interpreted in terms of four tetrads, rather than in terms of two octads. The present solubility study also reveals the three break points, and the tetrad effect reported Peppard et al.[3] was observed.

The solubility of sparingly soluble salts as a function of the static dielectric constant of mixtures has been related to the Born equation[17] or its modification.[18–20] An example of the relation between the logarithm of the solubility and the reciprocal of the dielectric constant of the mixtures is shown in Fig. 2 for samarium iodate-DMSO-water and lutetium iodate-DMSO-water systems. In addition to the solvent mixtures having DMSO concentrations of 5, 10, 20, and 40 mass percent, solvents of DMSO with concentrations of 15, 25, and 30 mass percent were also used to determine the solubilities of the two systems. The circles indicate the observed solubilities of the iodates and dash lines are from a modified Born equation.

In each system the logarithm of the solubility of the iodates decreases almost linearly with the reciprocal of the dielectric constant of the mixtures, as is expected from the Born equation[17] or its modification[18–20] when dealing with mixtures of the narrow dielectric constant range of 78.5—78.0, but when dealing with mixtures of the dielectric constant range of 78.0—76.0 deviation from the Born equation was found. The dielectric constant range of 78.5—78.0 where a plot of the logarithm of the solubility vs. the reciprocal of the dielectric constant of the binary aqueous solvent mixtures follows the modified Born equation is narrower than that of methanol-water[11] and ethanol-water[11] systems.

For example, the relation between the logarithm of the solubility of the sparingly soluble salts and the reciprocal of the dielectric constant of mixed solvents is given by Davis, Ricci and Sauter[18] as

$$\ln (S_w/S_x) = (Z_+Z_-e^2/2rkT)/(1/D_x - 1/D_w), \quad (1)$$

where S and D represent the solubility of the iodates based on the molar scale and the dielectric constant of the mixtures, respectively, and the subscripts w and x

Table 2. The 2r Values of Lanthanoid Iodates Systems Calculated from Eq. 1 (10^9 units)

Index	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
S_wS_5	2.3	2.9	3.2	3.2	3.3	3.5	3.5	3.3	3.4	3.0	3.4	3.4	2.8
S_wS_{10}	2.9	3.2	3.1	3.2	3.4	3.4	3.2	3.3	3.3	3.1	3.2	3.2	2.9
S_wS_{20}	4.0	3.9	3.9	4.1	4.1	4.1	4.0	3.9	3.7	3.6	3.6	3.5	3.3
S_wS_{40}	4.7	4.5	4.6	4.6	4.5	4.5	4.2	3.8	3.7	3.7	3.7	3.6	3.5
$S_{10}S_{20}$	5.5	4.6	4.8	4.9	4.9	4.8	4.7	4.3	4.1	4.0	3.9	3.7	3.7
$S_{10}S_{40}$	5.4	5.0	4.9	5.1	5.0	4.9	4.6	4.4	4.2	4.0	3.8	3.7	3.5

refer to the water system and the mixed solvent systems, respectively. Equation 1 corresponds to the first term of Koizumi's equation,[20] and the r value (solvation radius) was defined as Eq. 2:

$$1/r = (1/2)(1/r_+ + 1/r_-) \quad (2)$$

The 2r values calculated from Eq. 1 are given in Table 2. In "Index" column of Table 2, S_w and S_x (x=5, 10, 20, and 40) represent the solubility of iodates in water and that in the mixed solvent of the DMSO concentration x based on the mass percent scale, respectively, which were used to calculated the 2r values.

The physical properties of a DMSO–water system have been extensively studied.[13,21,22] These data point to strong interactions between water and DMSO in mixtures, which may be attributed to hydrogen bonding. Fox and Whittingham[21] have reported that the maximum interaction occurs in the region of about 0.3 mole fraction, enhancement of water structure expects perhaps at very low concentration (<0.01 mole fraction). The extensive literature[23] dealing with the DMSO–water interaction indicates that the solution properties of aqueous DMSO are dominated by 2:1 H_2O–DMSO complex, and only one result reported by Glasel[24] has been given 3:1 H_2O:DMSO complex.

When the electrolytes were added to DMSO–water solvent mixtures, the maximum interaction of DMSO and water changed distinctly. Indeed, Mastroianni, Pikal and Lindenbaum[25] have reported that the heats of dilution for lithium bromide in aqueous DMSO solutions exhibit a maximum around 20 mol% DMSO.

In a solubility study involving silver halides in DMSO–water mixtures,[26] the variation in the solubility data shows no simple correlation with the DMSO concentration in the mixtures. The solubility of silver chloride increases with an increase in the DMSO concentration, but those of silver bromide and iodide are reversed. From these results, the solubility phenomena of electrolytes in DMSO–water mixtures are no simple behavior.

In this study, as are given in Table 2 and shown in Fig. 2, the 2r values are classified into two categories. In each iodate system, one group consists of the 2r values for the lower DMSO concentration range (<2.5 mol%), and the other is those for the DMSO concentration of 20 and 40 mass percent (>5.0 mol%). The change of the slope depends on that of the solvation of lanthanoid ions, and it may also reflect the change of the DMSO–water interaction effected by lanthanoid ions.

Gibbs Free Energies of Transfer of Lanthanoid Iodates from Water into Aqueous DMSO Media. The aim of this section is to explore the dependence of the free energy of transfer for lanthanoid iodates from water into aqueous DMSO solutions on the lanthanoid atomic number.

The free energy of transfer of lanthanoid iodates from water into binary aqueous solvent mixtures is given by

$$\Delta G_t^\circ[\mathrm{Ln(IO_3)_3}] = RT \ln [K_{sp}(w)/K_{sp}(x)], \quad (3)$$

and the solubility product K_{sp} can be calculated from

$$K_{sp} = 27S^4\gamma_\pm^4. \quad (4)$$

Here, S and $\gamma_\pm$ represent the solubility of the iodates based on the molar scale and the molar activity coefficient of the iodates, respectively.

The solubilities of the iodates in water S_w and in DMSO–water mixtures S_x are related to the free energy of transfer from water into binary aqueous solvent mixtures:

$$\Delta G_t^\circ[\mathrm{Ln(IO_3)_3}] = 4RT \ln [S_w\gamma_\pm(w)/S_x\gamma_\pm(x)]. \quad (5)$$

From the solubility data, Blandamer, Burgess, and Duffield[27] have calculated the free energies of transfer of potassium cyanide from water into binary aqueous solvent mixtures. In the study, three methods were adopted to calculate the free energy of transfer. One approach was by an estimation of molar mean activity coefficients using the Debye–Hückel limiting law;[28] the other was also by an estimation of activity coefficients using the Güntelberg equation;[28] the rest was by the calculation of the quantity ΔG_t° on the molar scale from the observed solubility assuming $\gamma_\pm(w)/\gamma_\pm(x)\simeq 1$ in Eq. 5. For example, in pure DMSO the free energies calculated by using the Debye–Hückel equation and that calculated by using the Güntelberg equation were 21.8 and 21.9 kJmol^{-1}, respectively, and that calculated from the solubility assuming $\gamma_\pm(w)/\gamma_\pm(x)\simeq 1$ was 23.2 kJmol^{-1}. The relative average deviation is 2.7%. A comparison of the three results of the free energy of transfer to a series of pure solvent has been shown that the assumption $\gamma_\pm(w)/\gamma_\pm(x)\simeq 1$ was reasonable.

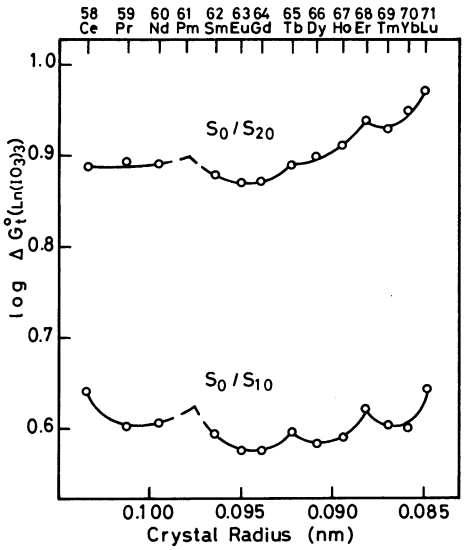

Fig. 3. Dependence of the logarithm of the free energy of transfer on the crystal radii (nm) of lanthanoid ions(III).

In this study, an estimation of molar activity coefficients used the Güntelberg equation[28] and the Davies equation.[28] Also, the free energies of transfer of the lanthanoid iodates from water into aqueous DMSO solutions were calculated from the observed solubility using Eq. 5. Further, Eq. 5 assuming $\gamma_{\pm}(w)/\gamma_{\pm}(x)\simeq 1$ was also used to calculate the free energies of transfer. From the results for samarium and lutetium iodate systems, the relative average deviation of the free energy of transfer calculated using the three methods was the range of 1.0—2.0%. The results are better than that of potassium cyanide in pure DMSO. Therefore, the free-energy values of the iodates calculated from the assumption $\gamma_{\pm}(w)/\gamma_{\pm}(x)\simeq 1$ were used in Fig. 3.

The dependence of free energy of transfer for lanthanoid iodates from water into aqueous DMSO solutions on the lanthanoid atomic number is shown in Fig. 3. The ratios S_0/S_{10} and S_0/S_{20} (Fig. 3) refer to the solubility ratio given explicitly in Eq. 5 and subscripts 0, 10, and 20 refer to the organic co-solvent concentrations of the mixtures. In Fig. 3, the points on a plot of the free energy of transfer against the lanthanoid atomic number can be divided into four curves with break points at atomic number 68 (erbium) and 65 (terbium) and in the 61—62 region. The behavior of trivalent lanthanoid ions is interpreted in terms of four tetrads, rather than in terms of two octads. Although the break points obtained in this free-energy study differ slightly from the behavior of the normal tetrad effect reported by Peppard et al.,[3] it can be seen that a tetrad-effect-like behavior is also observed in this free-energy study. However, Fujisawa and Suzuki[29] have reported that from a stability constant study the three break points were placed at 60 (neodymium), 64 (gadolinium) and 68 (erbium). Nugent[4] has stated that the variation in the interelectronic-repulsion-stabilization energy for the lanthanoid aqueous ions results in a tetrad effect at the 1/4, 1/2, and 3/4 filled shells of a 4f electronic configuration. However, a more detailed theoretical treatment as well as additional experimentation are necessary.

The figures referring to solubility ratios S_0/S_5 and S_0/S_{40} are not shown here, but the behavior of the curves is almost similar to that of S_0/S_{10} and S_0/S_{20}.

References

1) T. Moeller, "The Lanthanides, in Comprehensive Inorganic Compounds," ed by A. F. Trotman-Dickenson, Pergamon Press, London (1973), Vol. 4, p. 1.
2) S. Misumi, *Nippon Kagaku Zasshi*, **89**, 723 (1968).
3) D. F. Peppard, C. A. A. Bloomquist, E. P. Horwitz, S. Lewey, and G. W. Mason, *J. Inorg. Nucl. Chem.*, **32**, 339 (1970).
4) L. J. Nugent, *J. Inorg. Nucl. Chem.*, **32**, 3485 (1970).
5) S. Siekierski and M. Salomon, *J. Solution Chem.*, **14**, 473 (1985).
6) S. Siekierski, T. Mioduski, and M. Salomon, "Scandium, Yttrium, Lanthanum and Lanthanide Nitrates (IUPAC Solubility Data Series, Vol. 13)," Pergamon Press, London (1983).
7) S. L. Bertha and G. R. Choppin, *Inorg. Chem.*, **8**, 613 (1969).
8) F. H. Firsching and T. R. Paul, *J. Inorg. Nucl. Chem.*, **28**, 2414 (1966).
9) C. B. Monk, *J. Chem. Soc.*, **1951**, 2723.
10) C. B. Monk, *Trans. Faraday Soc.*, **47**, 1233 (1951).
11) H. Miyamoto, H. Shimura, and K. Sasaki, *J. Solution Chem.*, **14**, 485 (1985).
12) E. Tommila and A. Pajunen, *Soum. Kemistil. B*, **41**, 172 (1968).
13) R. L. Kay, G. A. Vidulich, and K. S. Pribadi, *J. Phys. Chem.*, **73**, 445 (1969).
14) IUPAC Commission on Solubility Data, "Solubility Data Series Guidelines for Compilers, Evaluators and Editors," ed by A. F. M. Barton, Pergamon Press, London, (1984).
15) Y. Marcus, *J. Solution Chem.*, **12**, 271 (1983).
16) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5237 (1954).
17) M. Born, *Z. Phys.*, **1**, 45 (1920).
18) T. W. Davis, J. E. Ricci, and C. G. Sauter, *J. Am. Chem. Soc.*, **61**, 3274 (1939).
19) P. B. Davies and C. B. Monk, *J. Chem. Soc.*, **1951**, 2718.
20) E. Koizumi, *Nippon Kagaku Kaishi*, **68**, 19 (1947).
21) M. F. Fox and K. P. Whittingham, *J. Chem. Soc., Faraday Trans. 1*, **71**, 1407 (1975).
22) For example: (Density and Viscosity) S. A. Schichman and R. L. Amey, *J. Phys. Chem.*, **75**, 98 (1971); (Heat of Mixing) H. L. Clever and S. P. Pigott, *J. Chem. Thermodyn.*, **3**, 221 (1971); (Vapor Pressure) S. Y. Lam and R. L. Benoit, *Can. J. Chem.*, **52**, 718 (1974); (Molal Volume and Heat Capacity) O. Kiyohara, G. Perron, and J. E. Desnoyers, *Can. J. Chem.*, **53**, 3263 (1975).
23) For example: E. M. Arnett and D. R. McKelvey, *J. Am. Chem. Soc.*, **88**, 2598 (1966); G. Yagil, *J. Phys. Chem.*, **73**, 1610 (1969); S. A. Schichman and R. L. Amey, *J. Phys. Chem.*, **75**, 98 (1971).
24) J. A. Glasel, *J. Am. Chem. Soc.*, **92**, 372 (1970).

25) M. J. Mastroianni, M. J. Pikal, and S. Lindenbaum, *J. Phys. Chem.*, **76**, 3050 (1972).
26) B. G. Cox and R. Natarajan, *J. Chem. Soc., Faraday Trans. 1*, **75**, 1780 (1979).
27) M. J. Blandamer, J. Burgess, and A. J. Duffield, *J. Chem. Soc., Dalton Trans.*, **1980**, 1.
28) See, for example, R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd edn., Butterworths, London, (1959), Chap. 9.
29) M. Fujisawa and Y. Suzuki, 30th Conference on Coordination Chemistry, Tokyo, Japan, (1980), p. 296.