J. Chem. Eng. Data **1982**, *27*, 81–84

Solubility Product Constant and Thermodynamic Values for the Terbium Trifluoride–Water System†

Manchery P. Menon

Department of Chemistry, Savannah State College, Savannah, Georgia 31404

The solubility and the solubility product of TbF_3 in aqueous solution were determined by three different methods. However, for the reasons discussed in the text, the radiometric values 3.59×10^{-5} M and 3.66×10^{-17} for the solubility and the solubility product, respectively, seem to be more acceptable than the others. The values for ΔH° and ΔG° at 298 K are positive, and that for ΔS° is negative for the dissolution of $TbF_3(s)$, indicating the reason for the slight solubility of this salt in water. The pH dependence of the solubility shows a minimum at a pH of about 4.2, a trend similar to what has been observed in the case of other rare-earth fluorides. The dependence of the solubility on fluoride concentration and the value for the stability constant of terbium monofluoride complex confirms the complexation of Tb^{3+} ion in aqueous solution.

Although the solubilities and the solubility products of slightly soluble halides of silver and other metals have been measured (*1*) only a very limited quantity of data on the solubility of the fluoride of the individual lanthanides are available in the literature (*2*). Even slight differences in the solubilities of the rare-earth fluorides in water or in fluoride solutions may be helpful in developing suitable separation procedures for lanthanides. Furthermore, the IUPAC solubility data project also requires detailed data on the rare-earth fluoride–water systems (*3*). Much of the work on the solubilities of rare-earth fluorides has been done by Russian scientists (*4–6*), but the solubilities were determined, in most cases, in various acids and in highly concentrated salt solutions. There is also considerable difference between the theoretical values for the pK_s (18–21.9) for lanthanide fluorides in aqueous solution predicted by Vasil'ev and Kozlovski (*7*) and those (15–18.9) measured by Frausto and Manuela (*8*) using a potentiometric method. No detailed study involving the measurement of thermodynamic functions for the solution of individual rare-earth fluorides and their complexation behavior in aqueous solution seems to have been undertaken in the past. This study makes use of three different techniques to measure the solubility and the solubility product of terbium trifluoride in aqueous solutions, to determine the thermodynamic functions for the solution process, and to estimate the stability constant for terbium monofluoride complex which is known to exist in aqueous solutions (*9*).

Experimental Section

Materials and Equipment. Terbium chloride ($TbCl_3 \cdot 6H_2O$, 99.9% pure) was supplied by Alfa Division of Ventron Corp., and ^{160}Tb (73-day half-life) (99.0% pure) was obtained from Amersham Corp. All other reagents used in this study were of reagent-grade quality. Distilled water (D-water) was used in making all solutions except for conductometric measurements for which doubly distilled water (DD-water) was used.

The equipment used in this study consisted of (*1*) a Yellow Springs Instrument Co. Inc. (YSI) Model 31 conductivity bridge and their Model 3401 conductivity cell, an Orion Ionalyzer Model 407A and their fluoride specific ion electrode, Model 96-09, a Burnell Model BB wrist-action shaker, a Dubnoff metabolic shaking incubator for equilibrating solutions at desired temperature, a Harshaw Model 3 × 3 in. NaI (T1) well crystal γ-ray spectrometer, and a Canberra Model 1431 single-channel analyzer with associated accessories.

Analytical Procedures. Procedures employed for the determination of the solubilities of terbium trifluoride by the three methods are similar to those reported elsewhere (*10*). In the conductometric method, the limiting equivalent conductance ($\Lambda^0_{TbCl_3}$) was first determined by measuring equivalent conductances of a number of dilute solutions of $TbCl_3$ of known concentration and plotting equivalent conductance (Λ) against the square root of C (see Figure 1). The ionic equivalent conductance of Tb^{3+} was obtained from $\Lambda^0_{TbCl_3}$ and the value for the ionic equivalent conductance of Cl^- ($\lambda^0_{Cl^-} = 76$ mho cm^2 g-equiv^{-1}, ref *11*). The value obtained for $\lambda^0_{Tb^{3+}}$ was 70 ± 2 mho cm^2 g-equiv^{-1}, which is in agreement with the reported value of 66.9 ± 0.1 mho cm^2 g-equiv^{-1} for this ion (*12*). Using the value for $\lambda^0_{F^-}$ ($\lambda^0_{F^-} = 54$ mho cm^2 g-equiv^{-1}, ref *11*), the limiting equivalent conductance of TbF_3, Λ^0_t) for Tb^{3+} and F^- ions at various temperatures was calculated by using the following equation (*12*):

$$\lambda_{t'} = \lambda_t[1 + C(t' - t)] \tag{1}$$

where t' is the desired temperature, $t = 18$ °C, and $C = 0.0238$. Terbium fluoride was precipitated by adding a slight excess of 0.1 M solution of sodium fluoride to 40 mL of 0.1 M $TbCl_3$ solution. The mixture was heated in a water bath for about 30 min and then centrifuged and decanted. The precipitate was washed several times with DD-water to ensure that no foreign ions were absorbed on the precipitate. Only polypropylene wares were used for processing fluoride solutions. The residue was dried at 110 °C. Portions of the precipitate were mixed with 50 mL of DD-water in two polypropylene bottles and agitated intermittently for more than 24 h with the wrist-action shaker. The bottles were kept in a clinical thermostat at 25 °C for 5 days before conductivity measurements were made. The molar concentration of TbF_3 in saturated solutions at various temperatures was computed with the use of the equation

$$C_{TbF_3}\,(\mathrm{M}) = \frac{1000\Theta L}{3(\lambda^0_{t'(Tb^{3+})} + \lambda^0_{t'(F^-)})} \tag{2}$$

where Θ is the cell constant and L the measured net conductance. The cell constant of the conductivity cell was 1.13 cm^{-1} and the specific conductance of DD-water was 3.4×10^{-6} mho cm^{-1}.

In the potentiometric method, the total concentration of the fluoride ion in saturated solutions of TbF_3 was measured with the Orion Ionalyzer and their specific fluoride electrode. Precipitation and purification of TbF_3 and the preparation of the saturated solution were carried out as described before. At the end of saturation, 10 mL of the supernatant liquid was centrifuged for about 15 min and 5 mL of the clear solution was used for analysis. Standard solutions ranging in concentration from 10^{-2} to 10^{-4} M were prepared from a standard solution of NaF (0.10 M) supplied by the dealers. The diluted standards and the

---

† This paper was presented at the ACS Southeast/Southwest Regional Meeting, New Orleans, LA, Dec 10–12, 1980.

0021-9568/82/1727-0081$01.25/0

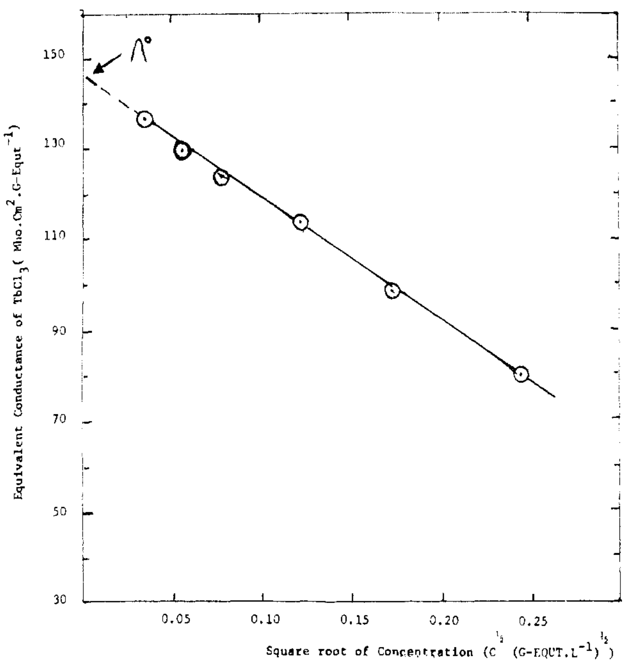

Figure 1. Equivalent conductance as a function of square root of concentration of $TbCl_3$.

reagent TISAB (total ionic strength adjustment buffer) were used to calibrate the instrument in the desired concentration range with 5 mL of the standard and 1 mL of TISAB. The sample was also processed in the same manner for analysis.

In the radiometric procedure, ^{160}Tb tracer (2 mC in 1 mL) was diluted to 4 mL with D-water and 0.5 mL of the diluted tracer was added to 40 mL of 0.1 M $TbCl_3$ solution. After the solution was mixed, radioactive $^*TbF_3$ was precipitated by adding a slight excess of 0.1 M solution of sodium fluoride to the labeled-$TbCl_3$ solution. After the contents were simmered in a hot water bath for about 30 min, the solution was centrifuged and decanted. The precipitate was washed several times with D-water, centrifuged, and dried at 110 °C.

A small fraction of the precipitate was weighed and dissolved in concentrated sulfuric acid in a Teflon beaker which was kept in a hot water bath. The resulting solution was diluted to 250 mL with D-water. A 5-mL aliquot of the diluted solution (standard) was pipetted into a counting tube and its γ activity measured to determine the specific activity of TbF_3 in cpm mol^{-1}.

Portions of the labeled precipitate were mixed with 50 mL of D-water in two polyethylene bottles and equilibrated in the same way as described before for other measurements. At the end of equilibration, 10 mL of the supernatant liquid from each bottle was transferred to another tube and centrifuged for 15 min at 5000 rpm. The second supernatant liquid was transferred to another tube, and 5 mL of this solution was counted in the γ-ray spectrometer. The solubility of the TbF_3 in the saturated solution was calculated by using the following equation:

$$C_{TbF_3}\ (\mathrm{M}) = 1000 R_{\mathrm{sample}} W/(5 R_{\mathrm{std}} M) \tag{3}$$

where R_{sample} and R_{std} are the net counting rates of the sample and the standard, W is the weight of the labeled fluoride in 5 mL of the standard, M is the molecular weight of TbF_3, and C_{TbF_3} is the concentration of TbF_3 in the saturated solution. A similar procedure was used to determine the total concentration of Tb^{3+} in fluoride solutions at constant ionic strength. In this case solutions with constant ionic strength (1 M), a pH of 3.1 ± 0.1, and the desired fluoride concentrations were made by mixing appropriate amounts of $NaClO_4$, NaF, and HCl. Radioactive $^*TbF_3$ was mixed with 50 mL of these solutions and allowed to equilibrate from 2 to 5 days at room temperature with intermittent shaking during the period.

Table I. Solubility and Solubility Product of TbF_3 in Aqueous Solution at 25 °C Obtained by Three Different Methods

method	10^5(solubility), M	mean activity coeff	K_{SO}
conductometric	5.87 ± 0.15	0.9380	2.48×10^{-16}
potentiometric	4.17 ± 0.17	0.9469	6.56×10^{-17}
radiometric	3.59 ± 0.52	0.9506	3.66×10^{-17}

Estimation of the Stability Constant of Terbium Monofluoride Complex. In this experiment 5 mL of the diluted $^*TbCl_3$ (0.1 mL of tracer diluted to 100 mL) was counted to determine its γ-ray activity. Ten milliliters of this solution was shaken with 0.5 g of purified, equilibrated and dry Dowex-50X4 cation-exchange resin (100–200 mesh) for 30 min. The supernatant liquid was centrifuged, and 5 mL of the solution was again counted. From these data, K_{eq}, the equilibrium constant for the exchange of free Tb^{3+} ion with the exchanger, was computed by using the relation

$$K_{eq} = \frac{(A_{\mathrm{soln(BE)}} - A_{\mathrm{soln(AE)}})V_{\mathrm{soln}}}{A_{\mathrm{soln(AE)}} m_{\mathrm{res}}} \tag{4}$$

where $A_{\mathrm{soln(BE)}}$ and $A_{\mathrm{soln(AE)}}$ are the activities of 5 mL of solution before and after exchange, V_{soln} is the volume of the solution phase, and m_{res} is the weight of the resin used. The experiment was repeated by shaking 10 mL of the saturated aqueous solution (supernatant liquid) of $^*TbF_3$ at 25 °C with 0.5 g of the same exchanger for 30 min and counting 5 mL of the centrifuged solution in a counting tube. In conductometric measurements the temperature was controlled within ±0.1 °C, but in all other cases where samples had to be centrifuged it was within ±1 °C.

Results and Discussion

In aqueous solution of TbF_3, the solid-solution equilibrium can be written as

$$TbF_3(s) \rightleftharpoons Tb^{3+}(aq) + 3F^-(aq) \tag{5}$$

or if complexation occurs

$$mTbF_3(s) \rightleftharpoons nTb^{3+}(aq) + (m-n)TbF^{2+}(aq) + (2m+n)F^-(aq) \tag{6}$$

provided that only monofluoride complex is formed (*9*). The thermodynamic solubility product, K_{SO}, in the absence of complexation is given by the expression

$$K_{SO} = a_{Tb^{3+}} a_{F^-}{}^3 = 27 C_{sat}{}^4 \gamma_\pm{}^4 \tag{7}$$

assuming that the dry powder of TbF_3 used for analysis is completely anhydrous (*13*). Even if it is a hemihydrate similar to other lighter lanthanide trifluorides (*14*), the above equation is valid because $a_{H_2O} \sim 1$. If all of the terbium ion exists as monofluoride complex

$$K_{S1} = K_{SO}\beta_1 = a_{TbF^{2+}} a_{F^-}{}^2 \tag{8}$$

where K_{S1} is the apparent solubility product and β_1 the stability constant of TbF^{2+}. This is probably not the case in aqueous solution. The mean activity coefficient was calculated from Davies' equation (*16*).

The solubilities, the mean activity coefficients, and the thermodynamic solubility product constants for the TbF_3–water system are listed in Table I. The errors in the solubility values are deviations from the mean of two measurements. It can be seen from this table that the values obtained for the solubility from potentiometric and radiometric measurements agree with each other within experimental errors. However, the solubility

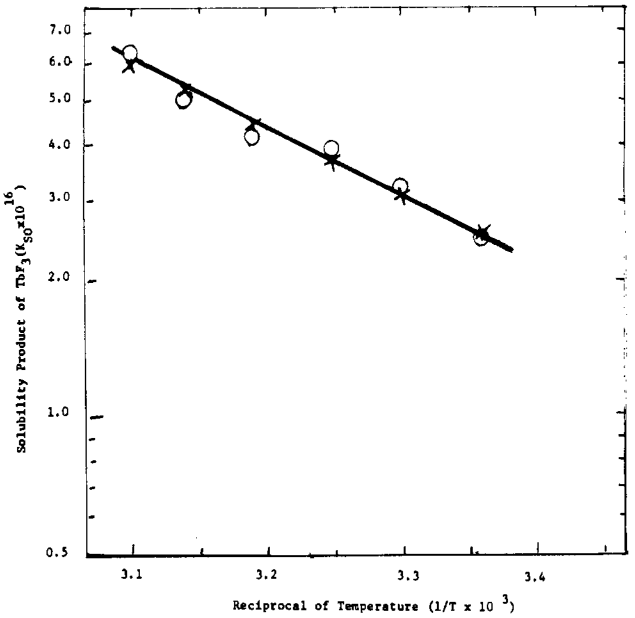

Figure 2. Temperature dependence of solubility product of TbF_3: (O) measured; (X) least-squares fit.

Table II. Values for the Standard Thermodynamic Functions for the Dissolution of TbF_3 at 25 °C

thermodynamic functions	measured values
$\Delta H°$,[a] kJ mol^{-1}	27.39 ± 0.46
$\Delta G°$, kJ mol^{-1}	93.78 ± 4.74
$\Delta S°$, J K^{-1} mol^{-1}	222.78 ± 16.0

[a] Enthalpy change. [b] Free energy change. [c] Entropy change.

measured by the conductometric method is somewhat higher than the other values. The solubility measured by this method is dependent on the limiting equivalent conductance used for TbF_3 which will be in error if the fluoride complex species is present. It has been reported by Weaver and Purdy (*15*) that the conductometric value obtained for K_{so} for CeF_3 is about 20 times higher than that obtained by the radiometric method. In our experiments K_{so} values for TbF_3 obtained from conductometric measurements differ only by a factor of 2. Since radiometric measurements which involve the determination of the radioactivity of total terbium are not affected by the presence of any foreign ion or complexed fluoride species, the radiometric value seems to be more acceptable than the other two. All of these values fall within the range of K_{so} values reported by Dilva and others (*8*) for lanthanide fluorides. The radiometric value for K_{so} was used to compute the standard free energy change for the solution process. The standard thermodynamic relations shown in ref *10* for $\Delta G°$, $\Delta H°$, and $\Delta S°$ were used to compute the respective values for the solution process at 298 K.

Figure 2 is a plot of K_{so} vs. $1/T$, the slope of which was used to evaluate $\Delta H°$ assuming that $\Delta H°$ remains constant in the temperature range 298–318 K. Values for the thermodynamic functions for the solution process are listed in Table II. Although positive values for $\Delta H°_{298}$ and $\Delta G°_{298}$ may be expected for the nonspontaneous dissolution of TbF_3(s), a negative value for the standard entropy change is somewhat surprising. However, the standard third-law entropies for F^- ion and Tb^{3+} ion have been reported to have negative values ($S°_{F^-} = -13.8$ J K^{-1} mol^{-1} and $S°_{Tb^{3+}} = -179$ J K^{-1} mol^{-1}) (*17*). Assuming that $S°_{298}$ for TbF_3 has a positive value, similar to $S°_{298}$ for CeF_3(s) ($S°_{298} = 115.53$ J mol^{-1} K^{-1} (*17*), it is reasonable to have a negative entropy change at 298 K for the solution process. Furthermore, hydration of Tb^{3+} ion and ordering of water molecules around it can also make ΔS negative.

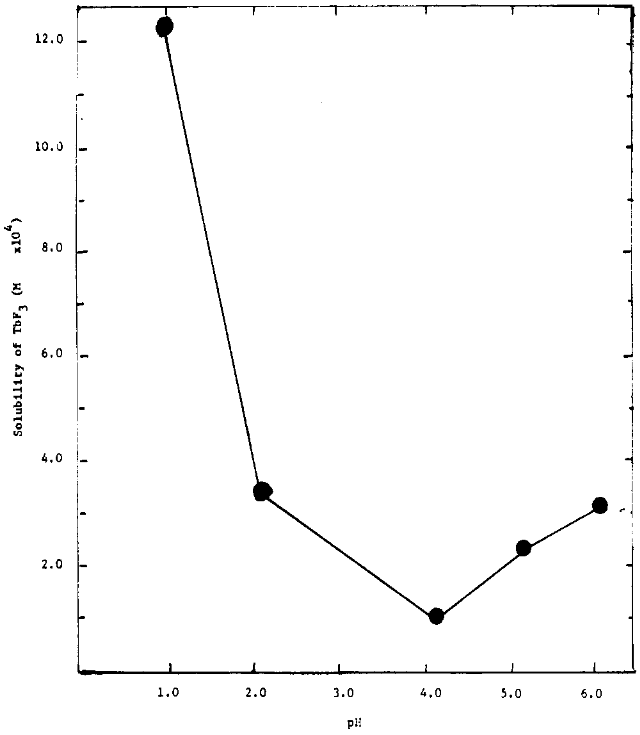

Figure 3. pH dependence of solubility of TbF_3 (potentiometric measurement).

The pH dependence of the solubility of TbF_3 is shown in Figure 3. The data for the plot were obtained from potentiometric measurements. A decrease in solubility with an increase in pH and a significant rise after pH 4.2, a trend similar to those reported elsewhere (*10*, *15*), is quite obvious from this curve. Since the apparent solubility product in acid solution of fluoride depends not only on Tb^{3+} and F^- ion concentrations but also on that of HF, the following equilibria have to be considered:

$$H^+ + F^- \rightleftharpoons HF \tag{9}$$

$$\beta_{HF} = a_{HF}/(a_{F^-}a_{H^+}) \tag{10}$$

where β_{HF} is the stability constant of HF. It appears that, in acid solution, the complexation of Tb^{3+} with F^- does not take place and the apparent solubility product is governed by the expression

$$K_{SIH} = K_{SO}\beta_{HF} = a_{Tb^{3+}}a_{F^-}{}^2 a_{HF}/a_{H^+} \tag{11}$$

Since $\beta_{HF} = 1.07 \times 10^3$ (*9*), it can be seen from eq 10 that, at pH 1 ($a_{H^+} = 0.1$), $a_{HF} = 107a_{F^-}$. It is obvious that more TbF_3 would dissolve in acid solution to furnish additional F^- ions for the formation of HF. The apparent solubility product for TbF_3 in acid solution will be higher by a factor of 1.07×10^3, which will result in an increased solubility. At pH 4 ($a_{H^+} = 10^{-4}$), where the minimum in solubility was observed, the complexation of F^- with H^+ and Tb^{3+} seems to have the least effect on solubility. The increase in solubility after pH 4 may be attributed to the complexation of F^- ion with Tb^{3+} in which case the apparent solubility product constant may be expressed by eq 8.

In Figure 4, the solubility of TbF_3 measured by radiometric technique is plotted against the fluoride concentration at an ionic strength of 1 M and a pH of 3.1. The sharp increase in solubility of TbF_3 may be attributed to the formation of terbium monofluoride complex, although the common ion effect of F^- may drive the solution process in the opposite direction.

The stability constant, β_1, of the terbium monofluoride complex was estimated from radiometric measurements of the concentrations of Tb^{3+} (free) and TbF^{2+} ions in saturated aqueous solution of TbF_3 by using equations similar to those

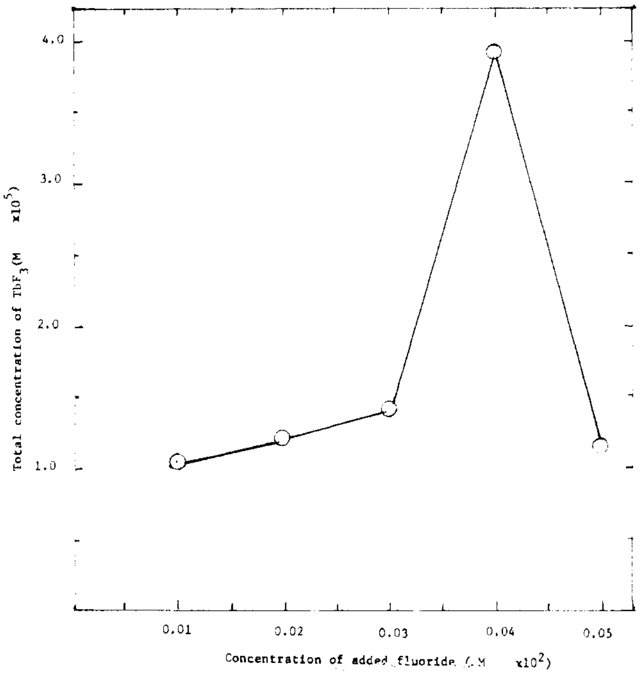

Figure 4. Fluoride dependence of the solubility of TbF_3 at 25 °C (radiometric measurement).

discussed in ref *10*. The value obtained from our measurements is 1831 ± 455, which is comparable with the values 1450 and 1950 reported by Moulin et al. (*18*) and Bilal et al. (*19*), respectively. The percent of total Tb^{3+}(aq) that is tied up as terbium monofluoride complex ion in aqueous solution was estimated to be 60.8.

Acknowledgment

Laboratory assistance by Eldret Parrish, a chemistry graduate, and Joan Smith, a senior in chemistry, is appreciated.

Literature Cited

(1) Anderson, K. P.; Butler, E. A.; Woolley, E. M. *J. Phys. Chem.* **1971**, *75*, 93.
(2) Stevenson, P. C.; Nervik, W. E. "The Radiochemistry of the Rare Earths, Scandium, Yttrium and Actinium", NAS-NS 3020, publication under Nuclear Science Series; USAEC, Office of Technical Services, Department of Commerce: Washington, DC, 1961; p 18.
(3) "IUPAC Solubility Data Project Combined, News Letter 1"; Pergamon Press: Oxford, England, Feb 1980.
(4) Dadahaeva G.; Ikarami, D. D. *Kokl. Akad. Nauk SSR* **1976**, *19*, 31.
(5) Ivanov-Emin, B. N.; Zaitseva, V. A. *Zh. Neorg. Khim.* **1967**, *12*, 2247.
(6) Galkin, N. P.; Shishkov, Y. D.; Khomyabov, V. I. *Radiokhimiya* **1978**, *20*, 136.
(7) Vasil'ev, V. P.; Kozlovski, E. V. *Zh. Neorg. Khim.* **1977**, *22*, 853.
(8) Da Dilva, J.; Frausto, J. R.; Manuela, Q. M. *Rev. Port. Quim.* **1973**, *15*, 29; *Chem. Abstr.* **1975**, 129929g.
(9) Walker, J. B.; Choppin, G. R. *Adv. Chem. Ser.* **1967**, *71*, 127.
(10) Menon, M. P. *J. Radioanal. Chem.* **1981**, *63*, 293.
(11) Willard, H. H.; Merrit, J. R.; Dean, L. L. "Instrumental Methods of Analysis", 5th ed.; Van Nostrand: New York, 1974; p 741.
(12) Speeding, F. H.; Nelson, R. A.; Rard J. A. *J. Chem. Eng. Data* **1974**, *19*, 379.
(13) Taylor, M. D. *Chem. Rev.* **1962**, *62*, 503.
(14) Batsonova, L. R.; Lukina, L. V. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1972**, *17*, 629.
(15) Weaver, J. L.; Purdy, W. G. *Anal. Chim. Acta* **1959**, *20*, 376.
(16) Davies, C. W. "Ion Association"; Butterworths: London, 1962.
(17) Karapetyants, M. Kh.; Karapetyants, M. L. "Thermodynamics Constants of Inorganic and Organic Compounds" (translated by J. Schmorah); Hemphery Science Publishers: Ann Arbor, MI, 1970.
(18) Moulin, N.; Hussonnois, M.; Brillard, L.; Guillaumont, R. J. *J. Inorg. Nucl. Chem.* **1975**, *37*, 2521.
(19) Bilal, B. A.; Kob, B. *J. Inorg. Nucl. Chem.* **1980**, *42*, 629.

Received for review May 22, 1981. Accepted October 16, 1981. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research through their grant no. 11218-B3.

Refractive Index of Molten Salt Hydrates. Mixtures of Tetrahydrates of Calcium and Cadmium Nitrates

Surender K. Jain* and Vijai V. Singh
Hindu College, University of Delhi, Delhi 110007, India

Refractive indexes of molten $Ca(NO_3)_2 \cdot 3.97H_2O$ + $Cd(NO_3)_2 \cdot 4.22H_2O$ mixtures have been measured as functions of temperature and composition. Refractive index–composition isotherms were found to be linear. Molar polarizations computed through the use of the Lorenz–Lorentz equation also varied linearly with composition. The expansivities calculated from the temperature coefficient of the refractive index were found to be nearly equal to those obtained by direct measurement.

Introduction

In the past few years, a number of reports concerning physicochemical investigations of molten hydrates have appeared in the literature. These include studies of conductance (*1*–*4*), viscosity (*1*–*4*), density (*2*–*6*), acid–base and electrochemical reactions (*7*, *8*), proton magnetic resonance spectra (*9*), ultrasonic absorption (*10*, *11*), Cd^{2+} diffusion coefficient (*12*), hydration and association equilibria (*13*), glass transition temperature (*14*), surface tension (*15*, *16*), and refractive-index measurements (*17*, *18*). It has been shown by Moynihan et al. (*19*) that, in the binary hydrate melt system containing tetrahydrates of calcium and cadmium nitrates, both of the cations, e.g., Ca^{2+} and Cd^{2+}, are equally hydrated and the system behaves almost ideally, at least above 60 °C. In order to complete the physicochemical measurements on this interesting system, we present in this paper refractive-index measurements for the binary system containing the tetrahydrates of calcium and cadmium nitrates.

Experimental Section

Analytical-grade tetrahydrates of calcium nitrate (BDH, India) and cadmium nitrate (SM, India) were used as such. Gravimetric analysis and comparison of the density data of the two pure, filtered, and matured melts used in the present study with the precise density vs. composition data of Ewing and Mikovsky (*20*) and Ewing and Herty (*21*) established that the actual H_2O/Ca^{2+} and H_2O/Cd^{2+} mole ratios were 3.97 ± 0.01 and 4.22 ± 0.01, respectively.

Mixtures of varying compositions were prepared by mixing the requisite amounts of the melts in glass flasks fitted with airtight ground-glass joints and filtering while hot through the

0021-9568/82/1727-0084$01.25/0 © 1982 American Chemical Society