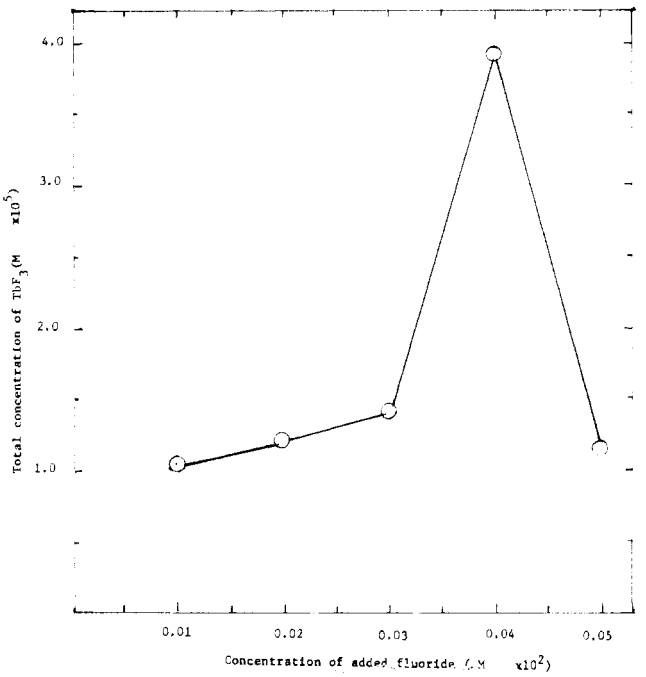

Figure 4. Fluoride dependence of the solubility of TbF_3 at 25 °C (radiometric measurement).

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.

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

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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

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Table I. Refractive Index-Temperature Equations and the Expansivities for Binary Mixtures Containing Tetrahydrates of Calcium and Cadmium Nitrates

Cd^{2+}, mol %	no. of data points	temp range, °C	$n = a - bt$			$10^4\alpha_{LL}$,[a] deg^{-1}	$10^4\alpha_{GD}$,[a] deg^{-1}	$10^4\alpha$,[a] deg^{-1}	α/α_{GD}
			a	10^3b	10^4(SE)				
0.0	6	30–69	1.4717	0.211	0.6	3.98	4.62	4.73	1.02
16.6	6	20–70	1.4760	0.211	0.3	3.94	4.57	4.94	1.08
19.8	6	30–71	1.4786	0.219	0.6	4.07	4.73	4.89	1.03
29.8	6	21–70	1.4822	0.224	0.5	4.13	4.80	5.06	1.05
39.4	6	21–70	1.4831	0.223	0.7	4.10	4.77	5.15	1.08
49.6	6	22–71	1.4854	0.224	0.8	4.09	4.77	4.98	1.04
59.6	6	30–70	1.4883	0.232	0.9	4.21	4.91	5.08	1.03
69.7	5	31–71	1.4906	0.222	0.4	4.09	4.67	5.05	1.08
79.8	5	31–71	1.4939	0.235	0.4	4.21	4.92	5.13	1.04
89.9	5	31–72	1.4971	0.242	0.1	4.31	5.04	5.16	1.02
100.0	4	32–71	1.4989	0.227	0.1	4.01	4.70	5.19	1.10

[a] All values are for 70 °C.

Table II. Refractive Index, Molar Volume, and Molar Polarization vs. Mole Fraction Isotherms for Binary Mixtures Containing the Tetrahydrates of Calcium and Cadmium Nitrates

temp, °C	Cd^{2+}, mole fraction	$n = A + BX$			V_m (cm^3 mol^{-1}) $= A' + B'X$			P_{LL} (cm^3 mol^{-1}) $= A'' + B''X$		
		A	10^2B	10^3(SE)	A'	B'	SE	A''	B''	SE
30	0–1.0	1.4657	2.64	0.43	135.02	3.07	0.30	37.32	2.76	0.09
50	0–1.0	1.4618	2.56	0.68	136.34	3.22	0.30	37.38	2.79	0.09
70	0–1.0	1.4575	2.52	0.64	137.69	3.36	0.32	37.45	2.82	0.09

sintered-glass filters (porosity G-3). The filtered melts were then maintained at about 60 °C to mature for a few hours.

Refractive indexes were measured on a PZO, Warszawa (Poland), refractometer (Model RL 1) whose prisms were maintained at the highest temperature (ca. 70 °C) by circulating water from a constant-temperature bath through the prism compartments. A drop of the melt was placed directly onto the lower prism and the upper prism was immediately clamped into position. The temperature was then lowered, and measurements were made at certain constant temperatures. In some cases the temperature was raised and measurements were made during the heating cycle also. The measured refractive indexes were reproducible to ±0.0002 unit.

Results and Discussion

Measured refractive indexes (n) for various mixtures of the $Ca(NO_3)_2{\cdot}3.97H_2O + Cd(NO_3)_2{\cdot}4.22H_2O$ system are presented in Table I in the form of least-squares-fitted equations of the type

$$n = a - bt(°C) \quad (1)$$

where a and b are arbitrary constants characteristic of the composition. The composition dependence of the refractive index of the system at 30, 50, and 70 °C is shown in Figure 1. The refractive index–composition isotherms are found to be linear and can be described satisfactorily by first-degree polynomials of the type

$$n = A + BX \quad (2)$$

where X is the mole fraction of Cd^{2+} in the mixture. The values of the constants A and B for three typical temperatures are presented in Table II.

Molar volumes (V_m) obtained from the measured densities were observed to be additive. The V_m–composition isotherms are recorded in Table II. Molar polarizations have been calculated by using the Lorenz–Lorentz equation

$$P_{LL} = [(n^2 - 1)/(n^2 + 2)]V_m \quad (3)$$

The linear P_{LL}–composition isotherm (at 70 °C) is shown in Figure 1, and presented in Table II (for 30 and 50 °C also), in the form of the equation

$$P_{LL}\ (cm^3\ mol^{-1}) = A'' + B''X \quad (4)$$

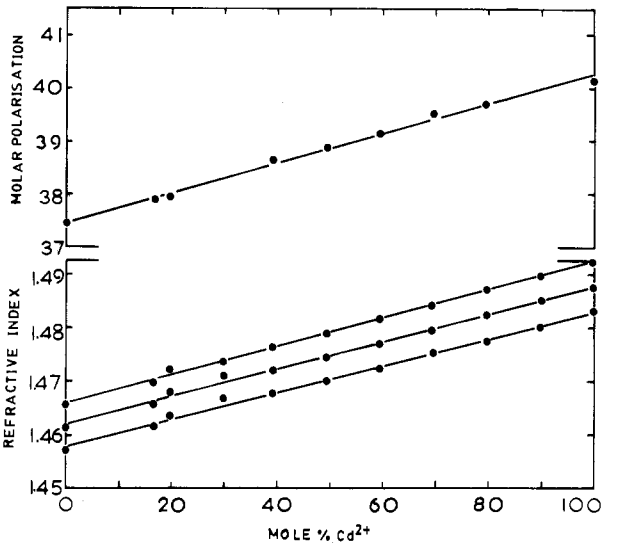

Figure 1. Refractive index at 30, 50, and 70 °C (in order from above) and molar polarization at 70 °C shown as functions of composition of the system.

Table III. Comparison of the Molar Polarization (P_{LL}) Values with Literature Values

salt	ref	P_{LL}(30 °C)
$Ca(NO_3)_2{\cdot}4.1H_2O$	*22*	38 (25 °C)
$Ca(NO_3)_2{\cdot}4.0H_2O$	*17*	37.31
$Ca(NO_3)_2{\cdot}4.05H_2O$	*3*	37.33
$Ca(NO_3)_2{\cdot}3.97H_2O$	present work	37.32
$Cd(NO_3)_2{\cdot}4.12H_2O$	*3*	39.39
$Cd(NO_3)_2{\cdot}4.22H_2O$	present work	40.08

where A'' and B'' are constants characteristic of temperature. Table III presents a facile comparison of the present P_{LL} values for the pure melts with those available in the literature. Taking advantage of the nearly temperature-invariant nature of P_{LL}, we calculated the expansivities of these melts from the temperature coefficient of the refractive index and the differential forms of the Gladstone–Dale and Lorenz–Lorentz equations, through the expressions (*22*)

$$\alpha_{GD} = [1/(n - 1)](dn/dT) \quad (5)$$

$$\alpha_{LL} = \{6n/[(n^2 - 1)(n^2 + 2)]\}(dn/dT) \quad (6)$$

The computed values of α_{GD} and α_{LL} are included in Table I. These are found to be smaller than the directly measured values of expansivities (α), the discrepancy being greater for α_{LL} than for α_{GD}. A similar observation has been made by Rao et al. (*22*), while analyzing their results on $Ca(NO_3)_2 \cdot 4.1H_2O + KNO_3$ mixtures, and also by Jain (*3*). In this study, the ratio α/α_{GD} has a value of 1.06 ± 0.04. This value agrees favorably with those reported earlier by Rao et al. (*22*) and Jain (*3*).

Thus, these studies further support the idea that binary mixtures containing the tetrahydrates of calcium and cadmium nitrates form an ideal molten system.

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Excess Volumes of Binary Mixtures of Isomeric Butyl Chlorides, Pivalonitrile, and Methylchloroform with Nonpolar Solvents

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Excess volumes V^E of binary mixtures of *n*-butyl chloride, *sec*-butyl chloride, *tert*-butyl chloride, pivalonitrile, and methylchloroform with benzene, carbon tetrachloride, cyclohexane, and *n*-hexane at 293.15 K have been computed from the experimental density data. Evidence exists to suggest that the respective molecular shapes of the components play a part in the determination of V^E values.

Introduction

Volume changes on mixing are of interest essentially to test theories of solution and to determine practically composition from density measurements (*1*). In this paper, we report the volumetric behavior of some polar substances (*n*-butyl chloride, *sec*-butyl chloride, *tert*-butyl chloride, pivalonitrile, methylchloroform) in nonpolar solvents (benzene, carbon tetrachloride, cyclohexane, *n*-hexane) at 293.15 K and atmospheric pressure. These measurements were made as part of a continuing study on the thermodynamic and electrical properties of liquid mixtures (*2-8*).

Experimental Section

Densities were measured with an accuracy of ±5 × 10^{-5} g cm^{-3} by the hydrostatical displacement method previously reported (*9*). The temperature was maintained at 293.15 ± 0.05

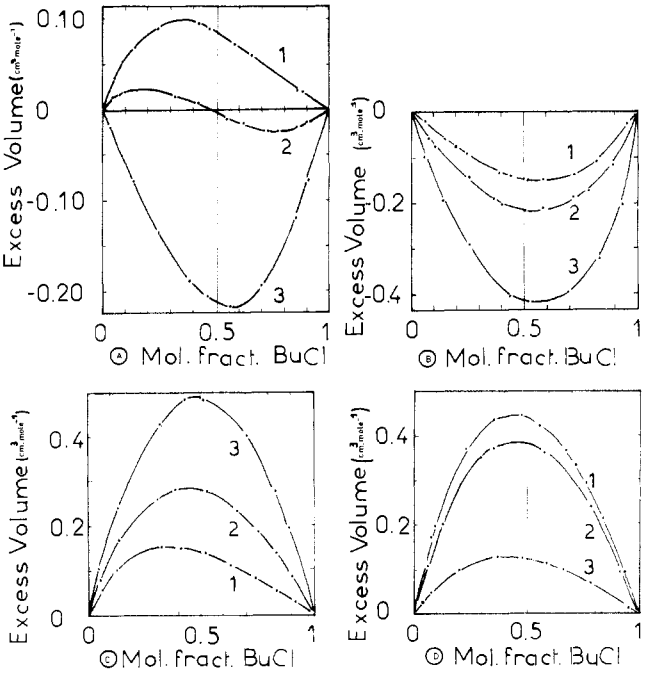

Figure 1. Molar excess volumes of mixtures of butyl chlorides ((1) *n*-butyl chloride, (2) *sec*-butyl chloride (3), *tert*-butyl chloride) with nonpolar solvents ((A) benzene, (B) carbon tetrachloride, (C) *n*-hexane, (D) cyclohexane) at 293.15 K.

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