ways to calculate B_{12} are possible; most points were calculated by using all pressures.

The errors must be related to direct measurement of temperature, pressure, and composition of mixture. The probable error in pressure measurements does not exceed ±0.02% at any pressure. The source of error in pressure are weight calibration, effective area of the piston and cylinder of the dead weight gauge, barometric pressure, hydraulic head correction, and the reading and "null" correction of the differential pressure indicator, as discussed in detail earlier (*7–9*). The temperature was kept constant to within less than 0.01 K. If long time drifts occurred during several hours of continuous operation of the thermostating bath, the pressures were corrected and all brought to the same temperature for the given expansion run. The resulting pressure error is far below the accuracy stated above and the error in temperature is estimated at ±0.01 K.

4. Discussion

The values of $B(T)$ and $C(T)$ for pure substances are in very good agreement (*7*, *9*) with literature data. Thus, the accuracy of $B(T,x)$ determination should be also satisfactory. An additional error arises, however, from indirect determination of composition by means of eq 4. The excess virial coefficients of binary mixtures ($2B_{12} - B_{11} - B_{22}$) are very high, being of the order of +280 $cm^3\ mol^{-1}$. This deviation is higher than the value of either virial coefficient of the pure components. The derived values of $B_{12}(T)$ are consistent with the accuracy of ±4 $cm^3\ mol^{-1}$. For the propane + helium system, $B_{12}(T)$ increases but slightly with temperature. This suggests that $B_{12}(T)$ is located, in the neighborhood of the maximum and is confirmed by a qualitative discussion based on the Lennard–Jones (6–12) potential. Application of the Lennard–Jones (6–12) potential with the pure component values of σ and ϵ taken from Hirschfelder et al. (*5*), i.e., $\epsilon/k = 6.03$ K and $\sigma = 2.63$ Å for helium, $\epsilon/k = 242$ K and $\sigma = 5.637$ Å for propane, yields the geometric mean $\epsilon_{12}/k = 38.2$ and arithmetical mean $\sigma_{12} = 4.133$ Å. These values predict $B_{12}(T)$ from 41.2 to 41.6 cm^3/mol^{-1} for T from 393.2 to 423.0 K—in fair agreement with our data from Table IV. The force parameters estimated from the pure component data (*9*) are $\epsilon/k = 4.65$ K and $\sigma = 2.662$ Å for He, $\epsilon/k = 225$ K and $\sigma = 5.811$ Å for propane, and $\epsilon/k = 240$ K and $\sigma = 5.34$ Å for propene. These values produce for the helium–propane system $B_{12}(T)$ equal to 45.5–46.1 $cm^3\ mol^{-1}$ and for helium–propene 38.1–38.6 $cm^3\ mol^{-1}$ for the same temperature range. The agreement with the mixture data is as good as can be expected as the Lennard–Jones potential was developed for spherical molecules. Moreover, large differences in size between helium and the hydrocarbon compounds require potential functions which would take this into account besides the orientational effects.

Unfortunately, our data reported here for B_{12} extend only from 398 to 423 K and any analysis in terms of intermolecular potential functions is thus prohibited. Therefore we have refrained from any fitting procedures; the above calculations are meant to show an order-of-magnitude agreement.

We hope to consider in future papers the details of the hydrocarbon–helium interaction in the context of the $B_{12}(T)$ values using all possible data, along with our data reported here, so as to extend as much as possible the temperature range and the range of molecular volume of the larger component.

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Refractive Index of Molten Lewis Acid Salt Hydrates: Mixtures of $Cr(NO_3)_3 \cdot 9H_2O + Ca(NO_3)_2 \cdot 4H_2O$

Surender K. Jain

Hindu College, University of Delhi, Delhi-110007, India

Refractive indices of molten $Cr(NO_3)_3 \cdot 9H_2O$ + $Ca(NO_3)_2 \cdot 4H_2O$ mixtures have been measured as a function of temperature and composition. Refractive index–composition (in mol % of $Ca(NO_3)_2 \cdot 4H_2O$) isotherms showed a "break" at ≈39 mol % of divalent ion salt hydrate. Molar polarizations, computed using the Lorenz–Lorentz equation, varied linearly with composition. Expansivities calculated from temperature coefficient of refractive index were found to be much smaller than those obtained from density measurements.

Volumetric, surface, and flow properties of $Ca(NO_3)_2 \cdot 4H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$ and a number of Lewis acid salt hydrates of metals belonging to 3d series of transition elements in pure (*3*, *5*) and mixed (*2*, *4*, *6*) states have recently been reported. In an effort to gather more evidence for the existence of hydration–dehydration tendencies in mixed melts, refractive index measurements on the system $Cr(NO_3)_3 \cdot 9H_2O + Ca(NO_3)_2 \cdot 4H_2O$ are reported in this paper.

Experimental Section

Material. $Ca(NO_3)_2 \cdot 4H_2O$ (BDH, India) and $Cr(NO_3)_3 \cdot 9H_2O$ (Ortanal, Italy) were of analytical reagent grade. The melting temperatures of these salts as determined by the cooling curve method were found to be 42.5 and 36.8 °C, the corresponding literature liquidus temperatures being 42.7 and 37 °C, re-

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Table I. Refractive Index Values for $Cr(NO_3)_3 \cdot 9H_2O$ + $Ca(NO_3)_2 \cdot 4H_2O$ Mixtures

Mol % $Ca(NO_3)_2 \cdot 4H_2O$	Temp, °C 25.0	50.0	75.0
0.0	1.4870	1.4829	1.4795
13.9	1.4845	1.4807	1.4769
28.1	1.4815	1.4777	1.4742
39.4	1.4800	1.4760	1.4722
54.5	1.4760	1.4720	1.4685
61.4	1.4740	1.4702	1.4668
67.7	1.4725	1.4685	1.4650
78.5	1.4695	1.4657	1.4622
85.2	1.4685	1.4642	1.4605
93.1	1.4658	1.4617	1.4583
100.0	1.4640	1.4602	1.4568

spectively. Agreement between the experimentally determined melting temperatures and those reported in the literature (*8*) leads one to believe that the salts were of stoichiometric compositions as reported by the manufacturers. This, however, was verified for $Ca(NO_3)_2 \cdot 4H_2O$ gravimetrically by vacuum dehydration of a small sample (ca. 5 g) at temperatures starting from melting to about 130–140 °C. Repeated cross-checks established the water content to be within ±0.01 of the stoichiometric value of four. Mixtures of varying compositions were prepared by melting the requisite amounts of the salts in hard glass flasks fitted with airtight ground glass joints and filtered through sintered glass filters (porosity G-3). Filtered melts were then maintained at about 60 °C for maturing.

Refractive indices were measured on a PZO, Warszawa (Poland) refractometer (Model RL 1) whose prisms were maintained at the highest temperature, 75 °C, by circulating water from a constant-temperature bath through the prism compartments. A drop of the melt was placed directly onto the prism and the prisms were immediately clamped into position. The temperature was then lowered and measurements made at 50 and 25 °C. The temperature was then raised and measurements were made during the heating cycle also. The measured refractive indices were reproducible to ±0.0002 units.

Results and Discussion

Measured refractive indices (*n*) for various mixtures of the system $Cr(NO_3)_3 \cdot 9H_2O + Ca(NO_3)_2 \cdot 4H_2O$ are presented in Table I. Variation of refractive indices with temperature could be described by linear equations of the type

$$n = a - bt \qquad (1)$$

where *a* and *b* are arbitrary constants characteristic of the system composition. These constants for all the mixtures investigated in this study are presented in Table II. Composition dependence of refractive indices of the system $Cr(NO_3)_3 \cdot 9H_2O + Ca(NO_3)_2 \cdot 4H_2O$ is shown in Figure 1. These isotherms show "discontinuity" at about 39 mol % of $Ca(NO_3)_2 \cdot 4H_2O$. Similar "breaks" have been observed (*6*) when fluidities, surface tensions, and equivalent volumes of this system were plotted against mole percent of $Ca(NO_3)_2 \cdot 4H_2O$. Thus, the present investigation appears to provide further support for the existence of hydration–dehydration tendencies in these mixtures. Equations describing the composition dependence of refractive index at 25, 50, and 75 °C are reported in Table III.

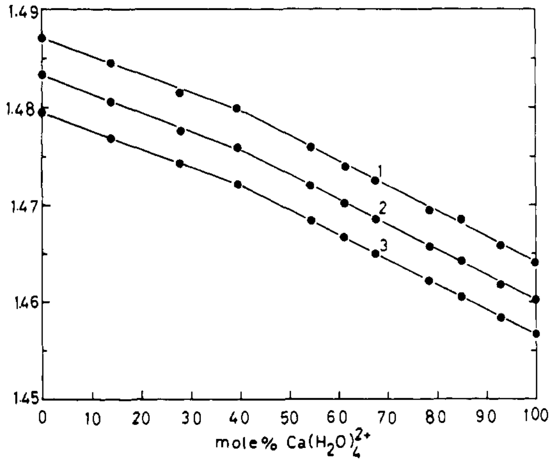

Figure 1. Plot of refractive index vs. mol % $Ca(NO_3)_2 \cdot 4H_2O$ for $Cr(NO_3)_3 \cdot 9H_2O + Ca(NO_3)_2 \cdot 4H_2O$ mixtures: (1) 25 °C, (2) 50 °C, (3) 75 °C.

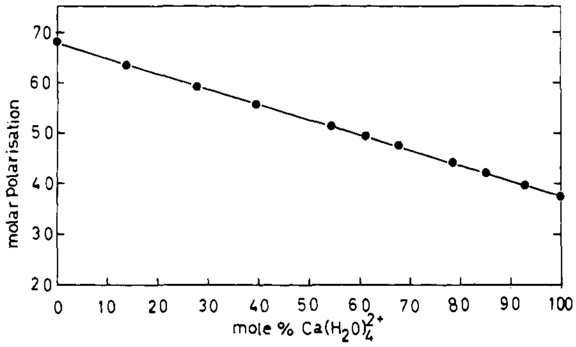

Figure 2. Molar polarizations (P_{LL}), at 50 °C, for $Cr(NO_3)_3 \cdot 9H_2O + Ca(NO_3)_2 \cdot 4H_2O$ mixtures shown as a function of composition.

Molar volumes (V_m) were computed from the densities of these mixtures reported elsewhere (*6*). V_m–temperature results are described in the form of least-squares fits in Table II. Molar polarizations at 50 °C have been calculated using the Lorenz–Lorentz equation

$$P_{LL} = \frac{(n^2 - 1)}{(n^2 + 2)} V_m \qquad (2)$$

These calculated values have been included in Table II and

Table II. Refractive Index–Temperature and Molar Volume–Temperature Equations and Related Parameters for $Cr(NO_3)_3 \cdot 9H_2O + Ca(NO_3)_2 \cdot 4H_2O$ Mixtures

Mol % $Ca(NO_3)_2 \cdot 4H_2O$	Temp range, °C	$n = a - bt$			Temp range, °C	$V_m = A + Bt$, $cm^3\ mol^{-1}$			P_{LL} (50 °C)	$10^4\alpha_{LL}$ (50 °C)	$10^4\alpha_{GD}$ (50 °C)	$10^4\ \alpha$ (50 °C)
		a	$10^3 b$	10^3SE		*A*	$10^2 B$	SE				
0.0	25-75	1.4906	0.150	0.28	32-87	230.71	14.15	0.112	67.89	2.65	3.11	5.89
13.9	25-75	1.4883	0.152	0.004	32-82	217.54	11.97	0.078	63.57	2.70	3.16	5.31
28.1	25-75	1.4851	0.146	0.12	28-82	203.75	11.84	0.102	59.29	2.61	3.06	5.61
39.4	25-75	1.4839	0.156	0.08	31-82	192.78	10.38	0.041	55.83	2.80	3.28	5.21
54.5	25-75	1.4797	0.150	0.20	17-82	177.98	9.90	0.078	51.22	2.72	3.18	5.41
61.4	25-75	1.4775	0.144	0.16	17-70	172.63	9.21	0.021	49.45	2.63	3.06	5.22
67.7	25-75	1.4762	0.150	0.20	16-80	166.13	9.18	0.019	47.49	2.75	3.20	5.38
78.5	25-75	1.4731	0.146	0.12	26-73	154.71	8.01	0.024	43.91	2.69	3.13	5.04
85.2	25-75	1.4724	0.160	0.24	27-82	147.88	7.58	0.013	41.86	2.96	3.45	5.00
93.1	25-75	1.4694	0.150	0.28	27-82	139.88	7.76	0.035	39.49	2.80	3.25	5.37
100.0	25-75	1.4675	0.144	0.16	15-84	133.63	6.39	0.064	37.47	2.70	3.13	4.66

Table III. Parameters of the Refractive Index-Mole Fraction Isotherms

Temp, °C	Composition range (mol %, $Ca(NO_3)_2 \cdot 4H_2O$)	$n = a - bx$		
		a	$10b$	10^3SE
25.0	0.0-39.4	1.4869	0.182	0.29
	39.4-100.0	1.4902	0.261	0.25
50.0	0.0-39.4	1.4830	0.179	0.24
	39.4-100.0	1.4863	0.261	0.13
75.0	0.0-39.4	1.4795	0.186	0.05
	39.4-100.0	1.4825	0.258	0.12

shown as a function of composition in Figure 2. A value of 37.47 for the molar polarization (P_{LL}) of $Ca(NO_3)_2 \cdot 4H_2O$ at 25 °C could be favorably compared with the value 38 estimated from the molar polarization values for $Ca(NO_3)_2 \cdot 4.1H_2O + KNO_3$ mixtures reported by Rao et al. (*7*).

The molar refractions have been evaluated by several empirical formulas (*1*) of which only the Lorenz-Lorentz relation appears to have a sound theoretical basis. However, Young and Finn (*9*) have shown that the Gladstone-Dale formula

$$P_{GD} = (n - 1)(M/\rho)$$

is quite adequate in giving temperature-independent molar refractions. If the molar polarizations were temperature independent, then the differential form of Gladstone-Dale and Lorenz-Lorentz equations would provide a direct relation between the coefficient of thermal expansion, α, and the temperature dependence of refractive index through the expressions

$$\left[\frac{1}{(n-1)}\right]\frac{dn}{dT} = \frac{1}{\rho}\frac{d\rho}{dT} = \alpha_{GD} \qquad (3)$$

$$\left[\frac{6n}{(n^2-1)(n^2+2)}\right]\frac{dn}{dT} = \frac{1}{\rho}\frac{d\rho}{dT} = \alpha_{LL} \qquad (4)$$

Computed values of α_{GD} and α_{LL} for all the mixtures are recorded in Table II. 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. (*7*) while analyzing their results on $Ca(NO_3)_2 \cdot 4.1H_2O + KNO_3$ mixtures. For the mixtures investigated in this study, the ratio α/α_{GD} lies between 1.5 and 1.9, which is much higher than the value 1.15 reported by Rao et al. (*7*) for the $Ca(NO_3)_2 \cdot 4.1H_2O + KNO_3$ system. It may be that due to the "release" of water from the coordination of trivalent chromium ion by NO_3^-, the thermal expansivity of this system is increased and is thus reflected in the ratio α/α_{GD}.

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Heats of Mixing of Binary Chloroalkane-*n*-Alkane and Chloroalkane-*n*-Alcohol Systems at 25 °C

T. Huong Doan-Nguyen, Juan H. Vera,* and Gerald A. Ratcliff[†]

Department of Chemical Engineering, McGill University, Montreal, Quebec H3A 2A7, Canada

Heats of mixing of six binary chloroalkane-*n*-alkane and nine chloroalkane-*n*-alcohol systems were measured in an isothermal dilution calorimeter. Experimental results expressed as $\Delta H/x_1x_2$ vs. x_1 were interpolated using the expanded spline-fit technique. Heats of mixing are reported at regular composition intervals.

Accurate heat-of-mixing data are extremely valuable for testing solution models. In order to understand the effect of molecular structure on thermodynamic properties of solutions, systematic information covering components of different structural characteristics is required. This work presents heats of mixing data for chloroalkanes with different *n*-alkanes and *n*-alcohols. Data on these systems are scarce in the literature. Only data for three chloroalkane-*n*-alkane systems have been previously reported (*3*). Measurements in this study were made at 25 °C.

Materials and Apparatus

Materials used in this work, together with their suppliers and specifications, are listed in Table I. Refractive indices of the pure components were measured in a Bausch & Lomb refractometer. Experimental and literature values of the index of refraction are also presented in Table I. The agreement between experimental and literature values of the index of refraction was considered satisfactory and the materials were used without further purification.

The heats of mixing measurements were made in an isothermal semicontinuous dilution calorimeter of Van Ness type (*6*) specially constructed to measure heats of mixing of endothermic systems. The basic features of this calorimeter have been described elsewhere (*5*). The principle of operation of the calorimeter is as follows: one component is introduced semicontinuously, at constant temperature and pressure, into a cell initially containing the other component. Electrical energy is added to the system in order to maintain the temperature constant during the mixing process. The amount of energy added is a measure of the heat of mixing. The entire heat of

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[†] Deceased July 1976.

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