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Surface Tensions and Refractive Indices of Molten Calcium Nitrate Tetrahydrate and Its Mixtures with Lithium Nitrate

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The surface tension and refractive index of $Ca(NO_3)_2 \cdot 4H_2O$ and its mixtures with $LiNO_3$ have been measured as a function of temperature and lithium nitrate content. Surface tension values show negative deviations from ideal behavior values and are observed to be a linear function of the surface layer mole fraction (x^σ). The enrichment factor(s) has been computed on the basis of Eberhart's equation. Surface enthalpies and entropies of mixing per unit area have also been computed. Refractive index–composition isotherms show a slight concavity toward the composition axis but the molar polarizations (P_{LL}), computed using the Lorenz–Lorentz equation, varied linearly with the mole fraction of $LiNO_3$.

Because of the extensive supercooling and quite often glass-forming tendencies, hydrated salts in the molten state provide media specially suited for low-temperature electrochemical investigations. In previous publications, various aspects of physicochemical behavior of such systems have been reported (*5–11*). This communication describes some of the observations made on $Ca(NO_3)_2 \cdot 4HO$ + $LiNO_3$ mixtures with respect to their surface and optical properties.

Experimental Section

Material. Analar (BDH) grade $Ca(NO_3)_2 \cdot 4H_2O$ and anhydrous lithium nitrate (Pro analysi, Carlo Erba, Italy) were used without purification except that the lithium nitrate was vacuum desiccated for about 24 h at room temperature. The water content of $Ca(NO_3)_2 \cdot 4H_2O$ was estimated gravimetrically as described earlier (*11*). Repeated cross checks established the water content to be within ±0.01 of the stoichiometric value of 4. Mixtures of varying compositions were prepared by melting the requisite amounts of the salts in hard glass flasks (ca. 100 cm^3) fitted with airtight ground glass joints and filtered through sintered glass filters (porosity G-3) under a slight positive pressure of dry air. The filtered melts were then maintained at about 60 °C for maturing.

Apparatus. The refractive indices (n) were measured on a PZO, Warszawa (Poland), refractometer (Model RL 1), whose prisms were maintained at about 75 °C by circulating water from a constant-temperature bath through the prism compartments. A drop of the melt was placed directly onto a prism, and the prisms were immediately clamped into the position. Under the conditions, the measured values of refractive indices were reproducible to ±0.0002 units.

Surface tensions (σ) were measured by the differential capillary rise method. The related details regarding experimentation have been described earlier (*9*). The measured values are estimated to be precise to ±0.25 mN m^{-1}. The temperatures of the constant-temperature bath were controlled and measured with a precision of ±0.1 °C.

Results and Discussion

Table I. Surface Tension (σ) Values for $Ca(NO_3)_2 \cdot 4H_2O$ + $LiNO_3$ Mixtures

temp, °C	σ, mN m^{-1}	temp, °C	σ, mN m^{-1}
10.0^a		20.0^a	
28.5	99.42	27.5	100.57
40.0	96.77	50.0	96.83
60.0	94.81	77.0	93.84
80.0	92.47		
30.0^a		40.0^a	
30.0	99.33	28.0	104.70
76.0	94.48	50.0	100.59
		75.0	96.58

^{a} Mol % $LiNO_3$.

Table II. Refractive Index Values of $Ca(NO_3)_2 \cdot 4H_2O$ + $LiNO_3$ Mixtures

	mol % of $LiNO_3$				
temp, °C	0.0	10.0	20.0	30.0	40.0
28.5	1.4638	1.4641	1.4652	1.4660	1.4679
60.0	1.4593	1.4600	1.4609	1.4624	1.4642
73.0	1.4575	1.4587	1.4594	1.4605	1.4624

The surface tension (σ) and the refractive index (n) values of $Ca(NO_3)_2 \cdot 4H_2O$ + $LiNO_3$ mixtures are presented in Tables I and Table II. The data were least-squares fitted into linear equations

$$\sigma(\text{mN m}^{-1}) = p - q(T - 273.16) \tag{1}$$

$$n = a - b(T - 273.16) \tag{2}$$

The coefficients p, q and a, b are characteristic of the melt composition. These coefficients are presented in Tables III and IV, respectively. The variation of surface tension (at 348 K) with mole fraction of $LiNO_3$ (x_{LiNO_3}) in the mixtures is shown in Figure 1. Extrapolation of the data to pure $LiNO_3$ was facilitated by extrapolating the values of $\sigma(LiNO_3)$ reported by Addison and Coldrey (*1*) to 348 K, a hypothetical supercooled state of $LiNO_3$. The system showed negative deviations. This behavior is usually explained qualitatively by the fact that the surface layer of the solution is *enriched* in the component of lower surface tension. If it is so, Eberhart (*4*) found it advantageous to describe the surface tensions in terms of surface layer mole fraction (x_i^σ) of the component through the expression

$$\sigma = x_1^\sigma \sigma_1 + x_2^\sigma \sigma_2 = (s x_1 \sigma_1 + x_2 \sigma_2)/(s x_1 + x_2) \tag{3}$$

where x_1 and x_2 are the mole fractions of the two components of the binary mixture and s is a factor called *enrichment factor*, which is described as

$$s = \frac{(x_1^\sigma / x_2^\sigma)}{(x_1 / x_2)} \tag{4}$$

where x_1^σ and x_2^σ are the mole fractions of the two components in the surface layer. Value of s (at 348 K) was determined by the method suggested by Eberhart (*4*), in which ξ is plotted against ξ/r in accordance with the equation $\xi = -s(\xi/r) + 1$; where

$$\xi = (\sigma - \sigma_1)/(\sigma_2 - \sigma_1)$$

$$r = x_2/x_1$$

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Table III. Surface Tension-Temperature Equations for $Ca(NO_3)_2 \cdot 4H_2O$ + $LiNO_3$ Mixtures

mole fraction of $LiNO_3$			σ(mN m^{-1}) = $p - q(T - 273.16)$				
bulk (x)	surface (x^σ)	temp range, K	p	10^2q	SE^b	$10^3(S^\sigma/A^\sigma)$, J m^{-2} K^{-1}	$10^2(H^\sigma/A^\sigma)$, J m^{-2}
0.0^a	0.0	318-354	102.46	13.10	0.13	0.131	13.82
0.1	0.018	301-353	102.55	12.81	0.60	0.128	13.75
0.2	0.040	300-350	104.04	13.50	0.55	0.135	14.09
0.3	0.066	303-349	102.57	10.64	0.002	0.106	13.15
0.4	0.099	301-348	109.42	17.24	0.25	0.172	15.64

^{a} Adopted from ref 9. ^{b} SE = standard error.

Table IV. Linear Refractive Index-Temperature Equations for $Ca(NO_3)_2 \cdot 4H_2O$ + $LiNO_3$ Mixtures

		$n = a - b(T - 273.16)$			P_{LL}, cm^3 mol^{-1}					
mol % $LiNO_3$	temp range, K	a	10^3b	10^3SE^c	28.5	60.0	73.0^a	$10^4\alpha_{LL}$, deg^{-1}	$10^4\alpha_{GD}$, deg^{-1}	$10^4\alpha$,^{b} deg^{-1}
0.0	301-346	1.4678	0.142	0.03	37.30	37.55	37.65	2.66	3.09	4.75
10.0	301-346	1.4676	0.123	0.22	34.60	34.87	34.99	2.30	2.67	4.84
20.0	301-346	1.4689	0.131	0.15	31.93	32.19	32.31	2.45	2.84	5.00
30.0	301-346	1.4695	0.122	0.23	28.95	29.54	29.62	2.27	2.64	5.22
40.0	301-346	1.4714	0.122	0.15	26.61	26.89	27.62	2.26	2.63	5.44

^{a} Values are in °C. ^{b} Values at 60 °C. ^{c} SE = standard error.

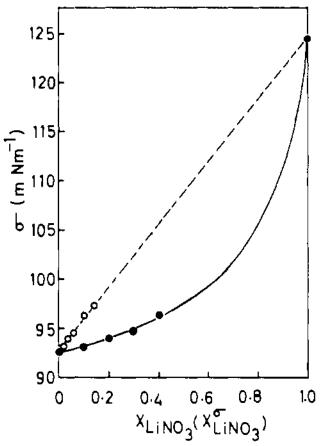

Figure 1. Surface tension (σ) of $Ca(NO_3)_2 \cdot 4H_2O$ + $LiNO_3$ mixtures (at 348 K) shown as a function of bulk (●) and surface layer (○) mole fraction of lithium nitrate.

ξ is thus the surface tension on a dimensionless scale varying from zero for pure 1 to unity for pure 2. The analysis of the data yields a value of 6.06 for the surface enrichment factor. Using this value of s, the surface tensions for the mixtures of different compositions were calculated and are shown as the solid curve in Figure 1. There is a striking agreement between the curve drawn and the experimental points. Taking this value of s = 6.06, the mole fractions of lithium nitrate in the surface layer ($x^\sigma_{LiNO_3}$) were calculated. In Figure 1, the measured surface tensions are also shown as a function of surface concentration of lithium nitrate. The linear plot, thus obtained showed that in these mixtures the surface tension is a linear function of the surface and not the bulk concentrations.

The surface tension of a liquid is defined as its surface free energy per unit area, i.e.

$$\sigma = G^\sigma/A^\sigma \tag{5}$$

where A^σ is the area of the surface. The surface entropy per unit area (S^σ/A^σ) and the surface enthalpy per unit area (H^σ/A^σ) are then described as

$$S^\sigma/A^\sigma = -\mathrm{d}\sigma/\mathrm{d}T \tag{6}$$

$$H^\sigma/A^\sigma = \sigma - T(\mathrm{d}\sigma/\mathrm{d}T) \tag{7}$$

As the temperature coefficient of surface tension for any mixture is constant, the quantity H^σ/A^σ is a constant and independent of temperature. Table III lists the values of H^σ/A^σ and S^σ/A^σ for all the mixtures investigated in this study. The magnitude of H^σ/A^σ appears to place these molten hydrates between highly ionized molten salts and the nonpolar liquids; the magnitude of this parameter usually lies around 0.2 J m^{-2} for the former and 0.05 J m^{-2} for the latter class of liquids.

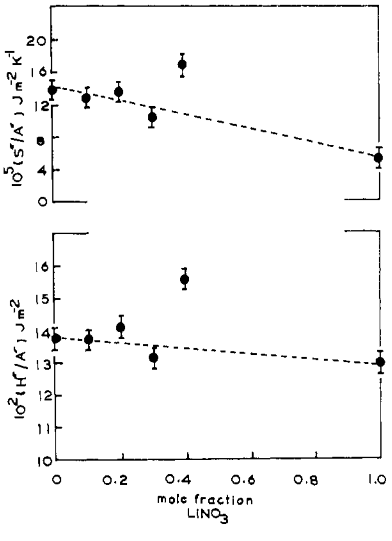

Figure 2. Surface entropy and surface enthalpy per unit area shown as a function of mole fraction of $LiNO_3$ in $Ca(NO_3)_2 \cdot 4H_2O$ + $LiNO_3$ mixtures.

Bloom et al. (*3*) interpreted the deviations in surface tension values from ideal behavior values in terms of surface enthalpy and surface entropy of mixing per unit area, described as

$$\Delta(H^\sigma/A^\sigma) = (H^\sigma/A^\sigma) - \{x_1(H^\sigma/A^\sigma)_1 + x_2(H^\sigma/A^\sigma)_2\} \tag{8}$$

$$\Delta(S^\sigma/A^\sigma) = (S^\sigma/A^\sigma) - \{x_1(S^\sigma/A^\sigma)_1 + x_2(S^\sigma/A^\sigma)_2\} \tag{9}$$

where (H^σ/A^σ) and (S^σ/A^σ) are the surface enthalpy and surface entropy per unit area for the mixture and the quantities with the subscript 1 and 2 refer to those of the pure components. These were evaluated through relations 6 and 7. The parameters H^σ/A^σ and S^σ/A^σ appear to be nearly additive but in view of larger deviations shown by the results at 40 mol % of $LiNO_3$,

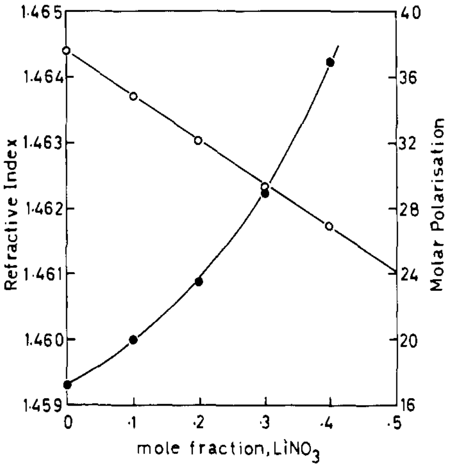

Figure 3. *Refractive index and molar polarization (at 60 °C) of* $Ca(NO_3)_2{\cdot}4H_2O + LiNO_3$ *mixtures, shown as a function of* $LiNO_3$ *mole fraction.*

no definite conclusions can be drawn from these plots.

The composition dependence of refractive index (at 60 °C) of the system $Ca(NO_3)_2{\cdot}4H_2O + LiNO_3$ is presented in Figure 3. Concavity in the isotherm indicates some interactions leading to the changes in ion-water dipole bonding, on the addition of lithium nitrate to molten $Ca(NO_3)_2{\cdot}4H_2O$. The molar volumes (V_m) corresponding to the compositions of the mixtures investigated herein were computed from the volumetric data on $Ca(NO_3)_2{\cdot}4H_2O + LiNO_3$ mixtures reported earlier (*5*). The V_m-temperature results are described in the form of least-squares fits in Table V. Molar polarizations, at 28.5, 60.0, and 73.0 °C, have been calculated using the Lorenz-Lorentz equation

$$P_{LL} = \frac{(n^2 - 1)}{(n^2 + 2)} V_m \qquad (10)$$

These computed values are reported in Table IV. Molar polarization values at 60 °C are shown as a function of composition in Figure 3.

The molar refractions have been evaluated by several empirical formulas (*2*) of which only the Lorenz and Lorentz relations appear to have a sound theoretical basis. However, Young and Finn (*13*) have shown that the Gladstone-Dale formula

$$P_{GD} = (n - 1)(M/\rho) \qquad (11)$$

is quite adequate in giving temperature-independent molar refraction. The molar polarization for these liquids varied by about 1-2.5% over the temperature range 28-73 °C. If, as a first approximation, this temperature variation is ignored, the differential forms of eq 10 and 11 would provide a direct relation between the coefficient of thermal expansion α, and the temperature dependence of refractive index through the expressions

Table V. Molar Volume-Temperature Equations for $Ca(NO_3)_2{\cdot}4H_2O + LiNO_3$ Mixtures

mol % $LiNO_3$	V_m(cm^3 mol^{-1}) = $A + Bt$			V_m(60 °C), cm^3 mol^{-1}
	A	10^2B	SE^a	
0.0	133.42	6.43	0.020	137.29
10.0	123.63	6.12	0.020	127.32
20.0	113.83	5.85	0.016	117.35
30.0	104.03	5.55	0.016	107.38
40.0	94.25	5.25	0.008	97.41

^{a} SE = standard error.

$$\frac{1}{(n-1)}\frac{dn}{dT} = \frac{1}{\rho}\frac{d\rho}{dT} = \alpha_{GD} \qquad (12)$$

$$\frac{6n}{(n^2-1)(n^2+2)}\frac{dn}{dT} = \frac{1}{\rho}\frac{d\rho}{dT} = \alpha_{LL} \qquad (13)$$

The computed values of α_{GD} and α_{LL} for all the mixtures are recorded in Table IV. These are found to be smaller than the directly measured values of expansivities (α), the discrepency being larger for α_{LL} than for α_{GD}. Similar observations have been made by Rao et al. (*12*) while analyzing their results on $Ca(NO_3)_2{\cdot}4.1H_2O + KNO_3$ mixtures and also by Jain (*10*) from his results on $Cr(NO_3)_3{\cdot}9H_2O + Ca(NO_3)_2{\cdot}4H_2O$ mixtures. In the present case, the ratio α/α_{GD} lies between 1.54 and 2.1; these are of the same order as observed for $Cr(NO_3)_3{\cdot}9H_2O + Ca(NO_3)_2{\cdot}4H_2O$ mixtures but are relatively higher than the value 1.15 reported by Rao et al. (*12*).

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