On the Additivity of Molar Volume and Refractivity of Molten $Ca(NO_3)_2 \cdot 3.18H_2O$–KSCN System

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Synopsis. Densities and refractive indices of $Ca(NO_3)_2 \cdot 3.18H_2O$–KSCN melts have been measured as functions of temperature and composition. Densities, molar volumes, and refractive indices show linear dependence on temperature. Molar volume, intrinsic volume, molar refractivity, and the product of refractive index and molar volume show additivity within ±2% error. The molten $Ca(NO_3)_2 \cdot 3.18H_2O$–KSCN system at ambient temperatures appears to behave like an ideal mixture of molten $Ca(NO_3)_2 \cdot 3.18H_2O$ and supercooled KSCN melt.

Earlier, we have reported the densities, viscosities, and equivalent conductances of molten $Ca(NO_3)_2 \cdot 3.99H_2O$–KSCN systems.[1] In that paper,[1] although we have mentioned about an interesting feature of this system, *i. e.*, its ideal behavior with respect to molar volume, our major emphasis was on the non-Arrhenius temperature dependence of viscosities and equivalent conductances. In order to understand more about the ideal behavior of such a binary system we have reported here the densities and refractive indices of molten $Ca(NO_3)_2 \cdot 3.18H_2O$–KSCN systems as functions of temperature and composition.

Experimental

Reagent grade calcium nitrate tetrahydrate, mp 43.5 °C, was used in the molten state. The exact number of moles of water per mole of calcium nitrate has been determined through EDTA titration method and is found to be 3.18. Potassium thiocyanate was recrystallized twice from double-distilled water. Preparation of samples of $Ca(NO_3)_2 \cdot 3.18H_2O$–KSCN and their density measurements were made as described earlier.[1] The refractive index (±0.1%) measurements were made corresponding to sodium light using the Abbe refractometer.

Results and Discussion

The molar volumes (V) of $Ca(NO_3)_2 \cdot 3.18H_2O$–KSCN melts are calculated from their measured densities and are represented in Table 1 in the form of a linear function

$$V = V_o' + b'T, \tag{1}$$

where V_o' and b' are constants at a particular concentration. As the system under study has an inherent tendency to supercool the temperature dependence of molar volume may also be represented as

$$V = V_0 + b'(T - T_0), \tag{2}$$

where T_0 is the ideal glass transition temperature and V_0 is the intrinsic volume. Comparison of Eqs. 1 and 2 gives that

$$V_o' = V_0 - b'T_0. \tag{3}$$

From Fig. 1a it may be noticed that both V_o' and b' vary linearly with mole fraction of KSCN, x_2. Presuming that V_0 and T_0 vary linearly with concentration,[1] Eq. 3 becomes on substituting the linear concentration dependences of all the terms

$$m_1 = m_2 - m_3T_{01} + b_1'm_4 - m_3m_4x_2, \tag{4}$$

where m_1, m_2, m_3, and m_4 are the respective slopes of linear variations of V_o', V_0, b', and T_0 with x_2. T_{01} and b'_1 are the values of T_0 and b', respectively for pure $Ca(NO_3)_2 \cdot 3.18H_2O$ melt. From Eq. 4 it may be understood that the observed constancy of m_1 appears to be explainable only when T_0 becomes almost independent of solute concentration. In such

Table 1. Parameters for Eqs. 1 and 6 for the molar volume and refractive index, respectively of $Ca(NO_3)_2 \cdot 3.18H_2O$–KSCN melts

x_2	b' / cm³ mol⁻¹ K⁻¹ or k_1	V_o' or k_2 / cm³ mol⁻¹	σ_1[a] / cm³ mol⁻¹ or σ_2[a]	V_0[b] / cm³ mol⁻¹
0.0	0.0675	106.90	0.027	120.81
	(1.0159)	(56.82)	(8×10^{-5})	
0.0265	0.0662	106.00	0.018	119.64
	(0.8917)	(72.14)	(8×10^{-5})	
0.1599	0.0618	97.97	0.022	110.70
	(0.9881)	(56.52)	(1×10^{-4})	
0.3533	0.0544	86.65	0.017	97.86
	(0.9664)	(53.69)	(1×10^{-4})	
0.4499	0.0509	80.81	0.020	91.30
	(0.9567)	(52.00)	(1×10^{-4})	
0.5414	0.0476	75.34	0.015	85.15
	(0.7025)	(72.23)	(1×10^{-4})	
1.0000[c]	(1.1821)	(22.85)	(4×10^{-5})	

Parameters for Eq. 6 (k_1 and k_2) are within the parantheses. a) $\sigma_1 = [\Sigma(V_{obsd} - V_{calcd})^2/N]^{1/2}$ and $\sigma_2 = \Sigma(n_{obsd} - n_{calcd})^2/N]^{1/2}$, N is the number of the data points. b) Intrinsic volume, $V_0 = V_o' + 206b'$. c) Data from Refs. 6 and 7.

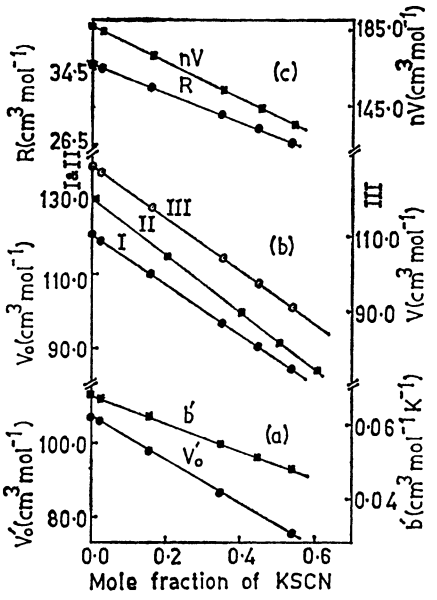

Fig. 1. Variations of (a) V_o' and b', (b) V_o (I-present work; II-Ref 1) and V (at 323 K), and (c) molar refractivity (R) and nV (at 323 K) with concentration for molten $Ca(NO_3)_2 \cdot 3.18H_2O$-KSCN systems.

a case $m_4 \approx 0$ and Eq. 4 reduces to

$$m_1 = m_2 - m_3 T_{o1}. \quad (5)$$

With the knowledge of the reported[1-3] values of T_o for calcium nitrate tetrahydrate, the T_o value for $Ca(NO_3)_2 \cdot 3.18H_2O$ may be considered as nearly equal to 206 K. Substituting this value for T_{o1} and also the values of $m_1 = 59.1$ cm^3 mol^{-1} and $m_3 = 0.037$ cm^3 mol^{-1} K^{-1} obtained from Fig. 1a in Eq. 5, the value of m_2 may be determined which is found to be 66.7 cm^3 mol^{-1}. This value of m_2 is also in agreement with the observed value of the slope of the plot of V_o versus concentration (Fig. 1b), the value of V_o (Table 1) being obtained from Eq. 3 after keeping T_o as 206 K. It is worthy to note that the present extrapolated value of $V_o = 54.0$ cm^3 mol^{-1} for pure KSCN coincides with the value obtained in a similar manner using computed values of V_o from the transport property data of $Ca(NO_3)_2 \cdot 3.99H_2O$-KSCN melts[1] (Fig. 1b). Such an agreement in the V_o value of pure KSCN estimated independently from the molar volume and transport property data appears to envisage that the assumption made regarding the concentration independent nature of T_o is justifiable. Accordingly, the T_o value of pure KSCN may be considered as nearly the same as that of $Ca(NO_3)_2 \cdot 3.18H_2O$ which we have taken as 206 K. This value is closely comparable with the value 203 K for T_o of KSCN computed from its electrical conductance data.[4] Moreover, it has been found that the concentration dependence of V_o predominantly governs the variation of V with x_2 for the $Ca(NO_3)_2 \cdot 3.18H_2O$-KSCN melts. As reported earlier[1] V is found to be additive within ±2% error. The molar volumes of pure KSCN at low temperatures required for testing the additivity of V are estimated from the same linear function for its density above the melting point.[5]

The measured refractive indices (n) of the systems under study also show a linear dependence on temperature. In this case, however, the least-squares fitted values of the intercepts and slopes do not vary linearly with x_2. Therefore, the composition dependence of refractive index has been described in terms of molar refractivity. Molar refractivities show negligible dependence on temperature but vary linearly with x_2 as illustrated with an isotherm at 323 K in Fig. 1c. It may be noted that the extrapolated value of molar refractivity (19.5 cm^3) for pure KSCN at 323 K coincides within ±2% with the value (19.11 cm^3) calculated from the refractive index and density values for molten KSCN obtained after extrapolating the high temperature data[5,6] to 323 K. Therefore, in a mixture of $Ca(NO_3)_2 \cdot 3.18H_2O$ and KSCN the formation of complex ions does not appear to take place.

Furthermore, an attempt to fit the n data to the Gladstone-Dale (G-D) equation,[7] $n = 1 + k/V$, has revealed that the present data fit into a slightly modified G-D equation of the form

$$n = k_1 + k_2/V. \quad (6)$$

The least-squares fitted values of the constants k_1 and k_2 are given in Table 1. Rearranging Eq. 6 and then by substituting the additive behavior of molar volume on the right hand side of the rearranged expression, we obtain

$$nV = A - Bx_2, \quad (7)$$

where $A = n_1V_1$ and $B = n_1V_1 - n_2V_2$. The terms with suffix 1 correspond to $Ca(NO_3)_2 \cdot 3.18H_2O$ and those with 2 to KSCN. In obtaining Eq. 7 k_1 and k_2 are considered to be independent of concentration. The least-squares fitted values of k_1 and k_2 (Table 1), on the other hand, are not exactly independent of concentration, but vary in a non-linear fashion. However, such changes in k_1 and k_2 do not seem to produce much deviation from Eq. 7 as apparent from the linearity of the plot of nV *versus* x_2 (Fig. 1c). It has also been found that the least-squares fitting of nV into Eq. 7 is reasonably good. Therefore, the applicability of the modified G-D equation seems to account for the observed additive nature of the product nV within ±2%.

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