Properties of KSCN-rich Molten NaSCN-KSCN Mixtures

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For molten (Na, K)SCN mixtures with more than 50 mol% KSCN the molar volume V_m, electrical conductivity, $\varkappa$, refractive index n, surface tension γ and heat capacity C_p were measured in dependence of composition and temperature. γ exhibited the minimum at ca. 70 mol% KSCN and C_p was 148 $JK^{-1}mol^{-1}$ in the range of 413 to 471 K. The electronic polarizabilities of the ions in the molten state were estimated by the semiclassical Clausius-Mossotti equation.

Key words: Molar volume, Electrical conductivity, Refractive index.

1. Introduction

KSCN-rich melts of (Na, K)SCN are used in the surface heat treatment of machine parts made of ferrous materials. In this treatment a plastic iron sulfide layer which prevents a wear of the treated materials, is formed. The melt plays an important role not only as thermal medium but also as electrolyte and sulfide ion source. Knowledge of the fundamental physico-chemical properties of the binary melt is therefore desirable, but only phase diagrams [1, 2], electrical conductivities [3, 4] and polarographic data [3] are available as yet.

NaSCN and KSCN form ionic crystals consisting of spherical cations and rod-shaped molecular anions [5–8]. The thiocyanate ion is also present in the melts near their melting point [9–11]. The physico-chemical properties of binary melts composed of salts with such rod-shaped anions are interesting in comparison with those of alkali metal halide and nitrate melts.

We have measured the molar volumes [12], refractive indices [12, 13], surface tension, and electrical conductivities [14] of a series of alkali thiocyanate single melts. The present study describes corresponding measurements, including heat capacity, on KSCN-rich molten (Na, K)SCN mixtures.

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2. Experimental

The chemicals were 99.9% pure (Rare Metal Co., Ltd.). They were dried at 30 K below their melting point (NaSCN: 583 K, KSCN: 446 K [15, 16]) under a reduced pressure of 0.13 Pa for 8 hours, melted at just above the melting points and then solidified. Known amounts of the salts were weighed in a glove box, mixed and melted at 473 K in a quartz tube under a nitrogen atmosphere. After 30 min, the melt was quenched to prevent segregation. The prepared samples were stored in ampoules.

The molar volumes were measured under nitrogen in a quartz dilatometer having a volume of about 5 cm^3. The so called "gold furnace" was used to heat the samples. This furnace has a uniform temperature over a range of more than 20 cm. Since the thermal expansion coefficient of quartz is small, viz., 5.5×10^{-7} K^{-1} [17], calibration runs were performed with distilled water. The error caused by the thermal expansion of quartz was estimated to be 0.05% at most. Details of the measuring procedure are described in [18].

The surface tension was measured with the maximum bubble pressure method described in [19], using argon which was purified by passing through chemical traps filled with molecular sieves (4 A) and titanium sponges at 1173 K to remove possible H_2O, O_2, and N_2. The reproducibility of the results was ca. $\pm 0.3\%$, similar to that in [19].

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The conductivity was measured with a conventional ac bridge method. The U-shaped conductivity cell of quartz had a capillary part of 3.5 mm inner diameter and 110 mm length. The disk-like platinum electrodes had an area of 1 cm^2. The noninductively wound gold furnace was used also in this case. The cell constant was determined with molten KNO_3 whose conductivity is kown [20].

A hollow prismatic cell made of fused silica was used for the measurements of the refractive index as described in [21]. The angle of minimum deflection was read with a precision of 1 minute. The relation between the refractive index, n_λ, and the angle of minimum deflection, δ_λ, is

$$n_\lambda = \sin((\delta_\lambda + A)/2)/\sin(A/2), \quad (1)$$

where A is the apex angle of the prismatic cell and the subscript λ refers to the wavelength. The apex angle A has been calibrated beforehand with a reference material whose refractive index has been accurately measured by Gustafsson and Karawacki [22]. The temperature of the melt was automatically controlled and recorded with a sheathed chromel-alumel thermocouple inserted into the melt. The light had nine wavelengths from 440 to 680 nm. The accuracy in the refractive index attained for an aqueous electrolyte solution has usually been $\pm 1 \times 10^{-5}$ [23], but in our case it was estimated to be $\pm 1 \times 10^{-4}$ because of the experimental difficulties at elevated temperatures.

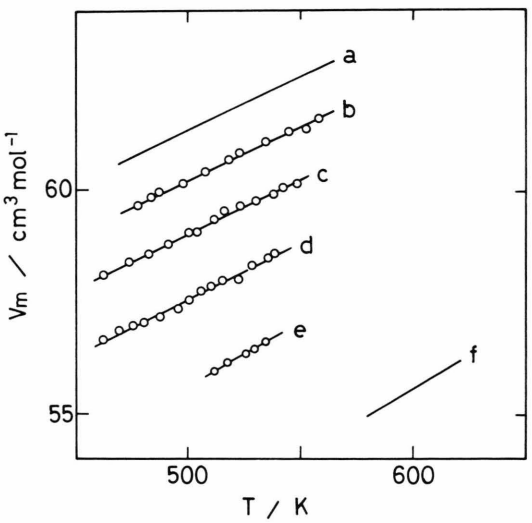

Fig. 1. Molar volumes of molten (Na, K)SCN mixtures. Circles indicate the observed values and solid lines those calculated from (2). a) 100, b) 88.5, c) 74.8, d) 59.6, e) 40.2, f) 0 mol% KSCN.

The heat capacity was measured with a differential scanning calorimeter (Rigaku Co., Lid., model DSC 8230 B) by the method of Angell et al. [24]. A synthetic sapphire crystal was used as reference material [25]. The DSC sample was prepared by putting a small amount of the chemical (ca. 15 mg) on a weighed aluminum pan and covering it with a lid in the glove box. The measurements were carried out with a heating rate of 5 K per min under nitrogen atmosphere. The accuracy of this experiment is thought to be within $\pm 7\%$ from the heat capacity measurement of KNO_3 in the solid and liquid states [26].

3. Results and Discussion

The molar volumes obtained are shown in Fig. 1 together with those of the pure melts. They can be expressed as functions of composition and temperature by the equation [27]

$$V_m(T, x) = \left(\sum_{n=0}^{3} a_n x^n\right) + \left(\sum_{n=0}^{3} b_n x^n\right) T, \quad (2)$$

where T is temperature in K and x the mole fraction of KSCN. The coefficients determined by a least squares fitting are

$$\begin{aligned} a_0 &= 0.37589 \times 10^2, & b_0 &= 0.29965 \times 10^{-1}, \\ a_1 &= 0.10768 \times 10^2, & b_1 &= -0.91635 \times 10^{-2}, \\ a_2 &= 0.78651 \times 10, & b_2 &= -0.51384 \times 10^{-2}, \\ a_3 &= -0.67777 \times 10, & b_3 &= 0.801578 \times 10^{-2}. \end{aligned}$$

In the calculation the molar volumes of the pure melts were taken from [12]. The standard error of the fit was

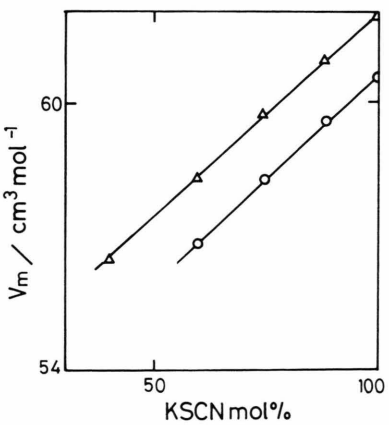

Fig. 2. Molar volume isotherms of molten (Na, K)SCN at 470 K (○) and 530 K (△).

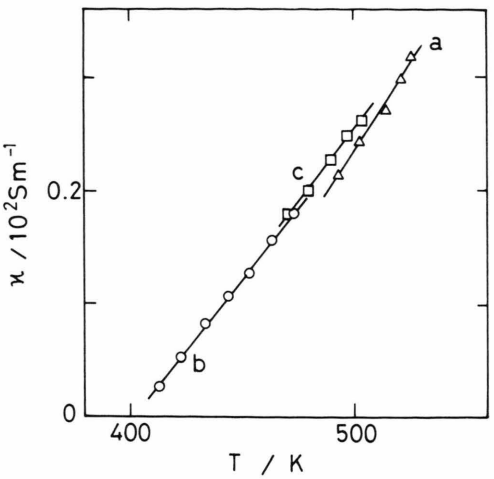

Fig. 3. Conductivities of molten (Na, K)SCN. a) 60.0, b) 74.8, c) 90.1 mol% KSCN.

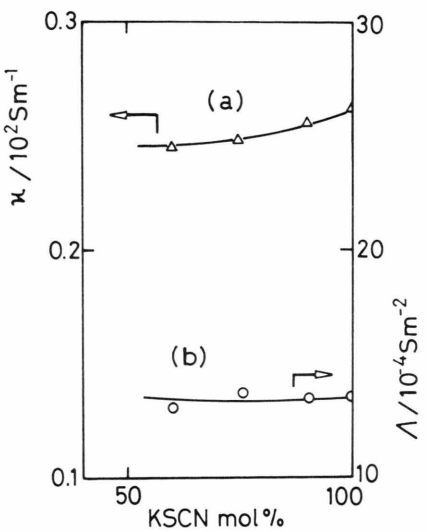

Fig. 4. Specific and equivalent conductivity isotherms of molten (Na, K)SCN at 500 K.

0.772×10^{-1}. Figure 2 shows the composition dependence of the molar volume at 470 and 530 K.

The shape of the SCN^- ion, as analyzed by an X-ray diffraction study of pure alkali thiocyanate melts [11], is linear with 0.115 nm C–N and 0.165 nm C–S distance. However, since the SCN^- ion does not form ligand bonds with the Na^+ and K^+ ions in the molten thiocyanates [9], it may behave as a sphere because of its three dimensional rotation. The effective radius of the SCN^- ion has been estimated to be 0.215–0.220 nm [13]. Therefore the molar volume isotherms are practically linear as those of the chloride and nitrate binary melts. The temperature dependencies of the electrical conductivities are given in Figure 3. Since in this study the temperature ranges were small, linear approximations were adequate. The results are listed in Table 1. Electrical conductivities of the melt at 73 w/o KSCN, i.e. 69.3 mol% KSCN, have been reported by Panzer and Schaer [3]. Making a due interpolation, our data are found to be by ca. 3% larger. Cingolani et al. [4] have measured the conductivities of this binary system in the range 560 to 650 K. Their values for 75 mol% KSCN, extrapolated to the temperature range of our data, are quite small. Probably the SCN^- ions partly decomposed because of the high temperature of their measurements.

Table 1. Electrical conductivity and surface tension equations. SE indicates the standard error of estimation.

Electrical conductivity $k = -a + b \times 10^{-3} T$

mol% KSCN	$-a$	b	SE	Temp. range/K
60.0	1.2241	2.936	6.53×10^{-1}	493–525
74.8	1.0172	2.532	1.92×10^{-1}	413–473
90.1	1.1022	2.715	5.74×10^{-1}	471–514

Surface tension $r = a - b \times 10^{-1} T$

mol% KSCN	a	b	SE	Temp. range/K
47.2	135.5	0.6305	0.297	506–566
68.3	124.2	0.4453	0.255	465–535
79.9	124.4	0.4416	0.135	486–539

The composition dependencies of the specific and equivalent conductivities are small, as for 500 K in Figure 4. Also the specific conductivity of pure NaSCN, extrapolated to 500 K using an empirical equation [14], is close to that of pure KSCN at the same temperature.

The refractive index of the 75.0 mol% KSCN melt, measured with light of a fixed wavelength, decreased linearly with increasing temperature (see Fig. 5a) and, measured at a given temperature decreased nonlinearly with increasing wavelength (see Figure 5b). For the refractive index of molten salts with normal dispersion we have proposed the following modification of Cauchy's equation:

$$n(\lambda, T) = \left(\sum_{i=0}^{2} P_i \lambda^{-2i} \right) + \left(\sum_{i=0}^{2} Q_i \lambda^{-2i} \right) T, \qquad (3)$$

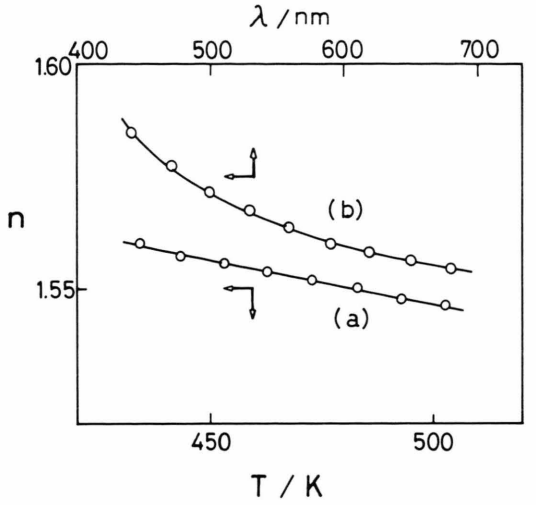

Fig. 5. Refractive index of 75.0 mol% KSCN melt (a) at 650 nm vs. temperature and (b) at 453 K vs. wavelength.

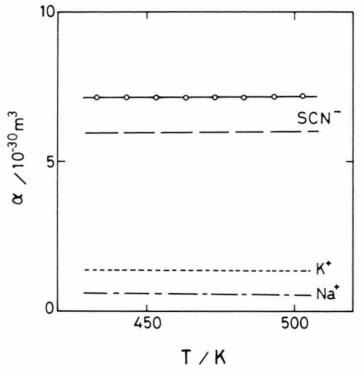

Fig. 6. Electronic polarizability of various ions in 75.0 mol% KSCN melt. Circles show the observed values and the solid line those calculated from (6) on the basis of additivity. The polarizabilities of the ions were taken from [13].

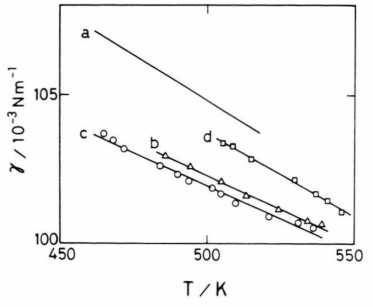

Fig. 7. Surface tensions of molten (Na, K)SCN. a) 100, b) 79.9, c) 68.3, d) 47.2 mol% KSCN.

where T is the temperature in K and λ the wavelength in nm. The physical interpretation of the P_i and Q_i parameters was outlined previously [28]. The parameters determined by the least-squares fit are,

$$P_0 = 0.16219 \times 10, \quad Q_0 = -0.18992 \times 10^{-3},$$
$$P_1 = 0.69110 \times 10^4, \quad Q_1 = 0.14425 \times 10,$$
$$P_2 = 0.14899 \times 10^{10}, \quad Q_2 = -0.29282 \times 10^7,$$

and the standard error in the calculation is 0.665×10^{-3}.

The electronic polarizability of a molecule, α, is defined by the Clausius-Mossotti equation, in which the dielectric constant is set equal to $\varepsilon = n^2$,

$$\alpha = (3/4\pi N_A)[n_\infty^2 - 1)/(n_\infty^2 + 2)]\, V_m\,, \tag{4}$$

where the subscript ∞ refers to infinite wavelenth and N_A is Avogadro's number. The variation of α with temperature is given in Fig. 6, where it can be seen that α increases slightly with increasing temperature ($\alpha = 7.14$ at 433 K and 7.19×10^{-30} m^3 at 503 K). The values of α for Na^+, K^+, and SCN^- in the measured temperature range were taken from the respective pure melts [13], in which the value of Na^+ was obtained by extrapolation. Their values at 433 and 503 K are 5.92 and 6.01 for SCN^-, 0.59 and 0.55 for Na^+, and 1.38 and 1.38×10^{-30} m^3 for K^+ ions, respectively. Besides (4), an alternative expression has been utilized for the purpose of further interpolation of the polarization phenomenon:

$$(n_\infty^2 - 1)/(n_\infty^2 + 2) = (4\pi/3) \sum N_i\, \alpha_i\,, \tag{5}$$

where N_i and α_i are the number and the electronic polarizability of the i-th ion in the unit volume, respectively. The electronic polarizabilities of the 75.0 mol% melt obtained experimentally and calculated on the basis of additivity are compared in Fig. 6 and found to be in good agreement. This proves the validity of (5) for this binary melt containing rod-shaped anions.

The surface tensions of the molten mixtures are shown in Fig. 7 together with that of pure KSCN melt. The surface tensions decreased linearly with increasing temperature. Thus, the values were expressed as linear functions of temperature by least squares fitting, with the results given in Table 1. As can be seen in Figure 7, the surface tension in this system seems to have a minimum at about 70 mol% KSCN. Such a minimum was not observed in the surface tension isotherms of molten (Na, K)Cl [29, 30] and (Na, K)NO_3 [31, 32] mixtures. The alkali metal and chloride ions in these melts are spherical, and also the nitrate ion is almost spherical. As mentioned above, also SCN^- appeared

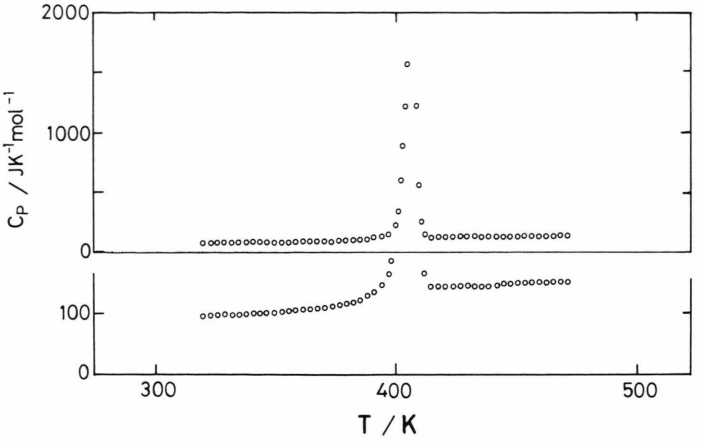

Fig. 8. Temperature dependence of the heat capacity of eutectic (Na, K)SCN. Lower curve: enlarged ordinate scale.

in the bulk to behave as if spherical due to the three dimensional rotation. However, since in the surface layer the three dimensional rotation is restricted, the nonsphericity of the ion may become effective in the surface tension.

In the DSC measurement of the 75.1 mol% KSCN mixture, only one peak at 405 K was observed, which is lower than the temperature 412 K for a solid-solid phase transition of pure KSCN. Piantoni et al. [2] have reported that the eutectic composition in this system lies between 73.8 and 75.6 mol% KSCN. Oparina and Dombrovskaya [1] reported the same. The melting point observed in this work was intermediate between 407 K for the former and 402 K for the latter composition. The experimental result on C_p for the eutectic composition in the solid and liquid state is presented in Figure 8. In the solid state the value of C_p increased slightly with increasing temperature, but in the liquid state it was almost constant, i.e. 148 $JK^{-1} \cdot mol^{-1}$ in the average, from 413 to 471 K.

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