   Bull. Chem. Soc. Jpn., 61, 2193—2194 (1988)

The Refractive Index of Molten $CaCl_2$-NaCl Mixtures

Kazuo IGARASHI* and Junichi MOCHINAGA
Department of Synthetic Chemistry, Faculty of Engineering, Chiba University, Chiba-shi, Chiba 260
(Received December 21, 1987)

Synopsis. The refractive indices of molten $CaCl_2$-NaCl mixtures were measured goniometrically with visible light at nine wavelengths and represented as a function of both the temperature and the wavelength using a modified Cauchy relation. Information on electronic polarization is also reported.

The knowledge of the refractive index of a melt is very useful for obtaining the hypersonic velocity which characterizes the high-temperature relaxation process.[1] Moreover the temperature derivatives of the indices are necessary for measuring the thermal conductivity of the liquids by means of wave-front shearing interferometry.[2] Furthermore the indices can be used to estimate the molar refractivity and the electronic polarizability in terms of the Lorentz-Lorenz equation and the Clausius-Mossotti equation, based on the evaluation of the effective local field around the species. We have measured the refractive indices for several binary chloride melts[3-7] and have evaluated the electronic polarizabilities of the ions in the mixture melts. The molten $CaCl_2$-NaCl mixture is of interest because the Ca^{2+} (0.100 nm) and Na^+ (0.102 nm) cations have nearly equal ionic radii.[8] For this molten system, we have already measured the molar volume[9] and the surface tension.[10] In the present study, the refractive indexes of this melt were measured, and the electronic polarizabilities of the ions were evaluated.

Experimental

A hollow prismatic cell made of fused silica was used for the goniometric measurement of the refractive index. The apparatus has been described in detail previously.[11] 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, σ_λ is:

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

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 by the use of a reference material whose refractive index has been accurately measured by Gustafsson and Karawacki.[12] The temperature of the melt was automatically controlled and recorded with a precision of 0.1 °C using a sheathed chromel-alumel thermocouple inserted into the melt. The light of nine wavelengths, from 434.1 to 680 nm, was used. The chemicals, $CaCl_2$ and NaCl, are of an analytical reagent grade and were dried by means of a conventional technique.[7]

Results and Discussion

The refractive indices at 560 nm of the binary melts measured are shown in Fig. 1, together with those of molten pure $CaCl_2$ and NaCl reported previously.[3,7] They decreased linearly with the increase in the temperature at fixed wavelengths over the whole range of $CaCl_2$ composition. Such behavior is the same as that reported previously.[3-7] The accuracy attained for an aqueous electrolyte solution has usually been $\pm 1\times10^{-5}$ in the refractive index,[13] but for the molten $CaCl_2$-NaCl mixture $\pm 1\times10^{-4}$ was estimated because of the experimental difficulty at elevated temperatures.

The refractive indices decreased non-linearly with the increase in the wavelength at a given temperature, as is shown in Fig. 2. For the refractive index of molten salt with a normal dispersion, we have already proposed the following modification of Cauchy's equation:

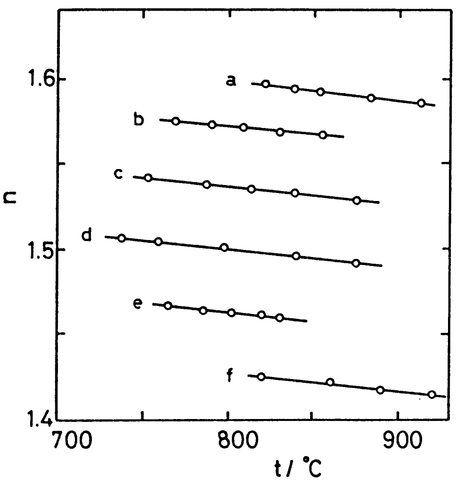

Fig. 1. Refractive indices of molten $CaCl_2$-NaCl at 560 nm. $CaCl_2$ mol%, a: 100.0, b: 79.2, c: 58.6, d: 39.1, e: 19.3, f: 0.0.

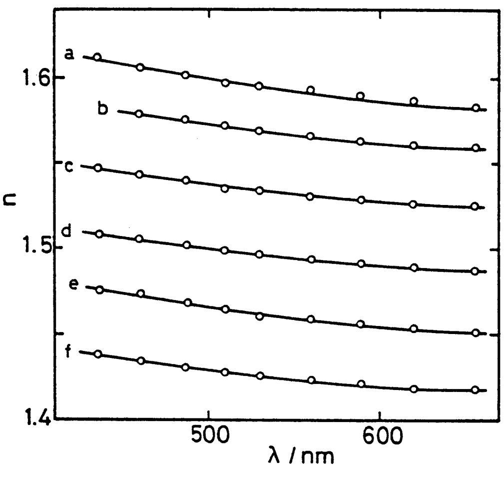

Fig. 2. Dispersions in refractive index of molten $CaCl_2$-NaCl at 850 °C. Symbols are the same as those in Fig. 1.

Table 1. Parameters of the Modified Cauchy Equation

$CaCl_2$ mol%	19.3	39.1	58.6	79.2
P_0	1.5718	1.5597	1.6003	1.6635
$P_1 \times 10^{-4}$	−2.1053	1.3311	8.6674	−1.0233
$P_2 \times 10^{-9}$	4.0838	−0.8439	−0.2582	2.0819
$Q_0 \times 10^{4}$	−1.6480	−1.0960	−1.0693	−1.4336
$Q_1 \times 10^{-1}$	3.5653	−0.4482	−0.3261	2.0814
$Q_2 \times 10^{-6}$	−5.1769	0.6514	0.5773	−2.3498
$\varepsilon \times 10^{4}$	4.49	3.05	3.25	3.41
Temp range/°C	765—830	738—875	753—875	769—855

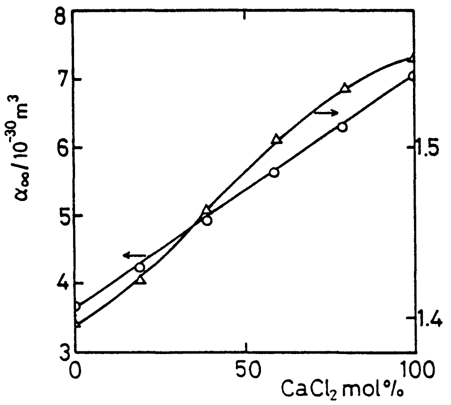

Fig. 3. Refractive index at infinite wavelength and electronic polarizability of molten $CaCl_2$–NaCl at 900 °C.

$$n(\lambda, t) = (\sum_0^2 P_i\lambda^{-2i}) + (\sum_0^2 Q_i\lambda^{-2i})\, t, \qquad (2)$$

where t is the temperature in °C and λ is the wavelength in nm. The physical interpretation of the P_i and Q_i parameters was outlined previously.[6] The parameters determined by the least-squares fit are listed in Table 1, in which ε is the standard error of estimation.

The molar refractivity, R_λ, is one of the best parameters for the polarization phenomenon; it is calculated from the refractive index, n_λ, and the molar volume, V_m, by the use of the Lorentz-Lorenz equation:

$$R_\lambda = (n_\lambda^2 - 1)/(n_\lambda^2 + 2)V_m. \qquad (3)$$

It is generally known in binary systems that R_λ possesses a linear dependence on the composition. For the molten $CaCl_2$–NaCl mixture, a strong linear dependende was also observed. The molar volume used in the calculation was taken from a previous report.[9]

The polarizability discussed here is the electronic one,[14] which is reduced to a scalar in the case of a dense ionic melt. The electronic polarizability of a molecule is defined by the Clausius-Mossotti equation, in which an optical dielectric constant is substituted for the static one:

$$\alpha_\infty = (3/4\,\pi N_A)[(n_\infty^2 - 1)/(n_\infty^2 + 2)]\,V_m, \qquad (4)$$

where the subscript ∞ indicates an infinite wavelength and N_A is Avogadro's number. The electronic polarizabilities of the Ca^{2+}, Na^+, and Cl^- ions in the pure $CaCl_2$ and NaCl melts at 900 °C are known to 0.61, 0.43, and 3.24×10^{-30} m^3 respectively.[3,7] The isotherm of the electronic polarizability for the molten mixture is shown in Fig. 3, together with that of the refractive index at an infinite wavelength, as calculated from Eq. 2 by interpolating λ to ∞. The refractive indices at an infinite wavelength deviate from additivity, while the electronic polarizabilities increase linearly, with an increase in the mole fraction of $CaCl_2$, and their values seem to lie on the additive line. This indicates that the electronic polarizability is approximately inherent in the ion, even in the case of condensed systems such as molten salt.

The authors would like to express their gratitude to Mr. Junji Tominaga for assistance in measuring the refractive index.

References

1) L. M. Torell, *J. Chem. Phys.*, **76**, 3467 (1982).
2) S. E. Gustafsson, *Z. Naturforsch.*, **22a**, 1005 (1967).
3) Y. Iwadate, K. Igarashi, and J. Mochinaga, *Denki Kagaku*, **48**, 97 (1980).
4) Y. Sasaki, K. Igarashi, and J. Mochinaga, *Denki Kagaku*, **50**, 226 (1982).
5) Y. Iwadate, K. Kikuchi, K. Igarashi, and J. Mochinaga, *Z. Naturforsch.*, **37a**, 1284 (1982).
6) Y. Iwadate, J. Tominaga, K. Igarashi, and J. Mochinaga, *Chem. Phys. Lett.*, **110**, 643 (1984).
7) K. Igarashi, Y. Iwadate, J. Mochinaga, and K. Kawamura, *Z. Naturforsch.*, **39a**, 754 (1984).
8) R. D. Shannon, *Acta Crystallgr., Sect. A*, **32**, 751 (1976).
9) K. Igarashi, Y. Iwadate, H. Ohno, and J. Mochinaga, *Z. Naturforsch.*, **40a**, 520 (1985).
10) K. Igarashi, Y. Iwadate, and J. Mochinaga, *Z. Naturforsch.*, **42a**, 853 (1987).
11) J. Mochinaga and Y. Iwadate, *J. Fac. Eng. Chiba Univ.*, **30**, 213 (1979).
12) S. E. Gustafsson and E. Karawacki, *Appl. Opt.*, **14**, 1105 (1975).
13) Y. Marcus and N. Soffer, *J. Solution Chem.*, **10**, 549 (1981).