Refractive Index of Molten $LaCl_3$-KCl, $LaCl_3$-NaCl, and $LaCl_3$-$CaCl_2$ Mixtures

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Z. Naturforsch. **39 a**, 754–758 (1984); received June 4, 1984

The refractive indexes of molten $LaCl_3$-KCl, $LaCl_3$-NaCl, and $LaCl_3$-$CaCl_2$ mixtures were measured goniometrically for nine wavelengths and represented by empirical formulas as functions of both temperature and wavelength. According to the obtained formulas and the molar volume data, the molar refractivities and the electronic polarizabilities were estimated.

Introduction

The refractive index 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.

From the measurement of the refractive indexes of molten nitrate mixtures, Bloom and Rhodes [1] concluded that little or no additional ionic interaction occurred in these mixtures since the obtained molar refractivity isotherms showed no deviation from additivity beyond the experimental errors. Also, the molar refractivity of molten salt has been reported to increase slightly with rising of temperature [1–7]. The electronic polarizability of an ion or a molecule has so far been evaluated from the refractive index of alkali halide crystal [8], liquid crystal [9], aqueous electrolyte solution [10], and organic liquid [11]. The values for pure melts have been summarized in a previous paper [12].

Our study aims at obtaining the molar refractivities and the electronic polarizabilities for molten salt mixtures in order to obtain information concerning the mutual influence of ions in the mixture.

Experimental

Chemicals and Melt Preparation

The chemicals NaCl, KCl, and $CaCl_2$ were of analytical reagent grade. The salts were dried under vacuum for 8 hours just below the respective melting points and then melted. The hygroscopic chemical $LaCl_3$ was synthesized according to the reaction $La_2O_3 + 6\ NH_4Cl \rightarrow 2\ LaCl_3 + 6\ NH_3 + 3\ H_2O$ and purified by sublimation at reduced pressure to remove impurities such as oxides, NH_4Cl, and water. The mole ratio of the mixtures was obtained by weighing out the components and was checked by chelate titration.

Method

A hollow prismatic cell made of fused silica was used for the goniometric measurement of the refractive index. For a sketch of the apparatus cf. [5, 6]. 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

$$n_\lambda = \sin\{(\sigma_\lambda + A)/2\}/\sin(A/2), \qquad (1)$$

where A is the apex angle of the prismatic cell and the subscript λ refers to the wavelength. The apex angle A was calibrated beforehand by use of a reference material whose refractive index has been accurately measured by Gustafsson and Karawacki [13]. 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. Light of nine wavelengths, namely 434.1, 460, 486.2, 510, 530, 560, 589.3, 620, and 656.3 nm, was used.

Results and Discussion

Refractive Index

Highly accurate measurements of the refractive indexes of molten salts have been carried out by

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Gustafsson and Karawacki [13] with wave-front shearing interferometry, which is capable of giving the most reliable data obtainable on the present technical level. In the low temperature range (< 400 °C), our data are in good agreement with theirs as shown before [7]. However, we estimated that the accuracy of wave-front shearing interferometry at higher temperatures [14] (> 800 °C) is nearly equal to that of goniometry. It should also be mentioned that very precise refractive indexes have little effect on the estimation of the molar refractivity and the electronic polarizability since the molar volume has been measured up to only four significant figures. Moreover, the refractive index changes near absorption bands (abnormal dispersion [15]). La^{3+}, however, possesses no absorption bands in the visible region [16].

The refractive index n_λ of the mixtures decreased linearly with increasing temperature in the same manner as described previously [12]. As pointed out by Gustafsson et al. [3, 13, 17], at low temperatures the refractive indexes could be better fitted by quadratic functions of temperature. At high temperatures, however, the index data were represented by linear functions because of experimental uncertainties [14]. The decrease of the refractive index with increasing wavelength was found to correspond to normal dispersion [15], i.e. it could be represented by the Cauchy dispersion formula

$$n_\lambda = P + Q/\lambda^2 + R/\lambda^4. \tag{2}$$

Other expressions have been proposed as dispersion formulas, but we have ascertained experimentally that (2) is best applicable to ionic melts [7, 12]. As before [7], we have used the empirical equation

$$n(\lambda, t) = (P + Q/\lambda^2 + R/\lambda^4) + (P_t + Q_t/\lambda^2 + R_t/\lambda^4)\, t, \tag{3}$$

where the constants P to R_t have been determined by the method of least squares. The results for molten $LaCl_3$-KCl, $LaCl_3$-NaCl, and $LaCl_3$-$CaCl_2$ mixtures are given in Table 1, where ε is the standard error on fitting. The refractive index extrapolated to infinite wavelength, which is needed to evaluate the electronic polarizability, is readily obtained from (3).

Molar Refractivity

Molar refractivities R_λ of the mixtures were calculated at particular temperatures and wavelengths using the data in Table 1 and the Lorentz-Lorenz (L-L) equation

$$R_\lambda = \{(n_\lambda^2 - 1)/(n_\lambda^2 + 2)\}\, V_m, \tag{4}$$

where V_m is the molar volume [18]. A slight increase in the molar refractivity with increasing temperature, estimated to be of the order 1×10^{-3} cm^3/°C, is generally observed. An appreciable decrease of R_λ with increasing wavelength is also found; it amounts to more than 4% between 434.1 nm and 656.3 nm for pure $LaCl_3$ melt.

Molar refractivity isotherms for molten $LaCl_3$-KCl, $LaCl_3$-NaCl, and $LaCl_3$-$CaCl_2$ are illustrated in Figure 1. The molar refractivities of molten NaCl and $CaCl_2$ were taken from the literature [6, 19]. The straight lines are drawn on the basis of additivity,

$$R_{mix} = X_1 R_1 + X_2 R_2, \tag{5}$$

where R_{mix} is the molar refractivity of the mixture, and X_i and R_i refer to the mole fraction and the molar refractivity of the i-th component, respectively. It is seen that the deviations from additivity are within a few percent.

Electronic Polarizability

As reported previously [12], the polarizability discussed here refers to the electronic one.

The electronic polarizability (α_∞) is defined by the semiclassical Clausius-Mossotti equation, analogous to the L-L equation,

$$\alpha_\infty = (3/4\pi N)\, [(n_\infty^2 - 1)/(n_\infty^2 + 2)]\, V_m, \tag{6}$$

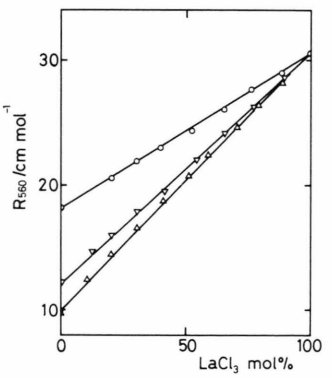

Fig. 1. Molar refractivity isotherms of molten $LaCl_3$-KCl (▽), $LaCl_3$-NaCl (△), and $LaCl_3$-$CaCl_2$ (○) at 560 nm wavelength and 900 °C. (R is in cm^3 mol^{-1}.)

Table 1. Coefficients of equation (3). The dimensions of λ and t are in nm and °C, respectively.
1) $LaCl_3$-KCl

$LaCl_3$/mol%	0.0	12.1	19.8	30.1	41.3
P	1.5179	1.8719	1.5925	1.6620	1.6717
Q	−1.4241E4	−1.2072E5	1.4013E4	1.1690E4	−8.9881E3
R	2.6325E9	1.7288E10	−7.9976E8	−2.1439E8	2.4954E9
P_t	−1.7046E-4	−5.3747E-4	−1.5740E-4	−1.9806E-4	−1.8505E-4
Q_t	2.0749E1	1.6282E2	−8.1679E0	−6.6690E0	1.8249E1
R_t	−2.7096E6	−2.2000E7	1.0727E6	5.6919E5	−2.6390E6
δ	2.97E-4	1.45E-3	9.58E-4	5.19E-4	7.74E-4
t/°C	852–960	750–845	669–925	739–904	752–910

1) $LaCl_3$-KCl

$LaCl_3$/mol%	54.3	65.7	77.1	89.5	100.0
P	1.7209	1.6759	1.7035	1.7794	1.7969
Q	−1.1331E4	3.0388E4	3.4105E4	1.0461E4	2.0417E4
R	2.7517E9	−2.1155E9	−3.1880E9	5.5226E8	−8.4774E8
P_t	−1.8634E-4	−8.3512E-5	−7.8022E-5	−1.3001E-4	−1.1806E-4
Q_t	2.2711E1	−2.8078E1	−3.0198E1	−1.6589E0	−9.9876E0
R_t	−3.0108E6	3.1090E6	4.1637E6	−1.7796E5	1.0968E6
δ	4.02E-4	6.09E-4	6.92E-4	3.92E-4	3.76E-4
t/°C	750–912	809–924	818–914	871–968	911–982

2) $LaCl_3$-NaCl

$LaCl_3$/mol%	0.0	10.6	19.9	30.3	40.8
P	1.4887	1.5825	1.6759	1.6310	1.8464
Q	1.7285E4	−6.5136E3	−2.3228E3	4.4637E4	−3.3913E4
R	−1.1201E9	1.6936E9	2.1655E9	−2.2623E9	7.2302E9
P_t	−1.0311E-4	−1.2266E-4	−1.8979E-4	−1.0256E-4	−3.0852E-4
Q_t	−1.2227E1	1.0950E1	1.0257E1	−4.4762E1	5.2018E1
R_t	1.3148E6	−1.2470E6	−2.1445E6	3.0905E6	−7.8614E6
δ	3.66E-4	8.25E-4	4.28E-4	9.63E-4	4.38E-4
t/°C	830–920	836–932	825–918	837–918	848–920

2) $LaCl_3$-NaCl

$LaCl_3$/mol%	50.8	59.0	70.5	79.1	89.1
P	1.8186	1.8236	1.8032	1.8277	1.7932
Q	−1.7358E4	−1.0966E4	1.7507E4	1.6975E4	2.6387E4
R	3.3958E9	3.1661E9	6.5674E7	−3.4327E8	−1.6388E9
P_t	−2.4801E-4	−2.2469E-4	−1.7265E-4	−1.8339E-4	−1.3381E-4
Q_t	2.9967E1	2.1536E1	−1.1365E1	−1.0146E1	−1.8054E1
R_t	−3.5543E6	−3.0945E6	5.6096E5	1.0763E6	2.2040E6
δ	4.14E-4	4.27E-4	4.41E-4	4.70E-4	4.83E-4
t/°C	839–918	839–911	836–916	845–910	848–918

3) $LaCl_3$-$CaCl_2$

$LaCl_3$/mol%	0.0	20.0	30.4	39.9
P	1.5603	1.6985	1.7932	1.7363
Q	5.8635E4	7.6826E3	−2.1346E4	−5.4729E3
R	−5.9429E9	1.5026E8	3.7015E9	2.7719E9
P_t	9.3908E-6	−1.1274E-4	−1.9705E-4	−1.2024E-4
Q_t	−6.1627E1	−6.0729E-1	3.4260E1	1.6368E1
R_t	7.3976E6	1.3114E5	−4.0373E6	−2.8731E6
δ	4.55E-4	3.67E-4	4.83E-4	1.56E-3
t/°C	821−912	861−969	862−971	851−962

3) $LaCl_3$-$CaCl_2$

$LaCl_3$/mol%	52.3	65.2	76.3	88.4
P	1.7649	1.8137	1.7354	1.8506
Q	5.7709E2	−1.1620E4	5.1569E4	1.2824E3
R	5.5761E8	3.0054E9	−5.3041E9	1.0821E9
P_t	−1.3928E-4	−1.7582E-4	−6.9758E-5	−1.8625E-4
Q_t	8.4433E0	2.2986E1	−4.4092E1	8.0668E0
R_t	−2.9643E5	−3.0332E6	5.9314E6	−7.0408E5
δ	1.50E-3	4.36E-4	4.14E-4	4.46E-4
t/°C	821−971	862−971	878−963	898−972

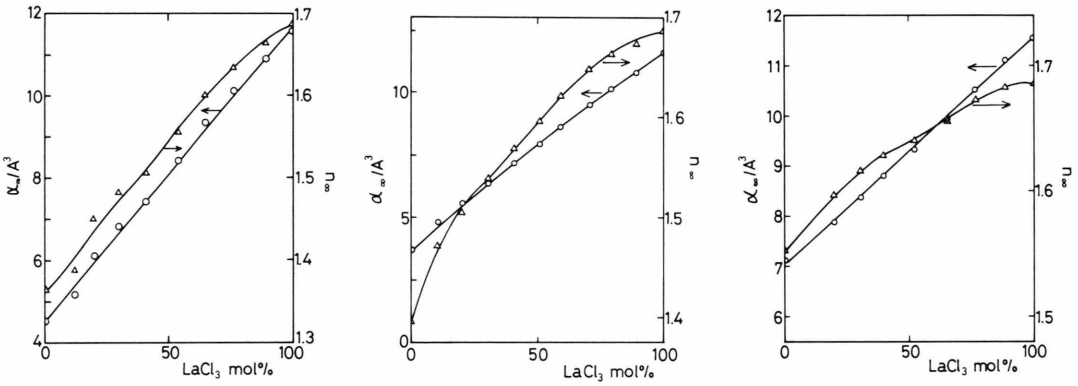

Fig. 2. Electronic polarizability and refractive index at infinite wavelength at 900 °C. a): $LaCl_3$-KCl, b): $LaCl_3$-NaCl, c): $LaCl_3$-$CaCl_2$.

where N is Avogadro's number and the subscript ∞ refers to infinite wavelength. The isotherms of the electronic polarizabilities for the mixtures are shown in Fig. 2 together with those of the refractive indexes at infinite wavelength calculated in terms of (3). The n_∞'s deviate from additivity while the α_∞'s increase linearly with increasing mole fraction of $LaCl_3$. This indicates that the electronic polarizability is approximately inherent in the ion even in case of condensed systems such as molten salts. The structure of these molten mixtures surely changes with adding $LaCl_3$. Structural data on molten $LaCl_3$-KCl mixtures measured with Raman spectroscopy are available [20, 21], indicating that in the potassium-rich $LaCl_3$-KCl melts the $[LaCl_6]^{3-}$ species, with a maximum concentration near 25 mol% $LaCl_3$, is the predominant configuration. Our results suggest that the electronic polarizability of an ion is nearly independent of the structure of the molten salt, which is supported by the fact that the

dispersion energy calculated from the ionization potential and the polarizability makes little contribution to the total potential energy; for alkali halides it was estimated by Okada et al. [22] to amount to only about 5%.

As reported by Tanemoto et al. [23], the refractive index and the density of molten $MnCl_2$-KCl mixtures deviate negatively from additivity in the KCl-rich range, but the effects of refractive index and density on the molar refractivity cancel, so that the molar refractivity obeys additivity. On the other hand, complex formation is reported for the molten $MnCl_2$-KCl mixture by Laser-Raman spectroscopic study [24]. Thus not only the molar refractivity but also the electronic polarizability does not necessarily afford a criterion for detecting the formation of complex ions in binary molten mixtures.

Further investigations on electronic polarization are desirable.

Acknowledgement

The authors would like to express their sincere gratitude to Mr. T. Suda for assistance in measuring the refractive index. The calculations were carried out with the computer in Chiba University (HITAC M-180). The facilities and computer time made available to them are gratefully acknowledged.

[1] H. Bloom and D. C. Rhodes, J. Phys. Chem. **60,** 791 (1956).
[2] H. R. Jindal and G. W. Harrington, J. Phys. Chem. **71,** 1688 (1967).
[3] E. Karawacki and S. E. Gustafsson, Z. Naturforsch. **31 a,** 956 (1976).
[4] Y. Uchiyama and E. Karawacki, Z. Naturforsch. **36 a,** 467 (1981).
[5] J. Mochinaga and Y. Iwadate, J. Fac. Eng. Chiba Univ. **30,** 213 (1979).
[6] J. Mochinaga and Y. Iwadate,Denki Kagaku **47,** 345 (1979); J. Mochinaga, Y. Sasaki, K. Igarashi, and T. Suda, J. Chem. Soc. Japan, No. **6,** 947 (1982).
[7] Y. Iwadate, K. Kawamura, and J. Mochinaga, J. Phys. Chem. **85,** 1947 (1981).
[8] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92,** 890 (1953).
[9] P. Adamski and A. D. Gromiec, Mol. Cryst. Liq. Cryst. **35,** 337 (1976).
[10] C. J. F. Böttcher, Recl. Trav. Chim. Pays-Bas **62,** 325, 503 (1943); ibid. **65,** 19, 91 (1946); H. R. Petty, J. A. Crumb, V. E. Anderson, E. T. Arakawa, and J. K. Baird, J. Phys. Chem. **81,** 696 (1977).
[11] J. D. Olson and F. H. Horne, J. Chem. Phys. **58,** 2321 (1973).
[12] Y. Iwadate, J. Mochinaga, and K. Kawamura, J. Phys. Chem. **85,** 3708 (1981).
[13] S. E. Gustafsson and E. Karawacki, Appl. Opt. **14,** 1105 (1975).
[14] R. Aronsson, H. E. G. Knape, and L. M. Torell, J. Chem. Phys. **68,** 3794 (1978).
[15] M. Born and E. Wolf, Principles of Optics, Pergamon Press, Elmsford, New York 1974, Chapter 2.
[16] K. A. Gschneidner, Jr. and L. Eyring, Handbook on the Physics and Chemistry of Rare Earths, Vol. 3, North-Holland Pub. Company, New York 1979, p. 175.
[17] L. W. Wendelöv, S. E. Gustafsson, N.-O. Halling, and R. A. E. Kjellander, Z. Naturforsch. **22 a,** 1363 (1967).
[18] K. Igarashi and J. Mochinaga, to be submitted for publication to Z. Naturforsch. a.
[19] Y. Iwadate, K. Kikuchi, K. Igarashi, and J. Mochinaga, Z. Naturforsch. **37 a,** 1284 (1982).
[20] V. A. Maroni, E. J. Hathaway, and G. N. Papatheodorou, J. Phys. Chem. **78,** 1134 (1974).
[21] G. N. Papatheodorou, Inorg. Nucl. Chem. Letters **11,** 483 (1975).
[22] I. Okada, R. Takagi, and K. Kawamura, Z. Naturforsch. **35 a,** 493 (1980); I. Okada and R. Takagi, ibid. **36 a,** 378 (1981); R. Takagi, I. Okada, and K. Kawamura, ibid. **36 a,** 1106 (1981).
[23] K. Tanemoto, Y. Takagi, and T. Nakamura, Japan. J. Appl. Phys. **15,** 1637 (1976).
[24] K. Tanemoto and T. Nakamura, Chem. Lett. No. **4,** 351 (1975).