Refractive Index of Molten $LiNO_3-KNO_2$ and $NaNO_3-NaNO_2$ Systems

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Goniometry was used to measure the refractive indexes of molten $LiNO_3-KNO_2$ and $NaNO_3-NaNO_2$ mixtures. The index data were smoothed as functions of temperature and wavelength using the modified Cauchy relation. Information on electronic polarization is also reported.

Knowledge of the refractivity of melts is needed in measurements of the hypersonic velocity [1] and the thermal conductivity by wave-front shearing interferometry [2]. The reciprocal system $LiNO_3-KNO_2$ and the additive system $NaNO_3-NaNO_2$ are promising as heat transfer media at relatively low temperatures [3], their lowest liquidus temperatures being 348 K at 44 mol% of KNO_2 [4] and 499 K at 32.5 mol% of $NaNO_3$ [5]. It therefore seemed worthwhile to measure the refractive indexes of these melts.

The chemicals used were of analytical reagent grade and dried as conventional [4]. Purified N_2 gas was bubbled through the nitrites for 30 min to remove trace amounts of water and depress the thermal decomposition. The intended mole ratios of the mixtures were checked by ultraviolet spectrophotometry [6]. The hollow prismatic cell used for the goniometry was made of optical fused silica. The apparatus and the evaluation of the refractive index have been described previously [7]. Calibration runs were performed using a reference material [8].

The refractive index n_λ for light of wavelength λ decreased linearly with increasing temperature. A curvilinear decrease of n_λ with wavelength, called normal dispersion, was also observed. These phenomena were well fitted by the equation

$$n(\lambda, T) = \left(\sum_0^2 P_i/\lambda^{2i}\right) + \left(\sum_0^2 Q_i/\lambda^{2i}\right) T,$$

where T is the absolute temperature. The physical interpretation of P_i and Q_i was outlined elsewhere [9]. The smoothed parameters P_i and Q_i are listed in Table 1. The electronic polarizability α_∞ was calculated from the semiclassical Clausius-Mossotti equation

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

where the subscript ∞ means infinite wavelength, and V_m is the molar volume [4]. The empirical equation

$$V_m = 30.94 - 5.19x + 33.49x^2 - 25.96x^3 + (0.0142 + 0.0222x - 0.0515x^2 + 0.0384x^3)\,T$$

holds for $LiNO_3-KNO_2$, x being the mole fraction of KNO_2. The density data for molten $NaNO_3-NaNO_2$ were taken from [5]. The n_∞'s were evaluated from the data in Table 1. For the $LiNO_3-KNO_2$ system, the isotherms of α_∞ and n_∞ at 603 K are illustrated in Fig. 1, where the data on molten $LiNO_3$ were taken from [10]. The plot of α_∞ vs. composition gives good linearity, percent departure from additivity ranging from 0.02% to 0.24%, indicating that even in condensed melts the electronic polarizability of an individual ion is little affected by the coexisting ions. The temperature dependence of α_∞ was found to be quite small, being of the order of $1 \times 10^{-33}\,m^3\,K^{-1}$. In an error-estimation approach one can write

$$d\ln\alpha_\infty = d\ln(n_\infty^2 - 1) - d\ln(n_\infty^2 + 2) + d\ln V_m.$$

The relative error in α_∞ is

$$|\Delta\alpha_\infty| = \alpha_\infty\,\{6n_\infty/(n_\infty^2 - 1)(n_\infty^2 + 2)\}\,|\Delta n_\infty| + (\alpha_\infty/V_m)\,|\Delta V_m|.$$

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Table 1. Refractive index equations.

i) $LiNO_3$–KNO_2 system

X($LiNO_3$)/mol%	90.0	79.9	59.6	49.1
Temp. range/K	569–638	564–643	523–614	543–623
P_0	0.15234E1	0.14640E1	0.15027E1	0.14936E1
P_1	0.30111E3	0.24171E5	−0.59701E4	0.23769E4
P_2	0.65931E9	−0.20200E10	0.20880E10	0.48306E9
Q_0	−0.15395E-3	−0.64568E-4	−0.15156E-3	−0.14687E-3
Q_1	0.87223E1	−0.33360E2	0.18489E2	0.52716E1
Q_2	−0.76582E6	0.39900E7	−0.31447E7	−0.59141E6
Standard error	0.316E-3	0.324E-3	0.338E-3	0.291E-3

X($LiNO_3$)/mol%	39.9	20.1	10.0	0.0
Temp. range/K	561–636	595–677	678–762	753–788
P_0	0.14538E1	0.14551E1	0.14627E1	0.14691E1
P_1	0.23018E5	0.15442E5	0.32809E4	0.22174E4
P_2	−0.22423E10	−0.89166E9	0.56631E9	0.55972E9
Q_0	−0.86198E-4	−0.10438E-3	−0.12381E-3	−0.13768E-3
Q_1	−0.29772E2	−0.16389E2	0.34111E1	0.26059E1
Q_2	0.39956E7	0.16250E7	−0.72675E6	−0.43458E6
Standard error	0.300E-3	0.378E-3	0.323E-3	0.233E-3

ii) $NaNO_3$–$NaNO_2$ system

X($NaNO_3$)/mol%	20.0	39.9	60.1	80.0
Temp. range/K	571–632	534–637	560–622	622–643
P_0	0.14704E1	0.14666E1	0.14375E1	0.15419E1
P_1	−0.00707E4	0.45791E4	3.1626E4	−2.6199E4
P_2	1.0363E9	0.29013E9	−3.8398E9	4.0294E9
Q_0	−1.2459E-4	−0.01101E-4	−0.55134E-4	−0.02229E-4
Q_1	0.99190E1	0.05213E1	−4.4728E1	5.1779E1
Q_2	−1.5329E6	−0.03959E6	6.8195E6	−6.3291E6
Standard error	3.40E-4	5.21E-4	3.72E-4	3.43E-4

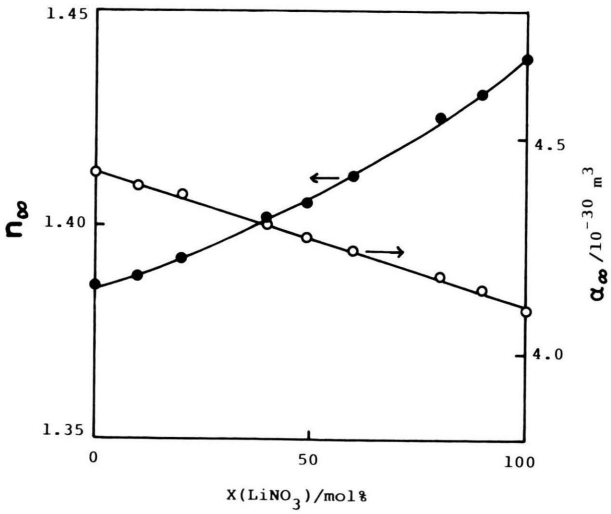

Fig. 1. The isotherms of n_∞ and α_∞ at 603 K.

As an example, we selected the molten $LiNO_3$-(90.0 mol%)–KNO_2(10.0 mol%) mixture at 603 K, in which $n_\infty = 1.4305$, $dn_\infty = 0.316 \times 10^{-3}$, $\alpha_\infty = 4.153 \times 10^{-30}$ m^3, $dV_m = 1.3 \times 10^{-8}$ m^3, and $V_m = 40.53 \times 10^{-6}$ m^3. Consequently, the relative error in α_∞ was computed to be 3.99×10^{-33} m^3. For the other mixtures, the errors were of the same order. Since α_∞ is regarded as a constant, the variation of the dispersion term $(n_\infty^2 - 1)/(n_\infty^2 + 2)$ with composition compensates that of the molar volume, so that these contributions are cancelled out. This fact implies that the refractive index, measured outside the abnormal dispersion region, may afford a criterion in detecting an error of the molar volume data, if there exists little ionic association in the melts.

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