The Electric Conductivity of Molten $(Na-Tl)NO_3$ Mixtures

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Electrical conductivities and densities of molten $(Na-Tl)NO_3$ mixtures have been measured in the temperature range between 192 °C and 400 °C.

At all compositions the specific conductivities appear to be linear functions of the temperature. While the equivalent conductivities of the mixtures deviate negatively from additivity, the apparent activation energies ΔE (from the relation $\Lambda = \Lambda_0 \cdot \exp(-\Delta E / R\,T)$ exhibit positive deviations from additivity.

This behavior is similar to that of other univalent binary systems with a common anion and seems to indicate that the polarization of the nitrate ion due to different cation sizes is the main cause of the additional hindrance to the electrical transport in mixtures.

In connection with other studies on the transport parameters of the $(Na-Tl)NO_3$ system[1], the electrical conductivity and the density of the system have been determined. In the literature the conductivity data of pure $TlNO_3$ present some discrepancies and few data on $NaNO_3-TlNO_3$ mixtures are available[2].

Experimental

An U type cell with a great cell constant, without connection to the liquid of the thermostatic bath[3] (thermoregulated to ±0.1 °C), was used. The bath, a $(Li, Na, K)NO_3$ eutectic mechanically stirred, was placed into a vertical Heraeus furnace. The temperature close to the cell was measured by means of a Cr—Al thermocouple, calibrated by comparison with a ITI * thermocouple of certified precision of ±0.1 °C.

The cell constant was determined by two different methods. First, H_2SO_4 solutions, titrated with 2‰ precision, whose conductivity values, precise to 1‰, were taken from the literature[4], were employed. Second, the calibration was repeated employing molten KNO_3 utilizing conductivity data of Kroger and Weissberger[5]. The cell constants were found to be 967.2 cm^{-1} and 967.9 cm^{-1}, respectively.

Resistance measurements were carried out with a LKB precision bridge at 2000 c/sec. The additional polarisation resistances were considered negligible at this frequency[6–8], taking into account the high cell constant. Accordingly very good agreement was found with the $NaNO_3$ conductivities obtained by extrapolation to infinite frequency[9].

Density measurements were carried out by the bob method, using a Mettler recording balance for the determination of the buoyancy of the bob[10]. The temperature was measured by means of a certified Cr—Al thermocouple immersed in the melt close to the bob. Reagent grade salts, after three cristallisations from water, were used.

Results and Discussion

Conductivity measurements at six different concentrations (0.0; 0.141; 0.25; 0.50; 0.75; 1.0 mole fraction of $TlNO_3$) were carried out at temperatures ranging from 190 to 400 °C[11]. Some runs were repeated several times in order to check the reproducibility. The experimental results are reported in Table 1. At each composition the specific conductivity was found to be a linear function of the temperature. The equations of the straight-lines, conductivity vs. T, as determined by the least squares method, are reported in Table 2. The densities expressed in terms of straigth-lines are given in Table 3.

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Mole fraction of $TlNO_3$	Temp. °C	$\varkappa$ Ω^{-1} cm^{-1}
0,00	306,25	0,9660
	309,75	0,9836
	312,00	0,9947
	312,25	0,9948
	315,25	1,0093
	316,25	1,0146
	317,25	1,0188
	317,75	1,0221
	321,25	1,0374
	329,75	1,0766
	337,00	1,1100
	340,75	1,1281
	345,50	1,1495
	350,75	1,1717
	359,00	1,2175
	368,00	1,2586
0,141	275,50	0,7004
	275,75	0,7019
	285,25	0,7418
	289,75	0,7676
	296,25	0,7870
	305,00	0,8226
	315,00	0,8635
	320,00	0,8889
	325,75	0,9076
	334,25	0,9370
	362,50	1,0560
0,25	267,25	0,6188
	278,00	0,6675
	289,00	0,6879
	297,00	0,7373
	298,00	0,7406
	322,00	0,8273
	335,75	0,8751
	367,25	0,9937
0,25	275,50	0,6232
	279,00	0,6616
	293,00	0,6983
	293,25	0,6999
	297,00	0,7060
	312,50	0,7486
	318,50	0,7768
	337,00	0,8611
	338,25	0,8673
	348,00	0,8775
0,50	234,00	0,4400
	244,75	0,4792
	251,25	0,5002
	257,50	0,5200
	259,00	0,5255
	260,25	0,5282
	265,25	0,5441
	270,00	0,5605
	280,00	0,5908
	281,50	0,5971
	390,50	0,6232
	300,50	0,6492
	312,50	0,6919
	329,75	0,7434
0,75	192,00	0,3080
	208,25	0,3559
	230,25	0,4222
	251,50	0,4841
	278,00	0,5628
	295,75	0,6148
	317,50	0,6756
0,75	193,25	0,3122
	212,75	0,3696
	225,50	0,4035
	240,20	0,4523
	257,75	0,5018
	268,50	0,5351
	293,75	0,6082
	319,75	0,6827
	329,00	0,7065
	360,00	0,7960
1,00	211,25	0,3587
	217,25	0,3736
	221,75	0,3851
	223,50	0,3908
	235,75	0,4223
	249,00	0,4568
	259,25	0,4825
	274,25	0,5204
	289,50	0,5579
	304,25	0,5967
1,00	208,75	0,3515
	209,00	0,3514
	209,25	0,3526
	219,75	0,3788
	234,25	0,4181
	237,75	0,4254
	268,75	0,5052
	295,00	0,5727
	301,25	0,5909
	330,75	0,6639
	334,75	0,6703
	349,50	0,7075

Table 1. Experimental values of specific conductivity of $NaNO_3$ and $TlNO_3$ and their binary mixtures.

Mole fraction of $TlNO_3$	Conductivity equations	Root mean square deviations	Temp. range °C
0,0	$\varkappa = 0{,}9938 + 4{,}6945\,(T - 312) \cdot 10^{-3}$	$1{,}6 \cdot 10^{-3}$	312—400
0,141	$\varkappa = 0{,}4718 + 4{,}0593\,(T - 285) \cdot 10^{-3}$	$3{,}4 \cdot 10^{-3}$	285—385
0,250	$\varkappa = 0{,}6209 + 3{,}6274\,(T - 270) \cdot 10^{-3}$	$15{,}0 \cdot 10^{-3}$	270—370
0,50	$\varkappa = 0{,}4466 + 3{,}1078\,(T - 234) \cdot 10^{-3}$	$2{,}5 \cdot 10^{-3}$	234—350
0,75	$\varkappa = 0{,}3103 + 2{,}9388\,(T - 192) \cdot 10^{-3}$	$7{,}5 \cdot 10^{-3}$	192—350
1,00	$\varkappa = 0{,}3683 + 2{,}5455\,(T - 215) \cdot 10^{-3}$	$1{,}5 \cdot 10^{-3}$	215—350

Table 2. Equations for the specific conductivity of $NaNO_3$, $TlNO_3$ and their binary mixtures.

Mole fraction of $TlNO_3$	Density equations	Root mean square deviations	Temp. range °C
0,00*	$d = 1{,}905 - 0{,}715\,(T - 307) \cdot 10^{-3}$	— —	307—427
0,201	$d = 2{,}605 - 1{,}035\,(T - 290) \cdot 10^{-3}$	$7{,}0 \cdot 10^{-3}$	290—400
0,334	$d = 3{,}054 - 1{,}084\,(T - 270) \cdot 10^{-3}$	$5{,}0 \cdot 10^{-3}$	270—370
0,529	$d = 3{,}642 - 1{,}173\,(T - 230) \cdot 10^{-3}$	$10{,}0 \cdot 10^{-3}$	230—350
0,668	$d = 4{,}058 - 1{,}600\,(T - 220) \cdot 10^{-3}$	$6{,}0 \cdot 10^{-3}$	220—350
0,790	$d = 4{,}430 - 1{,}647\,(T - 110) \cdot 10^{-3}$	$7{,}5 \cdot 10^{-3}$	180—350
1,00*	$d = 4{,}887 - 1{,}750\,(T - 217) \cdot 10^{-3}$	— —	217—427

* Data taken from ref. [13].

Table 3. Equations for the density of $NaNO_3$, $TlNO_3$ and their binary mixtures.

The standard deviations S were calculated by the formula[12]:

$$S = \sqrt{\Sigma (\delta_n)^2 / (h-1)}, \qquad (1)$$

where δ_n is the deviation of each measurement and h the numbers of measurements.

The conductivities of pure $NaNO_3$ and $TlNO_3$ are plotted in Fig. 1, together with some recent literature conductivity data[9, 13]. The present $NaNO_3$ values agree with those of other authors, while our $TlNO_3$ values agree with those of DE NOOJER[9] but differ by up to 4% from those collected by JANZ[13].

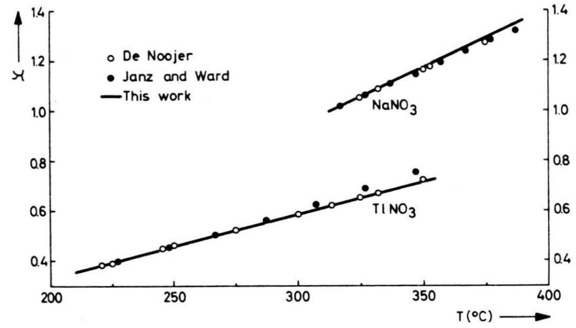

Fig. 1. Specific conductivities of pure $NaNO_3$ and $TlNO_3$.

Recently some specific conductivity data for $TlNO_3$ and $NaNO_3$ mixtures at three temperatures (200, 240, 320 °C) have been reported[2]. While these data generally agree with ours at the two lower temperatures, they differ by about 3% in the range $0.25 < X_{Tl} < 0.50$ at 320 °C.

The specific conductivity isotherms corresponding to the equations of Table 2 are shown on the left hand side of Fig. 2. In the same figure the isotherms of the equivalent conductivity $\Lambda = \varkappa V$ are presented.

The molar volumes, V, at each investigated composition were interpolated from the molar volumes calculated from the density equations of Table 3 (see Fig. 3).

According to the reported density data the molar volume isotherms do not deviate from additivity by

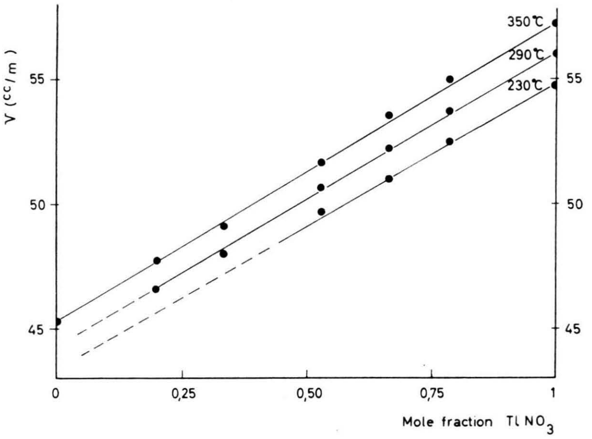

Fig. 3. Molar volume isotherms of the system (Na—Tl) NO_3 at three temperatures (230, 290, 350 °C).

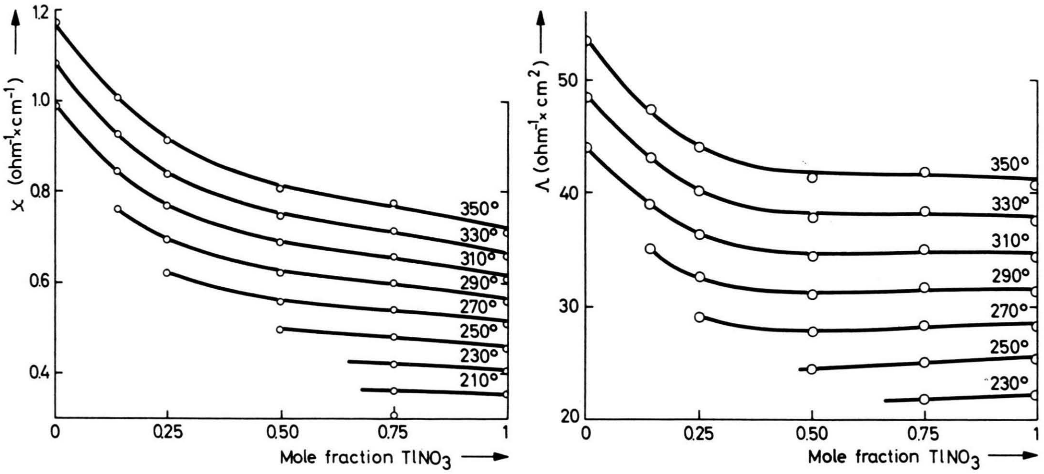

Fig. 2. Specific and equivalent conductivities of the (Na—Tl) NO_3 system.

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more than + (0.15 cc ± 0.1)/mole. Our density data do not confirme those of PROTSENKO et al.[2], who reported an S-shaped molar volume isotherm departing from a straight-line by about ± 1 cc/mole in the composition region of diluted mixtures.

The equivalent conductivity isotherms show rather marked negative deviations from additivity as compared with other binary nitrate systems containing $NaNO_3$[9].

From the relationship

$$\log \Lambda = \log \Lambda_0 - \Delta E / R\, T\,, \qquad (2)$$

the apparent activation energy[14] can be evaluated.

The ΔE values calculated by the least squares method are reported in Table 4, with the standard deviations $S_{\Delta E}$ calculated with the formula[12]

$$S_{\Delta E} = 1.986 \cdot S_{\log \Lambda} \cdot \sqrt{\frac{h}{h \sum 1/T_n^2 - (\sum 1/T_n)^2}}\,, \qquad (3)$$

where $S_{\log \Lambda}$ is the standard deviation of the function (2) calculated by a formula like the formula (1).

Mole fraction of $TlNO_3$	0,00	0,141	0.25	0,50	0,75	1,00
ΔE (Kcal)	3,41	3,51	3,49	3,46	3,52	3,20
Standard deviation	0,01	0,06	0,08	0,11	0,04	0,02

Table 4. Apparent activation energy of the system $NaNO_3$—$TlNO_3$.

The ΔE values at all compositions lie in the range 3.55 ÷ 3.20 Kcal/mole, in rather good agreement with the activation energies of other nitrate systems[13].

In particular the value 3.40 Kcal/mole of $NaNO_3$ agrees with the value 3.215 reported by JANZ[13] (at temperatures up to 427 °C), and with the values 3.35 ÷ 3.25 (at temperatures up to 450 °C) of BIZOUARD[15]. The 3.20 Kcal/mole value of $TlNO_3$ agrees with the value 3.16 that can be evaluated from the DE NOOJER data[9] and with the value 3.26 reported by JANZ[13].

The ΔE values of mixtures are higher than those calculated additively from the activation energies of the pure components. This characteristic is a rather general one for systems the cations of which have different sizes, as can be seen in Fig. 4, which presents the excess activation energies of two series of binary systems including $NaNO_3$ and $TlNO_3$ respectively; the conductivity data are taken from ref.[9, 15].

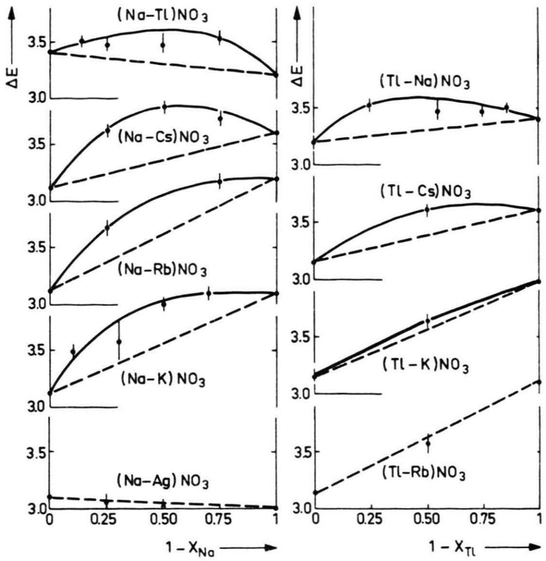

Fig. 4. Left hand: activation energy ΔE as a function of the composition of various systems (Na—Me)NO_3; Me=alkali, or Ag ion. Right hand: activation energy ΔE as a function of the composition for various systems (Tl—Me)NO_3; Me=alkali ion.

The ΔE deviations of the (Na – Tl)NO_3 system are intermediate between those of the (Na – Cs)NO_3 system and those (negligible) of the (Na – Ag)NO_3 system. The (Na – Tl)NO_3 system presents great deviations compared, for example, to the nearly ideal behaviour of the (Tl – Rb)NO_3 system. From these trends one can conclude that this effect is the larger, the larger the difference between the cationic radii.

On the other hand KETELAAR[16], by investigating negative deviations of equivalent conductivity from additivity, has found that for a large number of equimolecular binary mixtures of monovalent nitrates these deviations are proportional to $(\lambda_1 - \lambda_2)^2 / \lambda_1^2 \lambda_2^2$, where $\lambda = r_{\mathrm{cat}} + r_{\mathrm{an}}$. The polarisation energy term $(1/\lambda_1^2 - 1/\lambda_2^2)^2$ also increases with the difference between cationic sizes[17–20]. It must also be noted that the (Tl – Rb)NO_3 and (Na – Ag)NO_3 systems, the ΔE values of which are practically linear with composition, present nearly linear equivalent conductivity isotherms.

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The negative equivalent conductivity excess together with the positive activation energy excess indicate that the electrical transport is more hindered in mixtures than in the pure components. The nitrate anion is easily polarizable[21] and when inserted between cations of different radii will experience a net, permanent, electrical field. The resulting anion polarization increases the attraction between the nitrate and the smaller cation. These conditions will result in a higher resistance for the smaller cation to move relatively to the nearest nitrate; or, in other words, the mobility of the small cation relative to the nitrate will be reduced. Internal mobility[22] measurements in this system could be of interest just from this point of view.

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On the Growth of Ice in Aqueous Solutions Contained in Capillaries

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The growth rate of ice in supercooled water and in dilute aqueous solutions of various salts which dissociate in water into univalent ions was studied. The solutions contained in polyethylene tubes of small bore had concentrations between 10^{-6} and 10^{-1} moles liter^{-1} and were investigated at bath supercoolings between 1° and 15 °C. The growth rate of ice which in pure water was found to vary approximately with the square of the bath supercooling was affected in a systematic manner by the type and concentration of the salt in solution. At salt concentrations smaller than 5×10^{-2} moles liter^{-1} most salts did not affect the growth rate. However, the fluorides were found to increase the growth rate over and above the one in pure water. At concentrations larger than 5×10^{-2} moles liter^{-1} all the salts reduced the growth rate of ice below the one in pure water. By comparing solutions of salts with common anion it was found that at a particular bath supercooling and salt concentration the growth rate of ice was reduced most in lithium solutions and least in cesium and ammonium solutions. By comparing solutions of salts with common cation it was found that the growth rate of ice was reduced most in fluoride solutions and least in bromide solutions. It was concluded that in solutions with salt concentrations larger than 5×10^{-2} moles liter^{-1} the rate of dissipation of latent heat which controls the growth rate of ice is affected in a systematic manner by the freezing point lowering effects which result from pure mass transfer conditions prevailing at the ice-solution interface of a stagnant system. Some features of the observed growth rates are discussed in terms of the effect of dissolved salts on the growth forms of ice in aqueous solutions.

The problem of determining the growth rates and the growth forms of ice in water and aqueous solutions has occupied the interest of many scientists since the end of the 19th century[1–21]. Although the main importance of this problem lies in the realm of physical chemistry, recent studies in the

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