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Technical Paper

Chronopotentiometry of Ag^+ in Molten $\text{KNO}_3\text{-Ca}(\text{NO}_3)_2$ Mixtures*

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Interdiffusion coefficients of Ag^+ (D_{Ag^+}) in molten $\text{KNO}_3\text{-}x\text{ Ca}(\text{NO}_3)_2$ mixtures ($x=10, 20, 30$ and 40 mole%) have been determined using chronopotentiometry over a wide temperature range. Temperature-dependence of D_{Ag^+} was represented by equations of the type:

$$D_{\text{Ag}^+} = A \exp(-B/RT) \text{ for } x=10, 20 \text{ mole\% and}$$

$$D_{\text{Ag}^+} = A_1 \exp(-B_1/T - T_0) \text{ for } x=30, 40 \text{ mole\%}$$

The parameters A , A_1 , B , B_1 and T_0 have been evaluated.

1 Introduction

Temperature-dependence of transport properties in ionic melts which can be supercooled to a state of low fluidity or glassy state, exhibit markedly non-Arrhenius behaviour¹⁾. Observed data have, in general, been interpreted^{2)~6)} in terms of a three-parameter Vogel-Tamann-Fulcher (VTF) equation:

$$W_j = A_j \exp -B/(T - T_0)$$

where W_j is transport property $j = D_i T^{-1/2}$ (diffusion), $\phi T^{1/2}$ (fluidity) or $\lambda_i T^{1/2}$ (ionic conductance), A_j and B and T_0 being adjustable parameters*¹. This equation can be derived from the free volume theory of liquid transport (Cohen and Turnbull⁷⁾) and also the co-operative rearrangement transport mechanism in liquids (Adams and Gibbs⁸⁾); the significance of T_0 on the two approaches is, however, different. In the former, it is the temperature above which free volume commences to form and in the latter, the temperature at which the configurational entropy vanishes. Molten potassium nitrate-calcium nitrate mixtures have low liquidus temperature and some compositions can be supercooled even to $c 200^\circ\text{C}$ below the melting point of the alkali nitrate. Conduc-

tance⁹⁾ and viscosity⁹⁾ measurements in these systems have been carried out. Recently Welch and Angell¹⁰⁾ reported chronopotentiometric diffusion coefficients of Ag^+ (D_{Ag^+}) in $\text{KNO}_3\text{-Ca}(\text{NO}_3)_2$ (61.9: 38.1 mole%), the composition having slowest crystallization rate and thus permitting measurements over a wide temperature range. Growing interest in study of transport properties in supercooled melts led us to extend this study to molten $\text{KNO}_3\text{-}x\text{ Ca}(\text{NO}_3)_2$ mixtures, where $x=10, 20, 30$ and 40 mole%. Temperature-dependence of D_{Ag^+} over this composition range and the influence of increasing the divalent ion concentration in the solvent has been examined.

2 Experimental

Potassium and silver nitrate, both AnalaR (BDH) grade, were vacuum desiccated for several days and stored over anhydrous magnesium perchlorate until used. Calcium nitrate tetrahydrate, also AnalaR (BDH), was dehydrated by desiccation at room temperature followed by raising the temperature to about 300°C over a 12 h period in a vacuum oven. Weight analysis showed that the salt was thus completely dehydrated. It was mixed with calculated amount of

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*¹ The term $T^{1/2}$ in the transport properties is sometimes omitted, since in the low temperature region, where this equation is used, variation of transport property with temperature is rather rapid and is adequately accounted for by the exponential term alone.

KNO₃ in a dry box. About 200 gm of the mixture was loaded in a cylindrical pyrex glass vessel, c 380 mm long and 65 mm o.d. and fused in an inert (nitrogen) atmosphere. The solvent was matured (under vacuum) for 6~8 h before use. Its temperature was measured with an NPL calibrated chromel-alumel thermocouple, held in a glass sheath dipping into it and was controlled within $\pm 1^\circ\text{C}$ of the set value. Densities for solvents containing 10, 20 and 30 mole% Ca(NO₃)₂ were taken from Petersen et al.¹¹⁾ and that for 40 mole% from the equivalent volume values of McAuley et al.¹²⁾

The solvent in the cylindrical vessel was divided into several compartments by use of tubes with fritted-glass-bottom (porosity G-4). A three-electrode system was employed. Ag/Ag⁺ (c . 0.02 m) in the solvent in one of the compartments was the reference and a platinum foil (area c 2.5 cm²) dipping into another, the auxiliary electrode. Another platinum foil (area c 0.520 cm²), spot welded to a 26 gauge platinum wire sealed in soda-lead glass (Corning 0120) tubing and dipping in rest of the solvent in the cell, was used as the polarisable electrode¹²⁾. Chronopotentiograms were observed on a Hewlett and Packard (Model 122-A) oscilloscope and photographed with a Fairchild-Dumont (Type 450-A) 35 mm camera on ORWO-NP-7 panchromatic film. Time-base was provided by z -modulation of the electron beam with a square wave signal from an H & P (type 3300 A) Function Generator. Measurements were made from traces enlarged ($\times 100$) with a Nikon Profile Projector. Transition times were limited in the range 0.5 to 1.5 sec and were evaluated using the method proposed by Thalmayer et al.¹⁴⁾ with a precision better than $\pm 1.5\%$.

3 Results and Discussion

Chronopotentiograms were typical of those for a reversible one-electron process, without kinetic complications. In all cases Sand's equation:

$$D_{\text{Ag}^+} = 4I^2\tau/\pi F^2n^2A^2C^2 \quad (1)$$

where I is the applied constant current (amp.), τ , transition time (sec), A , electrode area (cm²), C , depolariser concentration (mole cm⁻³) and π , F , n having the usual meaning, was obeyed over a wide range of I/A and C . This enabled evaluation of D_{Ag^+} . Typical values at 573.2 K in KNO₃- x Ca(NO₃)₂ where $x=10, 20, 30$ and 40 mole% are presented in Table 1; values reported by Welch and Angell¹⁰⁾ at $x=38.1$ mole% Ca(NO₃)₂ are also included for comparison. Increase in divalent ion

Table 1 D_{Ag^+} in molten KNO₃-Ca(NO₃)₂ mixtures at 573.2 K

KNO ₃ - x Ca(NO ₃) ₂ (x mole%)	10	20	26	30	33	36	38.1	40
$D_{\text{Ag}^+} \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$ Chronopotentiometry	0.98	0.84	—	0.73	—	—	0.60*	0.54
Stokes-Einstein equation ^b	—	0.85	0.68	0.63*	0.50	0.53	—	0.47

a Welch and Angell¹⁰⁾

b Using data of E. Rhodes, W.E. Smith and A.R. Ubbelohde⁹⁾

* Interpolated

concentration in the solvent mixture is accompanied by a decrease in D_{Ag^+} . The comparison is done on the basis of cation field strength, $\sum_i n_i z_i / r_i$ where n_i is the mole fraction, z_i is the ionic charge and r_i is the radius of i th ion of the solvent. An increase in the cation field strength (Fig. 1) is accompanied by a decrease in D_{Ag^+} . Ionic migration in crystalline nitrates and also in chlorides, is generally enhanced by the incorporation of divalent ion into their lattices (Wagner effect). It has been pointed¹⁵⁾ out that for melts which are more compressible than corresponding crystals, an increase in cation field strength causes a shrinkage in the free volume, which would hinder the diffusion of an ion towards an electrode, as observed. These observations are also consistent with conductance measurements in molten halides¹⁶⁾, nitrates¹⁵⁾,¹⁷⁾ etc. where a decrease in ionic conductance is observed when a divalent cation replaces a univalent cation in the melt.

Diffusion coefficients could also be evaluated using Stokes-Einstein equation, which has been shown¹⁸⁾,¹⁹⁾ to give a reasonably good correlation between diffusion coefficient and viscosity for nitrate melts. Using equation in the form:

$$D_{\text{Ag}^+} = KT/a\pi\eta r_{\text{Ag}^+}$$

where η is the viscosity of the solvent (poise), r_{Ag^+} is the ionic radius (1.26×10^{-8} cm)²⁰⁾ and a is a constant with a value of 4.6 as given by Forcheri and Wagner¹⁸⁾ and also by others¹⁹⁾ for nitrate melts, D_{Ag^+} were calculated using the viscosity data of Rhodes, Smith and Ubbelohde⁹⁾. Calculated D_{Ag^+} at 573.2 K (Table 1) are seen to be in good agreement with the chronopotentiometric D_{Ag^+} reported in this study.

Temperature-dependence of D_{Ag^+} in different solvents has also been examined. Plots of $\log(D_{\text{Ag}^+})$ vs. $1/T$ at different compositions (Fig. 2) show a change from linear (Arrhenius) to non-linear with

$$D_{\text{Ag}^+} = (D_i)_{\text{Arr}} \exp(-E/RT)$$

increase in the divalent ion content in the solvent;

¹²⁾ Experimental arrangement for obtaining current time curves has been described earlier¹⁰⁾.

Fig. 1 Variation of D_{Ag^+} with cation field strength of molten KNO_3 - $Ca(NO_3)_2$ mixture at 573.2 K (▼, Ref. 10)

Fig. 2 Variation of $\log D_{Ag^+}$ versus $1/T$ in molten KNO_3 - x $Ca(NO_3)_2$

1: $x=0$, 2: $x=10$, 3: $x=20$, 4: $x=30$, 5: $x=40$ mole%, 1 Ref. 21

Table 2 Arrhenius and non-Arrhenius parameters for diffusion of Ag^+ in molten $\text{KNO}_3\text{-Ca}(\text{NO}_3)_2$ mixtures

$\text{KNO}_3\text{-}x$ $\text{Ca}(\text{NO}_3)_2$ (x mole%)	$(D_o)_{\text{Arr}}$ ($\text{cm}^2 \text{sec}^{-1}$)	E (cal. mole $^{-1}$)	T_o ($^\circ\text{K}$)	D_o ($\text{cm}^2 \text{sec}^{-1}$)	k ($^\circ\text{K}$)	Temp. range ($^\circ\text{K}$)
0*	0.65×10^{-8}	4340				613–696
10	0.53×10^{-8}	4529				576–656
20	1.03×10^{-8}	5454				494–621
30			355.0 ± 1.5	$1.73\text{--}1.82 \times 10^{-8}$	$366.6\text{--}382.7$	449–607
40			359.0 ± 1.0	$1.72\text{--}1.79 \times 10^{-8}$	$430.1\text{--}442.1$	462–599
40 ^a			309.5 ± 0.5			443–603
40 ^b			317 ± 1.0			453–603
40 ^c			325.5 ± 1.5			463–603
40**			320			—

*: Ref. 21, a, b, c: Ref. 9, **: Ref. 2

the latter could be represented by the three-parameter VTF equation:

$$D_{\text{Ag}^+} = D_o \exp \left[-k/(T - T_o) \right]$$

The different parameters obtained by least square fitting the data are presented in Table 2.

An increase in divalent ion content of the solvent is accompanied by an increase in T_o . This trend is also supported by others²¹. At 40 mole% $\text{Ca}(\text{NO}_3)_2$ in the solvent, T_o (this study) is higher than that obtained using the viscosity data⁹. It should be pointed out unless data for a sufficiently wide temperature intervals are available, T_o values will, to some extent, depend upon the temperature interval over which the data are taken. This difference appears to arise from the difference in the temperature intervals used in the two studies.

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