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SELF-DIFFUSION OF Ag^+ AND Na^+
IN MOLTEN $\text{Ca}(\text{NO}_3)_2 - \text{KNO}_3$

by

B. J. Welch and C. A. Angell

of the

Department of Chemistry

at

Purdue University

Lafayette, Indiana

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SELF-DIFFUSION OF Ag^+ AND Na^+
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B. J. Welch* and C. A. Angell

Department of Chemistry, Purdue University
Lafayette, Indiana, 47907

Abstract

In order to explore the behavior of diffusing ionic species in a molten salt in which non-Arrhenius behavior of other transport properties is established, the diffusivities of Ag^+ and Na^+ in dilute solution in 38.1% $\text{Ca}(\text{NO}_3)_2 + 61.9\% \text{KNO}_3$ have been measured. For both ions limited radio-tracer diffusion coefficients, determined using a diffusion-out-of-capillary method, are reported. D_{Ag^+} has also been measured by chronopotentiometry, by which means the range and reliability of the measurements were considerably extended. Chronopotentiometric and tracer data agree within expected errors of measurement. Both ionic diffusivities show a non-Arrhenius temperature dependence which is indistinguishable in magnitude from that of the electrical conductance of the solvent melt.

*On leave from Department of Applied Chemistry, University of N.S.W., Sydney, Australia.

INTRODUCTION

The glass-forming ionic liquid formed by mixing calcium nitrate and potassium nitrate in equal proportions by weight has been the subject of a number of recent detailed mass transport studies (1-5). So far these have been concerned with processes such as electrical conductance (1,3,4) and viscous flow (2,5) in which the system response is measured to a perturbation from equilibrium that affects all ionic species present. In self-diffusion measurements the equilibrium state of the system is perturbed only with respect to the distribution of a single ionic species, thus in principle some extra detail on the transport mechanism may be obtained. The present paper reports results of self-diffusion measurements on Ag^+ and Na^+ in the melt of composition 38.1 mole % $\text{Ca}(\text{NO}_3)_2$ - 61.9 mole % KNO_3 which was chosen because, according to Dietzel and Poegel (6), it has the slowest crystallization rate, hence permits longer studies in the supercooled condition.

The measurement of diffusion coefficients in supercooled melts by conventional tracer methods presents severe problems. Of the available tracer methods the diffusion-out-of-capillary method is considered the most reliable (7,8). However, even in the normal fluid melts where diffusion coefficients are of the order of $10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, capillary measurements require diffusion periods greater than six hours to achieve good accuracy. This diffusion time increases greatly when the smaller diffusion coefficients encountered in viscous melts are to be measured.

When the viscous melt is in the supercooled condition the experimentalist is faced with the additional problem that crystallization of the melt will probably commence before a suitable diffusion period has elapsed (9). Thus a method of measuring diffusion coefficients which can be carried out

on a short time scale must be found. One possibility would be the NMR pulse echo method which has been used to follow diffusion coefficients to very low values in supercooled o-terphenyl (10). However, this technique requires considerable specialized equipment. An alternative approach for short time scale diffusion coefficient determinations is provided by electrochemical methods in which electrodeposition rates of a suitable electroactive species are limited by its diffusivity. A convenient electrochemical technique which has been applied to molten salts by a number of authors (11) is chronopotentiometry, in which one determines the time taken, during passage of a constant current, for the potential of the electrode to rise above the value for the depositing ion.

There has, however, been some doubt that electrochemical methods have been free from all sources of systematic error (12) in their application to molten salts. It has been found (13,14) that deviations from the Sand equation (15) can occur due to kinetic complications for the electrodeposition reaction, as well as the normal design and mass transfer considerations (11). However, Laity and McIntyre (16) have demonstrated that in absence of the kinetic complications diffusion coefficients determined by chronopotentiometry should be identical with self-diffusion coefficients providing the required experimental precautions are taken.

In this work we have studied the diffusion of Ag^+ in molten $\text{Ca}(\text{NO}_3)_2 - \text{KNO}_3$ in stable and supercooled conditions using both tracer and chronopotentiometric techniques. We show that in the temperature range in which tracer methods are practicable the chronopotentiometric data agree with the tracer data within the uncertainty limits of the two techniques. Using the electrochemical technique, however, we have been able to extend the diffusivity data by an order of magnitude, covering in total values from $7.6 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ down to $6 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$. Tracer data for the Na^+ ion,

which could not be studied by electrochemical techniques, are also presented.

It was our original intention to study also the diffusion of Cd^{2+} and Bi^{3+} in the same solvent in order to establish whether a temperature range existed where the charge influences the temperature dependence of diffusion. However, in these cases kinetic complications were found probably due to oxidation of the deposited metal, by the nitrate melt (17).

EXPERIMENTAL

Materials

Malinckrodt A.R. grade KNO_3 and $Ca(NO_3)_2 \cdot 4 H_2O$ were used to prepare the solvent eutectic mixture. The silver nitrate used for the chronopotentiometric study was a refined A.R. grade. Platinum wire (0.5 mm diam.) and platinum foil (0.2 mm thick) were supplied by Engelhard Industries while the silver wire (0.5 mm diam.) and silver foil (0.2 mm thick) were chemically pure.

A. CHRONOPOTENTIOMETRIC DIFFUSION STUDIES

Apparatus

The melt was contained in a round bottomed tubular pyrex crucible 47 mm O.D. x 90 mm deep. Two holes positioned diametrically opposite each other and near the top of this crucible enabled it to be readily removed from the outer glass envelope that supported and positioned the crucible. The outer envelope was a pyrex tube, 58 mm O.D. x 270 mm long, sealed at one end. At the top was attached a Fischer and Porter 50 mm "solv-seal" joint. A side arm, positioned 40 mm from the top of the glass envelope and terminating in a S.J. 13/5 joint, served as a gas outlet. The electrodes were positioned, and the apparatus was sealed, with a machined teflon top that was fitted with an O-ring. The teflon top had five holes machined to accept standard taper ground glass joints and the electrodes were positioned through these holes.

The working or indicator electrode was similar in design to that used by Moynihan and Angell (18) although in this instance it was modified so that it could be readily removed from the melt without breaking the seal from the atmosphere. This was accomplished by use of a ground sliding joint. Both silver and platinum foil electrodes were used and in each instance they were welded to matching wire that had been sealed into the insulating glass. The

surface areas were approximately 2.5 cm^2 but the true areas were determined by careful measurement. Comparative areas could also be determined by comparing chronopotentiograms measured under identical conditions since the design enabled two electrodes to be immersed in the electrolyte simultaneously.

The counter electrode (anode) and its surrounding electrolyte were isolated from the rest of the melt by a tubular compartment that terminated in a fine porosity glass sinter. The sinter prevented mixing of the anolyte and catholyte while maintaining ionic contact. The upper section of the isolation compartment was welded to the lower part of a standard taper 19/38 inner joint which in turn was joined to a standard taper 14/35 outer joint. The latter served to both seal the compartment and precisely locate the glass tube that supported the platinum gauge anode. A thermocouple sheath could be positioned concentric with, and inside the electrode tube. Use of this design prevented possible interference from dissolution of the anode product.

An Ag/Ag^+ reference electrode was used with the silver ion concentration being similar to that in the bulk melt. This electrode was simply made of an 8 mm outside diameter glass tube that was drawn down to a fine capillary. This was filled with the working melt and had a silver wire immersed in it.

The melt could be stirred by means of a hollow shafted blade stirrer. Inert gas bubbling could also be used for either purification or stirring and this utilized the hollow shaft of the stirrer and emerged through a small hole near the centre of the blade.

A tapped tubular resistance furnace was used to heat the cell. The temperature gradient of the furnace was adjusted (by means of resistors across the tappings) so that there was a positive gradient over the melt. Such gradients stabilize the melt against convection currents, by producing a stabilizing density gradient. Temperature was controlled by a Melabs proportional controller

with platinum resistance sensor, and was measured with a chromel-alumel thermocouple.

Chronopotentiometry Instrumentation

The basic arrangement used by Moynihan and Angell (18) was modified to permit use of two working electrodes and also to enable current reversal to be applied. A Tektronix 564 storage oscilloscope was used for measurement of transition times that were too short for the strip chart recorder.

Procedure

Extreme care was taken to insure the absence of electroactive contaminants since these can have an adverse effect on the accuracy. Precautions were taken both with the cleaning of the cell assembly and with the purification of the solvent electrolyte.

Initially the glassware and electrodes were meticulously cleaned by normal procedures. They were then immersed in a pre-purified calcium nitrate-potassium nitrate eutectic and left to "soak" at 225°C for four days. This was to prevent contamination from exchange reactions that can occur between the salt and glass phases. Final cleaning of the cell was by washing in demineralized water and drying at 200°C in an atmosphere of nitrogen.

For all studies, a solvent composition of 38.1 mole % calcium nitrate plus 61.9 mole % potassium nitrate (50:50 wt. %) was used. Sufficient material to give the desired volume (approx. 75 ml.) of anhydrous melt was weighed into a cleaned beaker. The mixture was then heated to ca. 50°C and sufficient demineralized water added to form a homogeneous solution. By filtering the warm solution through a fine porosity glass sinter any insoluble (organic) material could be removed, the solution being filtered directly into the pre-cleaned cell crucible. The filtration was found necessary to avoid contamination of the melt with a carbonaceous material that otherwise interfered with the

cathode process.

The hot solution was dehydrated by slowly heating during purging with dried prepurified nitrogen. The final traces of water were removed by holding the melt at 250°C under a vacuum for 12 hours. The purity of the melt was checked both by the steady state current voltage curves using platinum electrodes and by running chronopotentiograms at very low current densities.

Weighed crystals of A.R. grade AgNO_3 solute were added to the purified solvent and the solution was thoroughly mixed by stirring. After an experiment the melt was chemically analyzed to check the silver nitrate composition.

In addition to the normal chronopotentiometric procedure, the method was varied to prevent errors due to variations in the surface area of the electrode that can arise from crystal or dendrite growth of the electrodeposit (11). While this could be prevented by current reversal on a platinum electrode such a technique could not be applied to silver working electrodes. The modified procedure involved intermittent introduction of a carefully cleaned and accurately measured platinum working electrode. The chronopotentiograms obtained on this electrode were then compared with those obtained on the normal working electrode and a ratio of the areas was thus obtained. In practice the variation did not exceed the limits of error.

B. TRACER DIFFUSION STUDIES

Tracer diffusion coefficients were measured by the diffusion out-of-capillary method using an apparatus and procedure essentially the same as that described by Angell and Tomlinson (20). In this procedure, labelled ions initially contained in twin 2 cm. capillaries of bore 1.0-1.3 mm, are allowed to diffuse into a bath of unlabelled salt of the same composition, and the total activity remaining in the capillary at the end of a suitable diffusion time is determined. The advantages of this method over others, particularly

over the diffusion-into-capillary method, have been discussed elsewhere (7,8). Most important of these is that the concentration of activity at the mouth of the capillary is zero once the diffusion profile is established. This assures that no changes in the capillary activity content are brought about when the salt at the capillary mouth is disturbed during removal of the capillary from the bath at the end of the run. In the diffusion-into-capillary procedure the activity concentration within the tube is a maximum at the mouth hence the inevitable hydrodynamic disturbances during withdrawal constitute a major source of error. Avoiding such errors was of particular importance in the present work because of the (undesirably) small total activity changes which had to be accepted (reasons given in the introduction). Initial immersion errors are readily avoided by providing the capillaries with a small excess of active salt. Any surplus not swept away during slow immersion is removed as soon as capillary rotation is commenced (20).

The radioactive salt sample with which the capillary was initially filled was prepared by adding some of the inactive bath salt to small quantities of dry $^{22}\text{NaNO}_3$ and $^{108}\text{AgNO}_3$ in a mixing bowl suspended above the bath (see ref. 20). This caused a concentration change amounting to only ~0.3 mole % which should not affect the diffusion coefficient significantly. In the case of $^{22}\text{NaNO}_3$ a small amount of inactive AgNO_3 was added to the active NaNO_3 before mixing with bath salt in order to compensate for the unstable density distribution which would have resulted from addition of NaNO_3 alone to the bath salt. If the capillary salt is even slightly less dense than the bath salt, unacceptable convective exchanges of salt between capillary and inactive bath will occur. Density differences in the opposite sense may be an advantage in that they help stabilize the system against thermal convection effects. To further guard against such convective exchanges a small positive temperature gradient was

maintained over the height of the bath. The stability of experimental conditions and absence of significant immersion errors are attested to by the good accordance of γ , the ratio of final to initial activity, for the two capillaries even in low temperature runs in which the total amount of activity diffused out is very small.

For runs carried out below the liquidus temperature, the system was inspected at regular intervals. If (slow-growing) crystals appeared (usually nucleating on the platinum capillary supports (20)) the run was terminated.

After the run the capillary contents were removed by solution in water, diluted to a total volume of 10 cc, and the activity counted using a liquid Geiger counter with demountable jacket. This activity was compared with that of the known sample weight of the salt with which the capillary was initially filled. Sufficient counts to give statistical accuracy of at least 0.2% for each sample were taken.

RESULTS

A. CHRONOPOTENTIOMETRY STUDIES

The shape of the chronopotentiograms was typical of that for a simple reversible process without kinetic complication and was consistent with one electron transfer in the overall electrode process. However, initial measurements carried out at a low silver nitrate concentration and under isothermal conditions showed that the product I^2t increased with time. This was subsequently found to be due to limited corrosion of the silver electrode that increased the concentration of silver ions in the melt. After an extended period reproducible results, that were independent of time, were obtained. Weight loss and chemical analysis confirmed the corrosion and results are given below.

(a) Verification of the Sand Equation

Transition times were measured over a range of currents and silver nitrate concentrations in order to test the applicability of the Sand Equation. This was to confirm that the experimental arrangement enabled precise and accurate measurement. Results obtained from a study of reproducibility of results for various transition times are presented in Table 1. Measurements were made for transition times from 0.153 to 12.7 seconds for two different electrode surfaces and for two different silver nitrate concentrations. The results show that the measurements are independent of transition time and the reproducibility for a given set of conditions is within $\pm 3\%$ while the agreement between sets of data is also within the same limits.

(b) Concentration Dependence

According to the Sand Equation, the product $I_t^{\frac{1}{2}}$ should be directly proportional to the concentration of silver nitrate. Furthermore the plot of the two variables should pass through the origin.

The results obtained at 505°K are presented in figure 1. For each electrode and concentration, at least four chronopotentiograms were measured. The reproducibility was generally found to be within $\pm 1\%$ although in some instances it was as poor as $\pm 2.5\%$. In the graphical presentation of these results, the silver nitrate concentration has been represented simply by mg of silver nitrate added since the true concentration differs from the synthesized value due to the dissolution of the silver working electrode. It can be seen from the two curves that they do not pass through the origin, although they tend to a common point when the value $I_t^{\frac{1}{2}}$ tends to zero. This matter is further dealt with below and in the discussion section.

(c) Temperature Dependence of Diffusion Coefficients

Diffusion coefficients were determined over the temperature range 412°K

to 572.8°K at two different concentrations of silver ions, viz. 16.78×10^{-6} mole cm^{-3} and 5.36×10^{-6} mole cm^{-3} based on the melt density at 573°K.

In each instance two different working electrodes of calibrated surface areas were used. The mean calibrated area of the platinum foil electrode was 2.69 cm^2 while the second electrode made from silver foil had a mean calibrated surface area of 2.89 cm^2 .

The definition of the chronopotentiograms was an optimum at temperatures near 500°K. Accuracy of derived diffusion coefficients fell off at both higher and lower temperatures because of the poorer definition.

The diffusion coefficient according to the Sand Equation is given by:

$$D = \frac{4I^2\tau}{\pi F^2 n^2 A^2 C_i^2} \quad (1)$$

where F is the Faraday constant, n the number of electrons required to electrodeposit the species i (Ag(I) in the present case), A is the electrode area, and C_i the concentration of i in mole cm^{-3} .

Over the temperature range investigated both A and C change due to expansion of the electrode and melt respectively. According to the data of McAuley, Rhodes and Ubbelohde (19), the molar volume of the melt would change by approximately 5% over the temperature range studied. Thus if constant volume were assumed the error in the diffusion coefficient would be up to 10% if the concentration at one of the extremes of temperature was adopted.

To compensate for this error, the basic Sand Equation was modified by employing the published molar volumes of the solvent components (19) to yield:

$$D = \frac{4}{\pi F^2} \frac{I^2 \tau}{A^2} \frac{(51.55 + 0.0219 T)^2}{M_i^2} \quad (2)$$

where M_i is the number of moles of Ag(I) per mole of melt and T the absolute temperature in degrees Kelvin. The change in A , on the other hand, amounts to

only 0.15% over our working range; the areas quoted are based on a temperature of 500°K. τ in all cases was determined from the chronopotentiogram by the construction recommended by Laity and McIntyre (16).

The derived diffusion coefficients for the different AgNO_3 concentrations and different electrode series, are collected in Tables 2 and 3. These results are plotted against reciprocal temperature in figure 2 along with the tracer results described below. The agreement between the results of these independent methods, particularly at higher temperatures where the uncertainties in the tracer data are smaller, is quite satisfactory. Agreement with chronopotentiometry data of good precision being published simultaneously by Ingram and Lewis is not quite as good, their results falling from 9% to 15% below the present measurements except at the low temperature extreme. Since details of their experimental work are not available to us we will not comment on possible reasons for these differences, except to note that overall uncertainties in ^{our} chronopotentiometric diffusion coefficients amount to ca. 10%, (more at lowest temperatures).

(d) Dissolution of Ag in the Nitrate Melt

As mentioned above this was indicated by the steady increase in transition time with the period of immersion of the silver working electrode. This inference was also supported by the self "stripping" of the silver off a platinum electrode after a chronopotentiographic measurement. The reference to working electrode potential versus time relationship showed three characteristic regions. The first region showed an asymptotic decay of the working electrode potential as the silver ion concentration is restored to a steady concentration. The electrode then exhibited a fairly steady potential at a potential identical with the potential of the Ag/Ag^+ reference electrode, the time the electrode remained at this potential being a function of the number of coulombs passed during the chronopotentiometric determination. The third region started with a

rapid decay in the potential of the platinum working electrode with the potential changing to a value characteristic of a freshly immersed platinum electrode in the same electrolyte.

The self-stripping rate increased significantly as the temperature was raised, but if Ag metal was also in contact with the melt, the stripping ceased after a considerable time.

The extent of the dissolution of silver has been measured in two independent corrosion tests. The duration of each test was one week and the temperature was programmed over the same range as that used in the chronopotentiometric measurements. In the first test, a melt initially containing 4×10^{-6} moles Ag(I) cm^{-3} was used, and in the second test a concentration of 10^{-5} moles Ag cm^{-3} was used. Results obtained are summarized in Table 4.

B. TRACER DIFFUSION STUDIES

Tracer diffusion coefficients for ^{109}Ag and ^{22}Na were calculated from the measured ratio of final to initial activity in the capillary, γ , using the equations:

$$D = 0.785(1-\gamma)^2 l^2/t \quad (3)$$

which is accurate to 0.1% for values of γ greater than 0.5 (22), and

$$D = 0.9336(l^2/t) \log_{10}(0.81057/\gamma) \quad (4)$$

which gives errors less than 0.2% when γ is less than 0.5 (14,22).

Values of $D_{109\text{Ag}}$ and $D_{22\text{Na}}$, together with the important experimental parameters, are collected in Tables 3 and 4. The uncertainties quoted for D are determined mainly by uncertainties in γ . Most runs yielded γ values greater than 0.5. Equation 3 shows that errors in this quantity are greatly magnified on proceeding to D . The uncertainty in γ itself arises principally from counting statistics, which reflect the rather low activity of the available radio-isotopes. However, some unassessed source of irreproducibility in γ (possibly temperature drift, or bubble growth during run) has clearly been present in the lowest temperature $D_{109\text{Ag}}$ run. Such experimental perils lead to high values of γ , hence, of D . The lower values of D should generally be regarded as the more reliable.

The data for ^{109}Ag are plotted in Figure 1 with chronopotentiometry results. Results for ^{22}Na are shown in Figure 2 where comparisons may be made with $D_{109\text{Ag}}$ and with the chronopotentiometric D_{Ag} data, the best fit of which is represented by the solid curve. Comparison of the temperature dependence of these diffusion processes with that for the conductance and viscous flow processes in the solvent is also made in Figure 2, and is discussed below.

DISCUSSION OF RESULTS

A. CHRONOPOTENTIOMETRY STUDIES

The Dissolution of Silver in the Melt

Although there have been no direct publications on the dissolution of Ag in molten $\text{Ca}(\text{NO}_3)_2 - \text{KNO}_3$ melts, Conte and Ingram (23) have reported corrosion rates for Ag in alkali nitrates. By comparing the rates for various additives they concluded the corrosion product was silver oxide with the oxygen potential being fixed by the nitrite-nitrate equilibrium. Conte and Ingram reported corrosion rates up to $21.5 \text{ mg cm}^{-2} \text{ day}^{-1}$ which is in qualitative agreement with our results where the rates were less than $5 \text{ mg cm}^{-2} \text{ day}^{-1}$. As the total reaction time was not reported by the former workers no quantitative comparison can be made, although their mechanism is supported by our spot test on samples of melt before and after contact with the electrolyte. The freshly purified melt showed that only trace amounts of nitrite were present while melts that had been in contact with silver for a prolonged time gave a stronger positive test for the presence of nitrite.

The observed reduction in corrosion when a higher concentration of silver ions is present further supports a dissolution mechanism such as proposed by Conte and Ingram since it would be expected to proceed to an equilibrium value. Environmental conditions such as temperature, silver ion concentration, and melt volume would therefore impose the limits.

It is therefore reasonable to expect that the corrosion results in an increase in silver ion concentration, and this is consistent with the good agreement found between the various measurements. Chemical analysis of the melt supported the weight loss measurements within experimental error. The weight loss, in turn, is in accord with results of extrapolating to $i_T^{1/2} = 0$ the plots of figure 1. Consequently, in calculation of the diffusion coefficients shown in figure 2, the concentration of $Ag(I)$ has been corrected for the contribution from initial corrosion.

Adsorption

Since the chronopotentiograms were well defined and since it was not necessary to correct for double layer charging, the data can be tested for effects of adsorption of electroactive species using a plot of $t^{1/2}$ versus reciprocal current at fixed concentration and temperature. A plot of data given in Table 1 gives a straight line passing through the origin, thus apparently no complications due to adsorption effects have arisen. This is further supported by the agreement in the calculated diffusion coefficients for the two different electrode surfaces. If adsorption occurred it is highly unlikely that the extent of adsorption would be identical for each electrode surface, it being known from the work of Inman and co-workers (see ref. 13) that adsorption is a function of electrode material.

B. GENERAL

Taken alone, the data shown in Figure 2 seem to establish that, when proper precautions are taken in performing the measurements, tracer and polarized electrode methods for the measurement of self-diffusion coefficients in molten salts yield results in quite satisfactory agreement. A similar conclusion may be reached from comparison of the recent chronopotentiometry results of Kawamura (24) and Sternberg and Herdlicka (25) for Ag^+ diffusing

in NaNO_3 , with the tracer results for the same system reported by Sjoblom and Behn (26). On the other hand, some doubts are raised by the fact that another set of chronopotentiometric data ^{on this present system} (21) falls below the tracer results by an amount somewhat greater than the expected uncertainty of the measurements. It should be borne in mind, however, that these measurements refer to a range of diffusion coefficients, $D_i < 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, in which accuracy greater than several % has always been difficult to achieve.

Temperature dependence of diffusion coefficients

Whereas, to date, self-diffusion coefficients measured in molten salts have always been well represented by Arrhenius equations (29), the temperature dependence of diffusion in the present $\text{Ca}(\text{NO}_3)_2 - \text{KNO}_3$ solution is strongly non-Arrhenius for both the ionic species studied. This finding parallels that of Moynihan's related study of various ions diffusing in a molten $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{ H}_2\text{O}$ solvent (18). One concludes that the departures from Arrhenius behavior observed in the transport properties of most molten salts at low temperatures have their origin in the nature of the mass transport mechanism for individual species rather than in a combination of Arrhenius ionic processes with different individual activation energies, as has frequently been suggested (27,28).

It is interesting, in this connection, to compare quantitatively the non-Arrhenius temperature dependence of the Na^+ and Ag^+ diffusion processes with that of the solvent $\text{Ca}(\text{NO}_3)_2 - \text{KNO}_3$ conductance and fluid flow processes. This comparison is made in Figure 3 where the tracer data for $^{22}\text{Na}^+$ and $^{109}\text{Ag}^+$ and a curve summarizing the D_{Ag^+} data of Figure 1 are compared with curves for specific conductance, κ , and fluidity, ϕ , based on data of Angell (1) for κ , and of Rhodes, et. al., (2) and Weiler, et. al., (5a) for ϕ . In making this comparison it is remembered that conductance and fluidity are mobility-

like properties related to the diffusivity by equations (30) of Einstein form:

$$D_i = \mu_i kT \quad (5)$$

where μ is a mobility, k the Boltzmann constant. Hence, κ and ϕ values have been multiplied by T at each temperature before plotting in Figure 3. Also, to bring the respective curves into approximate coincidence so as to better compare their temperature dependences, κ and ϕ values have been multiplied by an appropriate constant. Since the Figure 3 ordinate is a logarithmic scale, this simply amounts to displacing the ϕ and κ curves uniformly in the ordinate direction.

According to Figure 3, the temperature dependence for univalent cation diffusion is indistinguishable from that for the solvent conductance within the experimental precision of the diffusion data. In this temperature region both diffusion and conductance processes show a somewhat smaller temperature dependence than does the fluid flow process, which was also found to be the case in the $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ study (18).

It may be taken as evidence for the cooperative nature of mass transport processes in the non-Arrhenius region--an ion can only move when its neighbors (solvent species) also move.

It is unfortunate that the diffusion measurements could not be extended to still lower temperatures. Bose, et.al., (5a) have noted that although both fluidity and conductance in this melt conform to the VTF equation (1-5).

$$\kappa, \phi = A_{\kappa, \phi} \exp \left[-\frac{B_{\kappa, \phi}}{(T - T_0)} \right] \quad (6)$$

($A_{\kappa, \phi}$, $B_{\kappa, \phi}$ and T_0 , constants, $T_0 = 324^\circ\text{K}$), ^{for $T > 125^\circ\text{C}$} below this temperature both properties deviate from this form of temperature dependence and eventually return

(30) The equations referred to are the familiar, but only approximately valid, Nernst-Einstein and Stokes-Einstein equations.

to Arrhenius behavior before T_g is reached. However, they find that the conductivity becomes Arrhenius again at a markedly higher temperature than does the fluidity. It would be most interesting to determine which process the cation diffusivity follows most closely in this region, i.e., which, if either, of the Nernst-Einstein and Stokes-Einstein equations holds even approximately in this lower region. Interest is heightened by the possibility, exploited by Ingram (21), of studying anion diffusivity as well ^{by chronopotentiometry}. This suggests efforts should be made to understand the fading definition of the chronopotentiograms at low diffusivities with an aim to extending the measurements and elucidating this interesting region of behavior.

At high temperatures also, transport processes in molten salts tend towards Arrhenius behavior due, it is thought, to decreasing cooperativity in the transport mechanism. We had hoped to determine whether the common temperature dependence found for ions of different charges diffusing in $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (18) would persist in the higher temperature region $T/T_0 > 1.5$ of behavior accessible in the present solvent. Unfortunately our failure to obtain meaningful diffusion data for Cd^{2+} and Bi^{2+} has left this question unresolved. We might note, however, that Francini and Martini (31), in their oscillographic polarography study in the $\text{LiNO}_3 - \text{NaNO}_3 - \text{KNO}_3$ eutectic, found Tl^+ exhibiting Arrhenius behavior with the same Arrhenius coefficient as the divalent ions Cd^{++} , Pb^{++} , and Zn^{++} . The temperature range of their study corresponds to a temperature region $T/T_0 \approx 2.0-2.2$ (cf. 1.3-1.8 in the present study), according to recent T_g and T_0 determinations for molten alkali nitrates (32). There is some evidence in the work of Thalmayer, et al. (33) in the LiCl-KCl eutectic that, at higher temperatures still, some differences in Arrhenius coefficients for different ions do develop. This suggests that conditions probably do exist in which ionic diffusion probabilities are not predetermined by the solvent

rearrangement probability, but that such behavior is only to be found under highly fluid conditions.

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TABLE 1

The Reproducibility of $I^2\tau$ For Various Transition Times, At 512°K

AgNO ₃ Concentration = 4.1×10^{-5} moles/cc				AgNO ₃ Concentration = 4.81×10^{-5} moles/cc	
(a) PLATINUM ELECTRODE (2.59 cm ²)		(b) SILVER ELECTRODE (3.61 cm ²)		PLATINUM ELECTRODE (2.59 cm ²)	
τ (sec)	$I^2\tau \times 10^6$	τ (sec)	$I^2\tau \times 10^6$	τ (sec)	$I^2\tau \times 10^6$
6.55	2.44	12.7	4.73	10.2	3.35
4.27	2.46	8.05	4.72	1.14	3.45
2.71	2.41	5.27	4.66	0.61	3.45
2.45	2.42	4.85	4.75	0.36	3.35
2.25	2.48	3.20	4.67	0.270	3.25
1.62	2.38	2.04	4.61	0.153	2.25
0.82	2.41	1.61	4.73		

TABLE 2

Chronopotentiometric Diffusion Coefficients For Ag(I)

$$c_{\text{AgNO}_3} = 16.78 \times 10^{-6} \text{ moles/ml (at 573°K)}$$

[D_I , using platinum electrode: D_{II} , using silver electrode]

T (°C)	D_I ($\text{cm}^2 \text{ sec}^{-1} \times 10^6$)	D_{II}
299.7	7.32	7.21
298.6	7.095	7.40
288.3	6.35	6.49
284.0	6.40	6.02
276.2	5.52	5.33
271.3	5.32	5.20
266.5	4.90	4.62
258.2	4.39	4.34
243.9	3.20	3.54
238.0	3.09	2.94
235.2	3.00	2.94
229.1	2.62	2.54
224.0	2.35	2.33
220.2	2.26	2.30
214.2	1.96	1.93
210.2	1.83	1.91
204.2	1.86	1.81
203.0	1.62	1.63
193.4	1.19	1.19
191.5	0.957	1.00
181.2	0.732	0.727
180.5	0.687	0.729
174.8	0.589	0.629
167.1	0.326	0.372
164.5	0.400	0.405
153.0	0.138	0.136

TABLE 3

Chronopotentiometric Diffusion Coefficients For Ag(I)

$$c_{\text{AgNO}_3} = 5.36 \times 10^{-6} \text{ moles/cc (at 573°K)}$$

[D_I , using platinum electrode: D_{II} , using silver electrode]

T (°C)	D_I ($\text{cm}^2 \text{ sec}^{-1} \times 10^6$)	D_{II}
289.6	5.50	
289.0	5.81	
284.0	5.95	
263.7	4.83	
277.9		5.21
259.7	4.25	3.96
249.1	3.72	3.69
230.7		2.69
214.2	1.95	1.94
205.6	1.45	1.64
205.6	1.50	
200.8		1.52
200.4	1.27	1.53
199.9	1.36	
181.2	0.52	0.77
149.9	0.099	0.158
139.1	0.048	0.088

TABLE 4

Results of Corrosion Test

<u>Initial Ionic Ag(I)</u> (moles/cc x 10^6)	<u>Wt. Loss</u> Ag (g)	<u>Equivalent Conc.</u> <u>Increase</u> (moles/cc x 10^6)
4.0	0.015	1.72
10.0	0.0031	0.35

TABLE 5

Diffusion of ^{109}Ag in Molten 38.1% $\text{Ca}(\text{NO}_3)_2$ 61.9% KNO_3

Liquidus Temperature, 195°C

Temp. °C	t hrs.	γ	$D_{^{109}\text{Ag}}$ $\frac{\text{cm}^2}{\text{sec}} \times 10^6$	Uncertainty
158.0	48.50	.828	0.538	± 12%
		.827	0.511	
174.5	108.00	.695	0.760	± 6%
		.690	0.690	
190.0	41.50	.746	1.29	± 8%
		.755	1.27	
222.0	26.00	.726	2.47	± 7%
		.734	2.38	
252.0	18.52	.798	3.13	± 10%
		.805	3.03	
297.6	44.78	.361	7.73	± 2%
		.377	7.76	

TABLE 6

Diffusion of ^{22}Na in molten 38.1% $\text{Ca}(\text{NO}_3)_2$ 61.9% KNO_3

Temp.	t hrs.	γ	$D_{22\text{Na}}$ cm^2	Uncertainty	
<u>T</u>	<u>1/T</u>		$\text{sec}^{-1} \times 10^6$		
164.3	2.286	35.5	.881	0.352	$\pm 17\%$
			.885	0.318	
181.3	2.200	72.0	.755	0.731	$\pm 8\%$
			.738	0.824	
216.2	2.043	70.5	.607	1.92	$\pm 4\%$
			.601	1.96	
247.8	1.920	61.5	.522	3.19	$\pm 3\%$
			.501	3.52	

Figure Captions

Figure 1 $I\gamma^{1/2}$ dependence on additions of AgNO_3 for different electrodes. Ag electrode; area 2.89 cm^2 . Pt electrode; area 2.69 cm^2 .

Figure 2 Tracer self-diffusion coefficients (o) and chronopotentiometric diffusion coefficients (*, °) (see also Table 1) for Ag^+ diffusing in 38.1% $\text{Ca}(\text{NO}_3)_2$ + 61.9% KNO_3 solvent. The tracer data at $1/T = 2.32 \times 10^{-3} \text{ }^\circ\text{K}^{-1}$ are clearly in error, but there was no known experimental justification for rejecting the results. Statistical uncertainties in tracer data are indicated when in excess of symbol sizes.

Figure 3 Tracer self-diffusion coefficients for $^{22}\text{Na}^+$ (o) and $^{109}\text{Ag}^+$ (o) and chronopotentiometric diffusion coefficients for Ag^+ in 38.1% $\text{Ca}(\text{NO}_3)_2$ + 61.9% KNO_3 solvent compared with specific conductance and fluidity of the solvent. To facilitate comparison of the temperature dependences of the different processes, the latter properties have been multiplied by constant factors at each temperature to bring all the curves into close proximity. This amounts to an arbitrary adjustment of temperature-independent pre-exponential factors in equations of Equation 4 form, appropriate to each transport process. The fluidity curve has been interpolated from results for 37% $\text{Ca}(\text{NO}_3)_2$ (ref. 2) and 40% $\text{Ca}(\text{NO}_3)_2$ (ref. 5a) solutions.

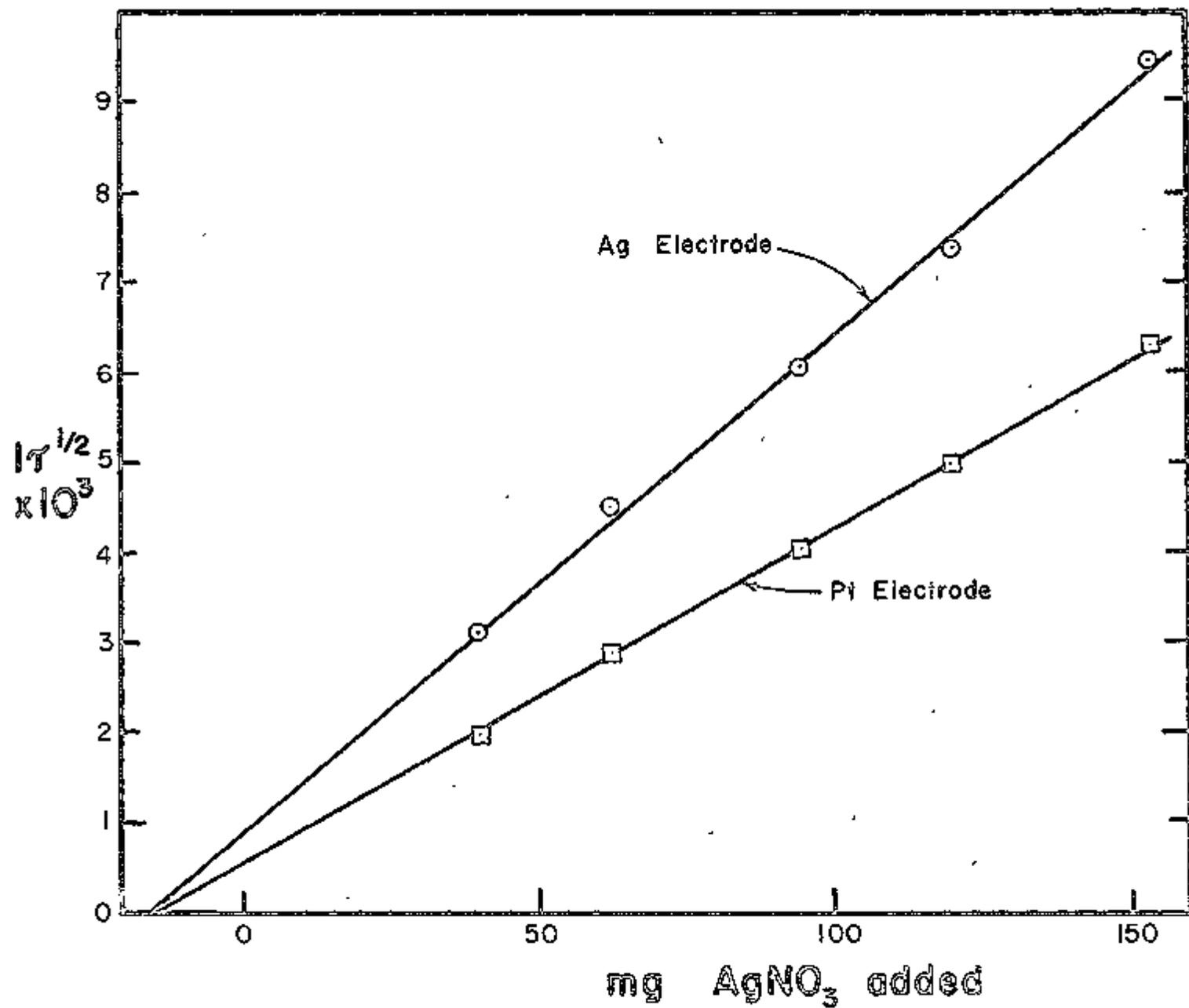


Fig. 1

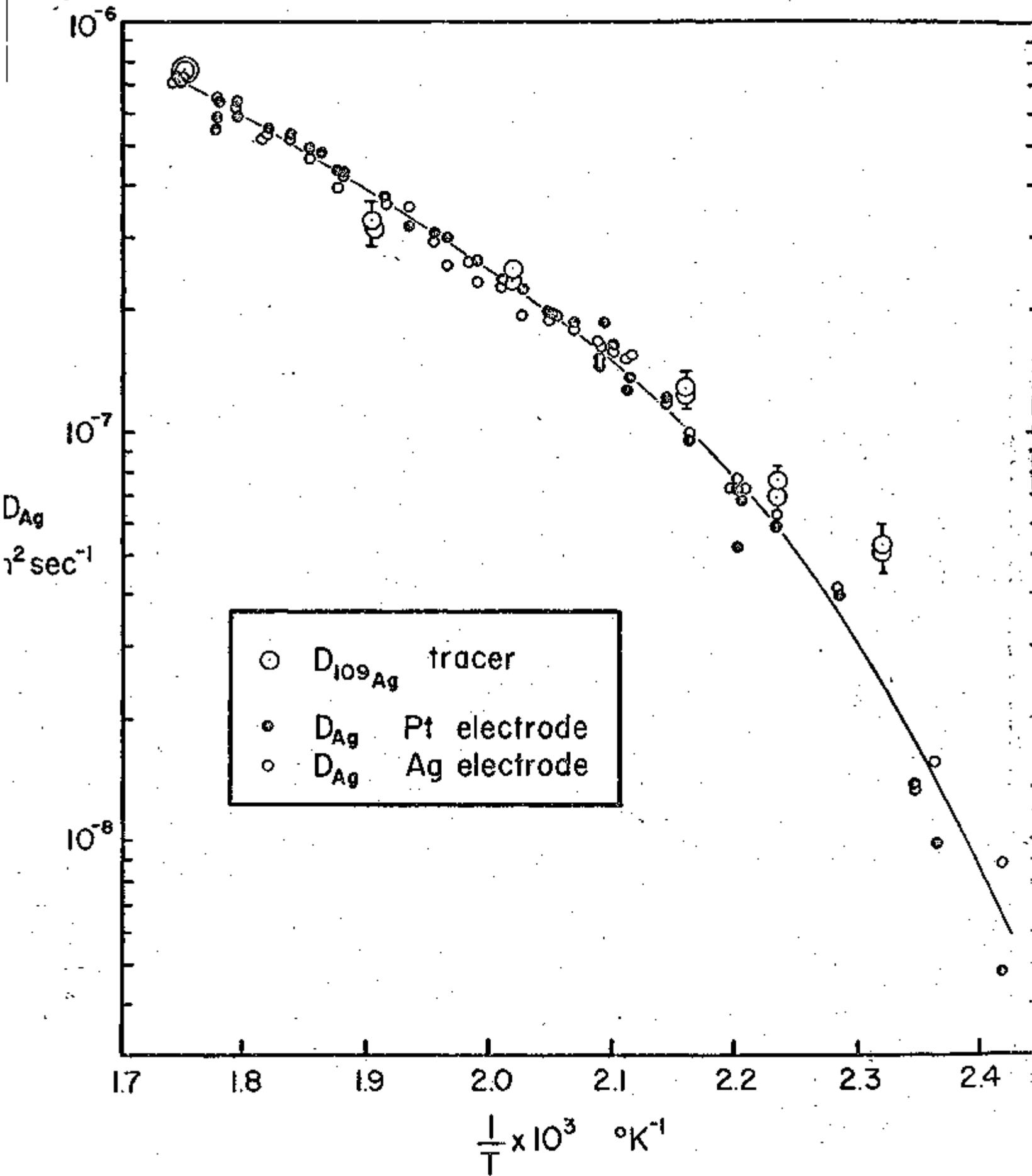


Fig. 2

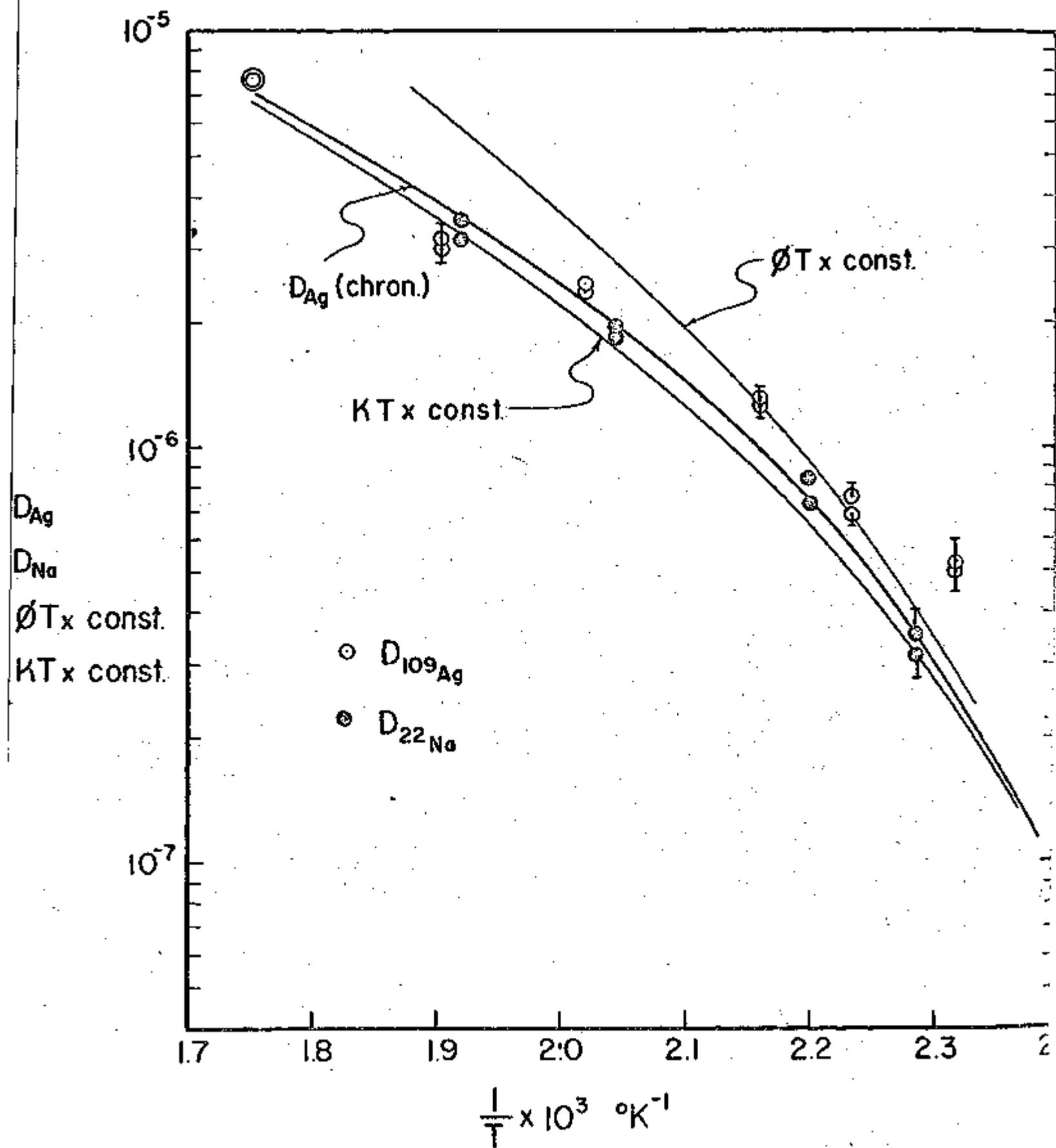


FIG. 3