Table 4 Data with glossmeter

No. of additive	wt. % of additive	Value of glossmeter's reading	
		at pH 9.0	at pH 10.5
1	0.1	201	171
	0.5	—	222
2	0.1	144	184
	0.5	—	—
5	0.1	154	83
	0.5	—	152
6	0.1	322	176
	0.5	—	207
No additive	—	105	88

are shown in Table 4. The difference of values of glossmeter between the original specimen and the resultant was big when aluminum is not dissolved and is kept the original surface, but the difference should be small when aluminum is corrosive. The difference values in case with addition of additives were decreased compared with those in case without additive and the stationary corrosion seemed to occur (the state of surface polishing), then the results from the surface state was not always coincided with those obtained from potential measurement.

4 Conclusion

Generally amines are considered to form stable

chelates with metal ions which are able to coordinate basic nitrogen atom as ligand but aluminum chelates with amines are quite unstable. So a remarkable difference was not seen between the amines which can form chelates and mono-amines, because amines are hydrolyzed to onium ions in aqueous solutions and were considered to be physically adsorbable on metal surface even in case of forming no compounds.

The results obtained from experiments and their discussion, lead to following conclusions:—

- 1) The corrosion was increased with addition of amines used in the experiment.
- 2) The corrosion value showed no big difference between mono- and poly-amines and no formation of chelate compound was apparently seen in case of poly-amine addition.
- 3) The addition of aromatic amines showed no influences to aluminum corrosion.

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Research Paper

Diffusion Coefficient of Silver Ion in $\text{LiNO}_3\text{-KNO}_3$ Melt

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The diffusion coefficients in dilute solution of silver ion have been measured with a chronopotentiometry, over a entire composition range of $\text{LiNO}_3\text{-KNO}_3$ system at the temperatures from 260°C to 360°C.

The obtained diffusion coefficients of silver ion decrease with increasing concentration of KNO_3 in KNO_3 rich side while decrease with decreasing concentration of KNO_3 in LiNO_3 rich side, indicating the limiting (maximum) value at the intermediate concentration of $\text{LiNO}_3\text{-KNO}_3$. Comparison with available diffusion coefficients of other monovalent cations such as lithium, sodium and potassium ions in $\text{LiNO}_3\text{-KNO}_3$ indicates that similar feature can be found for the case of potassium cation. Considering the fact that both silver cation and potassium cation are characterized by the high ionic polarizability, we may notice that the observed unique concentration dependence of diffusion coefficient of silver cation may be attributed to changes in short-range force due to the polarized silver cation in addition to the polarized large nitrate anion.

1 Introduction

Since the transport properties of the melt are largely determined by the (divergence of) short-range force^{(1),(2)}, it is of quite interest to examine how the parameters appeared in the short-range force alter the transport properties of melt. For ionic melts

it has been shown that the short-range force can be explained in terms of two parameters such as the ionic radius and the (induced) ionic polarizability⁽³⁾⁻⁽⁵⁾.

According to published data concerning the ionic radius and ionic polarizability as are shown in Table 1, the lithium cation has the smallest radius and

Table 1 Polarizabilities and radii of ions

Ion	Polariz. $\times 10^{-24} \text{ cm}^3$	Radius $\text{\AA}$
Li^{+}	0.03	0.66
Na^{+}	0.182	0.95
K^{+}	0.844	1.33
Rb^{+}	1.42	1.48
Cs^{+}	2.45	1.66
Ag^{+}	1.72	0.95
Tl^{+}	3.50	
Cl^{-}	3.66	1.81
Br^{-}	4.77	1.99
NO_3^{-}	4.13	2.19
I^{-}	7.10	2.23
F^{-}	1.04	1.36

smallest ionic polarizability while the potassium and silver cations have the relatively large ionic radius and the intermediate value of ionic polarizability in the listed various monovalent cations.

Since the diffusion coefficients in dilute solution of silver ion in $\text{LiNO}_3\text{-KNO}_3$ are not published elsewhere, this paper describes the diffusion coefficient of silver ion in $\text{LiNO}_3\text{-KNO}_3$ which has yielded new diffusion data for the above system from 260°C to 360°C over the entire range from pure LiNO_3 to pure KNO_3 .

In addition to being no published data on the diffusion coefficient of silver ion in $\text{LiNO}_3\text{-KNO}_3$, another strong motivation for investigating this system arises from the hope in examining how the high ionic polarizability of diffusing species such as silver cation affects the diffusion coefficient of diffusing species in the mixture of $\text{LiNO}_3\text{-KNO}_3$.

Combining the obtained diffusion coefficient of silver ion with the published diffusion coefficient of lithium, sodium and potassium cations in $\text{LiNO}_3\text{-KNO}_3$ ^{8),9)}, we hope to elaborate the effects of ionic radius and (induced) ionic polarizability of diffusing species on the transport properties of various monovalent diffusing cations such as silver, lithium, sodium and potassium.

2 Experimental

2.1 Preparation of sample

The $\text{LiNO}_3\text{-KNO}_3$ was purified from the reagent grade (special grade) material by filtering the melt through fritted silica under a dry nitrogen atmosphere followed by bubbling the dry nitrogen gas about two hours in the filtered melt in order to remove the small amounts of moisture in melt. The details of this purifying method have been reported previously^{8),9)}. Thereafter, small amounts of silver nitrate from reagent grade (special grade) material was added.

2.2 Measurement of diffusion coefficient of silver ion

The diffusion coefficients of silver cation were determined with the chronopotentiometry. Although a block diagram of chronopotentiometry are shown in Fig. 1, the apparatus and the procedures for instrument are substantially the same as discussed in previous publications¹⁰⁾⁻¹²⁾ involving the diffusion coefficients of silver cation in NaNO_3 , $\text{NaNO}_3\text{-KNO}_3$ and KNO_3 .

Fig. 1 Chronopotentiometry block diagram

2.3 Calculation of diffusion coefficient

The chronopotentiometric diffusion coefficients are calculated from the following

$$D = 4I^2\tau / (n^2F^2C^2\pi) \quad (1)$$

where D is the chronopotentiometric diffusion coefficient (cm^2/sec), I is the current density (A/cm^2), τ is the transition time (sec), nF is the numbers of coulombs of electricity per mole of electrode reaction, C is the concentration of silver nitrate in $\text{LiNO}_3\text{-KNO}_3$ and π is a constant.

The equation 1 shows the AgNO_3 concentration dependence of the $I\tau^{1/2}$ provided that the chronopotentiometric diffusion coefficients are independent on

Fig. 2 Relation between $I\tau^{1/2}$ and AgNO_3 concentration

AgNO_3 concentration. Most typical experimental relation between $I\tau^{1/2}$ and C are demonstrated in Fig. 2. It is obvious that the equation 1 fits well to the experimental data for the composition studied and the chronopotentiometric diffusion coefficients are determined from the slope of the line relating $I\tau^{1/2}$ to C at various temperatures.

3 Results

Table 2 shows the chronopotentiometric diffusion coefficients in the dilute solution of silver ion, together with the activation energy of the diffusion process, at various temperatures for almost whole range from pure LiNO_3 to pure KNO_3 . The diffusion coefficients of silver ion in pure LiNO_3 are determined by the oscillographic polarography of which method are already mentioned¹³⁾. Since it has been shown that the polarographic diffusion coefficients are agreed with the chronopotentiometric diffusion coefficients within an experimental error¹³⁾, the polarographic diffusion coefficients are also shown in Table 2. The data are all calculated from the slopes of computer fitted least square lines at each temperature. The range of accuracy is based on the results of simple statistical computation that the limiting error is mainly due to the uncertainty in determination of $I\tau^{1/2}$ term, which is calculated from three different transition times corresponding to three different current densities respectively while the concentration of silver ion and temperature are kept to be constant. The value of the probable errors in diffusion coefficient of silver ion indicated in Table 2 are also determined by the computer.

The only diffusion coefficient of silver ion in the dilute solution previously available was a single measurement by C. M. Sjöblom et al¹⁴⁾. Their results of the diffusion coefficients in dilute solution of silver ion in pure LiNO_3 and pure KNO_3 at 360 °C, measured with a porous frit technique by use of a radioactive tracer of silver, are 2.25×10^{-5} and $2.13 \times 10^{-5} \text{ cm}^2/\text{sec}$ respectively, in quite good agreement with present figures. The diffusion coefficient

obtained from porous frit technique is the volume fixed interdiffusion coefficient which is usually called the ordinary diffusion coefficient. The important experimental observations based on the measurement with the chronopotentiometry and porous frit technique are that the chronopotentiometric diffusion coefficients are identical with the ordinary diffusion coefficients in the dilute solution of silver ion, which was already pointed out theoretically by R.W. Laity et al^{15), 16)}. Thus, here after, the obtained chronopotentiometric diffusion coefficient can be considered identical with the ordinary diffusion coefficient in dilute solution.

4 Discussion

The diffusion coefficients in dilute solution of silver ion in LiNO_3 - KNO_3 , which are interpolated to the values at 350°C, are summarized in Fig. 3, together with the diffusion coefficients in dilute solution of various monovalent cations in LiNO_3 -

Solid line : based on present data
Dashed line : based on data of F. Lantelme and M. Chemla^{6), 7)}

Fig. 3 Diffusion coefficients of various monovalent cations in LiNO_3 - KNO_3 at 350°C

Table 2 Chronopotentiometric diffusion coefficients and its activation energies for silver ion in LiNO_3 - KNO_3 ($\times 10^{-5} \text{ cm}^2/\text{sec}$ and kcal/mol)

Temp. °C	LiNO ₃ mol %					
	100 p	80	60	40	20	0
360	2.17±0.07	2.30±0.05	2.48±0.07	2.46±0.04	2.24±0.03	2.05±0.06
340	1.88±0.05	2.01±0.04	2.18±0.05	2.11±0.03	2.04±0.03	1.85±0.06
315	1.50±0.04	1.81±0.03	1.86±0.05	1.90±0.04	1.79±0.03	
290	1.10±0.03	1.41±0.03	1.65±0.04	1.68±0.02	1.49±0.03	
260	0.93±0.04	0.98±0.03	1.26±0.03	1.35±0.03		
E_D	5.9±0.3	5.6±0.2	4.4±0.3	3.8±0.2	3.1±0.2	3.9±0.7

p : Polarographic diffusion coefficient

KNO₃ at 350°C* as reported by M. Chemla *et al.*^{(6),(7)}.

Some features of these curves are worth noting. The diffusion coefficients of various monovalent cations over the entire range of mixture of LiNO₃-KNO₃ decrease in the order of $D_{Li^+} > D_{Na^+} \geq D_{Ag^+} > D_{K^+}$. Since it is the general prediction that an smaller ion is mobile than an larger ion, the order of decreasing of diffusion coefficients corresponding to the order of increasing of ionic radii may be explained in terms of ionic radius.

It is noteworthy further that the diffusion coefficients of lithium and sodium cations in LiNO₃-KNO₃ decrease monotonously in the same direction with the increase of KNO₃ concentration in fused salt, while the diffusion coefficients of potassium and silver cations decrease in the same figure as those of lithium and sodium cations in KNO₃ rich side but decrease in the opposite figure in LiNO₃ rich side, indicating the limiting (maximum) values at the intermediate concentration of LiNO₃-KNO₃. Although the diffusion coefficients of various monovalent cations in LiNO₃-KNO₃ have been discussed by M. Chemla *et al.* in terms of complex formation⁽⁹⁾, the viewpoint that the fused salts such as alkali nitrates are composed only of simple ionic species rather than complex ions seems to be more appropriate. According to this viewpoint, however, it has been shown that the ionic interactions which contribute to the transport properties of fused salt are arisen from the polarization of the large anion like NO₃⁻ whose environment asymmetrical^{(7),(10)}, i.e., Li⁺NO₃-K⁺. In such circumstances the electron cloud of large nitrate anion tends to become polarized in the direction of the smaller of the two cations. Thus, the decrease of the diffusion coefficients of lithium and sodium cations in LiNO₃-KNO₃ with increasing KNO₃ can be explained as the result of the increase of the inducing ionic polarization in nitrate anion by the addition of larger potassium cation. Nor would such a view apply to the diffusion coefficients of potassium and silver cations with the limiting values at intermediate concentration of LiNO₃-KNO₃. In considering the fact that the cations such as potassium and silver are characterized by the high ionic polarizability as shown in Table 1, it is not surprising to see that their diffusion coefficients reveal the limiting value at intermediate concentration. In other words, such an effect of polarization in larger cation would account for the observed KNO₃ concentration de-

pendence of the diffusion coefficients of potassium and silver cations noted above. It should be noted that the diffusion coefficients of potassium and silver cations in LiNO₃-KNO₃ may correspond to the case where, in addition to the polarization of larger anion, the polarization of larger cations such as potassium and silver is also taking part of the transport properties, while the diffusion coefficients of lithium and sodium cations are limited to case where only the larger anion like NO₃⁻ is playing a important role in determining the transport properties.

To obtain the total (divergence of) short-range force for given set of many ions, it is necessary to convert the isolated ion pair results. In broader sense the total induced polarizability for any given ion may be regarded as a vector sum of all polarization due to the all electronic field sources surrounding this polarized ion. The local electronic field at the ion is the results not only of the entire set of ionic charges, but the other induced polarized ions as well, which themselves depend upon the entire set of ionic charges and induced polarizabilities. In other words the induced polarization interaction is in the strict sense unavoidably a many-body interaction in the fused salt system. Hence, it is quite difficult to elucidate the sole calculation of (divergence of) short-range force from polarization interaction and to test whether the calculated values of diffusion coefficients could agree with the obtained diffusion coefficients noted above quantitatively.

5 Summary

It is the present purpose to advocate that results of diffusion experiment in fused salt system may be expressed in terms of at least two parameters such as ionic radius and (induced) ionic polarizability which are appeared in the equation of (divergence of) short-range force. Hence, it is largely for this reason that the measurements of diffusion coefficient of large and polarizable silver ion with the chronopotentiometry are carried out in mixture of lithium nitrate and potassium nitrate.

Combining the obtained diffusion coefficient of silver cation with the other published diffusion coefficients of monovalent cations in LiNO₃-KNO₃, we can see that diffusion coefficients of various monovalent cations over the entire range of mixture of LiNO₃-KNO₃ decrease in the order of $D_{Li^+} > D_{Na^+} \geq D_{Ag^+} > D_{K^+}$. Since the order of decreasing of diffusion coefficient corresponds to the order of increasing of ionic radius, this feature may be explained in terms of ionic radius of diffusing species.

Further it should be noted that the diffusion coe-

* Although the tracer diffusion coefficients in dilute solution of monovalent cations in LiNO₃-KNO₃ are shown in Fig. 3, it should be noted that the tracer diffusion coefficient becomes to be equal to the ordinary diffusion coefficient at infinite dilution⁽¹⁰⁾.

fficients of silver ion decrease with increasing concentration of KNO_3 in KNO_3 rich side while decrease with decreasing concentration of KNO_3 in LiNO_3 rich side, indicating the limiting (maximum) value at the intermediate concentration of LiNO_3 - KNO_3 . Comparison with the diffusion coefficients of other monovalent cations in LiNO_3 - KNO_3 indicates that similar feature can be found for the case of potassium cation. Considering the fact both silver and potassium cations are characterized by the high ionic polarizability, we may notice that the observed unique concentration dependence of diffusion coefficient of silver ion may be attributed to changes in short-range force due to the polarized silver cation in addition to the polarized large nitrate anion.

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