POLAROGRAPHIC STUDIES IN AQUEOUS MELTS. II.*
THE CHARGE DEPENDENCE OF ION TRANSPORT

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Recent theoretical models of structure and transport in concentrated aqueous solutions suggest a significant dependence between the formal charge on an ion and its rate of transport. Previously derived polarographic diffusion coefficients tend to support this notion. A range of evidence indicates the presence of associated species in these media.

Half-wave potentials and diffusion coefficients for some metal ions in aqueous melts have been reported[1]. The diffusion data is directly useful for assessing new models of ion transport, whilst the half-wave potentials indicate the degree of interaction between the tracer cations and the other species in the medium, giving further, indirect information about transport processes.

The inadequacies of the Debye–Hückel theory for describing concentrated aqueous solutions are well known. A quasi-lattice model has been a popular approach to this problem[2-5]. Thus, the sum of the local charge-densities of both anions and cations, averaged over the entire medium, must equal the overall equivalent concentration of all these entities[5,6]. If the distribution laws are common to all ions, the sum of the site charge-densities of anions and cations will be constant and given by[2]:

$$\Sigma x_{j+}, x_{j-} = 2c_{j+}z_{j+} = 2c_{j-}(-z_{j-}),$$

$c_{j\pm}$ and $z_{j\pm}$ being the molar concentrations and formal charges, respectively, on the $j\pm$ ions. A constant, overall charge distribution results and mutual site exchange of anions and cations leads to the formation of ionic atmospheres. The transition-state based theory of transport by cooperative rearrangements of ions and ion groupings arrives at essentially similar conclusions[7]. Braunstein's[5] modified quasi-lattice model for aqueous melts, also accounts for the competitive equilibrium between anions and water molecules for coordination sites adjacent to cations; anion hydration cannot be neglected at elevated concentrations, however[8]. In Čeleda's formulation[2] (but see[3]), activity coefficients will be proportional to the solution normality, whilst the counter-ion cloud has a constant density, independent of the magnitude of the formal ionic charge. However, the thickness of the ionic atmosphere, and hence the effective ionic radius, will be a function of the formal ionic charge. Angell[9] had also adduced that the theoretical glass transition temperature, T_0, which is proportional to the mean ionic potential and is a principle

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transport-controlling parameter in some glassy melts, would be proportional to the solution normality. A correlation between the measured ionic diffusion coefficients and their formal ionic charges therefore, seems feasible.

RESULTS AND DISCUSSION

A plot of polarographic diffusion coefficients[1] against ionic charge for molten $Ca(NO_3)_2.4 H_2O$ at 50°C is shown in Fig. 1. In spite of its empirical nature, the data exhibits reasonable linearity.* The exact relationship between these parameters, implied by Čeleda[2], will be very complex. Plots of D-values against ionic potentials, (z/r), surface charge densities, (z/r^2), or $\sum I/r$, where I is the ionization potential[11], show no trends towards linearity when Pauling ionic radii are assumed[12].
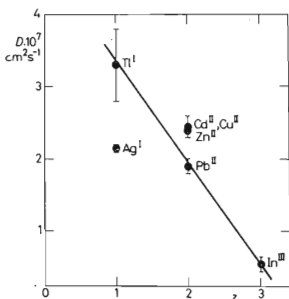

Fig. 1

Diffusion Coefficients of Metal Ions, Dissolved in $Ca(NO_3)_2.4 H_2O$ at 50°C vs Formal Ionic Charge (z)
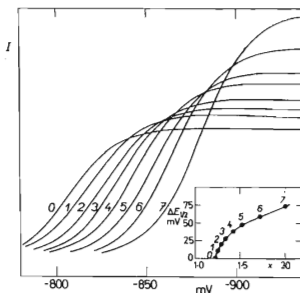

Fig. 2

Effect on Polarograms of Adding Water to a Solution of $0.85 . 10^{-3}$ m Cd(II) Ions in (initially) $Ca(NO_3)_2 . 4 H_2O + 56$ mol % KNO_3

50°C, capillary ($m . t_1$) product $= 7.9$ mg; arbitrary current scale; vs Ag/Ag$_{(I)}$ (0.023 m). Inset: Change in half-wave potential vs concentration of water ($x = $ mol H_2O/mol NO_3^-), corresponding to polarograms in main diagram.

* The diffusion coefficient for Ag$_{(I)}$ is much lower than expected: low values for this ion are often encountered in anhydrous melts, and in nitrate melts[10] activity coefficients can vary between $0.5 - 3.3$.

In anhydrous melts, the similarity between mobilities, or tracer diffusion coefficients for ions of like charge has been noted[13–15]. Some of these results can be quantified through a correlation with the ionization potentials[10], which can take account of partial charge-quenching on the ion[16]. Attempts to fit diffusion data to the Stokes–Einstein equation have also been successful in some cases[17–18]: a numerical constant of 4.6π in the equation (nearly complete slippage) was most appropriate.

A similar test for molten $Ca(NO_3)_2.4\,H_2O$ has been reported recently[19]. The general comments in that paper[19] are pertinent to this discussion, but the chronopotentiometrically determined diffusion coefficients reported there may be in error because the Sand equation is not obeyed and diffusion is not the limiting process[12]. In Table I, polarographically determined diffusion coefficients[1] are compared with values calculated from the Stokes–Einstein equation, using $a = 4.6\pi$, for molten $Ca(NO_3)_2$.$4\,H_2O$ at 50°C. Not only have the simple Pauling radii been used in these calculations, but also those of feasible complexes which might be present[20] in this system.

TABLE I

Comparison of Polarographically Determined and Calculated (Stokes–Einstein) Values of Diffusion Coefficients

Hypothetical species	Pauling ion radius, Å	"Associated radius," Å	$D_{calc} \cdot 10^7$ cm² s^{-1}	D_{obs}/D_{calc}
Cd^{2+}	0.97	—	7.28	0.3
$Cd(NO_3)^+$	0.97	2.90	2.43	1.0
$Cd(NO_3)_2(aq)_2$	0.97	4.29	1.65	1.5
$Cd(aq)_4^{2+}$	0.97	3.75	1.88	1.3
Ag^+	1.26	—	5.61	0.4
Ag_2^{2+}	1.26	2.52	2.80	0.8
Tl^+	1.47	—	4.81	0.7
$Tl(aq)^+$	1.47	2.86	2.47	1.3
$Cu(aq)_4^{2+}$	0.72	3.50	2.02	1.2
$Cu(aq)_2(NO_3)_2$	0.72	4.04	1.75	1.4
$Zn(aq)_4^{2+}$	0.74	3.52	2.01	1.2
$Zn(aq)_2(NO_3)_2$	0.74	4.06	1.74	1.4
$Pb(aq)_4^{2+}$	1.20	3.98	1.78	1.1
$Pb(aq)_2(NO_3)_2$	1.20	4.52	1.57	1.2
$Cu(NO_3)^+$	0.72	2.65	2.67	0.9
$Zn(NO_3)^+$	0.74	2.67	2.65	0.9
$Pb(NO_3)^+$	1.2	3.13	2.26	0.8
$In(aq)_{4\,or\,6}^{3+}$	0.81	3.59	1.97	0.3
$In(aq)_4(NO_3)_2^+$	0.81	4.67	1.52	0.4
$In(aq)_6(NO_3)_6^{3-}$	0.81	7.45	0.95	0.6

$(r(NO_3^-) = 1.93\ \text{Å},\ r(H_2O) = 1.39\ \text{Å}).$

The radii of the latter were considered to be the sum of the component ionic radii, as a first approximation. A rigorous model would need to account for the exact concentrations and individual diffusion coefficients of all the species present in mobile equilibrium. However, the ratios of observed : calculated diffusion coefficients, shown in the Table, closely approach unity in many cases, (compare[19]) Thus, the Stokes–Einstein equation may be a useful approximation for describing the transport of ions in aqueous melts, as well as in some anhydrous melts, provided that realistic species are considered when calculating effective radii. Agreement with the equation is poor for tervalent indium, but large, complex, hydrolysed species, perhaps with multinuclear centres, can be formed in neutral, aqueous solutions. Presumably a realistic value for the mean radius of such entities would improve the agreement.

Further evidence for the presence of mixed complexes in aqueous $Ca(NO_3)_2$. $.4 H_2O + KNO_3$ melts, at least for cadmium, ions is shown in Fig. 2. The mixed melt was progressively diluted with small amounts of water, and polarograms were recorded after each addition. The large half-wave potential shifts observed (see inset) clearly support an initial presence of complexes containing nitrate groups (and almost certainly water ligands, as well) which are progressively displaced in favour of aquo groups. Moreover, the curvilinear shape of the $\Delta E_{1/2} v.$ concentration plot indicates a step-wise displacement to form the aquo-complexes. Analysis in terms of the relevant stability constants is precluded by the absence of data for the corresponding anhydrous melt, at the present time.

However, the stability constants for $Cd^{2+} + Br^-$ in $Ca(NO_3)_2.4 H_2O$ at $50°C$ have been determined[12.21]: $\beta_1 = 500$; $\beta_2 = 0$; $\beta_3 = 1.7 . 10^7$; $\beta_4 = 6.0 . 10^8$.

This enabled the individual diffusion coefficients $(D . 10^6, cm^2 s^{-1}; D_0$ assumed) to be determined for each of the species in the step-wise equilibrium[12]: $D_0 = 0.25$; $D_1 = 0.28$; $D_3 = 0.25$; $D_4 = 0.17$.

The ratio of the diffusion coefficients for the final and initial species was found to be $D_4/D_0 = 0.68$. The final species is reasonably assumed[12] to be $[CdBr_4]^{2-}$, which would have an ionic volume $(\frac{4}{3}\pi r^3)$ of ~ 490 Å^3 based on summation of Pauling radii. If the initial species present in the melt (i.e. in the absence of bromide ions) is of the type $[Cd(NO_3)aq]^+$ or even $[Cd(NO_3)_2aq_2]$, then the effective ionic volume swept out in a random, tumbling model of the diffusion process would be ~ 330 Å^3, giving a ratio of ionic volumes of $V_4/V_0 = 0.68$, and equal to the observed ratio of diffusion coefficients: $CdBr_4^{2-} - r_{mean} = 4.89$ Å, $V_4 = 490$ Å^3; $CdNO_3^+ - r_{mean} = 2.90$ Å, $V' = 102$ Å^3; $Cd(NO_3)aq^+$ or $Cd(NO_3)_2aq_2 - r_{mean} = 4.29$ Å, $V_0 = 331$ Å^3; $Cdaq_4^{2+} - r_{mean} = 3.75$ Å, $V'' = 221$ Å^3; $Cd^{2+} - r = 0.97$ Å, $V''' = 3.8$ Å^3; $NO_3^- - r = 1.93$ Å; $H_2O - r = 1.39$ Å; $Br^- - r = 1.96$ Å.

The naïvety of the calculation is justifiable, since the ratios of the ionic volume of $[CdBr_4]^{2-}$ with other species such as $[Cd aq_4]^{2+}$, $[Cd(NO_3)_4]^{2-}$, Cd^{2+}, or dimeric entities are very different from the ratio of diffusion coefficients observed i.e. 0.68. A weakness of this approach, is that, as indicated above, the presence

of several species in equilibrium, in the melt is not taken into account. Nevertheless, strong supporting[20,21] evidence for the existence of metal nitrate complexes in aqueous nitrate melts is presented herein and the conclusions of Moynihan and co-workers[19] may need revising.

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