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## POLAROGRAPHIC STUDIES IN AQUEOUS MELTS: HALF-WAVE POTENTIALS, DIFFUSION COEFFICIENTS AND RELATED MEASUREMENTS

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Half-wave potentials and diffusion coefficients are reported for the reduction of a range of inorganic cations, at the d.m.e., in the aqueous melts  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ ,  $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$ ,  $\text{LiNO}_3 \cdot 3 \text{H}_2\text{O}$  and others. The data for Ni(II) is described in detail and related spectroscopic measurements provide additional information about the structure of these solutions, especially when compared with previous observations reported for anhydrous melts. Some problems of analysis in very concentrated media are considered.

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Aqueous melts are of interest for both theoretical and practical reasons. They lie intermediate between the normal concentration range of aqueous solutions and anhydrous molten salts. Studies of these highly concentrated media can be used to test theoretical models of structure, association and glass-forming behaviour, for example. On the other hand, data concerning mass transport and electrode processes is pertinent to battery research, electroplating and electro-polishing, and corrosion, in which fields such liquids are commonly encountered. Scholander<sup>1</sup> reviewed polarography in concentrated aqueous solutions two decades ago. However, that author was concerned to optimize the supporting electrolyte concentration for polarographic analysis. The competing influences of solvation, complex formation and viscosity (especially with regard to the applicability of the Stokes-Einstein equation) were also considered<sup>1</sup>. Only one paper has described polarographic studies in an aqueous melt<sup>2</sup>; no half-wave potentials were given. That paper<sup>2</sup> and the chronopotentiometrically determined<sup>3</sup> diffusion coefficients, also in molten  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ , have been criticized<sup>4,5</sup>.

The present communication described some basic polarographic and related data obtained in some recent studies of aqueous melts<sup>4</sup>; the implications in analytical work are discussed. The detailed investigation of the reduction of Cd(II) ions will be reported elsewhere.

### EXPERIMENTAL

*Reagents.* AR grade  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$  and  $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$  were used; batch-selected, (low chloride), laboratory reagent grade  $\text{LiNO}_3 \cdot 3 \text{H}_2\text{O}$  was the best available.  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{D}_2\text{O}$  was prepared by adding the calculated amount of  $\text{D}_2\text{O}$  to a sample of  $\text{Ca}(\text{NO}_3)_2$  which had been vacuum dried at 180°C. Other salts were AR grade, where available, and all were supplied by either B.D.H. or Hopkin and Williams. K and K Laboratories (U.S.A.) indium nitrate trihydrate

TABLE I  
Values of Half-Potentials and Diffusion Coefficients for Ions in Various Melts  
Method: d.c. manual or slow sweep.

Ion	Melt	°C	Reference electrode	$-E^{1/2}$ mV	$D \cdot 10^7$ $\text{cm}^2 \text{s}^{-1}$	H.I.E. slope mV	Comments
Cd(II)	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4 H <sub>2</sub> O	50	Ag/Ag(I) (10 <sup>-3</sup> m)	750 ± 10	2.45 ± 0.15	32	half-wave potentials derived from mean of a large number of similar values — large deviations from mean discounted
			Ag/AgCl(sat.), Cl <sup>-</sup> (5 · 10 <sup>-3</sup> m)	420 ± 20			
			Ag/AgCl(sat.) Hg/Hg <sub>2</sub> Cl <sub>2</sub> (sat.)	610 ± 20 780			
Pb(II)	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4 D <sub>2</sub> O	50	Ag/Ag(I) (10 <sup>-3</sup> m), in hydrate melt	710	1.84 ± 0.01	32	
			Hg/Hg <sub>2</sub> Cl <sub>2</sub> (sat.), in deuterate melt	710			
			LiNO <sub>3</sub> ·3 H <sub>2</sub> O	750			
Zn(II)	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4 H <sub>2</sub> O	50	Ag/AgCl	525 ± 15	6.0 ± 0.1	31	Pb <sup>II</sup> (NO <sub>3</sub> ) <sub>2</sub> not very soluble (<10 <sup>-3</sup> m) in this melt
			Ag/Ag(I) (10 <sup>-3</sup> m)	700 ± 5			
			Ag/AgCl(sat.)	555 ± 5			
Cu(II)	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4 H <sub>2</sub> O	50	Ag/Ag(I) (10 <sup>-3</sup> m)	140 ± 5	2.45 ± 0.10	~37	disproportionates, Cu <sup>I</sup> wave at ~ -0.15 V.
			Ag/AgCl	↑			
			CaCl <sub>2</sub> ·6 H <sub>2</sub> O	35			
Ag(I)	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4 H <sub>2</sub> O	50	—	↑	2.15 ± 0.05	—	deposits at potential of d.m.e., maximum similar to "second kind" at potentials > -400 mV.
			Ca(NO <sub>3</sub> ) <sub>2</sub> ·4 H <sub>2</sub> O	50			
			CaCl <sub>2</sub> ·6 H <sub>2</sub> O	35			

Tl(I)	Ca(NO <sub>3</sub> ) <sub>2</sub> .4 H <sub>2</sub> O CaCl <sub>2</sub> .6 H <sub>2</sub> O	49 35	Ag/AgCl(sat.) Ag/AgCl	820 ± 5 410	5 —	3.3 ± 0.5 —	59.5 61 <sup>c</sup>	maximum appears at conc. > 10 <sup>-3</sup> <i>m</i>
In(III)	Ca(NO <sub>3</sub> ) <sub>2</sub> .4 H <sub>2</sub> O	50	Ag/AgCl(sat.), Cl <sup>-</sup> (5 · 10 <sup>-3</sup> <i>m</i> ) Ag/AgCl(sat.)	465 ± 5 360 ± 5	5 5	0.55 ± 0.10	23	precipitation of hydro- lysis products at con- centrations > 10 <sup>-3</sup> <i>m</i>
	LiNO <sub>3</sub> .3 H <sub>2</sub> O CaCl <sub>2</sub> .6 H <sub>2</sub> O	47 35	Hg/Hg <sub>2</sub> Cl <sub>2</sub> (sat.) Ag/AgCl	710 ± 5 375	5 5	18 ± 2 3.5 ± 0.1	21 <sup>c</sup>	<i>D</i> -value estimated by comparison with a wave for Ni <sup>II</sup> in the same solution
Bi(III)	Ca(NO <sub>3</sub> ) <sub>2</sub> .4 H <sub>2</sub> O	50	Ag/AgCl (10 <sup>-3</sup> <i>M</i> )	230(I) <sup>d</sup> 420(II) <sup>d</sup>	—	— <sup>a</sup>	— <sup>c</sup>	ref. <sup>14</sup>
	CaCl <sub>2</sub> .6 H <sub>2</sub> O	35	Ag/AgCl	53	—	—	— <sup>c</sup>	<i>E</i> <sub>3/4</sub> - <i>E</i> <sub>1/4</sub> ≈ 30 mV. single wave only
Sn(II)	Ca(NO <sub>3</sub> ) <sub>2</sub> .4 H <sub>2</sub> O CaCl <sub>2</sub> .6 H <sub>2</sub> O	48 40	Hg/Hg <sub>2</sub> Cl <sub>2</sub> (sat.) Ag/AgCl	~ 520 ~ 350	—	~ 8.7	— <sup>c</sup> — <sup>c</sup>	not very soluble small maxima on pola- rograms even at lowest concentration, 6 · 10 <sup>-3</sup> <i>m</i>
Co(II)	CaCl <sub>2</sub> .6 H <sub>2</sub> O	35	Ag/AgCl	~ 550	—	~ 6.0	— <sup>c</sup>	half-wave potential showed marked tem- perature dependence
Ga(III)	CaCl <sub>2</sub> .6 H <sub>2</sub> O	35	Ag/AgCl	520 ± 10	10	± 50%	— <sup>c,d</sup>	ill-defined limiting cur- rent
UO <sub>2</sub> <sup>+</sup>	Ca(NO <sub>3</sub> ) <sub>2</sub> .4 H <sub>2</sub> O	60	Ag/AgCl(sat.)	~ 330	—	—	— <sup>d</sup>	single, highly irrever- sible, ill-defined wave

<sup>a</sup>Ratio I/II = 2/3. <sup>b</sup>Wave not discernable in manually plotted polarogram; therefore, *E*<sub>1/2</sub> and *D* determined by constr. method from slow scan wave. Rapid linear-sweep able to separate Zn(II) peak but wave shape shows irreversibility. <sup>c</sup>D.c., slow sweep. <sup>d</sup>Poor reversibility.

gave the same results as a sample which had been crystallized from c.  $\text{HNO}_3$  after dissolving pure indium metal in the AR grade acid<sup>6</sup>.

**Apparatus.** Pyrex cells, either dip-type or water-jacketted, were used throughout<sup>4</sup>. Temperature control was better than  $0.2^\circ\text{C}$  when a water bath was used, but only  $\pm 0.5^\circ\text{C}$  in the silicone oil thermostat used for temperatures above  $\sim 50^\circ\text{C}$ <sup>4</sup>. Manual polarograms were recorded with a Pye ballastic galvanometer ( $\tau$  17.8 s) with a lamp, stand and scale set at 1 m radius. Linear-sweep polarograms were recorded either with a Chemtrix SSP-2 (50 mV — 5 V s<sup>-1</sup>) or Tinsley 19/1 C in conjunction with a standard resistance box and Hitachi 165 chart recorder (1 mV range-potentiometric mode) for sweeps of 150 mV or 300 mV min<sup>-1</sup>. Capillaries (d.m.e.'s) had m.t. — products of either 5.9 mg or 7.9 mg. A hanging mercury drop electrode (h.m.d.e.) was used at the calibrated area 0.0212 cm<sup>2</sup> (Radiometer P 958 b). Mercury pool counter electrodes were used; various reference electrodes were used; these have been described elsewhere<sup>4</sup>. Visible spectra were recorded on the Hitachi/Perkin-Elmer EPS-3 T instrument.

**Procedure.** Generally, melts were purified by pressure filtration through a No 3 Pyrex frit; they were analysed for water content, subsequently<sup>4</sup>. Even low current density pre-electrolysis did not produce entirely satisfactory  $\text{LiNO}_3 \cdot 3 \text{H}_2\text{O}$  melts, as judged by their residual currents. Anhydrous solutes were vacuum dried for 1–2 days on a hotplate. Loss of water above  $\sim 100^\circ\text{C}$  was prevented by covering the melts with a di-n-butyl phthalate layer. All melts were briefly deoxygenated with pre-saturated, "wet"  $\text{N}_2$ , although the solubility of oxygen seemed to be negligible in all melts except  $\text{LiNO}_3 \cdot 3 \text{H}_2\text{O}$ .

## RESULTS AND DISCUSSION

### *Metal Ions, Excluding Ni(II)*

Table I shows the values of the half-wave potentials and diffusion coefficients for the ions examined, in various aqueous melts. In all cases linearity was observed between the limiting currents and the solute concentrations, which were usually within the range  $10^{-4}$ – $10^{-3}m$ . Reduction half-wave potentials normally lay well within the solvent decomposition limits, (Zn(II) ions were reduced very near the cathodic limit, Ag(I) ions were reduced at the potential of the d.m.e.). In nitrate melts the cathodic potential limit was anion reduction, and in chloride melts it was hydrogen evolution — both these processes exhibited kinetic complications<sup>4</sup>. Diffusion-control of solute ion reductions was confirmed by plots of  $i_d$  vs  $\nu^{1/2}$  (d.c. polarograms),  $i_p$  vs  $\nu^{1/2}$  (linear-sweep polarograms), and in the case of Cd(II) ions (the subject of a later communication), by current-time curve analysis, also. Diffusion coefficients were calculated from the simple, Ilkovic equation, as this has been shown<sup>4,7</sup> to be a useful approximation in practice. The value for Cd(II) is at variance with those reported by Braunstein and coworkers<sup>2</sup> and Angell and Moynihan<sup>3</sup>; in the latter case these authors do not appear to have worked in regions of pure diffusion control<sup>4,8</sup>. Most ions gave single, sigmoidal polarographic waves; therefore, since simple diffusion-control was also evident, the reversibility of the reduction was justifiably assessed from the slope of plots according to the Heyrovský-Ilkovic equation, (H.I.E.). Half-wave potentials were also derived from these plots, (*i.e.* where  $\log_{10}(i_d - i/i) = 0$ ). Less reliance is attached to potential data related to the Ag/AgCl (sat.) reference electrode, as these were not very reproducible<sup>4</sup> — this data is included in the table only as a guide for future work. The final column of Table I reports any unusual observations, *etc.* It should also be noted that salts of large cations, *e.g.*  $\text{Pb}^{2+}$ ,  $\text{UO}_2^{2+}$  were not very soluble in the aqueous melts. Since the solvent ions are already charge-shielded by solvation and complexation, weak-field solute cations probably find little incentive to enter the solution phase. Notably, Ag(I) often exhibits anomalously slow diffusion in molten salts, and this is apparently so in molten  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ , also.

## Results for Ni(II) ions

Table II gives the same kind of data as Table I, but for Ni(II) ions in various aqueous melts. Similar tests of diffusion-control and reversibility were applied as those described above. Linearity was always observed in plots of concentration of Ni(II) ions vs polarographic wave height.

It was not possible to resolve the wave for Ni(II) in  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$  at  $50^\circ\text{C}$  due to the intercedence of the  $\text{NO}_3^-$  decomposition wave. However, some early experiments indicated a half-wave potential shift to more positive values at higher temperatures ( $\sim 100^\circ\text{C}$ ). Irreversibility for this ion is normally associated with the tenacity of aquo-nickel(II) bonds in aqueous solutions<sup>9</sup> (cf. anhydrous molten nitrates<sup>10,11</sup>); it would appear that the Ni(II) ion is still predominantly coordinated by water, even at such low water activities, in a mixed aqueous melt. Fig. 1 shows the corresponding plots according to the H.I.E. and Oldham-Parry equation<sup>12</sup> (O.P.E.). Assuming an overall value<sup>13</sup> of  $n = 2$ , and using the value  $D = 1.75 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  (Table II, III), values of  $\alpha$ , the polarographic transfer coefficient<sup>14</sup> and the formal rate constant,  $k_r (10^{-3} \text{ cm s}^{-1})$ , were calculated according to the equation<sup>12</sup>  $E_{1/2} = E_r + (0.0642/\alpha \cdot n) \log_{10} [0.89 \cdot k_r(t/D)^{1/2}]$ ; This work ( $50^\circ\text{C}$ ),  $\alpha = 0.31$ ,  $k_r = 19 (E_r \equiv E_{1/2})$ . Molten  $\text{LiNO}_3\text{-NaNO}_3\text{-KNO}_3$  ( $140^\circ\text{C}$ ) (ref.<sup>10</sup>),  $\alpha = 0.41$ ,  $k_r = 6.2$ , ( $144^\circ\text{C}$ ) (ref.<sup>18</sup>),  $\alpha = 0.5$  (assumed),  $k_r = 5.0$ . Aqueous  $\text{NaClO}_4$ ,  $1\text{M}$  ( $25^\circ\text{C}$ ) (ref.<sup>9</sup>), — — —,  $k_r = 0.63$ ,  $4\text{M}$  ( $25^\circ\text{C}$ ) (ref.<sup>9</sup>), — — —,  $k_r = 4.5$ .

These values appear reasonable when compared with values from the literature for anhydrous molten nitrates and aqueous solutions. The comparison is particularly good when the results of Dandoy and Gierst<sup>9</sup> are extrapolated to higher concentra-

TABLE II  
Values of Half-Wave Potentials and Diffusion Coefficients for Ni(II)-ions in Aqueous Melts  
Method: d.c., manual.

Melt	Temp. °C	Reference electrode	$-E_{1/2}$ mV	Diff. coeff. $\times 10^7 \text{ cm}^2 \text{ s}^{-1}$	Typical H.I.E.slope mV
$\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{D}_2\text{O}$	50	$\text{Ag}/\text{Ag}(\text{I}) (10^{-3} \text{M})$	$940 \pm 5$	$1.45 \pm 0.05$	$100^a$
$\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O} +$ $+ 46 \text{ mol } \% \text{KNO}_3$	51	$\text{Ag}/\text{Ag Cl}(\text{sat})$	$725 \pm 5$	$1.75 \pm 0.10$	$103^a$
$\text{LiNO}_3 \cdot 3 \text{H}_2\text{O}$	47	$\text{Hg}/\text{Hg}_2\text{Cl}_2(\text{sat})$	$995 \pm 5$	$19.5 \pm 2.0$	$a, c$
$\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$	35	$\text{Ag}/\text{AgCl}$	$174 \pm 5$	$4.55 \pm 0.05$	$32^b$
	35	Hg pool	$363 \pm 5$		
	$115^d$	Hg pool	$260 \pm 5$	$39 \pm 1$	$\sim 43^{b, e}$
$\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$	$120^d$	Hg pool	$240 \pm 2$	$11 \pm 1$	$\sim 41^b$

Reversibility: <sup>a</sup>irrev., <sup>b</sup>good. <sup>c</sup>Complex wave shape. <sup>d</sup>Melt covered with di-n-butyl phthalate. <sup>e</sup>d.c.-manual, and slow speed.

TABLE III

Abridged, d.c. Polarographic Data for  $2.7 \cdot 10^{-3} M$ -Ni(II) in  $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O} + 46 \text{ mol } \% \text{KNO}_3$  at  $50^\circ\text{C}$

$i_d = 2800$  units,  $E_{1/2} = -725$  mV vs Ag/AgCl(sat.). Slope of Heyrovský-Ilkovič equation plot = 98 mV, slope of Oldham-Parry equation plot = 104 mV.

$-E$ mV	$i_{\text{corr.}}$ arbitr. units	$\log_{10} \frac{(i_d - i)}{i}$	$x = i/i_d$	$\log_{10} Y^a$
556.1	95	—	—	—
620.1	257	+0.995	0.092	-0.964
643.9	400	+0.778	0.143	-0.748
668.3	602	+0.562	0.215	-0.539
700.4	1 014	+0.246	0.362	-0.234
724.0	1 381	+0.011	0.493	-0.011
745.7	1 738	-0.214	0.621	+0.203
767	2 076	-0.458	0.741	+0.436
790	2 303	-0.666	0.823	+0.637
838	2 568	-1.044	0.917	+1.006
935	2 682	—	—	—
983	2 753	—	—	—

$$^a Y = x(5.5 - x)/5(1 - x).$$

TABLE IV

Absorption Bands in Aqueous Melts

Melt	Reference	$^\circ\text{C}$	Range, $m\mu$	$\nu_{\text{max}}$ , $m\mu$
<b>Ni(II)</b>				
$\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}^a$	same	50	340— 700	$395 \pm 1$
$\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{D}_2\text{O}^a$	$\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$	50	340— 700	$393 \pm 1$
$\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O} +$ $+ 46 \text{ mol } \% \text{KNO}_3^a$	same	29	340—1 750	$395 \pm 1^e$
$\text{LiNO}_3 \cdot 3 \text{H}_2\text{O}^a$	same	40	340— 700	$395 \pm 1$
$\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}^b$	same	30	280—2 600	$425 \pm 1^f$
<b>Cu(II)</b>				
$\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}^c$	same	50	600—2 600	—
$\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}^d$	same	50	600—2 600	—

<sup>a</sup>No evidence of tetrahedral bands at higher frequencies. <sup>b</sup>Beer and Lambert laws obeyed,  $\nu_{\text{max}}$  independent of temperature. <sup>c</sup>Many featured spectrum, indicating much distortion. Bands at 1250, 1163, 1050, 980 and 800  $m\mu$  + many shoulders. <sup>d</sup>Main peaks at 1460, 1170 and 980  $m\mu$ , but several shoulder evident, and considerable asymmetry. Other features: <sup>e</sup>688  $m\mu$ , 1075  $m\mu$ ; <sup>f</sup>784  $m\mu$ , 1350  $m\mu$ , 1650  $m\mu$ .

tions of the supporting electrolytes; the displacement of water molecules from the double layer clearly accelerates the reaction velocity, as expected from chemical considerations<sup>15</sup>. In all aqueous nitrate melts the asymmetric, visible absorption band remains stationary at 395  $m\mu$  (Table IV). On the basis of Angell and Gruen's extrapolation<sup>16</sup>, this would indicate that only one aquoligand has been displaced from the hexa-aquo nickel(II) ion found in aqueous solutions, (385  $m\mu$ ). Maybe a monodentate nitrato linkage is formed<sup>17</sup>. The weaker D-O interaction in  $D_2O$ , than H-O in  $H_2O$ , is reflected in the slightly higher absorption frequency (393  $m\mu$ , compared with 395  $m\mu$ ) for Ni(II) ions in molten  $Ca(NO_3)_2 \cdot 4 D_2O$ .

The formation of trinitratonickel(II) complexes in anhydrous nitrate melts<sup>17</sup> explains why the rate constant for their reduction was measurable<sup>10</sup> and their diffusion coefficient small<sup>7</sup> compared to Pb(II) and Cd(II) ions in the same melts. The results obtained in this work, therefore suggest that the important dehydration steps only occur for Ni(II) ions in the range between anhydrous and aqueous melts. Further investigations are necessary in this region.

Reynolds<sup>19</sup>, Vlček<sup>20</sup> and Tanaka and coworkers<sup>21</sup> have previously reported nearly reversible reduction of Ni(II) ions from concentrated  $CaCl_2$  solutions. The reduction of solutions containing blue  $NiCl_4^{2-}$  ions at the d.m.e. have not been investigated before, however, due to the incompatibility of mercury and most anhydrous, molten chloride solvents. Tetrachloronickelate ions are formed<sup>22</sup> in molten  $MgCl_2 \cdot 6 H_2O$ , but not in molten  $CaCl_2 \cdot 6 H_2O$ . Well-defined single-wave polaro-

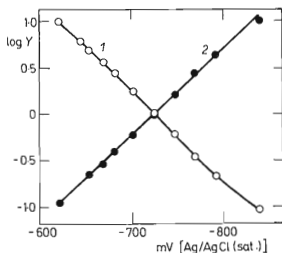


FIG. 1

Plots According to 1 the Heyrovský-Ilkovič Equation,  $Y \equiv i_d - i/i$  and 2 the Oldham-Parry Equation,  $Y \equiv x(5.5-x)/5(1-x)$ , where  $x = i/i_d$

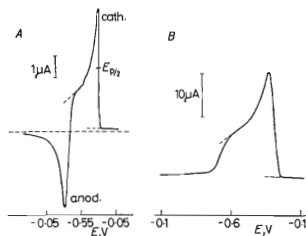


FIG. 2

Triangular Voltage Sweep for Ni(II) in  $CaCl_2 \cdot 6 H_2O$

$35^\circ C$ , h.m.d.e.,  $A 0.0212 \text{ cm}^2$ ,  $\nu 50 \text{ mV s}^{-1}$ , sweep direction from right to left. A  $1.423 \cdot 10^{-3} \text{ m-Ni(II)}$ ; B  $9.134 \cdot 10^{-3} \text{ m-Ni(II)}$  (showing effect of intermetallic formation on anodic stripping wave).

grams were obtained for solutions of Ni(II) ions in both of these aqueous chloride melts at  $\sim 120^\circ\text{C}$ , and also at  $\sim 30^\circ\text{C}$  for the latter. Wave-heights were proportional to concentration; plots according to the H.I.E. suggested simple, reversible behaviour, ( $n = 2$ ), — the mercury pool electrode should be an adequate reference at such elevated chloride concentrations. Thus, these single waves do not appear to resemble the Ni(II) prewaves referred to by Gierst and coworkers<sup>23</sup>. Although solutions of Ni(II) in  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  were dark blue, but yellow-green in  $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$  melts (at all temperatures) there does not appear to be any significant difference in the half-wave potentials. The higher (3 times) diffusion coefficient for the nickel(II) ion in  $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$  suggests that the outer sphere (or net) coordination number in  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  must be the larger. This is surprising, but many recent papers have described anomalous hydration numbers for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in aqueous solutions<sup>24</sup>. In  $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$  melts, the  $E_{1/2}$  shows a  $1.2 \text{ mV}/^\circ\text{C}$  shift, in the expected direction, over the range  $30 - 115^\circ\text{C}$ . The Arrhenius activation energy for diffusion in this range corresponds to  $6.4 \text{ kcal mol}^{-1}$ , *i.e.* approximately the same as Cd(II) ions<sup>4</sup>. Fig. 2 indicates that, for dilute solutions of Ni(II) ions in  $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$ , reversible behaviour is exhibited for reduction and subsequent reoxidation (stripping) at the h.m.d.e., for sweep rates up to  $50 \text{ mV} \cdot \text{s}^{-1}$ . The plots  $i_p - v^{1/2}$  show that the current is increasingly influenced by kinetic control at higher sweep rates. Furthermore, at higher Ni(II) concentrations the anodic wave height begins to decline due to intermetallic compound formation with the mercury<sup>25</sup>, (Fig. 2B); this effect was confirmed by current-reversal chronopotentiometry<sup>4</sup>. The spectrum for Ni(II) in this melt (Table IV) suggests that two aquo-ligands remain in the inner coordination sphere.

## CONCLUSIONS

Mass transfer is very slow in aqueous melts at temperatures not too far removed from their melting points, as evidenced by the diffusion coefficients shown in Tables I and II. Moreover, diffusion (and viscosity), is exponentially related to the "reduced" temperature<sup>26</sup>,  $(T - T_0)$ . Two implications of these results are that *a*) a high degree of temperature control will be necessary if reproducible analyses are to be obtained, *b*) small diffusion currents are obtained; these require careful and precise correction for residual currents, which in extreme cases may be of the same order of magnitude as the faradaic current. Nevertheless, media such as  $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$  may be useful for analytical studies, where the effective activity of water is very low. Problems of maintaining a constant water composition and preparing stable, reproducible reference electrodes should not be underestimated, however<sup>4</sup>.

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