mean square change in perihelion distance in 4.5 $\times 10^9$ years is

$$(\overline{\delta q_1^2})^{1/2} \cong 2\times 10^{-3}\ \text{A.U.} \qquad (41)$$

Therefore, for collisions between objects in typical meteorite orbits, the effect of this second mechanism is also seen to be small. For stone meteorites, it is probably smaller still, because they are unlikely to survive collision with projectiles as large as half their radius, as was assumed in these calculations. However by assuming higher values of the index p in the power law for the size distribution as well as highly inclined and eccentric orbits, which lead to higher relative velocities U' it may be possible to raise $(\overline{\delta q_1^2})^{1/2}$ by one or two orders of magnitude. Even stronger bodies would be required to survive this increased number of these higher velocity impacts, but it may be that meteoritic iron possesses this necessary strength. In this case multiple collisional scattering could provide a small supply of iron meteorites in Mars-crossing orbits in addition to those present at the time of origin of the solar system.

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Oscillographic Polarography in Molten Nitrates

I. The Behaviour of the Ions Tl^+, Cd^{++}, Pb^{++}, Zn^{++} and Ni^{++} in the Eutectic $LiNO_3$–$NaNO_3$–KNO_3

M. Francini and S. Martini

EURATOM C. C. R. Petten (N. H.)

Reactor Materials Department, Electrochemistry Group

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The polarographic investigation of Pb^{++}, Cd^{++}, Tl^+, Zn^{++} and Ni^{++} ions in a KNO_3-$LiNO_3$-$NaNO_3$ molten eutectic mixture was carried out by conventional and oscillographic (single-sweep) polarography. Experiments were carried out in the temperature range 150—200 °C, with a dropping mercury electrode as the cathode and a Ag/AgCl electrode as anode and reference. For ions with reversible behaviour (Cd^{++}, Pb^{++}, Tl^+) the polarographic diffusion coefficients calculated from conventional polarography data by means of the Ilkovič equation agree, within experimental errors, with those obtained from oscillographic data by the Randles-Sevčik equation at low potential change rates. At higher potential change rates deviations of the experimental peak currents from their theoretical values were observed. This is associated with a marked distortion of the wave and indicates a certain degree of kinetic control. The temperature dependence of the diffusion coefficients in the investigated range is the same for the ions with reversible behaviour and the corresponding activation energy is $E = -8.4$ kcal/mole.

1. Introduction

The feasibility of using the dropping mercury electrode (d. m. e.) in polarographic studies of molten nitrate melts was demonstrated some years ago by Steinberg and Nachtrieb [1]; their work indicated that in such low melting systems the d. m. e. could be used without particular difficulties and that the Ilkovič equation was quite valid.

The purpose of this work is to test, on the same system, the validity of the equation first established by Randles [2] and Sevčik [3] for the case of oscillographic polarography at linear voltage scanning. More recently Matsuda and Ayabe [4] carried out a complete analytical treatment of the single sweep oscillographic polarography including the cases of reversible, irreversible and "quasi" reversible electrode reactions; in this work the expressions derived by Matsuda are used.

For the case of the reversible electroreduction of a cation Matsuda obtained the following equations:

$$(i_\mathrm{p})_\mathrm{r} = 0{,}447\, n\, F\, A\, C\, D^{\frac{1}{2}} (n\, F\, v / R\, T)^{\frac{1}{2}}, \qquad (1)$$

$$(E_\mathrm{p})_\mathrm{r} = E_{\frac{1}{2}} - 1{,}11\, R\, T / n\, F\,, \qquad (2)$$

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[1] M. Steinberg and N. M. Nachtrieb, J. Am. Chem. Soc. **72**, 3558 [1950].

[2] J. E. B. Randles, Trans. Faraday. Soc. **44**, 327 [1948].

[3] A. Sevčik, Coll. Czech. Chem. Comm. **3**, 349 [1948].

[4] H. Matsuda and Y. Ayabe, Z. Elektrochem. **59**, 494 [1955]

$$(E_{p/2})_r = (E_p)_r = 2{,}20\, RT/nF \qquad (3)$$

where:

i_p = height of the oscillographic wave (Amp.);
A = electrode area (cm^2);
C = concentration of the cation ($moles/cm^3$);
n = number of electrons involved in the electrode reactions;
D = diffusion coefficient of the cation (cm^2/sec);
v = rate of voltage change (volts/sec);
T = absolute temperature;
$(E_p)_r$ = potential corresponding to the peak (or maximum value of) current (volts);
$(E_{\frac{1}{2}})$ = half-wave potential of conventional polarograms (volts);
$(E_{p/2})_r$ = potential at which the height of oscillographic wave reaches half its value (volts);
F, R = have their usual significance.

By expressing the electrode area as a function of the mercury mass flow m, of the drop lifetime τ at which the peak occurs and of the density of mercury d_t at the temperature considered, after grouping numerical constants, the following equations are obtained:

$$(i_p)_r = 2.247 \cdot 10^5\, n^{3/2} (m\,\tau/d_t)^{2/3}\, C\, D^{1/2} (v/T)^{1/2}, \qquad (4)$$

$$(E_p)_r = E_{\frac{1}{2}} - 1.11\, RT/nF, \qquad (5)$$

$$(E_{p/2})_r = (E_p)_r = 2.20\, RT/nF \qquad (6)$$

in which the following units are used: i_p in μA, m in mg/sec, τ in sec, d_t in g/cm^3, C in mMol/l, D in cm^2/sec, v in volts/sec and T in °K.

Conventional polarograms were carried out to obtain halfwave potentials and diffusion coefficients as requested for the check of the equations (5) and (4); these are calculated by means of the Ilkovič equation in the form:

$$i_d = 3.455\, n\, C\, D^{1/2} (m/d_t)^{2/3}\, \tau_{max}^{1/6} \qquad (7)$$

in which i_d is the limiting diffusion current in μA, τ_{max} is the drop lifetime in sec and the other symbols have the significance seen above.

2. Experimental

The description of the cell assembly as well as of the experimental procedures of preparing the base solvent and the reference electrode has been given elsewhere[5] and wil not be reported here.

3. Results and Discussion

In Fig. 1 the reduction wave of the Pb^{++} ion at low potential change rate is shown; the other ions give quite similar waves. The waves are well defined and quite reproducible and the determination of the peak current values does not present any difficulty. At potential change rates higher than 1 volts per sec distortions in the residual current base line appear that are due to the increase of the capacitive current (charging of the double layer) as well as to the instrumental characteristics of the apparatus. These distortions render the peak height evaluation more cumbersome; to overcome this difficulty, base lines of the pure solvent at different voltage change rates and temperature were recorded.

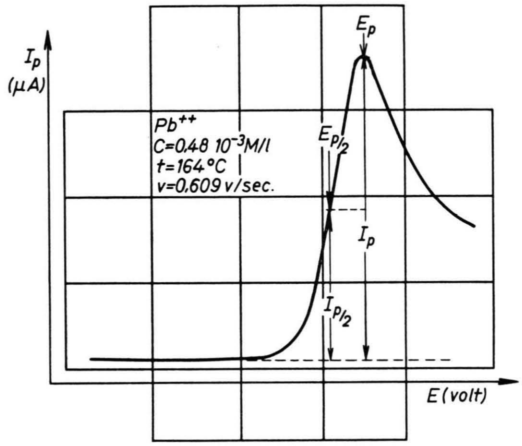

Fig. 1. Typical reduction wave.

For reversible electrode reactions the application of Eqs. (4), (5) and (6) reveal that:

1. The peak potential, whereas independent from concentration, is related to the half-wave potential. In Table 1 the measured E_p's at different concentrations and at constant voltage change rate are compared with theory. The $E_{1/2}$ values were obtained on the same solutions during the same run. The agreement between calculated and observed values is within the experimental uncertainty.

2. The peak potential is independent of the voltage change rate; this is true for Tl^+, Cd^{++}, Pb^{++} and Zn^{++} at least up to approximately 10 volts/sec, while for Ni^{++} the peak potential is always a function of the voltage change rate; then the coincidence between theoretical and experimental values observed in Table 1 is purely incidental.

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[5] M. Francini and S. Martini, Proc. 3rd Intern. Congr. Polarography, Southampton 1964, pp. 1153–1164.

Ion	t (°C)	C (10^{-3} M/l)	$E_{1/2}^{\text{obs}}$ (volt)	$E_{\text{p}}^{\text{theor}}$ (volt)	$E_{\text{p}}^{\text{obs}}$ (volt)
Pb^{++}	165	0.335	−0.375	−0.396	−0.398
	165	0.576	−0.375	−0.396	−0.398
	165	1.050	−0.375	−0.396	−0.398
	166	0.477	−0.378	−0.399	−0.398
Cd^{++}	162	0.140	—	—	−0.412
	162	0.620	−0.392	−0.413	−0.413
	162	0.930	−0.394	−0.415	−0.413
	165	1.07	−0.392	−0.413	−0.412
Tl^{+}	158	0.292	−0.534	−0.575	−0.577
	158	0.417	−0.534	−0.575	−0.577
	158	0.891	−0.534	−0.575	−0.577
	170	0.406	−0.546	−0.588	−0.587
	170	0.909	−0.546	−0.588	−0.587
	170	1.42	—	—	−0.585
Zn^{++}	163	0.577	−0.702	−0.723	−0.716
	163	0.950	−0.702	−0.723	−0.718
	163	1.149	−0.700	−0.721	−0.715
	170	0.807	—	—	−0.717
	170	1.402	—	—	−0.718
Ni^{++}	159	0.433	−0.277	−0.298	−0.295
	159	0.996	−0.277	−0.298	−0.298
	166	1.62	−0.279	−0.300	−0.292

Table 1. $V=0.609$ volts/sec.

3. The difference between the half-peak potential and peak potential is a function of the absolute temperature T and the number of electrons n involved in the electrode process. Good agreement between theoretical and experimental values exists for Tl^{++}, Cd^{++}, Pb^{++}, Ni^{++} and Zn^{++}, however yield values are greater than predicted by theory.

4. The peak currents are proportional to the square root of the voltage change rate. The observed Tl^{+} ion behaviour gives complete linearity in the whole range of voltage change rates explored (0 to 36 volts/sec) while for the other ions the linearity holds up to a potential change rate of approximately 10 volts/sec, increasing less than linearly beyond this limit. Departure from linearity is more marked at higher change rates [6].

Following DELAHAY [7] the departure from linearity can be explained by assuming that the rate of the electrode reaction is the factor controlling peak currents.

In fact, when linearity is no more fulfilled, an increase of the difference $(E_{\text{p}/2}-E_{\text{p}})$ is observed (from 83 mV, 42 mV, 45 mV, to 115 mV, 68 mV and 76 mV for Tl^{++}, Pb^{++} and Ni^{++} respectively). This increase of the $(E_{\text{p}/2}-E_{\text{p}})$ value is equivalent to a distortion of the wave that becomes smaller and rounded; this is in agreement with theory for the case of non reversible reactions.

From these results it is clear that:

1. Cd^{++}, Pb^{++} and Tl^{++} have reversible electrode reactions at voltage change rates lower than 10 volt /sec; the degree of irreversibility for higher sweep rates is in the following order: $Pb > Cd > Tl$.

2. Zn^{++} and Ni^{++} have irreversible electrode reactions and Zn^{++} is less irreversible than Ni^{++}.

This conclusions can be confirmed by evaluating the slopes of the $\log[i/(i_{\text{d}}-i)]$ vs. electrode potential plots as obtained from conventional polarograms. In Fig. 2 the obtained plots of $\log[i/(i_{\text{d}}-i)]$ vs. electrode potential are given. The reciprocal slopes of the obtained straight lines are 0.043, 0.043, 0.085, 0.043 and 0.045 (±1 mV) volts respectively for Pb^{++}, Cd^{++}, Tl^{+}, Zn^{++} and Ni^{++} and should be compared with the theoretical values of 0.0436, 0.0431, 0.0855, 0.0432 and 0.0429 volts. From the values of the measured slopes, Pb^{++}, Cd^{++}, Tl^{+} and Zn^{++} result to be reversible while for Ni^{++} there is a little difference between the calculated and experimental values. Furthermore the plot of Ni^{++} values does not yield a straight line, but is rather bent in agreement with a "quasi reversible" behaviour [8]. An additional proof of the non reversible behaviour of Ni^{++} can be deduced from the $\log i$ vs.

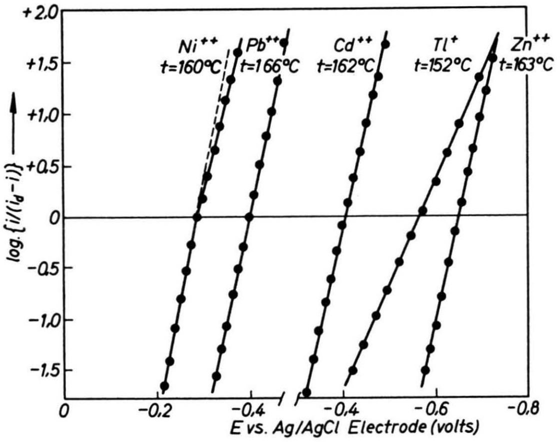

Fig. 2. Plot of the function $\lg\{i/(i_{\text{d}}-i)\}$ vs. electrode potential.

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[6] Quite similar behaviour was observed by DELAHAY [7] in aqueous solutions of ions with reversible electrode reactions.

[7] P. DELAHAY, J. Phys. Chem. **54**, 630 [1950].

[8] H. MATSUDA and Y. AYABE, Z. Elektrochem. **63**, 1164 [1959].

$\log h_{Hg}$ plots (where i is the diffusion current and h_{Hg} the height of mercury).

In Fig. 3 these plots are reported for the following current values: i_d, $\frac{2}{3}\, i_d$, $\frac{1}{3}\, i_d$. The plot $\log h_{Hg} + \log i_d$ has a slope 0.5 in perfect agreement with theoretical prediction. At lower current values (at the foot of a wave), a certain degree of independence of $\log i$ from $\log h_{Hg}$ is apparent. This is characteristic of non reversible behaviour, as pointed out by DELAHAY [9].

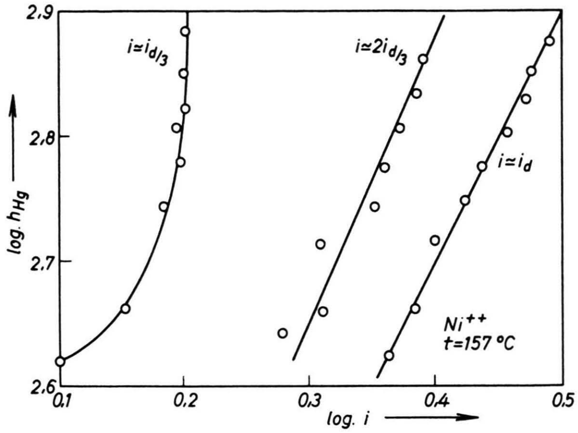

Fig. 3. Plot of $\lg h_{Hg}$ vs. $\lg i$ for different wave heights (conventional polarography).

From these observations it follows that:

1. Oscillopolarography is more sensitive than the conventional one for the detection of the degree of reversibility of electrode reactions;

2. The order of reversibility of the investigated ions is: $Tl > Cd > Pb > Zn > Ni$.

It is interesting to note that it was already proposed by PIONTELLI [10] to place Zn (along with Ag, Bi etc.), from the standpoint of its general electrochemical behaviour, in an intermediate position between the so called "normal" metals as Pb, Cd, Tl etc., and "inert" ones, as the transition metals, and that this point of view quite agrees with our conclusions, for this particular molten salt system. To complete the check of the validity of the Randles-Sevčik equation, the diffusion coefficients of the ions have been calculated by means of Eq. (4) and compared with those obtained by means of the Ilkovič equation (7), in the temperature range 150 ÷ 200 °C. In Fig. 4 and 5 their temperature dependences are given.

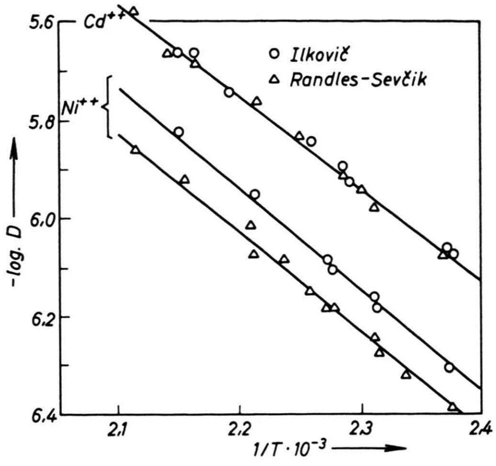

Fig. 4. Temperature dependence of diffusion coefficients.

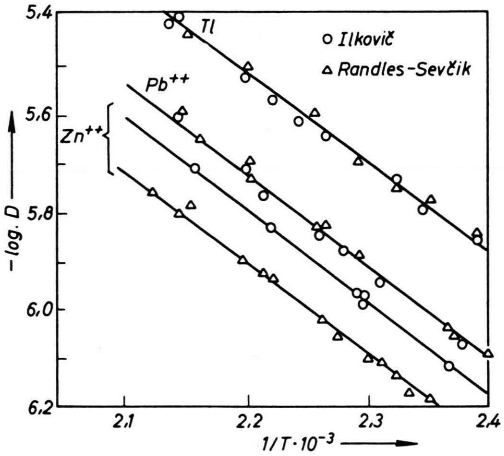

Fig. 5. Temperature dependence of diffusion coefficients.

From these plots the following conclusions can be drawn:

1. The agreement between the values calculated by Eqs. (4) and (7) is quite good for "reversible" ions as Pb^{++}, Cd^{++}, Tl^{+};

2. In the case of Zn^{++} and Ni^{++} there is some inconsistency, in agreement with the inert character of these ions;

3. The temperature dependence of diffusion coefficients is of the form $D = A \cdot \exp(-E/RT)$ where A is a constant and E is the activation energy of the diffusion process.

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[9] P. DELAHAY, New Instrumental Methods in Electrochemistry, Interscience Publ. New York 1954, p. 79.

[10] R. PIONTELLI, Comptes rendu de la III réunion du CITCE (1951), p. 71.

The obtained values of *E* are given in Table 2. There is a common value for Pb^{++}, Cd^{++}, Tl^{+}, Zn^{++}, whereas Ni^{++} yields a greater one. This can be easily explained taking in account its partial kinetic control of the current.

Ion	$E^{\text{R.S.}}$ (kcal/mole)	$E^{\text{Ilk.}}$ (kcal/mole)
Pb^{++}	−8.400	−8.400
Cd^{++}	−8.400	−8.400
Tl^{+}	−8.400	−8.400
Zn^{++}	−8.400	−8.400
Ni^{++}	−9.100	−9.100

Table 2.

4. Conclusions

1. The validity of the Randles-Sevčik equation (1) as well as of the other equations (2), (3) derived by MATSUDA in molten nitrate system was demonstrated.

2. In the case of fully reversible reactions [Eqs. (2) and (3) strictly obeyed] it is possible to calculate diffusion coefficients from oscillopolarographic data.

3. For not completely reversible reactions it seems not reasonable to calculate diffusion coefficients as well as activation energies of transport processes from polarographic data.

4. In every case (reversible or irreversible reactions) the peak currents are proportional to the concentrations up to a 10 volts/sec voltage change rate; thus oscillopolarography is a sensitive analytical tool also for these molten systems. The linearity between peak currents and concentrations has been verified in the range $1 \cdot 10^{-5} - 1 \cdot 10^{-2}$ moles/lt.