109. *Polarography in Fused Salts. The Dipping Platinum Microelectrode.*

By S. N. Flengas.

The behaviour of a dipping platinum microelectrode has been investigated in the case of silver nitrate dissolved in molten potassium nitrate–sodium nitrate. The solubility products of silver chloride and bromide, determined in this solvent by amperometric titration, agreed well with those determined by electrometric titration.

The application of the polarographic method of analysis to solutions of fused salts has been attempted only recently. Nachtrieb and Steinberg [1] studied the behaviour of the dropping mercury electrode in solutions of fused salts and obtained typical polarographic waves with several metallic cations dissolved in suitable low-melting solvents. However, the use of this electrode is obviously limited at higher temperatures by the volatility of mercury. An attempt, by the same authors, to use dropping electrodes of pure molten lead, bismuth, and silver was unsuccessful.

The use of a dipping platinum microelectrode in the analysis of fused salts was first described by Lyalikov and Karmazin.[2] Using molten potassium nitrate as a suitable solvent at 360°, they obtained well-defined polarograms for silver, cadmium, and lead cations and for the chromate anion. The decomposition potential of the solvent

[1] Steinberg and Nachtrieb, *J. Amer. Chem. Soc.*, 1948, **70**, 2613; 1950, **72**, 3558.
[2] Lyalikov and Karmazin, *Zavod. Lab.*, 1948, **14**, 144; *Zhur. Analit. Khim.*, 1953, **8**, 38.

electrolyte, under these conditions, was about −1·1 v against a platinum needle reference electrode. The use of silicate melts as solvents was also investigated but without success.

Since but few analytical methods are available for investigating fused salt systems, it was decided to make a further study of the behaviour of the dipping platinum electrode under controlled experimental conditions, and the method was applied to the determination of the solubility products of some sparingly soluble silver salts dissolved in a potassium nitrate–sodium nitrate eutectic melt.

Experimental

The current–voltage curves were recorded automatically on photographic paper by use of a Cambridge polarograph which was operated under a rate of potential change of 5·08 mv/sec. The microelectrode was similar to that of Lyalikov and Karmazin,[2] and is shown in Fig. 1. It consisted of a platinum needle, 1 mm. in diameter and 3 mm. long, sealed at the end of a soda-glass tube and surrounded by another glass tube open at the end. Dry, oxygen-free nitrogen was allowed to pass through this outer tube and escaped as bubbles, the electrode thus being periodically dipped and isolated from the surrounding solution. A constant rate of

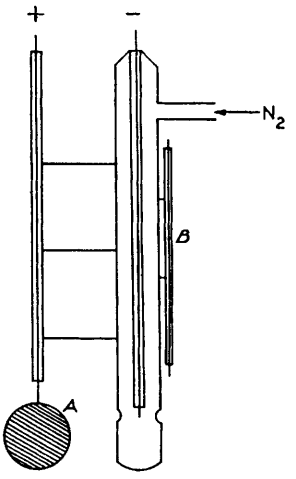

Fig. 1.

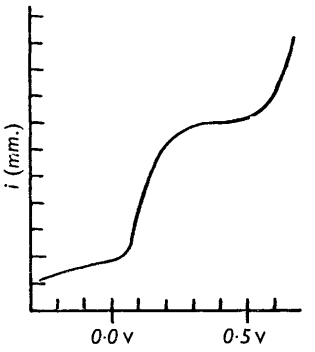

Fig. 2. *Polarographic wave of silver in the nitrate melt solvent at* 250° c.

nitrogen gas flow was achieved with the aid of a Mariotte flask, where, by adjusting the effective water level, it was possible to obtain bubbling rates of between 0 and 250 bubbles per min. (b. p. m.), the number being counted audibly.

A platinum disc (*A*) 2 cm. in diameter was used as a reference non-polarised electrode. The depth of immersion of the cathode, on which the hydrostatic back-pressure of the liquid in the outer tube depends, was maintained the same in all experiments, being adjusted with the aid of an auxilliary depth indicator electrode (*B*). The electrode system was rigidly clamped in position, and vertical movement was adjusted by means of a micrometer screw.

At the beginning of a run, the cathode terminal of the polarograph was connected to the indicator electrode, the anode terminal being always connected to the reference electrode. Then the electrode system was slowly lowered into the melt in the cell until a deflection of the spot of light in the galvanometer scale of the polarograph indicated that electrical contact had been established. The cathode terminal of the polarograph was then connected back to the dipping electrode, and the run started. The cell consisted of a 100-ml. Pyrex beaker in a tubular electric furnace, the temperature of which was controlled up to 350° with an accuracy of ±0·5° by means of a bimetallic strip and thermovalve regulator. Temperatures were determined with a 3″ partial immersion thermometer calibrated by suitable freezing-point measurements up to 327° (m. p. of lead).

At the end of a run the electrodes were cleaned by reversing the polarities and passing a current in the opposite direction for a few minutes.

To prepare the melts " AnalaR " salts were used. A stock of an equimolar mixture of

potassium nitrate and sodium nitrate was prepared by melting the two salts together and mixing them, and pouring the homogeneous melt into glass tubes where it was allowed to solidify quickly, thus avoiding the formation of density gradients by gradual cooling. These were then kept in a desiccator before use. Concentrated solutions of the metallic salts in this solvent were then prepared and used to prepare the more dilute ones.

Results.—The behaviour of the dipping platinum microelectrode with silver nitrate dissolved in the nitrate melt was first studied. The wave of the silver ion appears at about $-0{\cdot}05$ v against the platinum reference electrode (Fig. 2), and is as well defined as the polarographic waves obtained with the usual dropping electrode in aqueous solutions. The shape of the wave depends on the temperature of the melt: the nearer to the solidification point of the melt, the better the shape of the wave.

The residual current of the solvent melt is also dependent on temperature. On increase of temperature from 250° to 350°, the residual current increases and at the higher temperature the wave of silver ion is almost undetectable. Furthermore the decomposition potentials are also affected by temperature. In Table 1 the decomposition potentials of silver nitrate and of

TABLE 1. *Results for* $C_{AgNO_3} = 6{\cdot}7 \times 10^{-4}$ *mole*/1000 *g.*

	$-E_{dec.}$ (mv)			$-E_{dec.}$ (mv)			$-E_{dec.}$ (mv)			$-E_{dec.}$ (mv)	
t (°c)	$AgNO_3$	$KNO_3 + NaNO_3$	t (°c)	$AgNO_3$	$KNO_3 + NaNO_3$	t (°c)	$AgNO_3$	$KNO_3 + NaNO_3$	t (°c)	$AgNO_3$	$KNO_3 + NaNO_3$
242	50	670	260	45	620	294	40	520	322	30	440

the background solvent are shown for a temperature change of 100°. The decomposition potentials were measured on the photographic paper by drawing parallel tangents to the rising portions of the two waves.

From Table 1, it can be seen that the operable range of voltage in the polarograms decreases with increasing temperature, and at 350° only ions capable of reduction between 0·0 and 0·4 v can be detected. This is a serious drawback to the use of molten nitrates as solvent.

The small value for dE/dt for silver indicates that no appreciable activation polarisation is involved in the reduction at a bright platinum electrode: but the pronounced effect of temperature in the case of the background salt ($KNO_3 + NaNO_3$) indicates that a rather large activation polarisation is involved here.

The effect of temperature on the diffusion current of silver ion was also studied and is shown in Fig. 3(*a*), where results were obtained at a constant rate of bubbling and for constant salt concentration. The average value for di/dt is about 0·70% per degree. This low value again indicates a process controlled purely by diffusion.

For a constant rate of gas bubbling and at constant temperature the height of the polarographic wave was found to be strictly proportional to the salt concentration over a wide range of concentrations. This is illustrated in Fig. 3(*b*). On the other hand, for constant silver-ion concentration and constant temperature the diffusion current was found to depend on the bubbling rate (n). This is shown in Fig. 4, where the relation is tested for different temperatures and found to be linear. From the results in Fig. 4 the product $(i_d\sqrt{\tau})$, where i_d is the diffusion current in mm. and τ is the bubbling time expressed in sec. per bubble ($\tau = 60/n$), is found to be practically constant (Table 2). This relationship, which indicates that the diffusion current is

TABLE 2. $C_{AgNO_3} = 6{\cdot}85 \times 10^{-4}$ *mole*/1000 *g.*

$t = 242°$			$t° = 262°$			$t = 316°$		
i_d (mm.)	n (b.p.m.)	$i_d\sqrt{\tau}$	i_d (mm.)	n (b.p.m.)	$i_d\sqrt{\tau}$	i_d (mm.)	n (b.p.m.)	$i_d\sqrt{\tau}$
54	100	43·2	62	100	49·6	77	100	61·6
68	150	42·8	77	150	48·6	95	150	60·0
77	200	42·3	92	200	50·6	112	200	61·6

inversely proportional to the square root of the time of contact of the electrode with the surrounding solution, was predicted and found experimentally by Laitinen and Kolthoff [3] to apply also in the case of linear diffusion towards a plane platinum microelectrode. Thus the diffusion problem in the case of a periodically dipping cylindrical microelectrode approximates to one of

[3] Kolthoff and Lingane, "Polarography," I, Interscience, New York, 1952.

linear diffusion towards a plane microelectrode of the same total area which periodically increases and decreases. Probably during the short time of contact between the electrode and the surrounding solution, the diffusion layer cannot expand to a considerable distance into the solution and therefore the effect of curvature of the electrode surface is negligible.

Unfortunately, the hydrodynamics of the state of flow in the neighbourhood of a dipping microelectrode are not well defined owing to uncertainties concerning the layer of solution

FIG. 3.

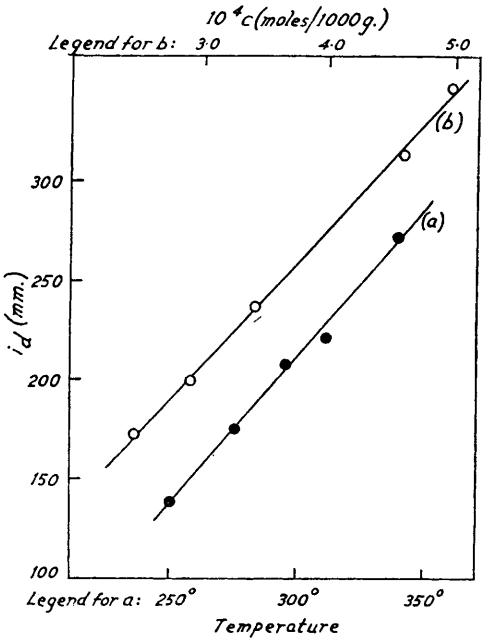

FIG. 5.

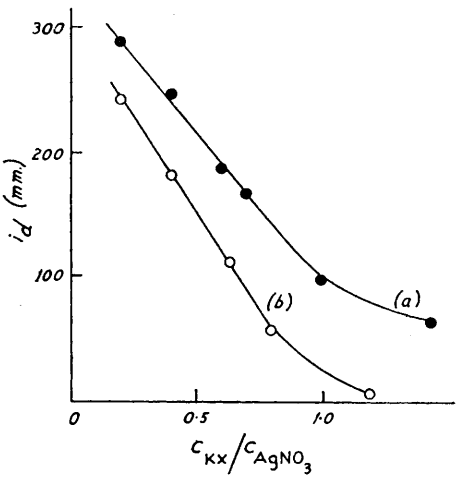

FIG. 3. Polarograph sensitivity = 1/100; n = 100 b.p.m.

(*a*) Temperature effect: $C_{AgNO_3} = 2{\cdot}44 \times 10^{-3}$ mole/1000 g.

(*b*) Calibration straight line: $t = 266°$.

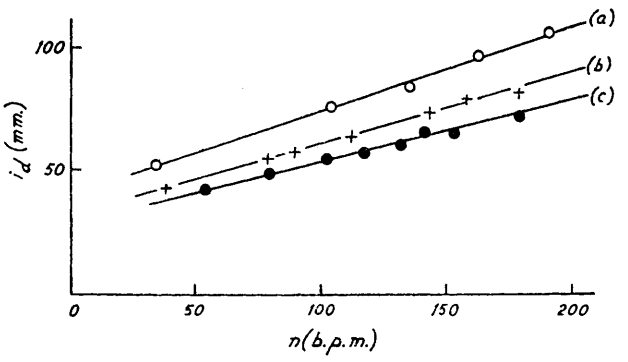

FIG. 4.

Polarograph sensitivity = 1/100; $C_{AgNO_3} = 6{\cdot}85 \times 10^{-4}$ mole/1000 g.

(*a*) $t = 316°$; (*b*) $t = 262°$; (*c*) $t = 242°$.

which is permanently adsorbed by adhesion and surface tension on the electrode surface, even when removed from the melt, etc., and the theoretical equation which can readily be derived on the above assumptions was found to agree only qualitatively with the experimental results. However, the shape of the current–time curve during a complete cycle (time τ), predicted by this equation, was in qualitative agreement with the one obtained experimentally on the screen of a low-frequency oscillograph.

The solubility products of some sparingly soluble salts of silver, *i.e.*, the chloride and bromide, in this melt were next measured by amperometric titration. A solution of silver nitrate in the melt was prepared, and the decrease of the silver wave was followed on the addition of increasing amounts of potassium chloride and bromide, severally. The results of these titrations are shown in Fig. 5, from which the solubility products can be calculated as follows.

We have $K_{s(AgX)} = [Ag^+][X^-]$, where $[Ag^+]$ is measured experimentally from the height of the polarographic wave and is the concentration of unbound halide ions. This is calculated from the total silver nitrate concentration and the total amount of added reagent by use of :

$$[X^-] = C_{KX} - (C_{AgNO_3} - [Ag^+])$$

The following average values are thus obtained for the solubility products at 250° : chloride, $(3{\cdot}95 \pm 0{\cdot}35) \times 10^{-6}$; bromide, $(7{\cdot}15 \pm 0{\cdot}75) \times 10^{-8}$. These are in good agreement with those obtained by electrometric titration,[4] *viz.*, $4{\cdot}89 \times 10^{-6}$ and $7{\cdot}61 \times 10^{-8}$, respectively.

Attempts to obtain polarographic waves for $Pb(NO_3)_2$, $CuSO_4$, $TlNO_3$, $ZnSO_4$, $Hg(NO_3)_2$, $Cd(NO_3)_2$, and $NiSO_4$, dissolved in this molten solvent at 250°, were unsuccessful.

Conclusions.—(1) The platinum dipping microelectrode can be used successfully to determine silver ions dissolved in a sodium nitrate–potassium nitrate melt. (2) The diffusion current is proportional to the silver salt concentration, and a linear function both of the rate of gas bubbling and of temperature. (3) Conditions for the reproducibility of the results are : constant rate of gas bubbling, same geometrical conditions of the electrode system, and constant temperature of the melt, which are in agreement with the results of Lyalikov and Karmazin.[2] (4) The use of the potassium–sodium nitrate melt as solvent is limited by the narrow operable range of potential.

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[4] Flengas and Rideal, *Proc. Roy. Soc.*, 1956, **233**, *A*, 443.