Chronopotentiometry in Fused Potassium Thiocyanate

By

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Introduction

There are a few investigations concerning with fused alkali thiocyanates. Paterno and Mazzuchelli¹⁾ found that the molten mass of potassium thiocyanates turned blue color, when it was heated to about 430°C. Feigl and Caldas²⁾ reported that in molten alkali thiocyanate at about 400°C there were conversions of metal oxides and sulfates into the corresponding sulfides. By freezing point measurements Kordes³⁾ and his co-workers showed the existence of the thiocyanate complex ions of various transition metals in molten potassium thiocyanate. Greenberg⁴⁾ et al. observed the spectra of various transition metal complex ions in the same kind of medium. Husband⁵⁾ measured the densities of several kinds of molten salts, including potassium thiocyanate.

Little is known concerning the electrochemical behaviours of the species present when metal compounds are dissolved in this molten medium, although Panzer and Schaer⁶⁾ conducted detailed polarographic and chronopotentiometric investigations of molten alkali thiocyanate melt itself using Ag/AgCl electrode as a reference.

The purpose of the present study is an evaluation of the use of molten potassium thiocyanate as a solvent in which voltammetric studies are conducted. Chronopotentiometric method was undertaken to lay the groundwork for future studies of diffusion process and behaviours of metal thiocyanate complexes dissolved in this melt.

Experimental Procedure

All chemicals used in this work were Analytical Reagent grade, without further purification. Anhydrous lead, cadmium and zinc chlorides were prepared by vacuum desiccation at suitable temperature and stored in desiccator with phosphorous pentoxide as a desiccative. Potassium thiocyanate (m.p. 173~175°C) was dried overnight in a vacuum oven at 100~110°C and stored in the desiccator under vacuum. No further purification was made, since the potential-time curves for the depolarizers were not interfered by the solvent, as is shown in Fig. 2, curve a.

A dropping mercury electrode of long drop time⁷⁾ (about 6 min.) was employed for an indicator electrode. The reference in the molten potassium thiocyanate runs was a platinum coil (1 mm. in diameter and 150 mm. in length), in direct contact with the melt. The working electrode was also made of platinum foil spot-welded to a platinum wire and had an area of about 3 cm². A conventional three-electrodes chronopotentiometric circuit shown in Fig. 1 was used. The constant current regulator was capable of supplying the

e_1 : indicator electrode
 e_2 : reference electrode
 e_3 : working electrode
P : constant high voltage source
V : synchroscope
A : D.C. micro-ammeter

Fig. 1. Electrolytic circuit.

cathodic current in the range of $3\sim 80\ \mu\text{A}$. The transition time measurement was performed with Iwasaki Synchroscope, Type SS-5302. The potential-time curve was recorded by opening the camera shutter, and closing it after the transition-time had been observed.

Toshiba silicone oil, TSF 433, was put in an oil bath and it was heated with a pipe heater (500 watt.) of which A.C. voltage was regulated by a temperature controller (the Chino temperature controller, Model E-660), and moderately agitated by compressed air in

order to attain the thermal equilibrium. This arrangement allowed the temperature to be controlled within $\pm 1^\circ\text{C}$.

Weighed salt mixture of potassium thiocyanate and metal chloride in an electrolytic cell made of borosilicate glass tube (5 cm. in diameter, 26 cm. in length) was drien for an hour under vacuum, melted in dry nitrogen atmosphere, and allowed for about half an hour bubbling dry nitrogen through it to attain thermal equilibrium prior to each run. The dropping mercury electrode was inserted into the melt of the salt mixture, of which temperature was controlled at desired value. The gas bubbling was stopped, and waited for a few minutes before chronopotentiometric runs were conducted. The electrolysis at dropping mercury electrode started at just 2 minutes after the beginning of the growth of new drop. The average area of a mercury drop at 2 minutes in fused salt solution was calculated to be $1.47\ \text{mm}^2$ by weighing the weight of 10 drops collected under the appropriate mercury height (102 cm.) at 191°C . The transition time of potential-time curve should be chosen within 2 seconds for the sake for reducing the change of surface area of a mercury drop less than 1% during electrosolysis.

Results and Discussion

When dropping mercury electrode was used as an indicator electrode, well-defined and reproducible chronopotentiograms were obtained. Fig. 2 shows examples of chronopotentiogram for reductions of the cadmium and ions in fused potassium thiocyanate at 191°C .

Fig. 2. Chronopotentiograms for the reduction of the pure malt (a), zinc(II) ($6.28\ \text{mM/kg KSCN}$, at $2.6\ \text{mA/cm}^2$) (b), and cadmium(II) ion ($6.05\ \text{gmM/k KSCN}$, at $2.7\ \text{mA/cm}^2$).

In order to determine the diffusion coefficient of the metal ions in this molten solvents, applicabilities of Sand's equation were examined. The products of the current density at the polarized electrode with the square root of transition time, $i_0\tau^{1/2}$, were determined at various current densities for reduction of each ion at the dropping mercury electrode. Curves a, b and c in Fig. 3 shows variations of the $i_0\tau^{1/2}$ values with reduction current densities in several concentrations of the cadmium ion. According to Delahay et al.,⁸⁾ the values of $i_0\tau^{1/2}$ are independent on the current density, when the mass transfer process at the electrode in unstirred solution is considered as the linear diffusion, while it is not independent in the case of spherical diffusion. The values of $i_0\tau^{1/2}$ are constant when the electrolysis time is so short, and it increases with increasing time of electrolysis for the metal ion, as is shown in Fig. 3. This increase at low current density is probably due to the effect of spherical diffusion and of natural convection.

Fig. 3. Relationship between $i_0\tau^{1/2}$ and i_0 and calibration curve (d) for Cd(II) ion at 191°C.
(a) 10.37 m mole/kg KSDN, (b) 6.45 m mole/kg KSCN, (c) 3.33 m mole/kg KSCN

Measurements were also carried out at various concentrations of depolarizers in this solvent. The result obtained from reduction of the cadmium ion are shown in Fig. 3, curve d. This clearly indicates that there is satisfactory linear relation between the value of $i_0\tau^{1/2}$ and bulk concentration of depolarizer in the present concentration range at around 10 mmole/kg. KSCN under the adequate current density.

Similar linear relation to that of the cadmium ion was observed in both reductions of the lead and zinc ions. It is consequently assumed that Sand's equation⁹⁾ can be safely applied to the present systems without introducing any significant correction. The slope of the above calibration curve as is shown in Fig. 3, curve d is given by a theoretical equation derived for a linear diffusion process in the following form,

$$i_0\tau^{1/2}/N = knd_T(D_T)^{1/2}, \quad (1)$$

where D_T is the diffusion coefficient at temperature $T^\circ\text{C}$, τ the transition time in seconds, i_0 the current density in mA/cm^2 , $k = \pi^{1/2}F/2 = 8.552 \times 10^4$, n the number of electrons involved in the electrode process, $d_T^{(*)}$ the density of the solvent at temperature T , in g/ml , and N the concentration in mmole/g . Using Eq. (1), one can calculate diffusion coefficient of metal ion at temperature T from the knowledge of the slope, $i_0\tau^{1/2}/N$, and n -value.

* $d_T = 1.6005 - 0.0008 (T - 173.5)$ $T : T^\circ\text{C}$

Fig. 4. Plots of $\log\{(\tau^{1/2} - t^{1/2})/t^{1/2}\}$ (a) and $\log(\tau^{1/2} - t^{1/2})$ (b) versus E for the reduction process of Pb(II) ion.

In order to obtain n -values involved in the electro-reduction of metal ions, the logarithmic plots¹⁰⁾ of time against electrode potentions, E , were taken. An example of the logarithmic plot is shown in Fig. 4 for the reduction process of the lead ion. A plot of $\log(\tau^{1/2} - t^{1/2})$ versus E yields no straight line, but the $\log\{(\tau^{1/2} - t^{1/2})/t^{1/2}\}$ versus E yields a straight line whose reciprocal slope is $2.3 \cdot RT/nF$. The reciprocal slopes of the logarithmic plot for lead and the similar plots for the cadmium and zinc ions calculated from the data are: Pb(II) , 0.043; Cd(II) , 0.067 and Zn(II) , 0.045, while the theoretical value is 0.046 in the case of $n=2$ at 191°C . The reciprocal slope for cadmium ion is somewhat too high, being 0.067 instead of 0.046, probably because of a slightly irreversible character of the process.

The results obtained from the logarithmic plot indicate that these three kinds of the metal ions are reduced at the dropping mercury electrode to metallic states followed by the amalgam formation. The diffusion coefficients ($\text{cm}^2/\text{sec} \times 10^6$) of those ions given by Eq. (1) in fused potassium thiocyanate at 191°C were evaluated as follows; Pb , 2.07; Cd , 1.94; Zn , 1.89, which are in good agreement with those in fused alkali nitrates¹¹⁾, in spite of the essential difference in characters of the fused solvents.

According to Sommer¹²⁾, potassium thiocyanate in molten state partly dissociates at elevated temperature (at about 400°C) in the following manner,

and yields highly reactive sulfur. In fact, precipitation occurred in the molten solution due to the formation of corresponding sulfide, when the molten potassium thiocyanate solutions containing each bivalent metal ion was heated up to 300°C , but at 250°C no precipitation was observed. It may be confirmed by the above experimental results that the dissociation reaction of molten potassium thiocyanate in Eq. (2) is negligibly small at lower temperatures than 200°C .

From measurements³⁾ of the freezing point and observations⁴⁾ of spectra in molten alkali thiocyanates, it is pointed out that various transition metal ions form complexes with thiocyanate. It seems to be interesting to do further reserches on a metal complex in molten salt media, and the quantitative discussions about the metal-thiocyanate complexes will be made in the following paper.

Summary

Lead, cadmium and zinc chlorides dissolved in fused potassium thiocyanate at about 300°C were converted into the corresponding sulfides, but at 250°C these metal sulfides did not appear in fused solutions.

Using dropping mercury electrode with a long drop time (about 6 min.), chronopotentiometric behaviours of lead, cadmium and zinc ions in fused potassium thiocyanate at 191°C were examined. Well-defined and reproducible chronopotentiograms were obtained for these three kinds of metal ions, and the products of current density with the square root of transition time, $i_0\tau^{1/2}$, were proportional to the bulk concentration for the depolarizers. Plots of $\log \{(\tau^{1/2} - t^{1/2})/t^{1/2}\}$ versus electrode potentials, E , for potential-time curve of each ion yielded straight lines whose reciprocal slopes are in good agreement with the theoretical value except the cadmium ion because of slight degree of irreversibility. From the experimental data the diffusion coefficients ($(\text{cm}^2/\text{sec}) \times 10^6$) for these metal ions in this fused solvent at 191°C were calculated to be as follows, respectively; Pb, 2.07; Cd, 1.94; and Zn, 1.89.

It can be concluded that the dissociation reaction of potassium thiocyanate in molten state is negligibly small at lower temperatures than 200°C.

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融解ロダンカリウム中でのクロノポテンシオメトリー

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Pb(II), Cd(II), Zn(II) 等の塩化物を融解ロダンカリウム(m.p. 173~175°C)中に溶解し, これを約300°Cにまで加熱するとこれらの金属イオンはそれぞれ対応する硫化物を形成し, 浴中に析出する. しかし250°C以下ではこれらの硫化物の析出は見られず, 均一な融液が得られる.

滴下時間の長い(約6分)滴水銀極を指示電極として, 乾燥窒素ガス雰囲気下, 191°Cにおいて, 融解ロダンカリウム中における Pb(II), Cd(II), Zn(II) イオンのクロノポテンシオメトリーの挙動を検討した. その結果, 図2に示すように, 上記二価金属イオンにつきいずれにも再現性のある良好なクロノポテンシオグラムが得られ, これらのグラムについて Sand 式の適用性を調べた. 図3, 曲線 a, b, c は Cd(II) イオンを復極剤としてその各濃度における $i_0\tau^{1/2}$ 値の電流密度に対する依存性を調べたものである. この図より明らかなように電流密度の増大と共に $i_0\tau^{1/2}$ 値はよい一定性を示していることが解る. 一方低電流密度側での $i_0\tau^{1/2}$ 値は, 電解時間(遷移時間)の延長による電極面積の増加を考慮してもなお, 増加しており, これは球面拡散および電解時間の延長にともなう対流等の影響に基因するものと考えられる. さらに図3, 曲線 d は Cd(II) イオンの濃度と $i_0\tau^{1/2}$ 値との関係を示したものであり, この曲線より調査した濃度範囲(~10 mmole/kg KSCN)内では両者の間に良好な比例関係の成立することが判った. Pb(II), Zn(II) イオンについてもそれらの $i_0\tau^{1/2}$ 値と電流密度およびそれらの濃度との関係は Cd(II) イオンについての場合と同様な結果が得られた. これらのことにより上記各金属イオンの還元過程は Sand 式に従うものと考えられる. これらの検量線の勾配 ($i_0\tau^{1/2}/N$) は Sand 式より $knd_T(D_T)^{1/2}$ となり, これより各イオンのこの溶媒中における拡散定数(D_T)を求めることができる. ここで N は

復極剤の濃度 (mmole/gr), $k=\pi^{1/2}F/2=8.552\times 10^4$, d_T は $T^\circ\text{C}$ における溶媒の密度, n は還元電子数である.

n の値を求めるために Reinmuth の方法に従って各イオンについて, それらの電位-時間曲線の解析を行なった. 図4は Pb(II) イオンについて示したものである. この図より, 電極電位(E)に対して $\log(\tau^{1/2}-t^{1/2})$ 値のプロットは曲線となり, これに対して $\log\{(\tau^{1/2}-t^{1/2})/t^{1/2}\}$ 値のプロットは直線を示していることがわかる. この直線の逆勾配は $2.3RT/nF$ で与えられ, 191°C, $n=2$ の場合における計算値は 0.046 となる. Cd(II), Zn(II) イオンについても Pb(II) イオンの場合と同様に, (E) に対して $\log\{(\tau^{1/2}-t^{1/2})/t^{1/2}\}$ 値のプロットの場合にのみ直線性が成立し, それらの直線の逆勾配は Pb(II), Cd(II), Zn(II) につきそれぞれ 0.043, 0.067, 0.045 であった. Pb(II), Zn(II) についての実験値は計算値とよく一致しているが Cd(II) のそれは計算値より大きな値を示しており, これはおそらく電極反応の非可逆性によるものと推察される.

以上の結果より, 上記二価金属イオンは融解ロダンカリウム中で金属状態にまで還元され, アマルガムを形成しているものと考えられる.

各イオンの 191°C でのこの溶媒中における拡散定数 ($\text{cm}^2/\text{sec} \times 10^6$) を求めると Pb(II), Cd(II), Zn(II) につきそれぞれ, 2.07, 1.94, 1.89 であった. これらの値は融解アルカリ硝酸塩中でのものとよく一致している.

一方, ロダンカリウムは融解状態において, 次式に示されるような解離平衡の状態にあり, 化学反応性の大きい遊離硫黄を放出すると考えられている.

しかし, 上記実験結果より, 200°C 以下では(1)式の解離平衡はほとんど無視できるものと推察される.