Studies on the Influence of Some Supporting Electrolytes
on the Diffusion Current and Half-wave Potential of the Reducible Ions
in the Polarographic Studies. I

Reduction of Cd^{++} Ions in CdCl$_2$ and Cd(NO$_3$)$_2$ Solution with Different Concentrations of Supporting Electrolytes — KCl, KNO$_3$, K$_2$SO$_4$ and NaCl

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Summary

The variations in the diffusion current (id) and half-wave potential (E$_{\frac{1}{2}}$) have been polarographically studied on the reducible Cd^{++} ions at different concentrations of the supporting electrolytes KCl, KNO$_3$, NaCl, and K$_2$SO$_4$. Apart from the prevailing view in favour of ionic strength, complex formation and viscosity etc. to explain the variations in id, the role of interfacial tension and liquid junction potential has been critically discussed as additional factors. Since experimental results show that the ILKOVIC's equation is dependent upon several other factors due to the nature of the environment, it has been suggested that each system should be considered as a specific one to probe into the parameters affecting the values of id and E$_{\frac{1}{2}}$, and arrive at a more convincing conclusion.

Introduction

Studies on polarography based on the ILKOVIC's equation, id $= 607$ n D$^{\frac{1}{2}}$ C m$^{\frac{2}{3}}$ t$^{\frac{1}{6}}$ has infused a lot of interest in the analytical field and in the study of the reaction mechanisms which are based on electro reduction and oxidation. While the technique of polarography is comparatively the recent one for the study of many problems which had or had not been studied by other methods, much remains yet to be done to explain the various factors on which the ILKOVIC's equation depends. In the recent communications of the last decade efforts have been directed to solve the multiparametric factors governing the current voltage relationship, but the trend of the results obtained by various workers in this field leads to suggest that more intensive and extensive experiments on the specific systems are necessary before we can explain the little variations in id or E$_{\frac{1}{2}}$ derived from the polarograms.

LINGANE and KOLTHOFF who were the pioneers in developing the technique of polarography[1]), had studied the variations in the limiting currents for a number of reducible ions, in the absence and in the presence of foreign electrolytes and modified the equation developed by HEYROVSKY by taking into account the change in the effective diffusion coefficient of the reducible ion caused by the addition of indifferent electrolytes. LINGANE[2]) discussed the thermodynamic significance of the equation of the C—V curves, and attributed the increase in $E_\frac{1}{2}$ of Tl^+, Zn^{++}, Pb^{++} and Cd^{++} at different concentrations (0.02 N-1 N) of KCl and KNO_3 to the decrease in the value of activity coefficient of the reducible metal ion. DONALD FORD and ANDERSON[3]) elaborated the role of ionic strength and character of ionic environment as being responsible for the variations in $E_\frac{1}{2}$ within wide limits under the concentration of supporting electrolytes (different nitrates) going up to 12 M. They emphasized further that the effect of ionic strength and nature of the ionic environment should be considered in the investigations of complex formation by the polarographic technique.

A. A. VLECK[4]) also observed that $E_\frac{1}{2}$ of Tl^+ and Pb^{++} ions was linear with $\sqrt{\mu}$ where μ was the ionic strength at different concentrations of the supporting electrolytes. He had further shown that in the case of Ni^{++} and Co^{++} ions the height of the wave increases with increasing concentrations of supporting electrolytes having different anions, the effect if Cl^- and SO_4^{--} ions being more than I^- ions, which suggests that some more factors play their part than merely the ionic strength and activity coefficient. KARL MICKA[5]) observed that in the case of Tl^+ and Zn^{++} ions $E_\frac{1}{2}$ values were dependent on the mercury flow rate and also that variations of $E_\frac{1}{2}$ were linear with $\sqrt{\mu}$.

In recent communications MUKHERJEE and Mrs. CHAKRAVARTI[6]) communicated their results on the variations of nature and concentration of a few supporting electrolytes on the $E_\frac{1}{2}$ and id of Cd^{++}, Zn^{++}, Ni^{++} and Co^{++} ions. They have attempted to explain the variations in id and $E_\frac{1}{2}$ by considering the role of (i) viscosity, (ii) probable complex formation, (iii) ionic strength, (iv) inter-ionic attraction and (v) hydrogen over-voltage.

In view of the conflicting position of the multiparametric influence on the role of concentration of a supporting electrolyte, it was deemed necessary to perform some simple experiments on the reducible Cd^{++} ions in the

[1]) LINGANE and KOLTHOFF, J. Amer. chem. Soc. **61**, 1045 (1939).

[2]) LINGANE, J. Amer. chem. Soc. **61**, 2909 (1938).

[3]) D. FORD and ANDERSON, J. Amer. chem. Soc. **72**, 3918 (1950).

[4]) A. A. VLECK, Chem. Listy **48**, 1474 (1954).

[5]) K. MICKA, Chem. Listy **50**, 203 (1956).

[6]) MUKHERJEE and CHAKRAVARTI, J. I. C. S., **38**, 12, 995 (1961); **39**, 3, 151 (1962).

presence of different concentrations of a few supporting electrolytes (KCl, KNO$_3$, K$_2$SO$_4$ and NaCl), and critically examine our observations in the light of some other factors such as interfacial tension and liquid junction potential which may affect the validity of the ILKOVIC's equation.

Experimental

Current voltage measurements were made with LANGE's polarometer in conjuction with a multiflex galvanometer. The conventional "H" type of cell was employed with the solution to be examined in one limb and saturated calomel electrode in the other. The two limbs of the "H" cell were separated by glass wool and an agar plug saturated with KCl[7]). Chemicals of B. D. H. and E. MERCK were used and the drop time was maintained at 3 seconds per drop. The solution was deoxygenated by bubbling nitrogen gas after passing it through alkaline pyrogallol for about 15 minutes. Gelatin of concentration 0.02% was used as maximum suppressor. All current measurements were of apparent maximum current, taken just as the drop fell.

Table 1
Cd^{++} as the reducing ion in CdCl$_2$ solution

Supporting Electrolyte Conc.	KCl		KNO$_3$		NaCl		K$_2$SO$_4$	
	id (μa)	E$_{\frac{1}{2}}$(volt)	id (μa)	E$_{\frac{1}{2}}$(volt)	id (μa)	E$_{\frac{1}{2}}$(volt)	id (μa)	E$_{\frac{1}{2}}$(volt)
M/2	9.170	0.630	7.700	0.595	9.36	0.62	—	—
M/4	—	—	—	—	—	—	8.98	0.615
M/10	8.800	0.620	7.700	0.595	8.990	0.610	8.97	0.610
M/25	8.550	0.605	7.710	0.600	8.990	0.595	8.55	0.615
M/100	7.900	0.604	7.710	0.595	8.810	0.595	8.55	0.620

id NaCl > id KCl > id K$_2$SO$_4$ > id KNO$_3$

Table 2
Cd^{++} as the reducing ion in Cd(NO$_3$)$_2$ solution

Supporting Electrolyte Conc.	KCl		KNO$_3$		NaCl		K$_2$SO$_4$	
	id (μa)	E$_{\frac{1}{2}}$(volt)	id (μa)	E$_{\frac{1}{2}}$(volt)	id (μa)	E$_{\frac{1}{2}}$(volt)	id (μa)	E$_{\frac{1}{2}}$(volt)
M/2	8.805	0.635	8.550	0.595	8.550	0.635	—	—
M/4	—	—	—	—	—	—	7.710	0.625
M/10	8.550	0.615	8.550	0,595	8.36	0.630	7.97	0.610
M/25	8.080	0.615	8.555	0.595	8.170	0.610	7.97	0.605
M/100	7.900	0.610	—	—	8.160	0.610	8.05	0.605

id KCl > id NaCl > id KNO$_3$ > id K$_2$SO$_4$

[7]) L. MEITES, „Polarographic Techniques", p. 21, Inter Science Publishers, New York 1955.

Table 3

Supporting Electrolyte	C_2/C_1	$E = \dfrac{2\,u}{u+v}\,\dfrac{RT}{N}\log\dfrac{C_2}{C_1}$ for faster cation	$E = \dfrac{2\,v}{u+v}\,\dfrac{RT}{N}\log\dfrac{C_2}{C_1}$ for faster anion	Ratio of EMF $KCl:KNO_3$; $K_2SO_4:NaCl$
KCl	50	—	0.1008	0.1008:
KNO_3	50	0.1032	—	0.132:
K_2SO_4	25	—	0.0850	0.0850:
NaCl	50	—	0.1202	0.1202

Discussion

It will be seen in table No. 1 that concentration effect of the supporting electrolytes (KCl, NaCl and K_2SO_4) in the range, M/2 to M/100, is to decrease the id value for the reduction of Cd^{++} ions of $CdCl_2$. The percentage decrease of id within this range of concentration of supporting electrolytes is as follows: 14% with KCl, 6% with NaCl and 5% with K_2SO_4. It will be also seen in table No. 2 which contains the results of $Cd(NO_3)_2$ that the percentage decrease in the value of id is 12% with KCl and 4% with NaCl, but with K_2SO_4 as supporting electrolytes the effect was reversed showing about 4% increase in id from dilution (M/4 to M/100). The corresponding values of $E_{\frac{1}{2}}$ also decrease with dilution of the supporting electrolytes, KCl and NaCl, but remain almost constant with K_2SO_4, and it is particularly interesting to note that when KNO_3 is used as supporting electrolyte the value of both id and $E_{\frac{1}{2}}$ remain constant in both cases. It has also been observed by previous workers that KNO_3 when used as supporting elctrolyte gives the best agreement with the ILKOVIC's equation. All these variations in id and $E_{\frac{1}{2}}$ observed by the different supporting electrolytes having monovalent cations need a critical examination of the factors involved.

The order of variations in id and $E_{\frac{1}{2}}$ for the reducible Cd^{++} ions (with Cl^- and NO_3^- as the anions and KCl and KNO_3 as the supporting electrolytes) is in agreement with those observed by MUKHERJEE and Mrs. CHAKARVATI (loc. cit.). They observed also that the concentration effect of these supporting electrolytes reversed the order of variations in the case of other reducible ions as Ni^{++}, Co^{++} and Zn^{++}. From this, it follows that, in practice, the values of id and $E_{\frac{1}{2}}$ are not only the functions of the nature of the reducible ion and the supporting electrolytes used, but also they are influenced by other factors which may alter the potential of the dropping mercury electrode. The possibility of the complex formation and ionic strength in the bulk of the systems, which have often been stressed by the previous workers, may be the additional factors. Such observations lead us to conclude that the effect of concentration of the supporting electrolytes is of

very specific nature and hence each system should be investigated as a specific case with punctilious attention to the changes brought about by the ionic environment of different supporting electrolytes in the parametric factors of the Ilkovic's equation.

Considering the basic parameters of the Ilkovic's equation, it is necessary that $id/\sqrt{P}$ or $id/h_{eff.}^{\frac{1}{2}}$ should remain constant at different concentrations of the supporting electrolytes for ascertaining whether the wave is a diffusion controlled one. In our experiments it was invariably necessary to make slight changes in the height of the mercury level in order to obtain the drop time of 3 seconds for all concentrations. It is also known that $P_{eff.}$ $\alpha_{1/si}$ $\alpha_{1/t}$ where Si = interfacial tension. Thus the drop time 't' is proportional to Si, which means that 't' is affected by the interfacial tensions of the supporting electrolytes and the suppressors. Inspite of this, the results are supposed not to be very much affected because $m^{\frac{2}{3}} t^{\frac{1}{6}}$ in most cases remains practically constant. Yet, the dependence of 't' on the interfacial tension cannot be set at nought, because mercury is able to show the positive adsorption with certain organic and inorganic substances.

W. C. Mc. Lewis[8]) and Patrick[9]) determined the adsorption of mercurous nitrate, salicylic acid, picic acid and neofuchsin at the interface of water and mercury and observed that the interfacial tension (σ ff) was lowered with increasing concentration of the dissolved substance according to the Gibb's adsorption equation. The quantity adsorbed was the function of the concentration which was shown by the adsorption curves[10]). In view of such observations it can be visualised that the interfacial tension at the water mercury interface may change with the nature and concentration of the supporting electrolyte due to positive or negative adsorption. The potential of the dropping mercury electrode is, therefore, influenced by the concentration and nature of the ions in the supporting electrolytes upto the point of the limiting adsorption.

Another factor of no less interest is the liquid junction potential of the cell, which also may not be negligible for obtaining the small changes in the values of id or $E_{\frac{1}{2}}$. The order of the EMF values has been shown allowing for the concentration differences (0.01—0.5 M) in table 3. These values are based on the assumption that appropriate concentration cells have been set up for determining the E M F from the thermodynamic equation for the concentration cells. The E M Fs of the concentration cells thus assumed are in the ratio $E_{KCl} : E_{KNO_3} : E_{K_2SO_4} : E_{NaCl}$ as 0.1008 : 0.1032 : 0.085 : 0.12.

8) W. C. McC. Lewis, Philos. Nag. (6), 15, 494 (1908); 17, 466 (1909).

9) Patrick, Z. physik. Chem. 86, 545 (1914).

10) Colloid and Capillary Chemistry by Freundlich, 1922.

Thus we see that the E M F of the K_2SO_4 concentration cell has the least E M F, when corrected for the liquid potential, while NaCl concentration cell has the maximum E M F. There is a fair agreement in the order of the variation in id in table 1, but not so in table 2 for $(Cd(NO_3)_2)$. If the liquid-liquid potential was the only factor for the deviation of id or $E_{\frac{1}{2}}$, the order of the changes in id or $E_{\frac{1}{2}}$ in the presence of different supporting electrolytes should have given full agreement with the E M Fs, which, however, is not uniformly satisfied. This kind of observations evidently suggest that the influence of the concentration of the supporting electrolytes is a complicated phenomenon which may vary from system to system, and consequently depend upon the factors which may be only determined, when a specific system is elaborately studied. Each system should, therefore, be regarded as a specific one and all parameters arising out of the change in the nature and concentration of supporting electrolytes should be thoroughly investigated before resorting to the formation of complexes or dependence on the ionic strength, which, of course, have been apparently a more common view to explain the variations in id or $E_{\frac{1}{2}}$.

More work is in progress.

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