

A polarographic study of zinc-thiocyanate complexes in mixed solvents

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Abstract. Complexes of zinc with thiocyanate were studied polarographically in aqueous mixtures of methanol, ethanol, dioxan and dimethyl formamide (DMF). The reduction, in most cases, was not reversible and the degree of irreversibility increased with the percentage composition of the mixed solvent as well as with the nature of the solvent in the order: alcohols < dioxan \approx DMF. The 'formal' potentials for reduction, determined by amalgam polarography at different thiocyanate concentrations in each solvent mixture, were used to calculate the standard rate constant, k_s , and the transfer coefficient, α , for the reduction from the current-potential data. The stability constants of the complexes, also evaluated from the 'formal' potentials, varied linearly with the dielectric constant of the medium.

Keywords. Polarography; zinc-thiocyanate; mixed solvents.

1. Introduction

The scope of voltammetry has been extended, in recent years, by increasing use of non-aqueous solvents. The physical properties of the solvent such as viscosity, dielectric constant, etc., have a pronounced effect on diffusion-as well as electron transfer processes. The double layer structure is altered by the solvent thus affecting the electrode reaction. Moreover, in many cases the tendency of metal ions to form complexes with ligands shows significant variations in different solvents.

The low solubilities of inorganic electrolytes in nonaqueous solvents pose special problems but these are circumvented by the use of aqueous mixtures of these solvents. Also, the use of mixed solvents enables one to study the progressive replacement of water by the solvent.

Thiocyanate complexes of metals are of importance in analytical chemistry (Sultanova *et al* 1973). They are of moderate stability and hence form excellent systems for the study of complexation characteristics in mixed solvents. A polarographic study of zinc-thiocyanate complexes in aqueous mixtures of methanol, ethanol, dioxan and dimethylformamide (DMF) is reported in this paper.

2. Experimental

A stock solution of zinc sulphate (BDH AR) was standardised with EDTA. Lithium nitrate (Allied and Co., Bombay, LR) was purified by pre-electrolysis and was estimated by an

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ion-exchange procedure. Methyl alcohol (BDH AR) was used as such. Ethyl alcohol and DMF (Koch-Light, England) were freshly distilled before use. Dioxan (E Merck, pro Analyti) was dried, refluxed over sodium hydroxide and then fractionally distilled before use. Potassium thiocyanate (Sarabhai Chemicals, GR) was used without purification and the stock solution was estimated by titration with silver nitrate.

Current potential curves were obtained at $30 \pm 0.1^\circ\text{C}$ on a manual set-up with a saturated calomel electrode (SCE) as the reference electrode. The reported currents have been corrected for the residual current. Viscosity measurements were made with an Ostwald's viscometer.

3. Results and discussion

Polarograms of 4×10^{-4} M zinc were recorded in the absence and presence of thiocyanate in 10, 25 and 50% (v/v) aqueous mixtures of methanol, ethanol, dioxan and DMF. The ionic strength was maintained at 1.0 with lithium nitrate.

Well-defined waves were obtained in all the media except in 50% DMF. The half-wave potentials were shifted to more negative values with increasing thiocyanate concentration. The reduction, however, was reversible only in 10% methanol, ethanol and DMF and in 25% methanol. Log-plots with curvature or high slopes in other media indicated quasi-reversible or irreversible processes.

The reversibility of the reduction was further investigated by calculating the standard rate constant, k_s , and the transfer coefficient, α . The 'formal' potentials, required for this purpose, were obtained from composite polarograms of zinc, recorded in different media, using a dropping zinc amalgam electrode. The kinetic parameters, k_s and α , were then evaluated from the data on cathodic waves by means of the expressions (Randles 1959),

$$i/i_d = \frac{1}{2} \left[1 + \tanh \left(-\frac{\beta\eta}{2} \right) \right] \phi(H) \quad (1)$$

and

$$\log \left[\frac{h}{(1 + \exp \beta\eta)} \right] = \log \left[\left(\frac{3}{7D} \right)^{1/2} k_s \right] - \frac{\alpha\beta\eta}{2.303}, \quad (2)$$

where β stands for nF/RT and η for $E - E_f^0$ (E_f^0 being the 'formal' potential) $\phi(H)$ is a function of H which is read from a plot of $\phi(H)$ vs H (Milner 1957). H is given by

$$H = h \cdot \tau^{1/2}, \quad (3)$$

where τ is the drop time. Thus, the parameter H (and hence, h) obtained from the current-potential data, yielded k_s and α from a plot of $\log [h/(1 + \exp \beta\eta)]$ vs η (equation 2).

It was observed from the current-potential data for the reduction of zinc in the presence of thiocyanate in different mixed solvents that the $E_{1/2}$ and E_f^0 were almost the same, in 10% methanol, ethanol and DMF, and in 25% methanol, which indicated reversible reduction. Calculation of k_s and α in other media was done by means of (1) and (2) and the values are presented in table 1.

The half-wave potentials as well as the 'formal' potentials shifted to more negative values with increasing thiocyanate concentration. The stability constants of zinc-thiocyanate complexes in different media, calculated by the methods of Lingane (1941)

Table 1. Values of α and k_s in different media.

[CNS]/M	Methanol		Ethanol		DMF		Dioxan		50%	
	α	$-\log k_s$	α	$-\log k_s$	α	$-\log k_s$	α	$-\log k_s$	α	$-\log k_s$
0.0	0.38	2.79	—	—	0.41	2.89	0.36	3.22	0.36	2.79
0.1	—	—	0.28	2.53	—	—	—	—	0.36	2.70
0.2	0.34	3.01	0.38	2.88	0.33	3.01	0.45	2.99	0.40	2.90
0.3	—	—	0.30	2.70	—	—	—	—	0.34	3.01
0.4	0.34	3.41	—	—	0.36	3.21	0.50	2.97	—	—
0.5	—	—	0.38	3.10	—	—	—	—	0.40	3.23
0.6	0.36	3.56	—	—	0.41	3.37	0.49	2.94	—	—
0.7	—	—	0.40	3.08	0.37	3.40	—	—	0.40	3.28
0.8	0.36	3.65	—	—	—	—	0.51	2.98	—	—
0.9	—	—	0.44	3.16	0.33	3.43	—	—	0.42	3.33
1.0	—	—	—	—	0.43	3.37	0.48	2.87	0.42	3.34

Table 2. Values of stability constants and the product $I\eta^{*1/2}$ in different media.

Solvent %	$\frac{1}{\epsilon} \times 10^2$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	I	$I \cdot \eta^{*1/2}$
Methanol							
10	1.33	—	1.78	—	2.57	1.24	1.36
25	1.43	—	1.93	1.98	2.70	1.10	1.35
50	1.67	—	—	2.90	4.48	1.04	1.36
Ethanol							
10	1.35	—	1.78	—	2.57	1.18	1.36
25	1.49	—	2.00	2.00	2.94	0.99	1.37
50	1.89	—	—	4.38	4.72	0.86	1.37
DMF							
10	1.31	—	1.78	—	2.57	1.20	1.33
25	1.37	—	—	—	3.90	1.01	1.25
Dioxan							
10	1.43	—	1.78	—	2.57	1.19	1.30
25	1.75	—	1.60	2.40	3.14	1.04	1.29
50	2.80	—	—	4.81	4.83	0.87	1.26

and DeFord and Hume (1951) using E_f^0 in the place of $E_{1/2}$, are tabulated in table 2.

The properties of the solvent that affect the polarographic behaviour are, mainly, the dielectric constant and viscosity, though chemical reactivity also plays a part. Ion pair formation between the depolarizer and the supporting electrolyte ions is enhanced in media of low dielectric constant. It has been observed in this study that the reversible half-wave potential, $E_{1/2}^r$ or the 'formal' potential, E_f^0 of the uncomplexed zinc is more positive than in water for all solvent mixtures. The shift in $E_{1/2}^r$ to positive values has been observed earlier (Schaap *et al* 1955; Koptenko and Migal 1975) and can be explained on the basis of electrostatic theory of solvation. The linear plot of E_f^0 vs $1/\epsilon$ where ϵ is the dielectric constant of the medium indicates a rough correlation between the electrostatic part of the free energy of transfer, ΔG_i^0 , from water to aqueous mixtures of the solvent and $(1/\epsilon)$ (Born 1920).

Since stability constants are related to E_f^0 , an attempt was made to correlate the stability constants with the dielectric constants of the media. The fourth species was identified in all the cases and hence a plot of $\log \beta_4$ vs $(1/\epsilon)$ was obtained which resulted in straight lines. Similar behaviour has been observed for a number of metal complexes (Arevalo, *et al* 1975; Tur'yan 1956, 1959, 1960).

The diffusion coefficients of the electroactive species are influenced by ion-solvent interaction which is manifest in the form of solvation and viscosity effects. The viscosity effect can be expressed by the Stokes-Einstein equation (1920) as

$$D = (RT/N)(1/6\pi\eta^*r), \quad (4)$$

where η^* is the viscosity of the medium. Since i_d is proportional to $D^{1/2}$, the constancy of the product, $i_d\eta^{*1/2}$ indicates that the change in diffusion current is mainly due to viscosity effects. In the present work, dropping mercury electrodes with different capillary characteristics were used. Hence, the diffusion current constant, I , equal to $i_d/m^{2/3}\tau^{1/6}$, was substituted for $i_d \cdot I \cdot \eta^{*1/2}$ was constant in alcohol media while it decreased in other media (table 2) indicating effects due to solvation as well.

The decrease in k_s in the presence of thiocyanate in the different media studied indicates the increasing role of the solvent in influencing the double layer structure as well as the electron transfer processes. The adsorption of the solvent and the preferential solvation of the electrode or the cation may result in the partitioning of the cation between the bulk of the solution and the interface, thereby influencing the electrode reaction (Behr *et al* 1979). An interesting observation was that while well-developed waves were obtained in dioxan (dielectric constant ~ 35), a drawn out and ill-defined wave was observed in 50% DMF with much higher dielectric constant (~ 65). This may be due to the chemical reactivity of DMF, in which zinc is extensively solvated, which hinders the reduction.

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