VOLTAMMETRIC INTERPRETATION OF POTENTIAL AT ION-SELECTIVE ELECTRODE USING
CURRENT-SCAN POLAROGRAPHY AT AQUEOUS/ORGANIC SOLUTIONS INTERFACE

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Although the measurement by the ion-selective electrode (ISE) belongs to the potentiometry, Koryta^{1,2)} and Fujinaga³⁾ advocate that the potential at the ISE and such important factors in the ISE measurement as Nernstian response, detection limits and interferences should be interpreted from the voltammetric viewpoint. To materialize the idea Koryta²⁾ presented many voltammograms at aqueous/organic solutions (A/O) interface which were simulated using extraction data under some assumptions.

The voltammetric concept on the ISE, however, has not yet found wide acceptance with most workers since the actual voltammograms available for the explanation of the potential-generating process at the ISE have scarcely been reported because of the difficulty in the measurement. The difficulty is attributable mainly to the ohmic potential drop (IR drop) in solution phases and solution/solution interface^{4,5}).

We have recently succeeded in recording accurate polarograms at the A/O interface employing the current-scan method⁶⁾ with a simple device⁷⁾. In this communication, the above-mentioned subjects concerned with the ISE are clearly interpreted comparing the polarographic results obtained by the current-scan method with the data found at the ISE. The membrane of the ISE is composed of the same organic solution as that used in the polarography.

The electrolytic cell used in the present work is similar to that proposed by Samec et al.⁸⁾ for the potential-scan polarography at the aqueous electrolyte dropping electrode, and is illustrated schematically in Fig. 1. The aqueous electrolyte solution was dropping upward into the nitrobenzene solution from a teflon capillary (1.4 mm $\varnothing$ x 3 mm) with the mean flow-rate $m = 0.018 \text{ cm}^3 \text{ s}^{-1}$ and the drop time t about 2.2 s. For the polarographic study the current, I , between CE1 and CE2 was scanned at a rate $v = 0.5 \mu\text{A s}^{-1}$ and the potential difference, ΔV , between RE1 and RE2 was detected. In order to compensate the IR drop caused by the resistance ($R = 0.53 \text{ k}\Omega$) between RE1 and RE2, a resistance, R_c , which is equivalent to R was put into the current supplying circuit in series and the voltage (IR_c) generated by R_c was subtracted automatically from ΔV ⁷⁾.

Fig. 1 Electrolytic cell

1, aqueous electrolyte dropping electrode;
2, teflon cylinder with small hole (1.4mm ϕ x 3mm); 3, nitrobenzene phase; 4, reservoir for aqueous solution;
RE1, RE2, Ag-AgCl electrode for potential measurement;
CE1, CE2, electrode for scanning current

Curve (1) in Fig. 2 is the polarogram at the aqueous electrolyte dropping electrode containing 0.05 M (1 M = 1 mol dm⁻³) in LiCl and 1 M in MgSO₄ as a supporting electrolyte which drops into the nitrobenzene solution containing 0.05 M in tetrabutylammonium tetraphenylborate (TBA·TPB). The polarogram does not sharply intersect the potential axis, where $I = 0$, at a definite potential suggesting that the A/O interface is polarized even when the current is small, since LiCl is hardly soluble in nitrobenzene and TBA·TPB is hardly soluble in water.

Curve (2) in Fig. 2 was obtained with the same solution-couple as that used in curve (1) but in the presence of both 5×10^{-4} M tetramethylammonium bromide (TMA·Br) in the aqueous phase and 5×10^{-4} M TMA·TPB in the organic phase. This polarogram shows the composite wave due to the reaction (1).

Where subscripts w and o denote the ions in the aqueous and organic phases, respectively. The polarogram sharply intersects the potential axis suggesting that the A/O interface is depolarized even when an appreciable current is flowing, since TMA⁺ is easily transferred from one phase to the other across the interface.

Curve (3) in Fig. 2 illustrates the polarogram obtained in the same condition as that of curve (2) but without TMA⁺ in the organic phase. The anodic wave in the polarogram is attributed to the reaction (2).

Fig. 2 Current-scan polarograms of TMA⁺ at the aqueous electrolyte dropping electrode

Supporting electrolyte, 0.05 M LiCl + 1 M MgSO₄ in aqueous dropping electrode and 0.05 M TBA·TPB in organic (nitrobenzene) phase

- (1) without TMA⁺ in both aqueous and organic phases
- (2) with 5×10^{-4} M TMA·Br in aqueous phase and with 5×10^{-4} M TMA·TPB in organic phase
- (3) with 5×10^{-4} M TMA·Br in aqueous phase and without TMA·TPB in organic phase

As there is no TMA^+ in the organic phase, the electrode interface is not completely depolarized, and the polarogram does not intersect the potential axis sharply.

Curve (1) in Fig. 3 is the relation between the concentration of TMA^+ in the test solution and the ISE potential at 25°C measured with the ISE system given in eq. (3).

SSE (Ag-AgCl, sat. KCl, aqueous)	0.05 M LiCl + 1 M MgSO ₄ + 5×10^{-5} M TMA·Br [Internal reference solution, aqueous]	0.05 M TBA·TPB + 5×10^{-4} M TMA·TPB [Liquid membrane, nitrobenzene]	0.05 M LiCl + 1 M MgSO ₄ + TMA·Br [Test solution, aqueous]	SSE (Ag-AgCl, sat. KCl, aqueous)

Curve (2) in Fig. 3 includes the result obtained by the same measurement as that of curve (1) but using the ISE cell without TMA·TPB in the liquid membrane.

Figures 2 and 3 clearly indicate that the ISE potential exhibits the Nernstian response only when the aqueous solution/organic membrane interface is completely depolarized by the objective ions, as pointed out by Koryta²⁾ or Fujinaga³⁾.

The zero-current potential ($E_{I=0}$) of the composite polarogram of TMA^+ [eq. (1)] shifts about 60 mV more negative when the concentration of TMA^+ in the aqueous phase is increased one order in the concentration range between 5×10^{-5} M and 5×10^{-1} M (see curves 2-6 in Fig. 4). The shift of $E_{I=0}$ in the polarograms corresponds to the Nernstian response at the ISE. As shown

curve (1) or (7) in Fig. 4, when the concentration of TMA^+ is less than 5×10^{-6} M or more than 5 M, the composite polarogram is influenced with the anodic or cathodic final rise of the residual current, respectively. Consequently, the shift of $E_{I=0}$ becomes smaller in these concentration ranges. Comparing the polarographic results with the results obtained by the ISE measurement [see curve (1) in Fig. 3], it is obvious that the dynamic range detectable at the ISE is controlled by the cathodic and anodic final rises in the residual current.

Curves (8), (9) and (10) in Fig. 4 are the polarograms of reactions (2), (4) and (5) which are recorded in the same conditions as curve (3) in Fig. 2. Curves (9) and (10), however, are obtained with 5×10^{-4} M Cs^+ and 5×10^{-4} M tetrapropylammonium ion (TPA^+), respectively, instead of TMA^+ in the aqueous solution. These polarograms indicate that TMA^+ transfers from water to nitrobenzene more easily than Cs^+ and less easily than TPA^+ .

Curves (11) and (12) are the composite polarograms of 5×10^{-4} M TMA^+ [curve (3) in Fig. 4] in the presence of 5×10^{-4} M Cs^+ and 5×10^{-4} M TPA^+ in the aqueous

Fig. 3 Relation between concentration of TMA^+ and ISE potential at liquid membrane ISE with 5×10^{-4} M (O) or without (●) TMA·TPB in the membrane

Fig. 4 Polarograms obtained in the same conditions as Fig. 2 but with various depolarizers listed below

Depolarizer in aqueous phase	Depolarizer in organic phase
1 5×10^{-6} M TMA·Br	5×10^{-4} M TMA·TPB
2 5×10^{-5} M TMA·Br	} as above
3 5×10^{-4} M TMA·Br	
4 5×10^{-3} M TMA·Br	
5 5×10^{-2} M TMA·Br	
6 5×10^{-1} M TMA·Br	
7 5 M TMA·Br	} none
8 5×10^{-4} M TMA·Br	
9 5×10^{-4} M CsBr	} as above
10 5×10^{-4} M TPA·Br	
11 5×10^{-4} M TMA·Br + 5×10^{-4} M CsBr	5×10^{-4} M TMA·TPB
12 5×10^{-4} M TMA·Br + 5×10^{-4} M TPA·Br	as above

phase, respectively. Since $E_{I=0}$ of curve (11) is identical to that of curve (3) but $E_{I=0}$ of curve (12) is shifted to fairly negative from that of curve (3), it is considered that the ISE potential of 5×10^{-4} M TMA⁺ may not be influenced by 5×10^{-4} M Cs⁺ but may be significantly affected by 5×10^{-4} M TPA⁺. In fact, in our ISE measurements of 5×10^{-4} M TMA⁺ by the ISE system of eq. (3), 5×10^{-4} M Cs⁺ had no effect and 5×10^{-4} M TPA⁺ gave 120–150 mV of negative error.

The above-mentioned results suggest that diverse cations which transfers from water to organic liquid membrane more easily than the objective cations give more serious interference in the ISE measurement.

Finally, on the ground of results obtained by the current-scan polarography, most of important factors in the ISE measurement such as the Nernstian response, the detection limits and the interferences have been clearly interpreted from the voltammetric viewpoint.

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