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Response of Copper(II) and Cadmium(II) Ion-selective Electrodes in Some Nonaqueous Solvents

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Synopsis. The response of cadmium(II) and copper(II) ion-selective electrodes was evaluated in methanol, ethanol, acetonitrile solutions and their mixtures with water. The electrodes showed an almost Nernstian behavior in nonaqueous solutions and their mixtures with water except in acetonitrile.

Application of ion-selective electrodes to nonaqueous solutions has been expanded by using solid membrane ion-selective electrode. Properties of the electrodes, *e.g.* their sensitivity, selectivity and response time are expected to be solvent dependent. Several authors reported the response of solid membrane electrode in a variety of organic solvents and their mixtures with water.[1–5] The response of solid membrane electrodes in different solvents is interesting but little is known about such solvent dependence.

This paper is concerned with the response of cadmium(II) and copper(II) ion-selective electrodes at direct potentiometry and potentiometric titrations in methanol, ethanol, acetonitrile and their mixtures with water.

Experimental

For the study, Ag_2S/MS (M=Cu or Cd) membrane disks were supplied by Denki Kagaku Keiki Co. LTD (Tokyo). A cross-section of the ion selective electrode made is shown in Fig. 1. Other apparatus were the same as in the previous report.[6]

Direct potentiometry and potentiometric titration in solution containing 0.1 M (1 M=1 mol dm^{-3}) sodium perchlorate were performed by the usual method. In every case, the electrode system was allowed to attain equilibrium (±0.1 mV) . Potentials at each titration became stable after a period of 5—30 min. All measurements were made at 25.0±0.1 °C.

Results and Discussion

Response of Cadmium(II) Ion-selective Electrode in Direct Potentiometry. Measurements by direct potentiometry of Cd (II) in methanol-water mixtures and pure methanol are shown in Fig. 2. Nernstian response in pure methanol was observed to 2×10^{-6} M at constant ionic strength of 0.1 M. The response becomes more ideal when some water is added.

In ethanol-water mixtures, the electrode responds similarly to the behavior in water-methanol mixtures.

In acetonitrile-water mixtures, the behavior of the electrode was different from the former cases. Approximate Nernstian response to cadmium concentration at constant ionic strength was observed from 10^{-3} M to 10^{-5} M at a solvent mixture containing 40 vol % acetonitrile and 60 vol % water (abbreviated as 40% acetonitrile solution). But intereference of an unknown nature gave very low readings in 80% acetonitrile solution.

Response of Copper(II) Ion-selective Electrode in Direct Potentiometry. In methanol-water mixture, the copper(II) electrode responds very well to copper concentration of 6×10^{-6} M and the Nernstian response was observed in the 80% methanol solution. But the electrode indicated the large shifts of the potential at the low concentration of copper(II) in 100% ethanol solution as shown in Fig. 3.

In ethanol-water mixtures, responses are linear in 20 and 40% ethanol solutions, but indicated the large

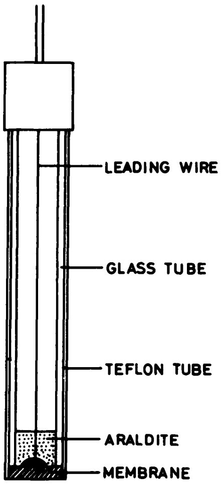

Fig. 1. Cross-section of metal sulfide membrane ion-selective electrode.

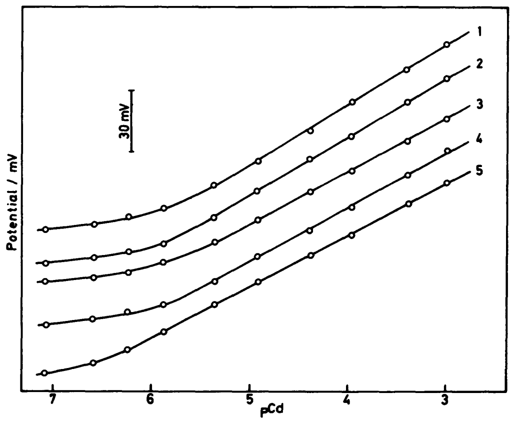

Fig. 2. Calibration curves for cadmium(II) ions in methanol–water mixtures
1; 100 % methanol, 2, 80 % methanol, 3; 40 % methanol, 4; 20 % methanol, 5; water

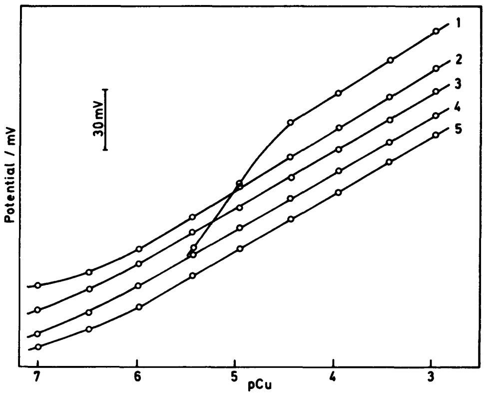

Fig. 3. Calibration curves for copper(II) ions in ethanol–water mixtures.
1; 100 % ethanol, 2; 80 % ethanol, 3; 40 % ethanol, 4; 20 % ethanol, 5; water

TABLE 1. RESPONSE OF COPPER(II) AND CADMIUM(II) ION-SELECTIVE ELECTRODES IN VARIOUS SOLVENTS

Solvent		Cu(II) electrode		Cd(II) electrode	
		Slope[a)]	Lower limit of usable range[b)]	Slope[a)]	Lower limit of usable range[b)]
		−mV/decade	pC_{Cu}	−mV/decade	pC_{Cd}
Water		31	6.2	29	6.5
Methanol	20%	30	6.2	29	5.8
	40%	30	6.2	28	5.8
	80%	31	6.2	30	5.7
	100%	28	4.4	31	5.7
Ethanol	20%	32	6.4	29	5.9
	40%	32	6.4	29	5.9
	80%	32	4.8	31	5.6
	100%	32	4.8	35	5.7
Acetonitrile	20%			26	4.6
	40%			26	4.6

a) Extending over the range $3<pC<5$. b) Evaluated as the point of intersection of the approximately linear segments of the curve in the regions $3<pC<5$ and $6<pC<7$.

TABLE 2. SELECTIVITY COEFFICIENTS FOR SEVERAL CATIONS

Solvent		Cu(II)-electrode	Cd(II)-electrode
		$\log K_{Cu,Fe}$	$\log K_{Cd,Zn}$
Water		0.8	5.0
Methanol	20%	0.8	5.3
	40%	0.4	5.2
	80%	1.5	5.4
Ethanol	20%	1.1	5.3
	40%	1.5	5.4
	80%	1.8	5.5
Acetonitrile	20%		5.3

shifts of potential at 80% ethanol and 100% ethanol concentration.

The results of these electrode responses are present in Table 1.

Evaluation of Selectivity Coefficients. The selectivity coefficients of these electrodes were determined by the mixed solution method. The values of the selectivity constants of the electrodes for two metals are given in Table 2. The selectivity coefficients in methanol-water and ethanol-water mixtures were somewhat larger than those in water.

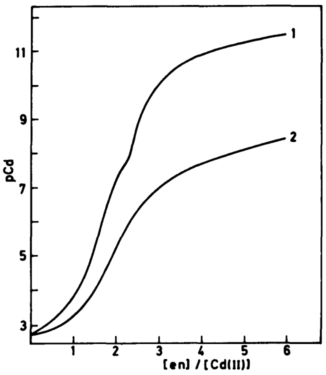

Fig. 4. Titration curves of 2×10^{-3} M $Cd(ClO_4)_2$ with 0.1 M en in 100 % methanol and ethanol solutions. 1; 100 % ethanol, 2; 100 % methanol.

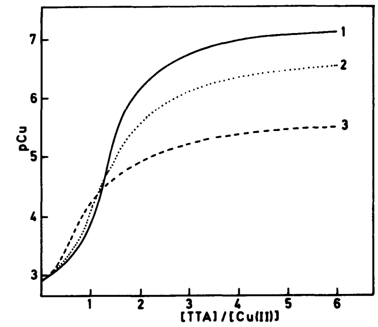

Fig. 5. Titration curves of 2×10^{-3} M $Cu(ClO_4)_2$ with 0.1 M TTA in 80 % ethanol solution.
1; pH=6.9, 2; pH=5.1, 3; pH=4.1.

Complex Formation Studies. In Figs. 4 and 5 are shown the potentiometric titration curves of cadmium(II) solution with ethylenediamine(en) in 100% methanol and ethanol solutions and copper(II) solution with thenoyltrifluoroacetone(TTA) in 80% ethanol solution. None of the titration curves showed any distinct break. The successive formation of complexes is proposed and more detail discussion is required for the determination of successive formation constants.

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