Behavior of the Cadmium Ion-Selective Electrode in Alcohol-Water Mixtures

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In an investigation on the behavior of a cadmium ion-selective electrode in methanol-water and ethanol-water mixtures, potential measurements were carried out with a digital pH/mV meter, a cadmium ion-selective indicator electrode and a silver-silver chloride reference electrode. The calibration curves, slopes of the response, response times, effects of temperature, relation between the potential and the pH-meter reading and selectivity of the electrode were discussed. The response of cadmium ions (electromotive force) was linear between 10^{-7}—10^{-2} mol dm^{-3} in water. However, the linear range became narrower with an increase in the alcohol content. The slopes in alcohol-water mixtures (27—33 mV/decade in methanol-water mixtures, 21—29 mV/decade in ethanol-water mixtures) were nearly equal to the Nernstian slope (29.6 mV/decade). The response times of the cadmium ion-selective electrode in 99 v/v% methanol and in 99 v/v% ethanol were somewhat long, but were still within 5 min for all solutions consisting of 10^{-5}—10^{-1} mol dm^{-3} of cadmium ions. The selectivity of the cadmium ion-selective electrode in various media was examined by the mixed-solution method using potassium, sodium, calcium and magnesium ions as the interfering ions. It was found that a cadmium ion-selective electrode could be used to determine cadmium ions in an alcohol-water solution, although the response time became longer and the linear range of the response became narrower with an increase in the alcohol content.

Ion-selective electrodes are used mainly for the determination of inorganic ions in aqueous solutions.[1,2] The behavior of ion-selective electrodes (halide ion-selective electrode,[3-6] copper ion-selective electrode,[7] lead ion-selective electrode[8] and so on) in nonaqueous solvents has already been reported. However, no study has been reported regarding the properties of a cadmium ion-selective electrode in organic solvents. When ion-selective electrodes are to be used in organic solvents, their properties (such as sensitivity, selectivity, and response time) might be expected to be strongly dependent on the solvents.[9] The effects of alcohol on the potentiometric chelatometric titration of cadmium ions with a cadmium ion-selective electrode was examined by the authors.[10]

This paper is concerned with the detailed behavior of a cadmium ion-selective electrode in methanol, ethanol, and their mixtures with water.

Experimental

Apparatus. A cadmium ion-selective electrode (Orion, Model 94-48A) was used in conjunction with a reference electrode (TOA, Model HS-205C) that was appropriate for the particular solvent used. In 99 v/v% methanol and ethanol solutions, a saturated aqueous potassium chloride solution in the reference electrode was replaced by a saturated solution of potassium chloride in methanol or ethanol.[11]

Reagent. Stock solutions (0.1 mol dm^{-3}) of cadmium chloride in water, in 25, 50, 75, and 99 v/v% methanol and in 25, 50, 75, and 99 v/v% ethanol were prepared and diluted as needed. Calcium nitrate tetrahydrate and magnesium sulfate heptahydrate were dehydrated by heating. All other reagents were analytical-reagent grade from Wako Pure Chemicals.

Procedure. All potentiometric measurements were carried out under constant stirring with a Teflon-covered stirring bar and a magnetic stirrer. The cell consisted of a 50-cm^3 glass beaker fitted with a rubber stopper, bored out for the insertion of electrodes and a thermometer. Successive runs were made by the immersion method in a series of cadmium-ion solutions (10^{-8}—10^{-1} mol dm^{-3}) in decade steps of increasing concentrations.

Results and Discussion

Calibration Curves. Calibration curves for the cadmium ion-selective electrode in water and in 25, 50, 75, and 99 v/v% methanol are shown in Fig. 1.

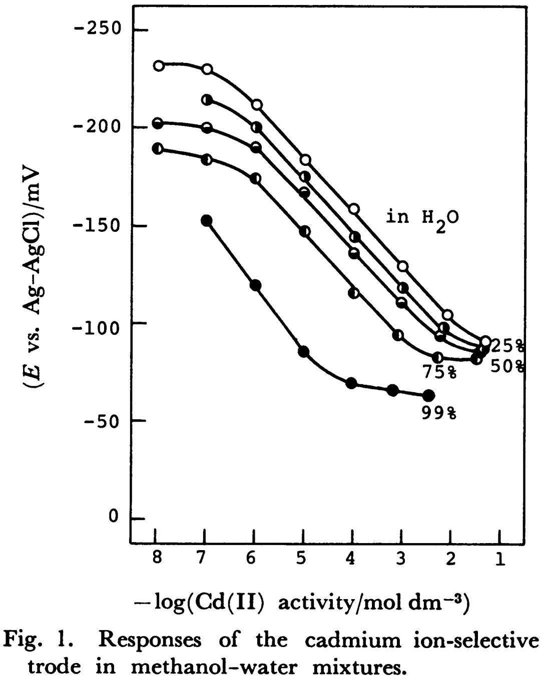

Fig. 1. Responses of the cadmium ion-selective electrode in methanol-water mixtures.

Cadmium-ion solutions of 10^{-8}—10^{-1} mol dm^{-3} are discussed. The logarithm of the cadmium ion activity, calculated by the Debye-Hückel approximation[12] (Eq. 1), was plotted along the X-axis.

$$\log \gamma_{\pm} = -\frac{A|Z_{+}Z_{-}|I^{1/2}}{1+BaI^{1/2}} \qquad (1)$$

$\gamma_{\pm}$; Mean activity coefficient, Z; Electric charge, I; Ionic strength, A and B; Constants of the Debye-Hückel theory,[13] and a; Ion-size parameter.

The permittivities of alcohol-water mixed solutions (ε_{AW}) were obtained using the following equation;

$$\varepsilon_{AW} = \varepsilon_W - (\varepsilon_W - \varepsilon_A)X_A \qquad (2)$$

ε_W; Permittivity of water, ε_A; Permittivity of alcohol, and X_A; Molar fraction of alcohol.

Curves shifted to more positive values with an increase in the alcohol content. The response was linear between 10^{-7}—10^{-2} mol dm^{-3} in water, but the range became narrower with an increase in alcohol content. Linearity was lost at higher cadmium-ion concentrations, presumably because ion pairs were formed by association in 50—99 v/v% methanol.

Figure 2 shows the calibration curves of the cadmium ion-selective electrode in water and in 25, 50, 75, and 99 v/v% ethanol. The results obtained in ethanolic solutions were similar to those in methanolic solutions.

The activity coefficients in alcohol-water mixed solutions were influenced by several factors compared with those in water. It was known that Eq. 1 could be used for aqueous solutions at ionic strengths of less than 0.1. However, in this work it was found that the activity coefficients could be calculated by the Debye-Hückel approximation within the following ranges; less than 10^{-2} mol dm^{-3} of cadmium ions in a 25 v/v% alcohol-water mixed solution, less than 10^{-3} mol dm^{-3} of cadmium ions in 50 and 75 v/v% alcohol-water mixed solutions and less than 10^{-5} mol dm^{-3} of cadmium ions in a 99 v/v% alcohol-water mixed solution.

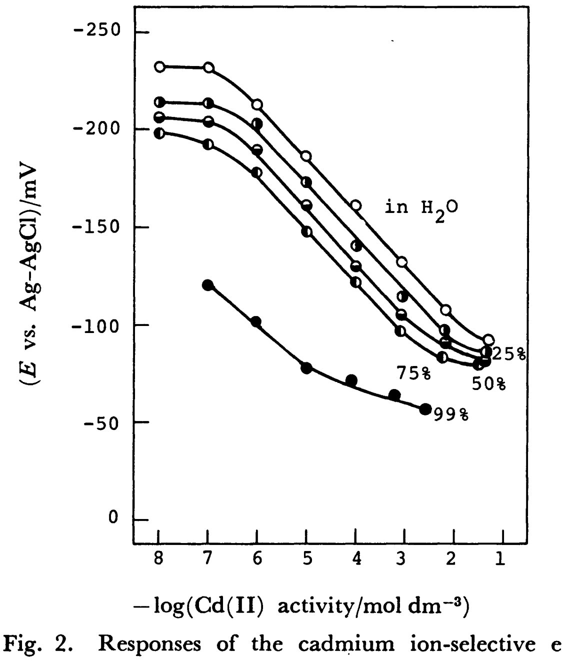

Fig. 2. Responses of the cadmium ion-selective electrode in ethanol-water mixtures.

Slopes of the Response. The slopes of the responses of the cadmium ion-selective electrode in various media are shown in Table 1. The slopes in alcohol-water mixtures (27—33 mV/decade in methanol-water mixtures and 21—29 mV/decade in ethanol-water mixtures) were similar to the Nernstian slope (29.6 mV/decade) and the correlation coefficient was nearly equal to 1. Good correlations were obtained between cadmium-ion activities and the observed potentials.

Response Time. The response times of the cadmium ion-selective electrode obtained in various media are shown in Table 2. The response time tended to decrease with an increase in the cadmium-ion concentration for all the solutions. The response times of the electrode in 99 v/v% methanol and in 99 v/v% ethanol were especially long, but the response times were less than 5 min in all solutions of 10^{-5}—10^{-1} mol dm^{-3} of cadmium ions.

Effects of Temperature. The effects of temperature on the slopes of the responses are shown in Table 3. Electrode potentials were measured between 0—50 °C. In all the solutions, the electrode potentials shifted to more positive values almost linearly with an increase in temperature. The theoretical slope calculated using the Nernst equation increased by ca. 1 mV per 10 °C rise in temperature. A similar tendency was observed in alcohol-water mixtures.

The Relation between the Potential and ΔpH. The relation between the electrode potential and the change in the reading of pH meter, ΔpH, upon an

Table 1. Slopes of the Response of the Cadmium Ion-Selective Electrode in Various Media

Solvent	Cd^{2+} Concn / mol dm^{-3}	Slope/mV	Coefficient of Correlation
99% MeOH	10^{-7}—10^{-5}	33.2	0.9999
75% MeOH	10^{-6}—10^{-3}	28.0	0.9991
50% MeOH	10^{-6}—10^{-3}	26.9	0.9969
25% MeOH	10^{-6}—10^{-2}	26.8	0.9976
99% EtOH	10^{-7}—10^{-5}	20.8	0.9982
75% EtOH	10^{-6}—10^{-3}	28.1	0.9995
50% EtOH	10^{-6}—10^{-3}	29.4	0.9993
25% EtOH	10^{-6}—10^{-2}	28.3	0.9960
H_2O	10^{-7}—10^{-2}	26.2	0.9978

Table 2. Response Times of the Cadmium Ion-Selective Electrode in Various Media

Cd^{2+} Concn mol dm^{-3}	Response time/min							
	Methanol in v/v%				Ethanol in v/v%			
	99	75	50	25	99	75	50	25
10^{-1}	—	0.0	2.5	1.0	—	3.0	0.0	0.0
10^{-2}	1.5	0.0	1.0	1.0	4.0	0.0	1.0	1.0
10^{-3}	4.0	0.0	1.0	1.0	3.0	0.0	1.0	0.0
10^{-4}	3.0	2.5	1.0	1.0	3.0	5.0	1.0	0.0
10^{-5}	1.0	4.0	1.0	1.0	1.5	1.0	2.5	1.0
10^{-6}	1.0	5.0	5.0	6.0	6.0	0.0	2.5	1.0
10^{-7}	5.0	6.0	8.0	6.0	8.0	7.0	11	7.0
10^{-8}	10	5.0	8.0	12	13	5.0	10	4.0

Table 3. Slopes of the Response of the Cadmium Ion-Selective Electrode at Various Temperature

Solvent	Cd^{2+} Concn	Slope/mV					
	mol dm^{-3}	5 °C	10 °C	20 °C	30 °C	40 °C	50 °C
99% MeOH	10^{-7}—10^{-5}	33.7	33.2	33.2	34.5	35.7	36.3
75% MeOH	10^{-6}—10^{-3}	26.5	26.9	28.0	27.9	28.1	30.8
50% MeOH	10^{-6}—10^{-3}	24.5	25.5	26.9	28.1	30.4	31.0
25% MeOH	10^{-6}—10^{-2}	25.6	26.0	26.8	27.7	29.0	30.0
99% EtOH	10^{-7}—10^{-5}	17.8	19.6	20.8	22.6	25.3	28.4
75% EtOH	10^{-6}—10^{-3}	26.3	28.3	28.9	33.2	35.7	36.1
50% EtOH	10^{-6}—10^{-3}	29.8	29.6	29.4	29.5	32.5	35.0
25% EtOH	10^{-6}—10^{-2}	23.4	24.4	28.3	29.5	28.2	29.2
Nernstian slope		27.6	28.1	29.1	30.1	31.1	32.1

addition of acid was examined (Fig. 3). The pH meter was calibrated with a glass electrode, a saturated calomel electrode and a pH standard aqueous solution. The ΔpH values of samples were adjusted with acetic acid. The electrode potentials were constant at a ΔpH of 3.5—5.0 in alcohol-water mixtures. The deviation increased for a ΔpH below 3.5.

Selectivity of the Cadmium Ion-Selective Electrode. The selectivity of the cadmium ion-selective electrode in various media was examined using the mixed-solution method (Table 4). Interferences by potassium, sodium, calcium and magnesium were investigated. The selectivity coefficients for potassium ions in 25—99 v/v% methanol (7.2×10^{-3}—5.0×10^{-2}) and in ethanol (3.6×10^{-3}—4.2×10^{-3}) were greater than those reported in the literature for an aqueous solution (6.7×10^{-8}).[14] Similarly, those for sodium ions in 25—99 v/v% methanol (3.9×10^{-3}—8.4×10^{-2}) and in ethanol (2.4×10^{-3}—1.4×10^{-1}) were greater than those reported in the literature (3.2×10^{-8}).[14] The selectivity coefficients for calcium ions in 25—99 v/v% methanol (2.0×10^{-4}—3.6×10^{-4}) and in 25—99 v/v% ethanol (3.3×10^{-5}—2.1×10^{-4}), for magnesium ions in 25—75 v/v% methanol (5.2×10^{-4}—1.1×10^{-3}) and in 25—50 v/v% ethanol (1.9×10^{-4}—5.6×10^{-4}) were in fair agreement with those reported in the literature (2.2×10^{-4} and 1.6×10^{-4}),[14] respectively.

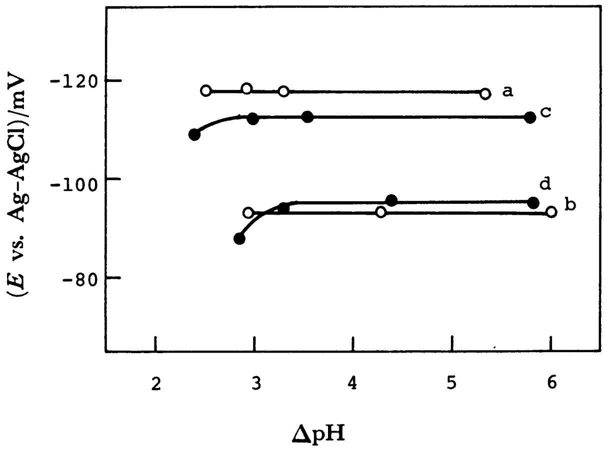

Fig. 3. The relation between the potential and ΔpH in methanol-water mixtures and ethanol-water mixtures: 10^{-3} mol dm^{-3} cadmium ion in (a) 25, (b) 75 v/v% methanol and in (c) 25, (d) 75 v/v% ethanol.

The cadmium ion-selective electrode could be used

Table 4. Selectivity Coefficient of the Cadmium Ion-Selective Electrode in Various Media

Solvent	Selectivity coefficient[a]			
	Interfering ion			
	K^+	Na^+	Ca^{2+}	Mg^{2+}
99% MeOH	5.0×10^{-2}	8.4×10^{-2}	2.7×10^{-4}	—
75% MeOH	7.2×10^{-3}	5.7×10^{-3}	2.2×10^{-4}	9.3×10^{-4}
50% MeOH	2.2×10^{-2}	3.9×10^{-3}	2.0×10^{-4}	5.2×10^{-4}
25% MeOH	7.2×10^{-3}	4.3×10^{-2}	3.6×10^{-4}	1.1×10^{-3}
99% EtOH	—	1.4×10^{-1}	2.1×10^{-4}	—
75% EtOH	4.0×10^{-3}	5.7×10^{-2}	1.0×10^{-4}	—
50% EtOH	3.6×10^{-3}	3.8×10^{-3}	9.9×10^{-5}	5.6×10^{-4}
25% EtOH	4.2×10^{-3}	2.4×10^{-3}	3.3×10^{-5}	1.9×10^{-4}
H_2O[b]	6.7×10^{-8}	3.2×10^{-8}	2.2×10^{-4}	1.6×10^{-4}

a) Mixed solution method. b) Literature value.

in alcohol-water solutions.

References

1) J. Motonaka, S. Ikeda, and N. Tanaka, *Anal. Chim. Acta,* **105**, 417 (1979).

2) W. S. Selig, *Ind. Eng. Chem., Prod. Res. Dev.,* **23**, 1, 140 (1984).

3) N. A. Kazarjan and E. Pungor, *Anal. Chim. Acta,* **51**, 213 (1970).

4) W. H. Ficklin and W. C. Gotschall, *Anal. Lett.,* **6**, 217 (1973).

5) G. J. Kakabadse, H. A. Maleila, M. N. Khayat, G. Tassopolos, and A. Vahdati, *Analyst,* **103**, 1046 (1978).

6) N. A. Kazarjan and E. Pungor, *Anal. Chim. Acta,* **60**, 193 (1972).

7) G. A. Rechnitz and N. C. Kenny, *Anal. Lett.,* **2**, 395 (1969).

8) G. A. Rechnitz and N. C. Kenny, *Anal. Lett.,* **3**, 259 (1970).

9) J. F. Coetzee and M. W. Martin, *Anal. Chem.,* **52**, 2421 (1980).

10) J. Motonaka, S. Ikeda, and N. Tanaka, *Bunseki Kagaku,* **33**, 551 (1984).

11) R. H. Cundiff and P. C. Markunas, *Anal. Chem.,* **28**, 792 (1956).

12) R. G. Bates, B. R. Staples, and R. A. Robinson, *Anal. Chem.,* **42**, 867 (1970).

13) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed., Butterworths, London (1959), Chap. 9.

14) M. J. Brand, J. Millitello, and G. A. Rechnitz, *Anal. Lett.,* **2**, 523 (1969).