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The Responses of the Monovalent Cation-sensitive Glass Electrode to the Cationic Activities in Different Solvents

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Synopsis. The responses of the glass electrode to the cationic activities in different solvents have been studied for several monovalent cations in several dipolar aprotic and protic solvents by comparing the potentials of the amalgam electrode with those of the glass electrode.

The Nernstian responeses of cationic glass electrodes to cations in partially aquated solvents[1,2] and in non-aqueous systems[1,3,4] have been well established. Cations are known to have quite different activities according to the solvent in which they are dissolved, and there have been some investigations in methanol[1] and hydro-organic madia[5] which confirm that the cationic glass electrodes can also respond to such a solvent effect on the cationic activities. In the present report, the potentials of the monovalent cation-sensitive glass electrode immersed in solutions of various monovalent cations were compared, in a variety of solvents, with the potentials of the corresponding amalgam or metal electrodes. To carry this out, the emf's of the following two cells were measured:

$$\text{Glass electrode} \mid \underset{(A)}{10^{-2}\,\text{M Et}_4\text{NClO}_4,\ x\text{M M}^+\text{ClO}_4^-\ (\text{D})} \underset{J_1}{\|}$$

$$\underset{(B)}{0.1\,\text{M Et}_4\text{NClO}_4\ (\text{AN})} \,\|\, \underset{(C)}{5\times10^{-3}\,\text{M AgNO}_3\ (\text{AN}) \mid \text{Ag}}$$

Cell I

$$\text{M(Hg)}^* \mid \underset{(A)}{10^{-2}\,\text{M Et}_4\text{NClO}_4,\ x\text{M M}^+\text{ClO}_4^-\ (\text{D})} \underset{J_2}{\|}$$

$$\underset{(B)}{0.1\,\text{M Et}_4\text{NClO}_4\ (\text{AN})} \,\|\, \underset{(C)}{5\times10^{-3}\,\text{M AgNO}_3\ (\text{AN}) \mid \text{Ag}}$$

Cell II

(* Ag wire for $M^+ = Ag^+$)

In these cells, D shows such solvents as 1,2-dichloroethane (DCE), acetonitrile (AN), propylene carbonate (PC), methanol, water, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), and M^+, such monovalent cations as lithium, sodium, potassium, cesium, thallium, and silver ions. The concentrations of $M^+ClO^-_4$ in the compartments (A) are shown in Table 1. It should be noted that the salt bridge (B) and the reference electrode (C) in Cells I and II are always the same as each other.

TABLE 1.

	Concentration of metal in amalgam (M)	Concentration of the ion[a] in Cells I and II[b]; x values
Lithium	6.58×10^{-2}	1.00×10^{-3}
Sodium	3.02×10^{-2}	1.00×10^{-3}
Potassium	2.25×10^{-2}	5.000×10^{-4}
Cesium	1.03×10^{-2}	5.000×10^{-4}
Thallium	1.84×10^{-2}	5.00×10^{-4}
Silver	Wire	1.00×10^{-4}

a) When the solvent was DCE, saturated solution of each ion was used, and methanol solution of the cesium ion was also saturated solution. b) See text.

Experimental

Apparatus. The glass electrode was a Beckman 39047. The constructions of the cell and the amalgam electrodes have been described previously.[6,7] The reference electrode was a silver wire immersed in 5×10^{-3} M silver nitrate in AN. The salt bridge consisted of 0.1 M tetraethylammonium perchlorate in AN instead of the 0.1 M tetraethylammonium picrate in AN used in the previous report.[6,7] Except when the D solvent was water, the junction potentials of J_1 and J_2 changed by only several millivolts upon the change in the salt bridge electrolyte.[8] When the D solvent was water, the change in the junction potential was somewhat larger. The test solution in Cell II were deoxygenated by bubbling in nitrogen gas. The metal contents in the amalgams were determined titrimetrically: the amalgams were decomposed in an excess of a 0.1 M perchloric acid solution, and then the excess acid was titrated with a standard sodium carbonate solution. For the emf measurements, a Hitachi-Horiba pH meter, model F-7ss (for Cell I), and a voltmeter equipped with a voltage follower with an input impedance of $10^{11}\Omega$ (for Cell II) were used.

Reagents. The potassium perchlorate of an analytical-reagent-grade substance was recrystallized. The cesium perchlorate was prepared from cesium carbonate and perchloric acid. These perchlorates were dried at 150 °C under a vacuum. The thallium perchlorate was prepared by passing an aqueous solution of thallium formate through a column of Amberlite IRA 411 exchange resin in the OH-form and by then neutralizing it with perchloric acid. It was dried at 70 °C under a vacuum. The silver perchlorate and silver nitrate were of an analytical-reagent-grade substance and were used after drying. The lithium perchlorate, sodium perchlorate, and tetraethylammonium perchlorate were the same as those in previous papers.[6,7] The 1,2-dichloroethane was purified by the method of Coetzee and Lok.[9] The acetonitrile, dimethylformamide, dimethyl sulfoxide, propylene carbonate, and methanol were purified by conventional methods.

Results and Discussion

The relations between the potentials of the glass electrode and those of the metal amalgam or silver wire electrodes in various solvents are shown in Fig. 1. Except for the case of the silver ion, the values of the potentials were referred to those in AN. In deaerated solutions, the potentials of the amalgam electrodes soon reached their equilibrium values and were stable

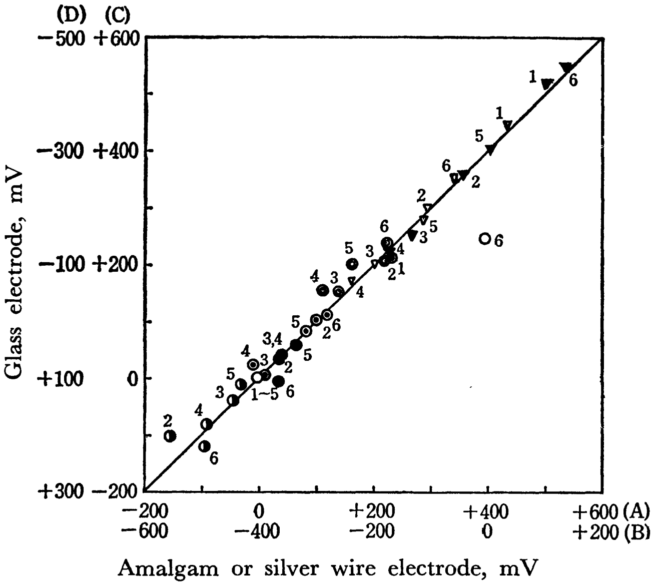

Fig. 1. The responses of the monovalent cation-sensitive glass electrode in various solvents.
(A) $E_{M(Hg)_{AN}} - E_{M(Hg)_D}$, Potentials of the amalgam electrode, (B) $E_{(Ag)_{AN}} - E_{(Ag)_D}$, Potentials of the silver wire electrode, (C) $E^{M}_{(Gl)_{AN}} - E^{M}_{(Gl)_D}$, Potentials of the glass electrode for M^+, (D) $E^{Ag}_{(Gl)_D}$, Potentials of the glass electrode for Ag^+.
M: 1; Li, 2; Na, 3; K, 4; Cs, 5; Tl, 6; Ag
D: ◑ DCE, ○ AN, ● PC, ⊙ methanol, ◎ water, ▽ DMF, ▼ DMSO

enough during the period of the measurements. When oxygen was introduced, however, the potential changed, especially when the measurements were carried out in methanol. Generally, the response of the glass electrode was slower than that of the amalgam electrodes. To reach the equilibrium potentials, it usually took about fifteen to twenty minutes. For various cations in water and for the silver ion in AN, the stabilizations of the glass electrode potentials needed a longer time, however. In Fig. 1, the potentials of the glass electrode for the cesium, and the thallium ions in water and the sodium ion in 1,2-dichloroethane deviate somewhat from the values of the amalgam electrodes. The potential change for the silver ion in 1,2-dichloroethane, propylene carbonate, and particularly in AN also deviates from the change in the potential of the silver wire electrode. Except for these exceptional cases, though, the correspondences of the potential changes of the glass electrode with those of the amalgam or silver wire electrodes are good enough for the cations investigated in this work.

In conclusion, if we consider that the amalgam or silver wire electrodes always make Nernstian responses to the solvent effects on the activities of monovalent cations, the glass electrode can also be considered in many cases to respond in the same ways. However, it should be remembered that there exist exceptional cases in which the Nernstian response cannot be obtained.

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