

## THE SPECIFIC ADSORPTION OF ALKALI METAL IONS AT THE MERCURY-FORMAMIDE INTERFACE

George H. Nancollas and David S. Reid.

State University of New York at Buffalo, Buffalo, N.Y. 14214.

### Introduction

The possibility of specific adsorption of the alkali metal ions at a mercury-solution interface has been investigated by a number of workers, but as yet no firm conclusions have been reached. Most of the work has been done in aqueous solutions, for which there are now abundant data. In a recent paper we reported results of measurements of the surface excesses of potassium and chloride ions at the interface between a mercury electrode and a solution of potassium chloride in formamide which indicated that specific adsorption of the potassium ion was occurring. In an attempt to clarify the situation, the surface excesses of anion and cation have been determined from electrocapillary and double layer capacity measurements for a mercury electrode in contact with a cesium chloride solution in formamide. The results for both the potassium chloride and cesium chloride solutions have been subjected to a components of charge analysis.

### Experimental

The procedures used for the purification of reagents and preparation of solutions have been described previously. Interfacial tensions were measured as a function of applied potential, using a capillary electrometer<sup>1</sup> in 0.050, 0.0889, 0.100 and 0.179 molal solutions of cesium chloride in formamide. The reference of potential was a silver-silver chloride electrode in the same solutions, and interfacial tensions were reproducible to  $\pm 0.2$  erg cm<sup>-2</sup> except at the most cathodic potentials, where the agreement was  $\pm 0.5$  erg cm<sup>-2</sup>.

### Results

Figure 1 shows the variation of interfacial tension,  $\gamma$ , with applied potential for the concentrations of cesium chloride studied. From the variation of interfacial tension with chemical potential,  $\mu$ , at constant potential  $E_0$ , the surface excesses of cesium and chloride ions can be evaluated. This has been done for 0.100 m cesium chloride, following the procedure outlined by Bockris et al.<sup>2</sup> The magnitude of the electrode charge at a given potential was obtained from previously reported capacitance data<sup>1</sup>. Figure 2 shows a plot of the surface excesses  $z \pm F. \Gamma \pm$  as a function of potential for 0.100 m cesium chloride and for comparison the surface excesses in 0.071 m potassium chloride<sup>1</sup>.

## Discussion

The form of the surface excess plots in figure 2 indicates that specific adsorption of cations is occurring in the far cathodic region in both potassium and cesium chloride solutions. The surface excess of anions reaches a minimum value and then increases as the potential becomes more cathodic.

Payne<sup>3</sup> has shown that iodide ions are not specifically adsorbed at electrode charges more cathodic than  $-10 \mu\text{coul.cm}^{-2}$ . Since the chloride ion would be expected to be specifically adsorbed to a smaller extent than iodide, it is reasonable to assume that beyond  $-1.2 \text{ v}$ , at which the electrode charge is approximately  $-13 \mu\text{coul.cm}^{-2}$ , there is no specific adsorption of chloride ions. In this region, therefore, the charge due to specifically adsorbed cations,  $q_+^1$ , can be calculated from the relationships

$$z_- F \Gamma_- = -q_-^{2-s} \quad (\text{a})$$

$$q_-^{2-s} = -A(e^{19.46 \phi_2} - 1) \quad (\text{b})$$

$$q_+^{2-s} = A(e^{-19.46 \phi_1} - 1) \quad (\text{c})$$

$$q_+^1 = z_+ F \Gamma_+ - q_+^{2-s} \quad (\text{d})$$

where the symbols have their usual meanings. In both potassium chloride and cesium chloride, a plot of  $q_+^1$  vs  $E_-$  was linear, and similar linear relationships involving  $q_-^1$  have been obtained in aqueous solutions for specifically adsorbed anions<sup>4,5</sup>. It is reasonable to assume that this linear relationship in formamide solution will hold so long as there is no anionic specific adsorption. Extrapolation to lower potentials gives values of  $q_+^1$ , from which  $q_-^1$  can be calculated by means of the following relationships.

$$q_+^{2-s} = z_+ F \Gamma_+ - q_+^1 \quad (\text{e})$$

$$q_-^1 = z_- F \Gamma_- - q_-^{2-s} \quad (\text{f})$$

together with (b) and (c) above.

The results of this calculation, figure 3, show that  $q_-^1$ , the anionic specific adsorption, is zero at potentials more cathodic than  $-0.9 \text{ v}$ . When  $q_-^1$  has a negative value, corresponding to specifically adsorbed anion, it is not possible to assign any more than qualitative importance to the results. At the present time there is no way of analysing for simultaneous specific adsorption of both anions and cations.

In the region where the anion specific adsorption is zero, the amount of specific adsorption appears essentially equal for both potassium and cesium ion. The extent of specific adsorption occurring at the cathodic extreme is worthy of note, and it is interesting to compare this with previous results. Payne<sup>3</sup> found no specific adsorption of cation to occur in solutions of potassium iodide in formamide. Recent surface excess results, however, in sodium and cesium chloride solutions in formamide, obtained by Damaskin<sup>6</sup>, while slightly lower than the present data, lead to similarly large values of the cation specific adsorption.

The amount of cation specific adsorption occurring at a given cathodic potential appears to be constant for the potassium, cesium and sodium ions, and probably also for the rubidium ion. At first sight this is difficult to understand, but by considering the behaviour of these ions in water and in formamide we can rationalise the observation. Somsen and Coops<sup>7</sup> have measured the heats of solution of the alkali halides in formamide, and calculated  $\Delta H^{\circ}_{sol}$ , the heat of solution at infinite dilution, in each case. Comparison of these  $\Delta H^{\circ}_{sol}$  values with similar values obtained for the solution of the alkali halides in water shows that  $[\Delta H^{\circ}_{sol}(H_2O) - \Delta H^{\circ}_{sol}(HCONH_2)]$  is a constant for each series of salts of the four alkali metals K, Na, Rb, Cs with a given halide ion. Using Van Eck's approach to the solvation of ions<sup>8</sup>, this has been explained as being due to the constancy of the term  $(\Delta H_s + \Delta H_c)$  for all four cations in each solvent where symbols have the same meaning as in (7). If we accept Grahame's<sup>9</sup> suggestion that specific adsorption can be considered as solvation of the ion by mercury, a solvent of infinite dielectric constant, then if all four cations are desolvated to the same extent the enthalpy change on specific adsorption would be constant and given by

$$\begin{aligned} -\Delta H &= k (\Delta H_s^f - \Delta H_s^m) \\ &= k (\Delta H_c^f + \Delta H_{nc}^f + \Delta H_h^f - \Delta H_{nc}^m - \Delta H_h^m - \Delta H_c^m) \\ &= k (\Delta H_c^f - \Delta H_c^m + \text{constant}) \end{aligned}$$

In this equation  $\Delta H_s$  is the ionic enthalpy<sub>c</sub> of solvation, f and m refer to formamide and mercury respectively, and the value of k is a measure of the extent of desolvation, k = 1 indicating complete desolvation.  $-\Delta H_c$  for inert gas-type cations has been shown to be equal to the sum of the ionisation potential and the electron affinity of the corresponding metal ions in both water and formamide. The same is probably also true for mercury, and so  $-\Delta H = \text{constant}$ , since  $\Delta H_c^f - \Delta H_c^m = 0$ . It is reasonable to assume a small or constant entropy of specific adsorption, since we have considered all the cations to be desolvated to the same extent. This would mean that the free energy of specific adsorption would be constant, resulting in an equivalent amount of specific adsorption in each case.

Extending this approach to the halide salts of a given cation,  $[\Delta H^{\circ}_{sol}(H_2O) - \Delta H^{\circ}_{sol}(HCONH_2)]$  increases in the order  $Cl^- < Br^- < I^-$ .

Since the anions are of similar size,  $\Delta H_{ac} + \Delta H_b$  will again be constant in each solvent, and the increase reflects an increase in  $(\Delta H_C^w - \Delta H_C^f)$  along the series. It is reasonable to assume that  $(\Delta H_C^f - \Delta H_C^m)$  will show a similar increase since in each case we are going from the solvent of lower dielectric constant to the solvent of higher dielectric constant.  $-\Delta H (= \Delta H_C^f - \Delta H_C^m + \text{constant})$  will increase in going from chloride to iodide and the free energy of specific adsorption can be expected to follow the same trend, resulting in the observed increase in specific adsorption.

Similar arguments can be advanced for the mercury electrode in aqueous systems, so that we would expect

- 1) equality of cation specific adsorption.
  - 2) an increase in specific adsorption along the series  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ .
- The latter is in accordance with the known behaviour of these anions at the mercury-water interface.

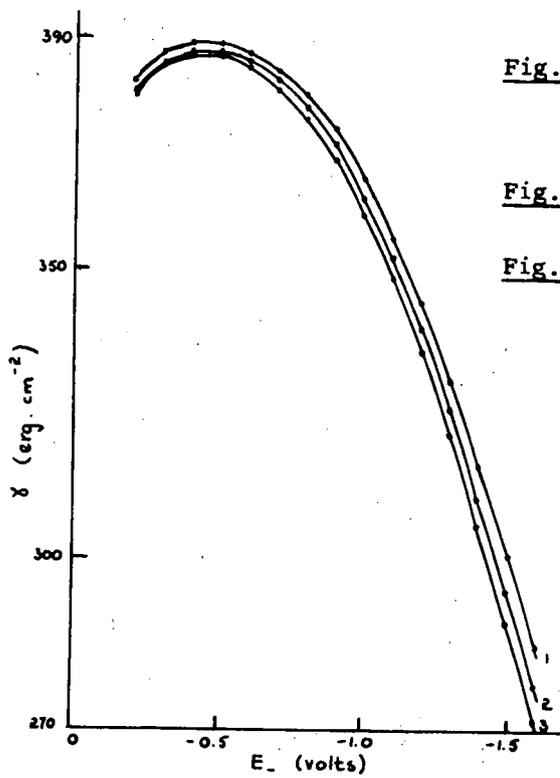
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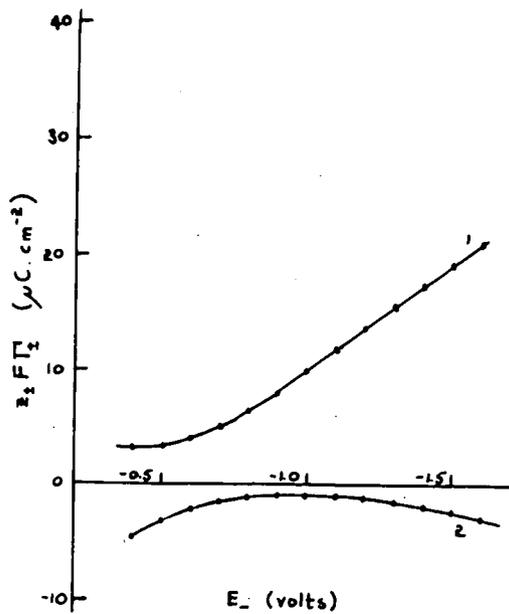
**Fig.1.**  $\gamma$  as a function of  $E_-$  for cesium chloride, (1) 0.050 m; (2) 0.0889 and 0.100 m; (3) 0.179 m.

**Fig.2.** Surface excesses. (1)  $K^+$  and  $Cs^+$ ; (2)  $Cl^-$

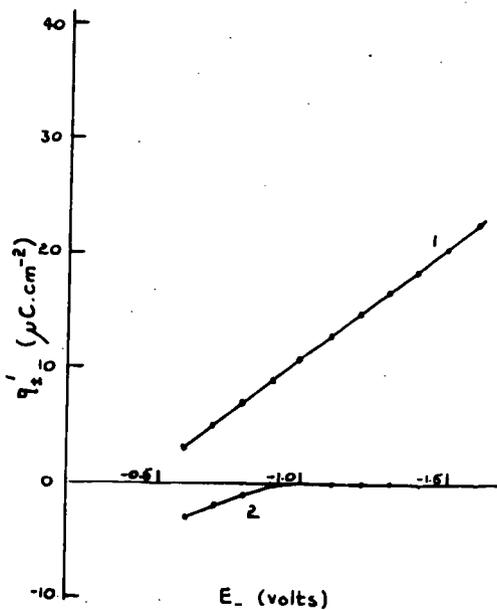
**Fig.3.**  $q_+^1$  as a function of  $E_-$  for cesium chloride. (1)  $q_+^1$ ; (2)  $q_-^1$



**Fig.1.**



**Fig.2.**



**Fig.3.**