THE ADSORPTION OF IODIDE ANION ON THE DROPPING MERCURY ELECTRODE IN WATER + 10% ETHANOL MIXTURE

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The adsorption of iodide anion on the dropping Hg electrode from KI + KF solutions at a constant ionic strength in water and water + 10% ethanol mixture at 25°C has been studied. Results show that I^- adsorption is qualitatively similar in both systems. The adsorption equilibrium in both cases can be described through a Frumkin-type adsorption isotherm, although the corresponding parameters depend on the metal charge density and the solvent composition. In the presence of ethanol, the adsorption of I^- ions decreases drastically. This fact appears to be mainly related to changes in the solvent structure, rather than due to the competitive adsorption of solvent molecules and I^- anions.

The adsorption of inorganic ions on mercury electrodes has been widely studied in both aqueous and organic solvents[1-10]. However, despite of the theoretical and practical interest in this subject, the number of publications dealing with the adsorption of inorganic ions in water + organic solvent mixtures is limited. For systems involving water–ethanol solvent mixtures, a mutual influence of ions and organic solvent molecules on the adsorption process has been observed. The effect depends on the solvent composition, and usually the lower the cosolvent concentration, the clearer the influence of the cosolvent on ionic adsorption.

Owing to its large size and polarizability, the I^- ion exhibits very unusual electrocapillary properties. This has been demonstrated by Grahame[11] and Dutkiewicz and Parsons[12] for aqueous solution of very low concentration, the ionic strength of which was adjusted with KF. The purpose of this work is to study the adsorption of the I^- anion in a water + 10% ethanol mixture at a constant ionic strength and to determine the influence of ethanol in I^- adsorption on mercury.

EXPERIMENTAL

Differential capacity measurements were made in the −0·3 to −1·4 V range (relative to the

SCE) with an impedance bridge similar to that described by Sluyters-Rehbach et al.[13]. The C_d values were measured at 1 kHz with an amplitude of 5 mV.

The surface tension was determined with a capillary electrometer controlled by a Ruska-type manostat which has been described elsewhere[14]. The capillary electrode was calibrated in 0·1M KCl by using interfacial tension data taken from the literature[15]. The accuracy of the surface tension data was 0·1 mN m^{-1}.

The zero charge potential, E_z, was determined with a streaming mercury electrode[16].

The capillary for the dropping mercury electrode (DME) was internally treated with dimethyldichloroxylane vapour. The counter electrode consisted of a Hg pool. The reference electrode was a saturated calomel electrode (SCE).

Chemicals of p.a. grade were purchased from Merck. The ionic strength of KI solutions (0·005 – 0·500 mol l^{-1}) was adjusted to 0·500 mol l^{-1} with KF. KF was recrystallized from twice distilled water by using platinum vessels. KI was firstly dissolved in water at 60°C, then filtered and finally the solution was cooled with ice. Both salts were dried under vacuum at 25°C for 72 h and kept under Ar in a desiccator. There was no evidence indicating the presence of impurities during measurements. Ethanol was distilled and water was distilled twice from alkaline $KMnO_4$. Mercury was purified by using a standard procedure.

All measurements were made at 25°C with solutions which were de-aerated using 99·98% purity argon.

RESULTS AND DISCUSSION

Figure 1a and 1b show the differential capacity vs potential curves for KI + KF in aqueous and water + ethanol solutions, respectively. In any case, the capacity increases with the increasing KI concentration. In aqueous solutions, the capacity increases steeply towards more positive potentials, the effect being well pronounced as the potential is more positive than −0·500 V. This behaviour, which is similar to that observed with other ions like Br^- and SCN^- (refs[17–18]), indicates a strong adsorption of I^- ion on Hg. In the presence of ethanol the shape of the capacity curves changes considerably. The appearance of a capacity maximum and minimum is related to the adsorption and desorption of ethanol, respectively, the former being accompanied by a drop in capacity, in particular at potentials close to the potential of zero charge.

Table I summarizes the values of E_z and the surface tension at the electrocapillary maximum for different solutions. The value of E_z shifts negatively and the surface tension decreases markedly as the I^- concentration increases. In the presence of ethanol, the values of E_z become more positive, and those of the surface tension decreases slightly as the I^- concentration increases.

In order to analyse the specific adsorption of I^- ions the method of Hurwitz[19] and Dutkiewicz and Parsons[12] was applied. The charge q^1 due to the specifically adsorbed I^- anion was evaluated according to the procedure[20]. The adsorption of F^- was neglected and the activity coefficients of the KI and KF were assumed to be equal. Their values were obtained with the help of the Davis' equation[21].

TABLE I

Coordinates of the electrocapillary maximum

KI mol l^{-1}	Water		Water–ethanol	
	$-E_z$ V	γ mN m^{-1}	$-E_z$ V	γ mN m^{-1}
0·005	0·596	421·2	0·542	404·0
0·010	0·619	420·2	0·570	403·3
0·025	0·653	416·7	0·604	402·7
0·050	0·677	413·7	0·627	400·8
0·075	0·690	413·2	0·645	400·5
0·100	0·699	412·2	0·654	400·0
0·250	0·730	407·5	0·690	396·7
0·500	0·755	405·2	0·720	395·3

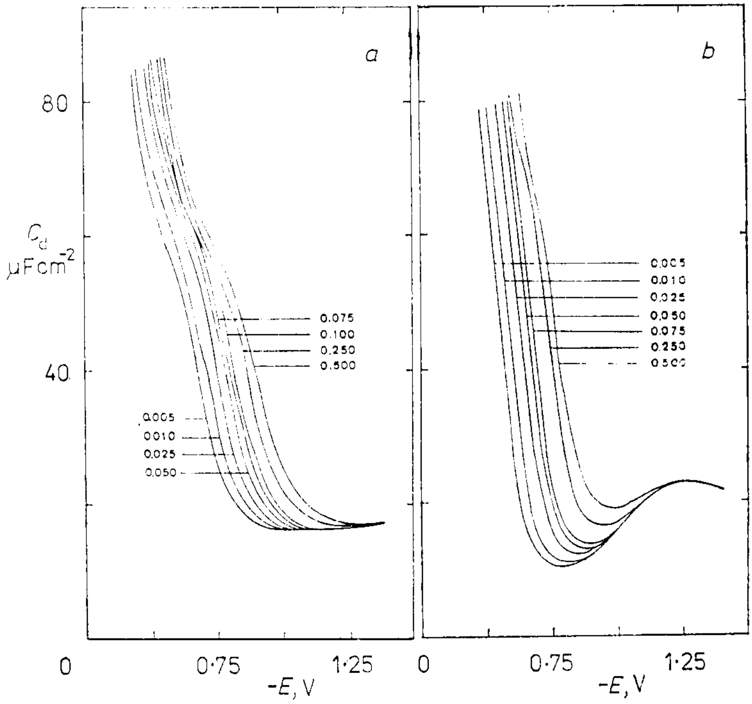

FIG. 1

Differential capacity vs potential curves. x M KI + (0·50 − x) M KF. The values of x are indicated. Ethanol free solutions (a), 10% ethanol containing solutions (b)

Figure 2 shows q^1 vs q plots, where q denotes the charge density on the metal. In any case, the value of q^1 increases with both q and the I^- concentration. These plots are practically linear, although the q^1 values in the presence of ethanol are lower than those resulting in ethanol free solutions. At the highest I^- concentrations and the most positive values of q that difference is small, but in the presence of ethanol and for the most diluted solutions, q^1 is about one half the value obtained in the absence of ethanol. It should be noted that a similar behaviour has been reported for the SCN^- anion in water + acetone and water + ethanol solutions[6,10].

At high ionic concentrations, the contribution of the diffuse layer to the total capacity is small, so that the features of the C_d vs E plots are then determined by the inner layer capacity, C^i. The reciprocal of C^i can be written as the sum of two contributions[22]

$$1/C^i = 1/{}_qC^i + (1/{}^1_qC^i)(\delta q^1/\delta q), \qquad (1)$$

where ${}_qC^i$ stands for the capacity of the inner layer measured for a constant amount

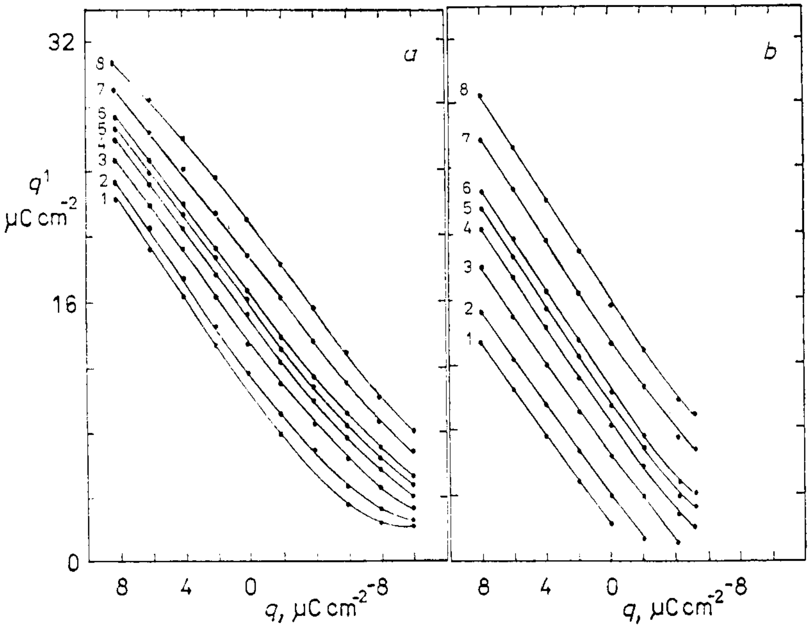

FIG. 2

q^1 vs q plots. x M KI + (0·50 − x) M KF. The values of x are indicated. Ethanol free solutions (*a*), 10% ethanol containing solutions (*b*): 1 0·005, 2 0·010, 3 0·025, 4 0·050, 5 0·075, 6 0·100, 7 0·250, 8 0·500 of adsorbate, and ${}^1_qC^i$ is the capacity measured for a constant charge density on the metal. The properties of the inner layer were studied by plotting ϕ^{m-2}, the potential drop across the metal and the outer Helmholtz plane (OHP), as a function of q^1 at constant q. The value of ϕ^{m-2} was calulated from the measured electrode potential by substracting the potential of the electrocapillary maximum in the absence of specific adsorption, and ϕ^2, the potencial of the OHP, calculated from the Gouy–Chapman theory. In these calculations it was assumed that neither K^+ nor F^- were specifically adsorbed.

The ϕ^{m-2} vs q^1 plots for both EtOH free and EtOH containing solutions (Fig. 3) show a set of almost parallel straight lines, although the presence of ethanol changes both the slope and the intercepts at $q^1 = 0$. From these results, the capacity of the inner layer measured a constant q can be replaced by the corresponding integral capacity ${}^1_qK^i$, which is the reciprocal slope of the lines drawn in Fig. 3. From the intercept, the integral capacity at $q^1 = 0$ due to the charge present on the metal ${}_qK^i$, can be obtained. According to Grahame[23] it is possible to calculate the thickness ratio $(X_2 - X_1)/X_2$ through the equation:

$$ {}_qK^i/{}^1_qK^i = \varepsilon^i_2(X_2 - X_1)/\varepsilon^i_{2,1}X_2 \,, \tag{2}$$

where X_1 and X_2 are the distances of the inner and outer Helmholtz planes from electrode respectively, and ε^i_2 and $\varepsilon^i_{2,1}$ are the electrical permitivities between metal and OHP and between IHP and OHP, respectively. Provided that $\varepsilon^i_2 = \varepsilon^i_{2,1}$, a reasonable value for the thickness ratio can be obtained.

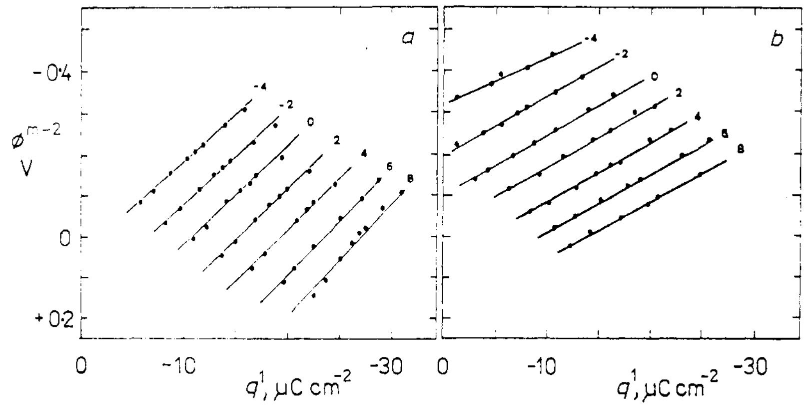

FIG. 3

ϕ^{m-2} vs q^1 plots. The metal density charges studied are indicated. Ethanol free solutions (*a*), 10% ethanol containing solutions (*b*)

The values of $1/{}^1_qK^i$, ${}_qK^i$ and $X_2 - X_1/X_2$ are given in Table II for the two systems studied. For all cases, the integral capacity at zero specific adsorption ${}_qK^i$ decreases as q increases and its value is about 11 μF cm^{-2} higher in the presence of ethanol. Although $1/{}^1_qK^i$ in the water + ethanol mixture is lower than in the ethanol free solutions, the corresponding thickness ratio is lower and decreases slightly in water–ethanol solutions. Otherwise, the thickness ratio remains approximately constant for $q > 0$ in the EtOH free solutions. The distance X_1 is probably the same for both systems as it should be determined by the size of I$^-$ anion. However, the properties of the inner layer as well as its thickness X_2 may be strongly dependent on the nature and structure of the solvent. This is not surprising as there are differences in the dielectric constant (28·3 for ethanol and 78·4 for water at 298 K) and the length of the solvent molecules (0·594 nm for ethanol and 0·154 nm for water) for the solvent constituents. For $q > 0$ the thickness ratio is close to 0·383 in the absence of ethanol, and is only slightly dependent on q. If one admits that the thickness of the inner region X_2 is about 0·40 nm, which corresponds to the radius of hydrated K$^+$ ion[24], the value of X_1 becomes close to 0·24 nm. The latter agrees with the radius of I$^-$ ion. Hence, the preceding assumption that $\varepsilon_2^i = \varepsilon_{2,1}^i$, which

TABLE II
Parameters of the inner layer

q μC cm^{-2}	$1/{}^1_qK^i$ cm^2 μF^{-1}	${}_qK^i$ μF cm^{-2}	$(X_2 - X_1)/X_2$
		Water	
−8	0·023	23·82	0·550
−6	0·022	21·62	0·491
−4	0·022	19·80	0·448
−2	0·022	18·26	0·413
0	0·022	16·94	0·388
2	0·022	15·79	0·379
4	0·024	14·80	0·377
6	0·027	13·92	0·380
8	0·029	13·14	0·388
		Water–ethanol	
−2	0·015	26·69	0·400
0	0·014	26·29	0·368
2	0·014	25·91	0·363
4	0·014	25·54	0·358
6	0·014	25·18	0·353
8	0·014	24·83	0·348

seems to be a good approximation in aqueous solutions, appears to be an unsatisfactory one for the water + ethanol system.

The Adsorption Isotherm

The congruence of the isotherm with the charge on the metal was established[25] by plotting the surface pressure Φ vs the logarithm of the solute activity for the different values of q. For the two systems superimposable plots are obtained by translation along the X-axis (Fig. 4). The average deviation from the common curve is below $0{\cdot}5\ \mathrm{mN\,m^{-1}}$ in the entire KI concentration range. Therefore, the adsorption isotherm should be congruent with respect to the metal charge. From these curves it is possible to determine a value of the maximum surface excess concentration Γ_m (ref.[26]). The result $\Gamma_m = 3{\cdot}48 \,.\, 10^{-10}\ \mathrm{mol\,cm^{-2}}$ is independent of the presence of ethanol, and agrees with that found from the $1/\Gamma$ vs $1/C$ plots extrapolated to $1/C = 0$ ($3{\cdot}50 \,.\, 10^{-10}\ \mathrm{mol\,cm^{-2}}$). Accordingly, the area covered by one adsorbed ion is close to $0{\cdot}48\ \mathrm{nm^2}$, a value which coincides with the plane projection of the hydrated I^- ion[24] ($0{\cdot}41\ \mathrm{nm^2}$).

The experimental adsorption data can be fitted to a Frumkin isotherm[27],

$$\Theta/(1 - \Theta)\exp(A\Theta) = \beta a\,, \tag{3}$$

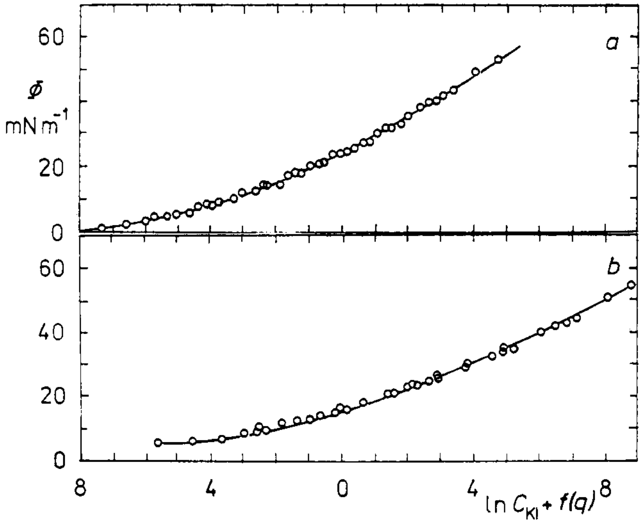

FIG. 4
Surface pressure vs ln C_{KI} activity + $f(q)$ composite plots. Ethanol free solutions (*a*), 10% ethanol containing solutions (*b*)

where Θ is the surface fraction covered by the adsorbate, a is the mean bulk activity, A is the lateral interaction parameter, and β is related to the standard free energy of adsorption by the relationship

$$\Delta G^0_{\text{ads}} = -RT \ln (55{\cdot}5\beta)\,. \qquad (4)$$

The value of the standard Gibbs energy ΔG^0_{ads} refers to unit molarity of adsorbate and $\Theta = 0{\cdot}5$ on the electrode surface[28].

In order to trace the possible dependence of the isotherm parameters on the charge on the metal, the linear test based on the Frumkin isotherm was applied. Characteristic $\log(\Theta/(1 - \Theta)\,a)$ vs Θ plots at the different density charges are shown in Fig. 5, where the series of straight lines confirm the validity of the Frumkin isotherm. From the corresponding slopes the interaction parameter was obtained, and from their intercepts at $\Theta = 0$ the standard free energy of adsorption at zero coverage $(\Delta G^0_{\text{ads}})_{\Theta=0}$ was calculated. The results are summarized in Table III. The interaction parameter A is positive in all cases studied. In the ethanol free solutions it becomes practically independent of q for $q < 4\,\mu\text{C cm}^{-2}$, but increases slowly for more positive values of q. In the presence of ethanol, the parameter A is considerably lower than in EtOH free solutions, and it seems to reach a maximum value at $q = 4-6\,\mu\text{C cm}^{-2}$. These results suggest that the adsorption process involves a significant adsorbate interionic repulsion, which is lowered by the presence of ethanol. Otherwise, $(\Delta G^0_{\text{ads}})_{\Theta=0}$ decreases as q increases, which is to be expected for the adsorption of anions. On the other hand, in ethanol containing solutions a minimum value of $(\Delta G^0_{\text{ads}})_{\Theta=0}$ is observed for $q = 6\,\mu\text{C cm}^{-2}$.

CONCLUSIONS

From the present results one can definitevely conclude that the adsorption of I^- ion on Hg is strongly influenced by the presence of ethanol in the solution. In order to advance an explanation of this effect, two main approaches can be considered. The first and perhaps the simplest one is to think in terms of the adsorption of ethanol molecules themselves at the interface causing a decrease in the amount of adsorbed I^- ions. However, this explanation is difficult to sustain, because it is well known that ethanol adsorption on Hg takes place at a charge density on Hg of about $-3{\cdot}5\,\mu\text{C cm}^{-2}$, i.e. rather far from the charge density range covered in the present work. Therefore, an interpretation in terms of a competitive adsorption between ethanol and I^- ions is not very realistic.

The second possibility consists in the influence of ethanol on the I^- adsorption on Hg through the ethanol–water solvent structure. The complexity of alcohol–water mixtures is clearly demonstrated by their thermodynamic and volumetric properties[29,30]. The formation of the ethanol–water mixtures implies a negative entropy excess which reaches a minimum for an ethanol molar fraction between 0·2–0·3. The large negative excess entropy of mixing hardly suggests a general breakdown in the structure of water upon the introduction of ethanol. The increase in order resulting from the binary solution with respect to the ideal mixture, has been explained through the formation of clathrate-type lattices, which are stabilized

TABLE III
Parameters of the isotherm

q μC cm^{-2}	Water		Water–ethanol	
	$-(\Delta G^0_{ads})_{\theta=0}$ kJ mol^{-1}	A	$-(\Delta G^0_{ads})_{\theta=0}$ kJ mol^{-1}	A
−4	23·11	5·6	—	—
−2	26·00	5·6	—	—
0	34·40	5·7	14·21	2·8
2	39·46	5·7	18·23	3·0
4	47·65	6·3	25·00	3·5
6	59·52	7·2	27·59	3·4
8	64·58	7·5	25·50	2·2

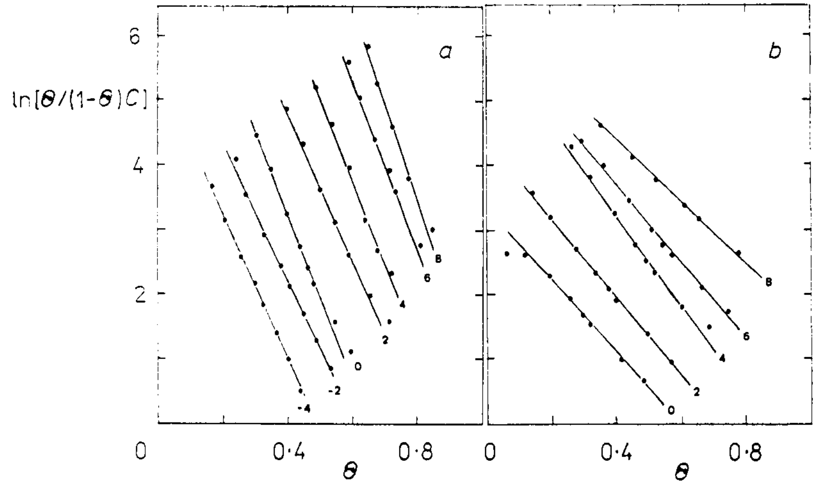

FIG. 5

Linear test of the Frumkin isotherm at different metal density charges. Ethanol free solutions (*a*), 10% ethanol containing solutions (*b*) through the presence of ethanol molecules, the latter occupying the empty cavities and restructuring the entire phase through hydrogen bonding. In addition to this effect, a competition between ethanol and water molecules in entering the coordination sphere of ions plays a significant role. In this case, the largest size of the ethanol molecule as compared to water, produces a considerably decreases of the ion diffusion coefficients. Therefore, from these structural considerations one should expect a greater interaction of ethanol and water molecules with the I^- ions in solution, and correspondingly, a decrease in the ion-metal surface direct contact interaction. This second approach provides an explanation better than the first one, as it becomes in principle, independent on the charge density at the metal.

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