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THE ADSORPTION OF SCN^- IONS ON MERCURY ELECTRODE FROM H_2O -ACETONE SOLUTIONS

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The adsorption of inorganic ions on mercury electrodes has been widely studied in recent years, not only from aqueous but also from organic solvent solutions. However, there are only few papers on adsorption from H_2O -organic solvent mixtures¹⁻³. This problem, interesting theoretically, has got also some practical importance in view of analytical applications of the double layer capacity measurements. The capacity changes have been used for detection of isomers of surface-active substances separated chromatographically with use of clathrate sorbents^{4,5}. This method requires adjusting of the separating properties of the chromatographic system with the content of organic solvent in the mobile phase.

The subject of this work is the influence of additions of acetone on the adsorption of thiocyanate ion on mercury electrode. The choice of the system studied was dictated by its significance in clathrate chromatography. The adsorption of SCN^- from aqueous solutions has been studied earlier by several authors⁶⁻¹⁰.

EXPERIMENTAL

The double-layer capacity data were obtained from impedance measurements of the dropping mercury electrode after 4 s. of the drop growth, using a Schering-type bridge, as previously¹¹. The frequency used was ca 800 c.p.s. At low SCN^- concentrations the measurements at several frequencies have been performed and the results have been found to be frequency independent.

The working anode was the mercury pool, the reference electrode aqueous 1M-NaCl calomel electrode. The zero charge potentials were measured with a streaming mercury electrode. The surface tension was measured with a conventional capillary electrometer with an accuracy of 0.2 dyne cm^{-1} . The reproducibility was $0.5-1 \text{ dyne cm}^{-1}$. All measurements were performed at 25°C .

Analytical grade reagents were used, acetone was purified by fractional distillation, water was twice distilled from alkaline KMnO_4 . Polarographically pure mercury was used. Air was removed from the solutions with hydrogen. Before introducing into the cell hydrogen was bubbled twice through the H_2O -acetone mixture at 25°C of the composition used in the experiment. Otherwise time dependent results were obtained.

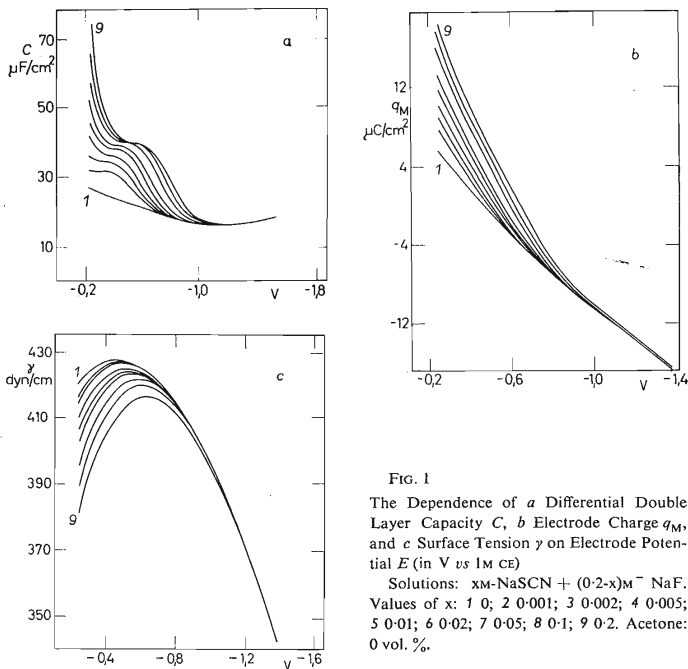


FIG. 1

The Dependence of *a* Differential Double Layer Capacity *C*, *b* Electrode Charge q_M , and *c* Surface Tension γ on Electrode Potential *E* (in V vs 1M CE)

Solutions: $x\text{M-NaSCN} + (0.2-x)\text{M}^- \text{NaF}$. Values of *x*: 1 0; 2 0.001; 3 0.002; 4 0.005; 5 0.01; 6 0.02; 7 0.05; 8 0.1; 9 0.2. Acetone: 0 vol. %.

RESULTS

To investigate the specific adsorption of SCN^- ions the method of Hurwitz¹² and Dutkiewicz and Parsons¹³ has been applied.

The series of solutions of x M-NaSCN + $(0.2-x)$ M-NaF in H_2O -acetone mixtures have been investigated. Acetone concentrations were 0, 2, 5, 10, 20 vol.%. If it is assumed that F^- ion is not specifically adsorbed and that activity coefficients of both salts are equal, surface excesses of spe-

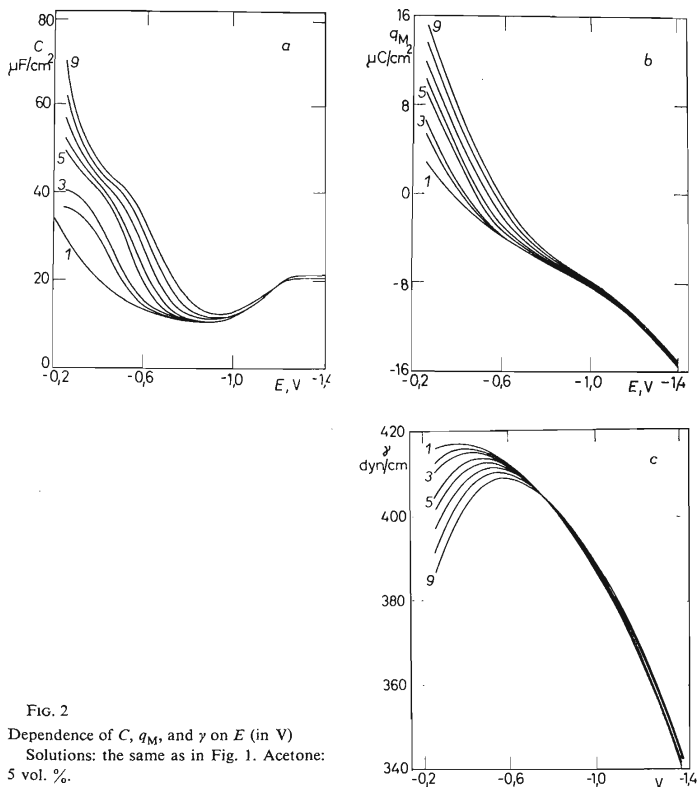


FIG. 2

Dependence of C , q_M , and γ on E (in V)

Solutions: the same as in Fig. 1. Acetone: 5 vol. %.

cifically adsorbed SCN^- ions q_1 are obtained by either of two methods: differentiation of surface tension γ at constant potential E , or of the Parsons function $\xi = \gamma + q_M E$ (ref.¹³) at constant electrode charge q_M , in respect to $RT \ln x$.

For all solutions the double layer capacity C vs potential E curves and zero charge potentials

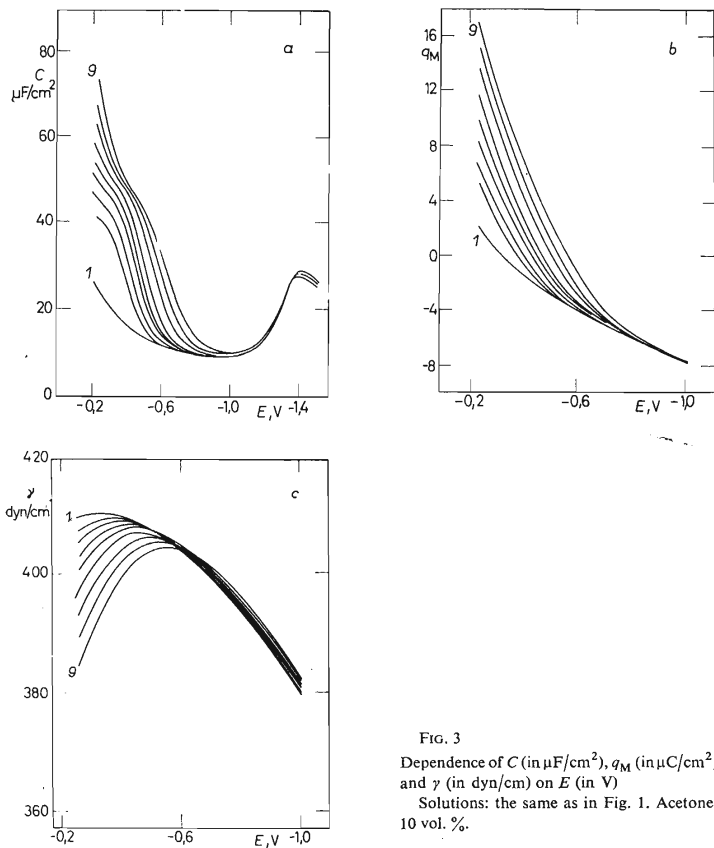


FIG. 3
Dependence of C (in $\mu\text{F}/\text{cm}^2$), q_M (in $\mu\text{C}/\text{cm}^2$) and γ (in dyn/cm) on E (in V)
Solutions: the same as in Fig. 1. Acetone: 10 vol. %.

E^z have been measured. The capacity curves have been numerically integrated to get the electrode charge vs potential curves, using $q_M = 0$ at E^z as the integration constant.

In order to get the surface tension γ vs potential curves the second integration has been performed. In the case of aqueous solutions and of 20% acetone the sets of curves for different SCN^- concentrations overlap at negative potentials. So it was justified to use the method of back integration, assuming the experimentally found value of 346 dyn/cm at -1.4 V for all aqueous

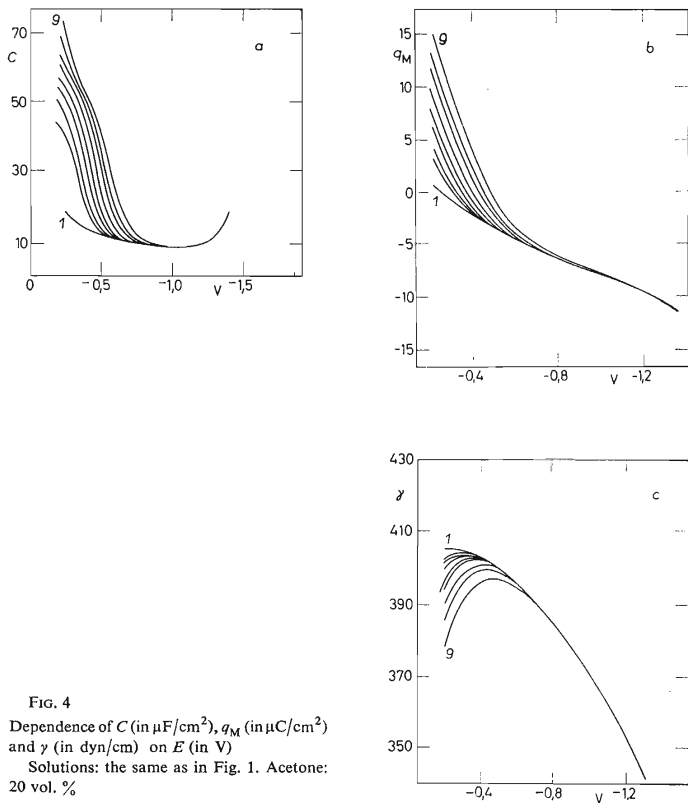


FIG. 4

Dependence of C (in $\mu F/cm^2$), q_M (in $\mu C/cm^2$) and γ (in dyn/cm) on E (in V)

Solutions: the same as in Fig. 1. Acetone: 20 vol. %

solutions and 335 dyne/cm for 20% acetone solutions. At other acetone concentrations the surface tension values at electrocapillary maximum were measured and used as integration constants. To check the agreement between the integrated curves and electrocapillary data several complete $\gamma-E$ curves have been measured. The result was in most cases satisfactory — the deviations were less than 1 dyne cm^{-1} .

The $C-E$, q_M-E and $\gamma-E$ curves for 0,5, 10 and 20% acetone solutions are shown in Figs 1–4. The double layer capacity at the minimum gets lower with acetone concentration, and the adsorption — desorption peak of acetone is shifted towards more negative potentials. The hump produced by SCN^- ions in aqueous solutions becomes much less pronounced in H_2O -acetone mixtures. The capacity values on the side of high positive electrode charge are higher in acetone containing solutions in the presence of SCN^- ions than in water. Accessible for experiments positive electrode charges are lower in H_2O -acetone solutions than in water. The potential range is limited by anodic dissolution of mercury. The potential of zero charge measured vs. aqueous 1M calomel electrode is shifted towards less negative potentials on addition of acetone. In the case of NaF in 20% acetone solution the zero charge potential can be hardly reached. This is visible as well on q_M-E as on $\gamma-E$ curves.

In all solutions the zero charge potential E^z is shifted with increasing SCN^- concentration towards more negative potentials. This is graphically represented in Fig. 5. At the assumptions made, the changes of potential measured vs. aqueous 1M calomel electrode are equal to those referred to the electrode reversible to the cation. The slope $(F/RT)(\partial E^z/\partial \ln c_{\text{SCN}^-})$ (the E -Stern-Markov coefficient) at the highest SCN^- concentrations is 1.45 ± 0.1 independent of acetone content in good agreement with the value found by Minc and Andrzejczak for aqueous solution⁹. It is also similar to the $(\partial q_1/\partial q_M)_x$ value in 0.2M-NaSCN at low electrode charge.

Surface excess of specifically adsorbed SCN^- ions q_1 were found by graphical differentiation

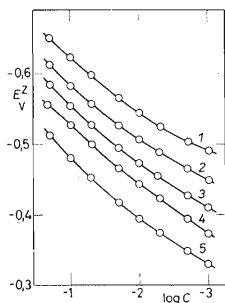


FIG. 5

Zero Charge Potential E^z vs. $\log c_{\text{SCN}^-}$ for Solutions of Various Acetone Concentrations

1 0; 2 2; 3 5; 4 10; 5 20 vol. % acetone.

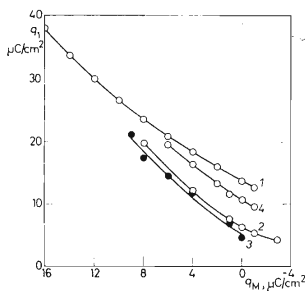


FIG. 6

The Dependence of Specifically Adsorbed SCN^- q_1 on Electrode Charge q_M

0.1M-NaSCN + 0.1M-NaF in acetone solution containing: 1 0; 2 5; 3 10; 4 20 vol. % acetone.

of γ vs $RT \ln c_{\text{SCN}^-}$ plot at constant potential and/or of ξ vs $RT \ln c_{\text{SCN}^-}$ plot at constant electrode charge. The accuracy of the results was estimated to be c. 10%. The dependence of q_1 on q_M for 0.1M-NaSCN, 0.1M-NaF in 0, 5, 10, 20% acetone is shown in Fig.6. At high positive electrode charge the value of $(\partial q_1 / \partial q_M)_x$ increases and so does the slope of E vs $\ln c_{\text{SCN}^-}$ at constant q_M . As pointed out by Dojlido, Ivanova and Damaskin¹⁴ the experimentally found validity of the equation

$$\left(\frac{\partial E}{\partial \ln c_{\text{SCN}^-}} \right)_{q_M} = \frac{RT}{F} \left(\frac{\partial q_1}{\partial q_M} \right)_x$$

can be regarded as a proof of the equality of the activity coefficients of both salts NaF and NaSCN. This equation is not well fulfilled at lower SCN^- concentrations.

DISCUSSION

It follows from our results that acetone influences significantly the adsorption of SCN^- ions and *vice versa*. In the investigated acetone concentration range q_1 is always lower than in aqueous solutions, as well in the case of constant electrode charge, as at constant potential. Several q_1 -% acetone curves are shown in Fig. 7. It is seen that the surface excess of SCN^- ions specifically adsorbed at mercury electrode of zero charge goes through a minimum at 10% acetone, and again increases at 20% acetone. This may be qualitatively explained as follows. The solution layer at the electrode may be regarded as the surface phase of the composition different from that of the bulk. One of the important factors which should determine specific adsorption from mixed solvents is the influence of organic solvent content on the chemical potential of the investigated surface-active agent. As a rule, the mole fraction of organic solvent in the surface phase increases strongly at low bulk concentrations, approaches unity, and then undergoes only slight changes at further increase of the bulk concentration. Therefore, at low

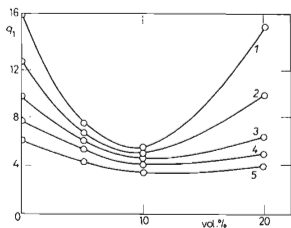


FIG. 7

Amount of Specifically Adsorbed SCN^- , q_1 ($\mu\text{C}/\text{cm}^2$), at E^z as a Function of Concentration of Acetone

Values of x : 1 0.2; 2 0.1; 3 0.05; 4 0.02; 5 0.01.

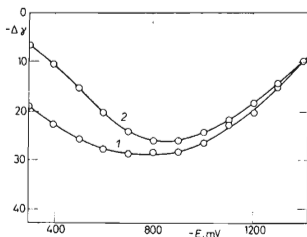


FIG. 8

The Lowering of Surface Tension (dyn/cm) of Mercury Electrode in Solutions of 0.2M-NaF (curve 1) and 0.2M-NaSCN (curve 2) Caused by Changing the Solvent Composition from Pure H_2O to 20 vol.% Acetone

increasing bulk concentrations of organic solvent the partition of the investigated substance between the bulk and the surface phase enhances or diminishes its adsorption in dependence on whether the chemical potential of this substance decreases or increases.

At further increase of the bulk concentration of organic solvent, when the surface phase is nearly saturated, the difference of solvent composition in both phases diminishes, and the large initial effect should decrease. Therefore, in the case when partition between the bulk and surface phases favours that enriched in organic solvent, the adsorption of the investigated substance should initially increase and then decrease with the increasing bulk concentration of the solvent; in the opposite case the effect should be opposite — the adsorption may go through a minimum, as observed in the case described in this paper.

Additionally, the competition of the investigated substance and of the solvent at the surface should be considered. The competition should always diminish the adsorption, according to classical theories of localized adsorption following the Langmuir type isotherms. In our case the effect of SCN^- on acetone adsorption may be explained by competition effects. As shown in Fig. 8 the surface tension at the mercury electrode-solution interface is lowered much stronger by acetone in NaF than in NaSCN solutions. This effect of SCN^- ions is visible only within the potential range of their specific adsorption.

It should be mentioned that our q_1 values for 0.2M-NaSCN calculated from the set of measurements at constant ionic strength are considerably higher (c. 40%) than the values of q_1 obtained by Wróblowa, Kovač and Bockris⁸, Parsons and Symens¹⁰ and by Minc and Andrzejczak⁹ from experiments with pure NaSCN or KSCN solutions. This discrepancy was observed in spite of good agreement of our surface tension data for 0.2M-NaSCN with those interpolated from the data of other authors.*

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