In our investigations the interactions between solvent molecules and ions as well as the intraionic and intramolecular interactions of ions and molecules have been considered at a mercury electrolyte solution interface.

The effect was studied of geometric isomerism and intramolecular rotational isomerism of fumarate, maleate, succinate and 1,2-dihalogenoderivates of ethane on solvent structure and electric permittivity at an electrode electrolyte interface.

The molecular and intramolecular interactions in the electrical double layer region were investigated using both experimental and theoretical methods. The differential capacities measured by bridge method as a function of applied potential at presence of molecules and ions under investigation, were analysed theoretically.

Our investigations lead us to the conclusion that some experimental observations concerning some electrical properties of an interface region can be explained as specific molecular interaction.

Solute–Solvent Interactions and Double Layer Effects. Adsorption of Hexafluoropropan-2-ol on Hg

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The need to enlarge the extent of the thermodynamic analysis on the state of the solutes involved in adsorption phenomena at electrified interfaces has been already underlined [1].

Attention has been consequently given to the system hexafluoropropan-2-ol (HFIPA)–Na_2SO_4–H_2O/Hg electrode, in order to study the interfacial behaviour of fluorinated compounds, HFIPA in particular, whose unusual behaviour in aqueous solution is known (*see e.g.* [2]). The possible interactions in solution, between solutes and solvent, in the above system, which can result in a more or less marked influence on the activity of both organic and inorganic solute are analyzed: *a*) through e.m.f. measurements of galvanic cells without transport; *b*) by means of non electrochemical techniques as density and calorimetric measurements. For sake of comparison parallel measurements are performed on the totally hydrogenated isomer iPrOH. Condition are selected in order to keep Na_2SO_4 activity constant with varying HFIPA concentration. Parallel series of electrocapillary and differential capacity measurements on Hg electrode are performed on solutions of HFIPA respectively at $a_{Na_2SO_4}$ and $C_{Na_2SO_4}$ constant. The whole of the experimental results is analyzed and discussed mainly in terms of significance of the adsorption isotherm obtained in both cases, prior to entering more deeply into detailed questions as to congruence problems or to considering a detailed picture of double layer structure and composition.

References

1 H. Nakadomari, D. M. Mohilner and P. R. Mohilner, *J. Phys. Chem., 80,* 1761 (1976).
2 J. Murto, A. Kivinen *et al., Suomen Kemistilehti, 40,* 250 (1967); *ibid., 40B,* 258 (1967); *ibid., B40,* 298 (1967).

On the Inhibitory Effect of Normal Aliphatic Alcohols upon Cd^{2+}, $Pb(OH)_3^-$ and Bi^{3+} Electroreductions on Mercury at High Surface Coverages

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A detailed investigation of the inhibitory effect of normal aliphatic alcohols, from n-butanol to n-octanol, upon Cd^{2+} and Bi^{3+} reductions and $Cd^\circ(Hg)$ oxidation in perchloric medium, as well as upon $Pb(OH)_3^-$ reduction and $Pb^\circ(Hg)$ oxidation in (NaF + NaOH) mixtures, was carried out at different ionic strengths on dropping mercury and amalgam electrodes. Experiments were conducted under conditions in which the coverage θ of the electrode surface by the surface-active alcohols is almost complete ($\theta \cong 1$). The experimental values of the ratio ($k_{\theta=1}/\kappa_{\theta=0}$) of the rate constant for the electrode reaction at high surface coverages to the corresponding rate constant in the absence of the alcohols, were compared with a theoretical expression of the form [1]

$$k_{\theta=1}/k_{\theta=0} = (c_S^*/c_W^*)^{-n_{\neq}/n_S}$$

$$\exp(n_{\neq}\Delta G^\circ_{ads}/n_S RT)\exp(-cn_{\neq}\Delta G_{lat}/RT) \qquad (1)$$

Here c_S^* and C_W^* are the bulk concentrations of the alcohol(S) and of water (W), $n_{\neq}$ and n_S are the numbers of adsorbed water molecules displaced from the electrode surface by one adsorbing particle of the activated complex for the electrode reaction ($\neq$) and by one adsorbing molecule of the surfactant S, respectively, and ΔG°_{ads} is the standard free energy