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

FERNANDO PULIDORI*, GIANNA BORGHESANI, RODOLFO PEDRIALI and ROSARIO CANNOLETTA

Institute of Chemistry, University of Ferrara, Italy

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

G. PEZZATINI, M. L. FORESTI and R. GUIDELLI

Institute of Analytical Chemistry, University of Florence, Florence, Italy

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 ($k_{\theta=1}/k_{\theta=0}$) 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]

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

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

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 of adsorption of S. Moreover, c is the coordination number in the adsorbed monolayer and ΔG_{lat} measures the energy involved in the process

$$\mathrm{S{-}S} + \mathrm{W} \neq \rightarrow \mathrm{W{-}S} + \neq - \mathrm{S}$$

where the hyphen denotes lateral interactions between contiguous particles in the adsorbed monolayer. The derivation of eqn. (1) relies on the following assumptions: (*i*) the activated complex for the electrode reaction is specifically adsorbed and is the same independent of whether it is formed by displacement of adsorbed solvent molecules or of adsorbed surfactant molecules; (*ii*) the theory of absolute reaction rates applies; (*iii*) the surfactant is adsorbed under equilibrium conditions. The expression for ΔG_{lat} depends both on the particular model of the adsorbed monolayer and on the particular mechanical statistical treatment of this model.

For all systems investigated the quantity ($\mathrm{c}n_{\neq}\,\Delta G_{\mathrm{lat}}/\mathrm{RT}$) turns out to be notably positive. This behaviour can be explained by the ability of adsorbed water molecules to establish strong ion–dipole interactions – and, possibly, further interactions of a more specific nature – with the charged activated complex, no such strong interactions with this complex being established by adsorbed aliphatic molecules.

The experimental dependence of $\mathrm{k}_{\theta=1}$ for $\mathrm{Pb(OH)_3^-}$ and $\mathrm{Bi^{3+}}$ reduction and for $\mathrm{Pb^{\circ}(Hg)}$ oxidation upon the bulk concentration of n-butanol, under certain experimental conditions, suggests a gradual passage from the mechanism previously outlined to an alternative mechanism in which the rate determining step involves the tunnelling of the transferring electron for the $\mathrm{Me(II)} + \mathrm{e} \rightleftharpoons \mathrm{Me(I)}$ charge-transfer step, across the adsorbed monolayer of the alcohol. This gradual passage takes place as the n-butanol bulk concentration is progressively decreased.

The dependence of the rate constant $k_{\theta=1}$, suitably corrected for diffuse-layer effects, upon the applied potential in the presence of the various normal aliphatic alcohols, is in qualitative agreement with an expression which accounts for the progressive increase in the compact-layer thickness with an increase in the length of the hydrocarbon chain.

Reference

1 R. Guidelli, M. L. Foresti and M. R. Moncelli, 'On the Inhibitory Effect of Neutral Organic Surfactants upon Simple Electrode Reactions at High Surface Coverages', *J. Electroanal. Chem.*, submitted.

Solvent Effect on the Electrode Reduction Mechanism of Phenyl Substituted Ethylenes

G. FARNIA, G. SANDONÁ, M. G. SEVERIN and E. VIANELLO

Institute of Physical Chemistry, University of Padua, Padua, Italy

This communication presents some preliminary results on the electrochemical reduction of tri- and tetraphenylethylenes in dimethylformamide (DMF) and hexamethylphosphoramide (HMPA), as part of a more extensive study on the correlation between kinetic and thermodynamic properties of radical anions and electrode reaction mechanism of the parent molecules.

Triphenylethylene (ϕ_3E)

Cyclic voltammetry of ϕ_3E in DMF with 0.1 *M* TBAP as supporting electrolyte shows two reversible reduction peaks, corresponding to the formation of the anion radical ($\mathrm{R} + \mathrm{e} \rightleftharpoons \mathrm{R}^{\overline{\cdot}}$) and of the dianion ($\mathrm{R}^{\overline{\cdot}} + \mathrm{e} \rightleftharpoons \mathrm{R}^{=}$), provided the solvent is carefully anhydrified, the last traces of water being eliminated by addition of alumina or molecular sieves directly into the cell. Traces of $\mathrm{H_2O}$, in fact, cause the irreversibility of the second reduction peak (disappearance of the corresponding anodic peak) even at a scan rate of 400 V $\mathrm{sec^{-1}}$. Further addition of $\mathrm{H_2O}$ affects also the reversibility of the first reduction peak, which increases in height giving eventually a single irreversible two-electron peak.

Macroscale electrolysis in the presence of $\mathrm{H_2O}$ yields quantitatively triphenylethane.

The anion radical $\mathrm{R}^{\overline{\cdot}}$, stable in absence of proton donors, undergoes a relatively slow decay in the presence of $\mathrm{H_2O}$ at low temperatures (–30 °C) according to the following mechanism:

$$2\,\mathrm{R}^{\overline{\cdot}} \underset{\mathrm{k_{-d}}}{\overset{\mathrm{k_d}}{\rightleftharpoons}} \mathrm{R} + \mathrm{R}^{=} \qquad (1)$$

$$\mathrm{R}^{=} \xrightarrow[\mathrm{HS}]{\mathrm{k_p}} \mathrm{RH_2} \qquad (2)$$

HS being the proton donor. Holding for $\mathrm{R}^{=}$ the stationary state hypothesis the decay rate of $\mathrm{R}^{\overline{\cdot}}$ results $-\mathrm{dC_{R^{\overline{\cdot}}}/dt} = 2\mathrm{k'_p k_d C^2_{R^{\overline{\cdot}}}}/(\mathrm{k'_p} + \mathrm{k_{-d}C_R})$ with $\mathrm{k'_p} = \mathrm{k_pC_{HS}}$. This results in a second order reaction when $\mathrm{C_R} \gg \mathrm{C_{R^{\overline{\cdot}}}}$, so that $\mathrm{C_R}$ is practically constant. Values of $\mathrm{k_d}$, $\mathrm{k_{-d}}$ and $\mathrm{k'_p}$ can thus be obtained, the equilibrium dismutation constant having been derived from the peak potential separation. On the other hand, for $\mathrm{k_{-d}C_R} \ll \mathrm{k'_p}$ one has $-\mathrm{dC_{R^{\overline{\cdot}}}/dt} = 2\mathrm{k_dC^2_{R^{\overline{\cdot}}}}$. These conditions, which can be realised at higher temperatures in voltammetric conditions,