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Electrocapillary Curves of Concentrated Solutions of Acids

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For dilute solutions of acids, the adsorption of the anion ($\Gamma_{A'}$) and of the cation ($\Gamma_{H\cdot}$) may be calculated from the values of the shift of the cathodic and anodic branches of the electrocapillary curve upon a change in the composition of the solution according to the familiar formula[1]:

$$\left(\frac{\partial\varphi}{\partial\mu_{H\cdot}}\right)_{\sigma} = \frac{1}{F}\frac{\Gamma_{H\cdot} + \Gamma_{A'}}{\Gamma_{H\cdot} - \Gamma_{A'}} \tag{1}$$

in conjunction with Lippmann's equation

$$\left(\frac{\partial\sigma}{\partial\varphi}\right)_{\mu_{H\cdot}} = -\varepsilon = -F(\Gamma_{A'} - \Gamma_{H\cdot}), \tag{2}$$

where $\mu_{H\cdot}$ is the chemical potential of the hydrogen ion, φ—the potential difference between the electrode and the solution and σ the interfacial tension at the interface electrolyte-mercury.

For this calculation, the measurements are carried out with respect to some constant auxiliary electrode (for example, a normal calomel electrode).

Lippmann's equation holds for any concentrations, but the first equation is not applicable to concentrated solutions, since in this case neither the value of φ nor that of $\mu_{H\cdot}$ can be determined,

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1 See Frumkin, „Electrocapillary Phenomena and Electrode Potentials" (Russ.), p. 138 (1919). Gouy, Ann. physique, (9) **7**, 129 (1917). Frumkin, Z. physik. Chem., **103**, 55 (1922).

the former owing to the impossibility of completely eliminating the diffusion potential between the auxiliary electrode and the concentrated solution, and the latter because of the impossibility of determining the individual activity coefficients in concentrated solutions. However, it is not difficult to derive an equation which would hold for any concentration of the acid. In order to obtain the data for which the calculations could be carried out the electrocapillary curves should be measured with respect to a reversible electrode in the same solution — for example, to a hydrogen electrode or an electrode of the second kind (in the case of HCl — a calomel electrode).

If we denote by φ_r the potential with reference to a hydrogen electrode in the same solution, by $\Gamma_{Hg_2A_2}$ the adsorption of the mercury salt, by Γ_{HA} the adsorption of the acid and by $\mu_{Hg_2A_2}$ and μ_{HA} the chemical potentials of these substances, where A is the anion of the acid, then the equation of Gibbs as applied to the mercury-solution interface will assume the following form (the adsorption of water is by definition assumed to be zero):

$$d\sigma = -\Gamma_{Hg_2A_2}\, d\mu_{Hg_2A_2} - \Gamma_{HA}\, d\mu_{HA}. \tag{3}$$

At the potential of the reversible hydrogen electrode, a condition of equilibrium is preserved on the mercury surface for the reaction:

$$H_2 + Hg_2A_2 = 2Hg + 2HA$$

from which

$$(\mu_{H_2})_0 + \mu_{Hg_2A_2} = 2\mu_{HA} + \text{const.},$$

where $(\mu_{H_2})_0$ is the thermodynamic potential of hydrogen at atmospheric pressure. Such a relation will also exist at any other potential, but instead of $(\mu_{H_2})_0$, the quantity μ_{H_2} will appear, which corresponds to the pressure of hydrogen that can exist in equilibrium with an electrode polarized to a given potential φ_r:

$$\mu_{H_2} + \mu_{Hg_2A_2} = 2\mu_{HA} + \text{const.}$$

Since

$$\varphi_r = \frac{1}{2F}\left[\mu_{H_2} - (\mu_{H_2})_0\right],$$

from the condition $\varphi_r = \text{const.}$ it follows that $\mu_{H_2} = \text{const.}$ Therefore, at constant φ_r,

$$d\mu_{Hg_2A_2} = 2d\mu_{HA}. \tag{4}$$

If we substitute equation (4) into (3), we obtain

$$-\left(\frac{\partial\sigma}{\partial\mu_{HA}}\right)_{\varphi_r} = 2\Gamma_{Hg_2A_2} + \Gamma_{HA},$$

but $2\Gamma_{Hg_2A_2} + \Gamma_{HA} = \Gamma_{A'}$, where $\Gamma_{A'}$ is the total adsorption of the anion, from which

$$\Gamma_{A'} = -\left(\frac{\partial\sigma}{\partial\mu_{HA}}\right)_{\varphi_r}. \tag{5}$$

Further, Lippmann's equation may be written in the form:

$$\frac{1}{F}\left(\frac{\partial\sigma}{\partial\varphi_r}\right)_{\mu_{HA}} = -\frac{\varepsilon}{F} = -(\Gamma_{A'} - \Gamma_{H\cdot}). \tag{2a}$$

From equations (2a) and (5) we obtain:

$$\left(\frac{\partial\varphi_r}{\frac{1}{F}\,\partial\mu_{HA}}\right)_{\sigma} = -\frac{\Gamma_{A'}}{\Gamma_{A'} - \Gamma_{H\cdot}}. \tag{6}$$

Making use of equations (2a) and (6), the values of $\Gamma_{A'}$ and $\Gamma_{H\cdot}$ may be easily calculated from the electrocapillary curves. The adsorption of the anion may be calculated also with the help of equation (5) from the change in σ with the concentration at $\varphi_r = \text{const.}$

For dilute solutions, we have

$$d\mu_{HA} = 2d\mu_{H\cdot} \quad \text{and} \quad d\varphi_r = d\varphi - \frac{1}{F}\,d\mu_{H\cdot}.$$

Substituting these relations into equation (6) we get:

$$\frac{1}{2}\left(\frac{\partial\varphi_r}{\partial\mu_{H\cdot}}\right)_{\sigma} = \frac{1}{2}\left(\frac{\partial\varphi}{\partial\mu_{H\cdot}}\right)_{\sigma} - \frac{1}{2F} = -\frac{1}{F}\,\frac{\Gamma_{A'}}{\Gamma_{A'} - \Gamma_{H\cdot}}$$

which is identical to equation (1).

Further, it will be noted that if the measurements in concentrated solutions of acids are carried out not with respect to a hydrogen electrode, but to an electrode of the second kind (Hg, Hg_2A_2 in the same solution), the calculation of the adsorption may be most conveniently made by means of an equation which is easily obtained from equation (3):

$$\Gamma_{HA} = \Gamma_{H^+} = -\left(\frac{\partial \sigma}{\partial \mu_{HA}}\right)_{\varphi_{Hg_2A_2}},$$

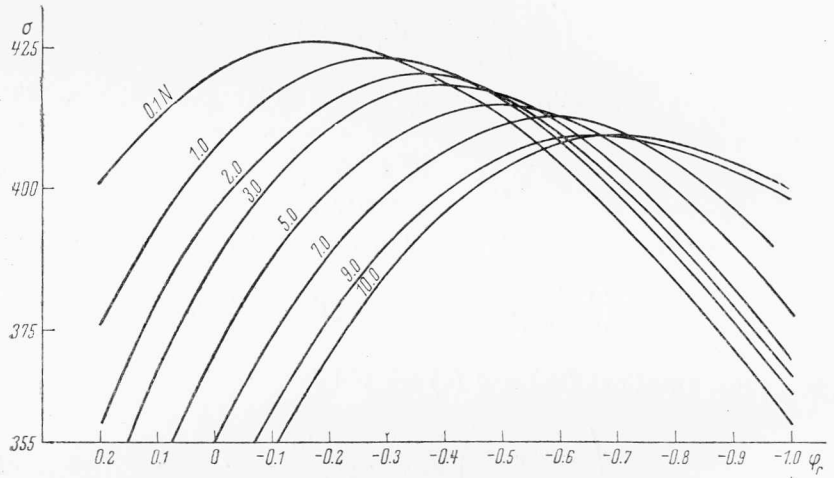

Fig. 1.
Electrocapillary curves for HCl solutions measured with reference to a hydrogen electrode in the same solution.

where $\varphi_{Hg_2A_2}$ is the potential measured with the help of the electrode of the second kind, as the condition $\varphi_{Hg_2A_2} = \text{const.}$ is equivalent to the condition $\mu_{Hg_2A_2} = \text{const.}$ In practice, the use of a hydrogen electrode in concentrated solutions of acids is, however, much more convenient than the use of electrodes of the second kind.

Table 1

c	0.1 N	1 N	2 N	3 N	5 N	7 N	9 N	10 N
$(\varphi_{max})_r$	—0.185	—0.293	—0.355	—0.407	—0.495	—0.595	—0.670	—0.710
σ_{max}	425.7	423	420.7	418.1	414.6	412	408.7	409.3

By way of an example of the application of the equations derived above, we may quote the results of calculation of the adsorption of ions in concentrated solutions of hydrochloric acid, making use of the electrocapillary curves shown in Fig. 1. These curves (for 0.1; 1.0; 2.0; 3.0; 5.0; 7.0; 9.0 and 10.0 N HCl) were obtained with respect to hydrogen electrodes in the same solutions. Table 1 shows data for the values of $(\varphi_{max})_r$ and σ_{max} for all these

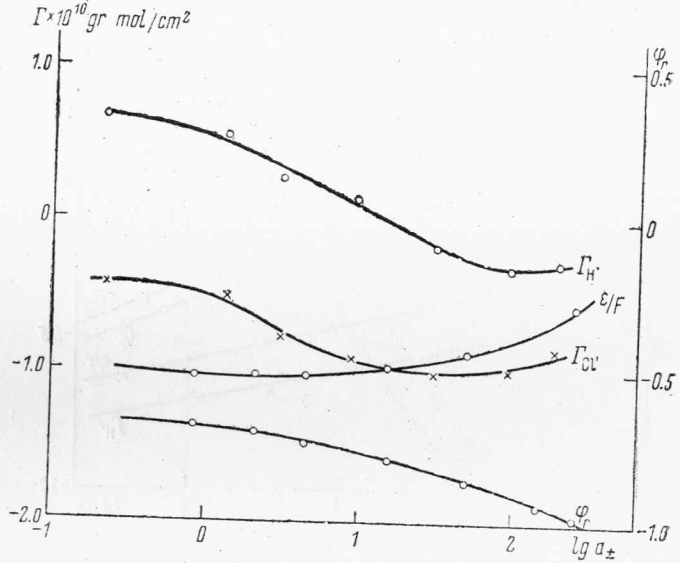

Fig. 2.
$\Gamma_{Cl'}$, Γ_{H^+}, ε/F and φ_r at $\sigma = 400$ dynes/cm. on the descending branch of the electrocapillary curve, as functions of $\lg a_{\pm}$.

solutions, which determine the position of the maxima of the electrocapillary curves.

The results of calculations of Γ_{H^+} and $\Gamma_{Cl'}$ obtained with the help of equations (2a), (5), and (6), for potentials corresponding to a value of σ equal to 400 dynes/cm. and for various concentrations, are represented in the form of curves, Γ_{H^+} *vs.* $\lg a_{\pm}$ and $\Gamma_{Cl'}$ *vs.* $\lg a_{\pm}$ in Fig. 2 (for the cathodic branch of the electrocapillary curve) and in Fig. 3 (for the anodic branch of the electrocapillary curve). In the same figures are given the potentials φ_r to which the calculated values of the adsorption correspond. As is evident from an examination of the curves of Fig. 2, for low concentra-

tions on the cathodic branch, the value of Γ_{H^+} is positive, while the value of $\Gamma_{Cl'}$ is negative, as was to be expected. With an increase in the concentration, the total negative adsorption of the ions is superimposed on the electrostatic adsorption, so that the value of Γ_{H^+} decreases, passes through zero, and then becomes negative, while the value of $\Gamma_{Cl'}$ becomes still more negative. In the most concentrated solutions, the negative value of $\Gamma_{Cl'}$ again falls somewhat owing to the approach of the chosen value of σ to the maximum of the electrocapillary curve.

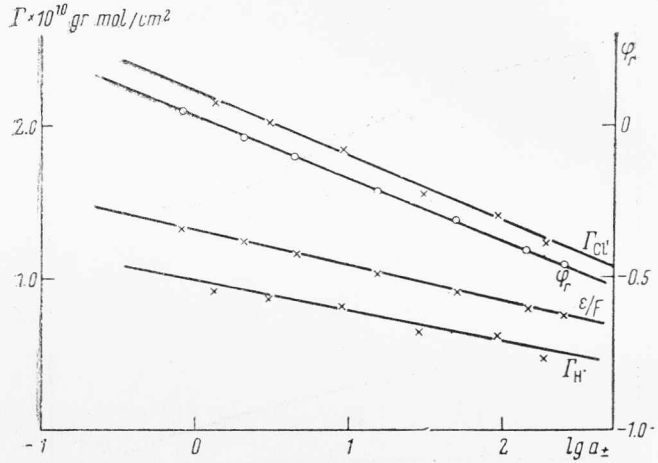

Fig. 3.
$\Gamma_{Cl'}$, Γ_{H^+}, ε/F and φ_r at $\sigma = 400$ dynes/cm. on the ascending branch of the electrocapillary curvre as functions of lg $a_{\pm}$.

On the anodic branch (Fig. 3), on account of the strong specific adsorption of the chlorine ion, the value of $\Gamma_{Cl'}$ is throughout positive and exceeds the surface charge, so that Γ_{H^+} is also positive. With increasing concentration, owing to the approach to the maximum, these values decrease. Finally, at the maximum, as can be seen from the position of the electrocapillary curves (see Fig. 1), the values of Γ_{H^+} and $\Gamma_{Cl'}$ are positive up to a definite concentration, then pass through zero, and finally become negative. This transition from positive to negative adsorption at high concentrations is often observed in the case of the adsorption of electrolytes[2].

[2] B. Bruns a. A. Frumkin, Z. physik. Chem., **147**, 125 (1930).

It is also of interest to follow the change in adsorption of each ion with change of polarization. To characterize this dependence, in Fig. 4 are presented data for $C = 3N$ and $C = 10N$ in the form of curves Γ_{H^+} *vs.* φ_r and $\Gamma_{Cl'}$ *vs.* φ_r. As is evident from this figure, $\Gamma_{Cl'}$, from a positive value on the anodic branch, passes through zero

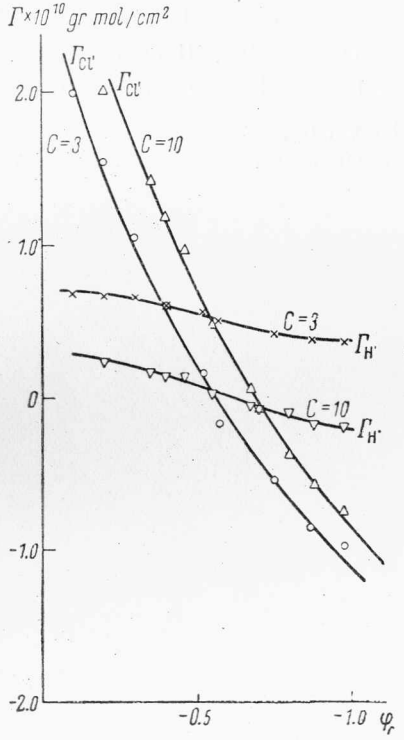

Fig. 4.
$\Gamma_{Cl'}$ and Γ_{H^+} as functions of φ_r for $C = 3N$ and $C = 10N$ HCl.

and reaches a considerable negative value on the cathodic branch. The positive adsorption of Cl′ is observed also along a part of the cathodic branch of the curve, *i. e.*, $\Gamma_{Cl'}$ is within certain limits positive at potentials more negative than φ_{max}, with the exception of only of the highest concentration (10 *N*). [$(\varphi_{max})_r$ for 3 *N* is — 0.407 V and for 10 *N* — 0.710 V]. Γ_{H^+}, owing to the strong specific adsorption of the anion in not very concentrated solutions, is positive

throughout the whole curve, while in concentrated solutions, as has already been pointed out, it passes over to a negative value. Here an apparently paradoxical result is obtained: the cation is adsorbed positively on the ascending branch of the electrocapillary curve, and negatively on the descending one.

In the russian version of this paper[3] there are presented electrocapillary curves and calculations of the adsorption of the anion and cation for concentrated solutions of hydrobromic and sulphuric acids, which confirm the results obtained with hydrochloric acid.

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[3] A. Frumkin a. S. Jofa, J. Phys. Chem. (Russ.), in print.