My first meeting with A.N. Frumkin

$\Delta t = 37$ years
My first teacher: Dr. Ol’ga I. Vorob’eva
My first supervisor:
Prof. Nina V. Nikolaeva-Fedorovich
Prof. Tatyana A. Kryukova

1953
My first topic, already in a new building of the Faculty of Chemistry:

\[
S_2O_8^{2-} + 2e^- = 2SO_4^{2-}
\]

Adsorption of inorganic cations

Peculiarities of weak ionic adsorption

Unfortunately I had no Fr+...
Lectures on physical chemistry and electrochemistry in Moscow University

Professor
Alexander N. Frumkin

A.N. Frumkin, V.S. Bagotsky, Z.A. Iofa, B.N. Kabanov,
Kinetics of the Electrode Processes,
Moscow, 1952
A.N. Frumkin, V.S. Bagotsky, Z.A. Iofa, B.N. Kabanov, 
Kinetics of the Electrode Processes,
Moscow, 1952

Our textbooks in Electrochemistry

Translated to Chinese, Portugal, and Spanish

Fast progress of electrochemistry in China?
Three famous soviet scientists answer the student’s question:

Mandel’shtam: Sorry, I gave you poor explanation, I shall propose something more simple and transparent;

Landau: If you are such a fool, I can repeat once again;

Frumkin: I do not understand how one can not understand it!
We were happy to become electrochemists during the period of active interest to adsorption phenomena at electrochemical interface....

R. Parsons, J.O’M. Bockris, other people of this fantastic generation....
A favorite technique: differential capacity

Fortunately I had La(III)…
**Frumkin adsorption isotherm**

\[
\beta c = \frac{\theta}{1 - \theta} \exp(-2a\theta)
\]  

(1)

- \(c\) - bulk concentration of organic substance;
- \(\theta\) - coverage of the electrode surface with organic substance;
- \(\beta\) - adsorption equilibrium constant
- \(a\) - parameter of lateral interaction

Different lateral interaction parameters:

- \(a = 4\)
- \(a = 2\)
- \(a = 1\)
- \(a = 0\)
- \(a = -2\)
Model of two parallel capacitors

- Scheme

- Electrode charge density

\[ \sigma = \sigma_0 (1 - \theta) + C_1 \theta (E_0 - E_N) \]  \hspace{1cm} (2)

\[ E_0 \] – electrode potential related to potential of zero charge (PZC) in the surface-inactive electrolyte;

\[ E_N \] – shift of PZC when switching from \( \theta = 0 \) to \( \theta = 1 \);

\[ \sigma_0 = \int_{0}^{E_0} C_0 dE \]
Model of two parallel capacitors

- Approximate Gibbs equation:

\[ d\gamma = -\sigma dE - RT \Gamma d\ln c \]  \hfill (3)

- Expression for \( \ln \beta \) as a function of \( E_0 \):

\[
\ln \beta = \ln \beta_0 - \frac{\Delta \gamma_0 + C_1 E_0 (E_N - E_0 / 2)}{RT \Gamma_m}
\]  \hfill (4)

\[ \Delta \gamma_0 = \int_{E_0}^{E_N} \sigma_0 dE \]  
(decrease of surface tension in supporting solution caused by deviation of potential from PZC)

- Decrease of surface tension due to adsorption of organic molecules at \( E_0 = \text{const} \):

\[ \Delta \gamma = -RT \Gamma_m [\ln(1 - \theta) + a\theta^2] \]  \hfill (5)
Electrocapillary curves of a mercury electrode in 1M NaCl solutions containing *tret-pentanol* additives:

1 - 0; 2 - 0.01; 3 - 0.05; 4 - 0.1; 5 - 0.2; 6 - 0.4 M

**Experimental data**

**Calculated**
Starting from 1960

Frumkin’s theory for interpreting differential capacity curves in solutions of aliphatic compounds

Five adsorption parameters \( (\beta_0, \ a, \ \Gamma_m, \ C_I, \ E_N) \)

- \( C_0, E_0 \)-curve in surface-inactive electrolyte solution
- Equations shown above

Expression for equilibrium differential capacity can be derived:

\[
C = C_0 (1 - \theta) + C_1 \theta + \frac{[\sigma_0 + C_1 (E_N - E_0)]^2 \theta(1 - \theta)}{RT \Gamma_m [1 - 2a\theta(1 - \theta)]}
\]

(6)
Experimental and simulated differential capacity curves, $a=\text{const}$

t-C$_5$H$_{11}$OH
$c=0.1\ \text{M}$ ;
$da/dE=0$. 

$C$, $\mu\text{F/cm}^2$

E, V
Lateral interaction parameter (“attraction coefficient”) vs. electrode potential

For an arbitrary dependence of \( a \) on \( E \):

\[
\ln \beta = \ln \beta_0 - \frac{\Delta \gamma_0 + C_1 E_0 (E_N - E_0 / 2)}{RT \Gamma_m} + (a_0 - a) \quad (7)
\]

\[
C = C_0 (1 - \theta) + C_1 \theta - RT \Gamma_m a \cdot \theta (1 - \theta) + \left[ \sigma_0 + C_1 (E_N - E_0) + RT \Gamma_m a'(1 - 2\theta) \right]^2 \theta(1 - \theta) \frac{RT \Gamma_m}{RT \Gamma_m[1 - 2a\theta(1 - \theta)]} \quad (8)
\]

where \( a_0 = a(E_0 = 0) \); \( a' = da/dE \); \( a'' = d^2a/dE^2 \)
Experimental and simulated differential capacity curves: linear $a, E$ - dependence

$t$-C$_5$H$_{11}$OH
$c=0.1$ M ;
$da/dE=0.46$ $V^{-1}$
Beyond the model of two parallel capacitors

• Parsons’ model

\[ E_0 = \frac{\sigma}{C_0} (1 - \theta) + \left( E_N + \frac{\sigma}{C_1} \right) \theta \] (9)

• Hansen’s model

\[ \sigma = (E_0 - E_N \theta) [C_0(1 - \theta) + C_1 \theta] \] (10)
Generalization

\[
\sigma = \frac{[C_0(1-\theta) + nC_1\theta]E_0 - nC_1E_N[k(1-\theta) + \theta]\theta}{1 + n\theta - \theta}
\]

(11)

- \(n = k = 1\): Frumkin’s model
- \(n = C_0/C_1; k = 1\): Parsons’ model
- \(n = 1; k = C_0/C_1\): Hansen’s model
Parameters $n$ and $k$ for aliphatic compounds

- **graphical analysis:**
  - parameter $n$ : $0.60 - 1.45$
  - parameter $k$ : $0.21 - 1.20$

- **regression analysis:**
  - $n = 1$ gives satisfactory agreement
  - parameter $k$ : $0.69 - 1.92$
Summary of 50-60ties period

Initiated by A.N. Frumkin

Translation edited by R. Parsons

Translation edited by K. Schwabe
Sorry for the quality of our old film…

Professor Frumkin and his fox-terrier Foma
Types of molecules we adsorbed (and enjoyed)
Coadsorption of two solution components.
Combination of two mixed Frumkin isotherms

\[ \sigma = \sigma_0 (1 - \theta_1 - \theta_2) + C_1 \theta_1 (E_0 - E_{N1}) + C_2 \theta_2 (E_0 - E_{N2}) \]  \hspace{1cm} (12)

\[ \beta_1 c_1 = \frac{\theta_1}{n_1 (1 - \theta_1 - \theta_2)^{n_1}} \exp \left( -2n_1 a_{11} \theta_1 - 2n_1 a_{12} \theta_2 \right) \]  \hspace{1cm} (13a)

\[ \beta_2 c_2 = \frac{\theta_2}{n_2 (1 - \theta_1 - \theta_2)^{n_2}} \exp \left( -2n_2 a_{22} \theta_2 - 2n_2 a_{12} \theta_1 \right) \]  \hspace{1cm} (13b)
One of the simplest equations in my life

\[
F(\theta_1, \theta_2) = \frac{\Delta G}{RT \Gamma_m} = -a_{11} \theta_1^2 - a_{22} \theta_2^2 - 2a_{12}\theta_1\theta_2 + \frac{\theta_1}{n_1} \ln\left(\frac{\theta_1}{n_1\beta_1c_1}\right) + \frac{\theta_2}{n_2} \ln\left(\frac{\theta_2}{n_2\beta_2c_2}\right) + (1 - \theta_1 - \theta_2) \ln(1 - \theta_1 - \theta_2) + \frac{\theta_1(n_1 - 1)}{n_1} + \frac{\theta_2(n_2 - 1)}{n_2}
\]  

(14)
\[ p_1 \left( \frac{\partial^2 F}{\partial \theta_1^2} \right)_{\theta_2} = \frac{1}{n_1 \theta_1} + \frac{1}{1 - \theta_1 - \theta_2} - 2a_{11} \quad (15a) \]

\[ p_2 \left( \frac{\partial^2 F}{\partial \theta_2^2} \right)_{\theta_1} = \frac{1}{n_2 \theta_2} + \frac{1}{1 - \theta_1 - \theta_2} - 2a_{22} \quad (15b) \]

**Conditions of extremum:**

\[ p_1 > 0, p_2 > 0 \quad \text{minimum} \]

\[ p_1 < 0, p_2 < 0 \quad \text{maximum} \]

\[ p_1 > 0, p_2 < 0 \quad \text{or} \quad p_1 < 0, p_2 > 0 : \text{saddle point} \]
$\theta_2$, $\theta_1$ relationships corresponding to two equations of mixed Frumkin isotherms
Models of two and three parallel capacitors taking into account diffuse part of the electrical double layer

\[ C_0(1 - \theta) \]

\[ C_1\theta \]

\[ C_{\text{dif}} \]

\[ C_0(1 - \theta_1 - \theta_2) \]

\[ C_1\theta_1 \]

\[ C_2\theta_2 \]

\[ C_{\text{dif}} \]
The most important applications

- Diluted electrolyte solutions.

- Ionic adsorption decreasing double layer capacity (systems like $x c \text{NaA} + (1-x)c \text{NaF}$).

- Coadsorption of neutral organic molecules and surface active anions (like bromide)
Further development of the theory of adsorption of ions and organic molecules on electrodes suggests transition to molecular models. However, I would like to point out that conclusions of molecular models should not contradict phenomenological models I just talked about.

The longer I live the more I see that I am never wrong about anything, and that all the pains that I have so humbly taken to verify my notions have only wasted my time.

George Bernard Shaw
I was always happy to work with active and creative people, especially women.
Our atmosphere
1965. Presentation of Frumkin portrait (attributed to Picasso)
Less scientific events at the Department