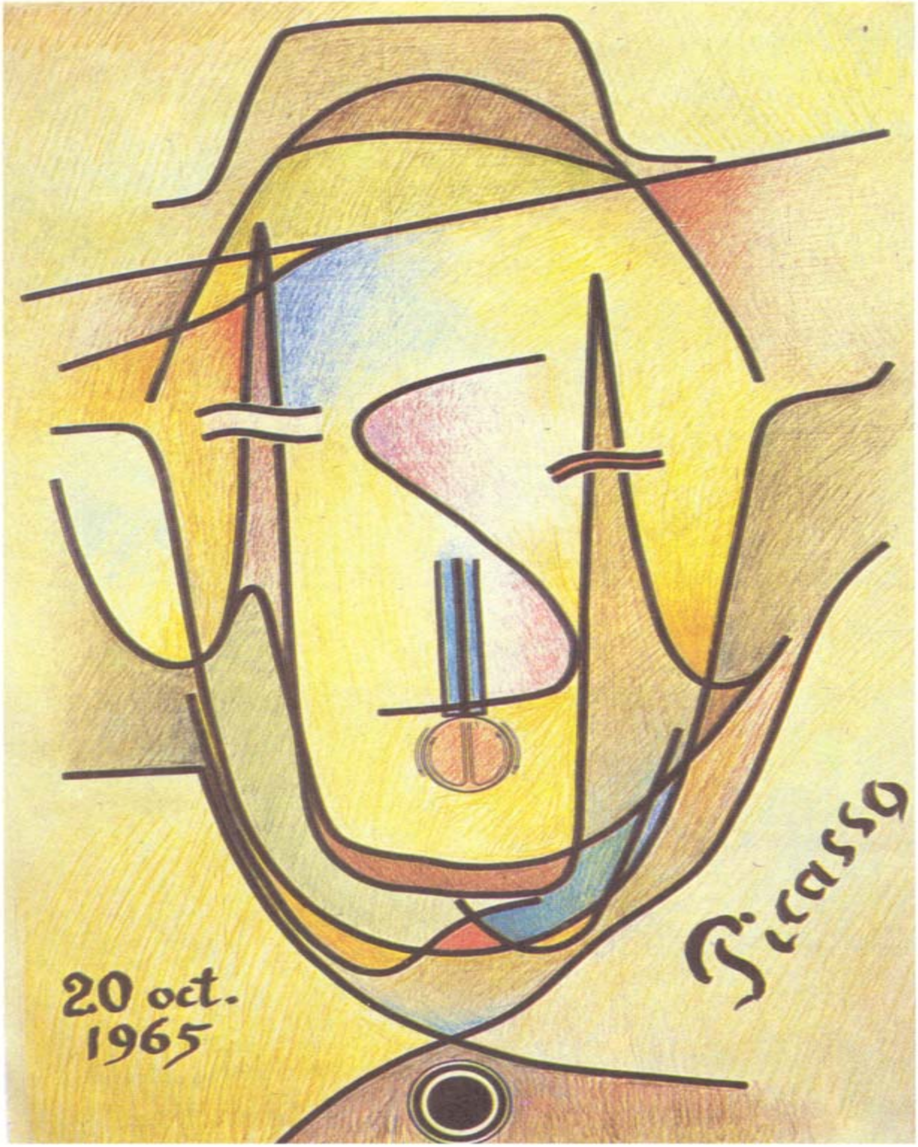
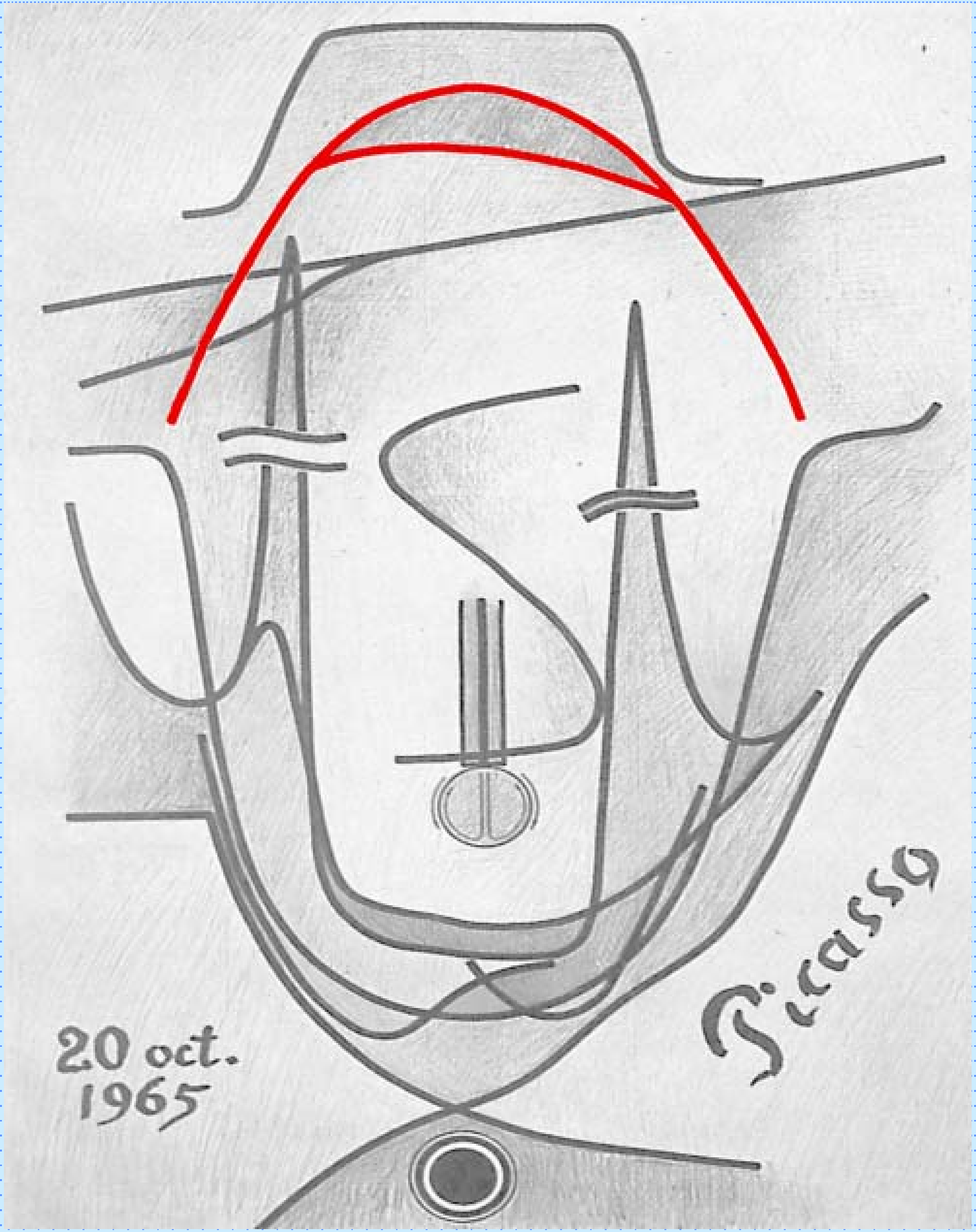
Свежий взгляд на портрет Фрумкина a la Picasso

Б.Б.Дамаскин



Здесь вместо носа появилась изотерма


20 oct.
1965
Picasso

G. Lippmann “Relations entre les phenomenes electriques et capillaries”,
Ann. chim. phys. (5), **5**, 494 (1875)
G. Gouy “Sur la fonction electrocapillaire I”,
Ann. chim. phys. (7), **29**, 145 (1903)
G. Gouy “Sur la fonction electrocapillaire II”,
Ann. chim. phys. (8), **8**, 291 (1906)
G. Gouy “Sur la fonction electrocapillaire III”,
Ann. chim. phys. (8), **9**, 75 (1906)
A. Frumkin “Zur Theorie der Elektrokapillaritat. I.”,
Ztschr. phys. Chem.,**103**, 43 (1923)
A. Frumkin “Zur Theorie der Elektrokapillaritat. II.”,
Ztschr. phys. Chem.,**103**, 55 (1923)

RELATIONS ENTRE LES PHÉNOMÈNES ÉLECTRIQUES ET CAPILLAIRES;

PAR M. GABRIEL LIPPMANN,
Ancien élève de l'École Normale supérieure.

HISTORIQUE.

La forme d'une surface liquide en équilibre satisfait à l'équation bien connue donnée par Laplace. On sait que l'analyse de Laplace s'appuie sur l'hypothèse de certaines forces moléculaires agissant au voisinage de la surface; l'expérience a toujours confirmé les résultats de cette analyse. On peut diviser l'étude expérimentale de la capillarité en deux parties : 1° vérification expérimentale de l'équation de Laplace, notamment de la loi de Jurin, qui en est une conséquence; 2° détermination numérique du coefficient unique que contient l'équation de Laplace, et qu'on a appelé depuis *constante capillaire* ou *tension superficielle*. Si la première partie a donné des résultats satisfaisants, il n'en est pas de même de la seconde. Pour une surface de nature donnée, pour la surface de contact eau-mercure par exemple, l'expérience fournit des valeurs qui varient sans raison apparente, qui diminuent avec le temps. Ces variations ont été d'abord constatées par M. Quincke (¹). Ce physicien a trouvé que la tension superficielle des surfaces liquides qu'il a étudiées (eau-air, mercure-air, eau-mercure, alcool-mercure, etc.) allait en diminuant d'une manière continue à partir du premier moment

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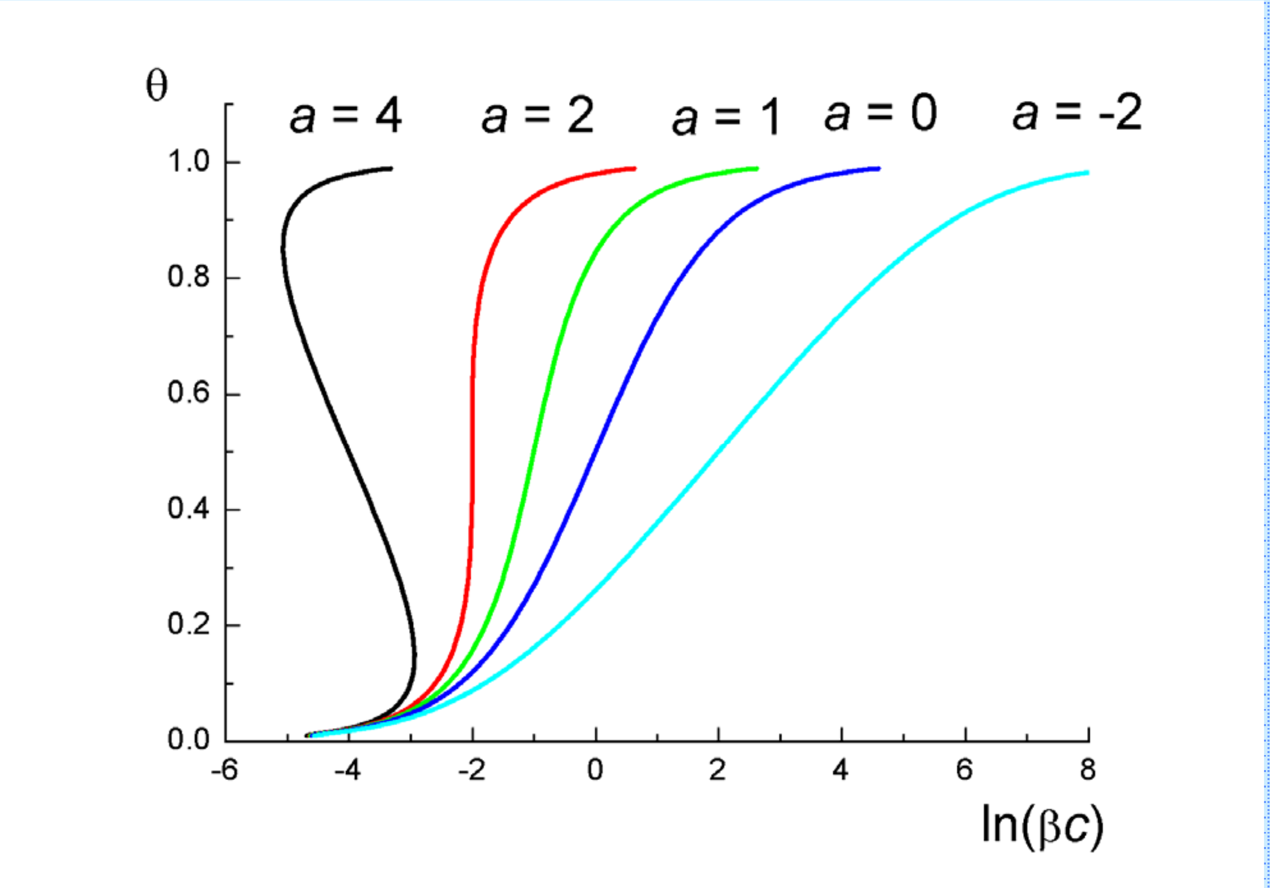
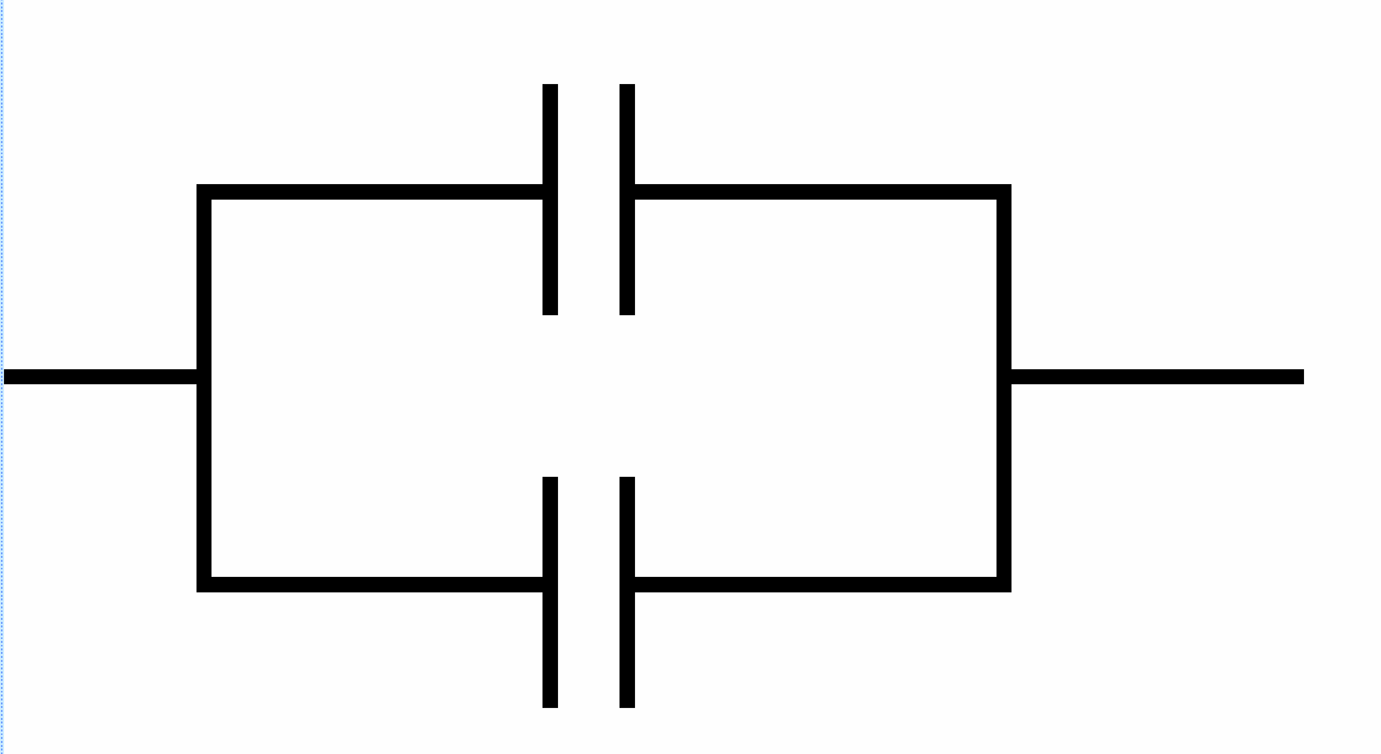
(¹) *Annales de Poggendorff*, t. CXXXIX, p. 1; 1870.

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



$$q = q_0(1-\theta) + C_1(\varphi - \varphi_N)\theta$$

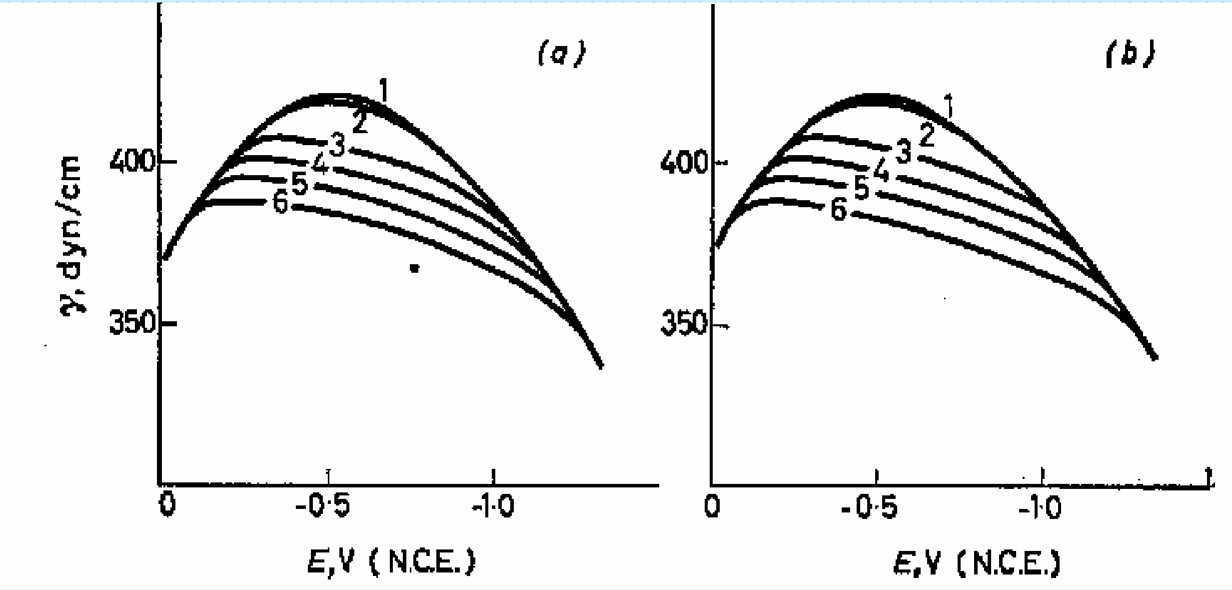
$$C_{\theta=0}(1-\theta)$$



$$C_{\theta=1}\theta$$

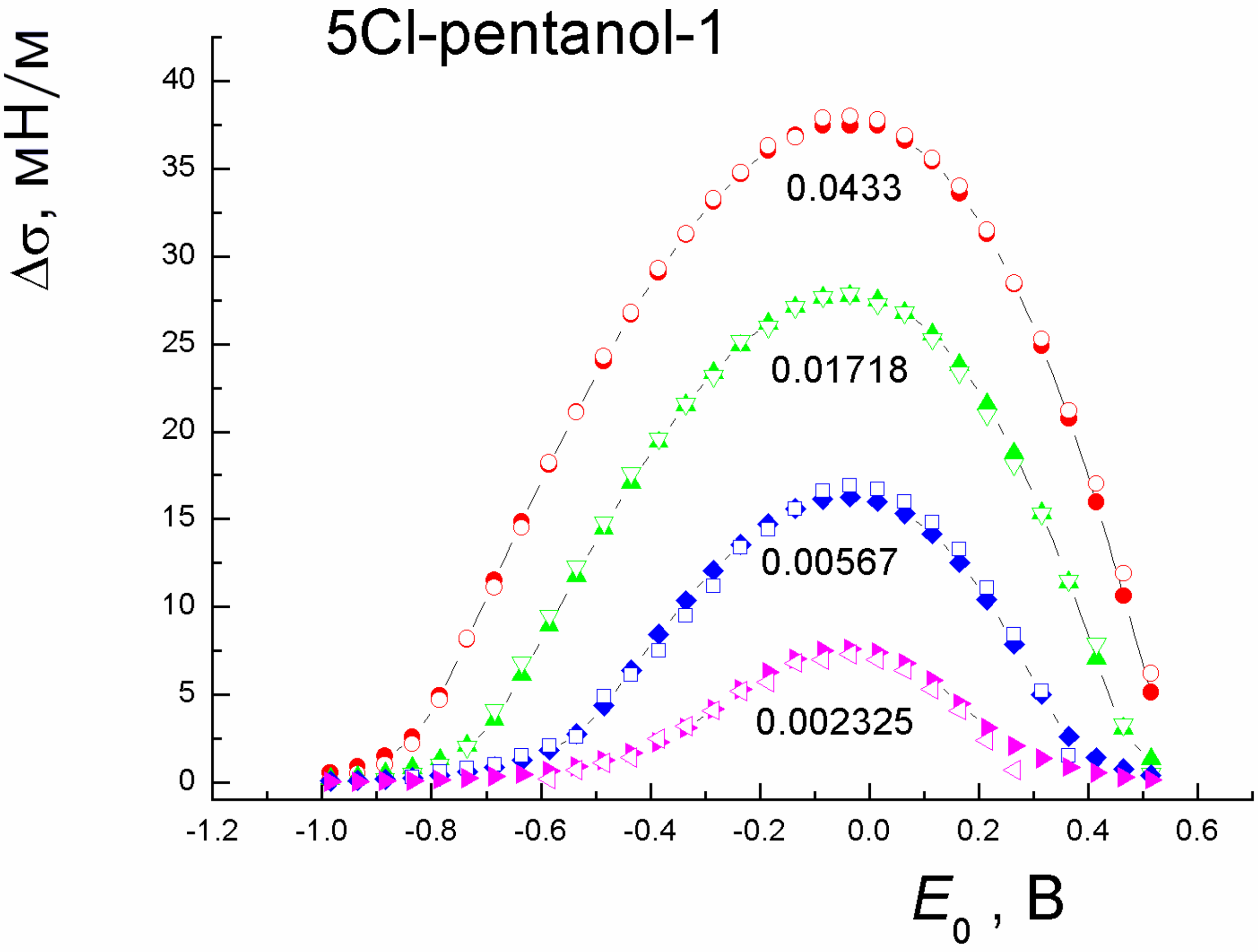
Electrocapillary curves of a mercury electrode in 1M NaCl solutions containing *tret-pentanol additives*:

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

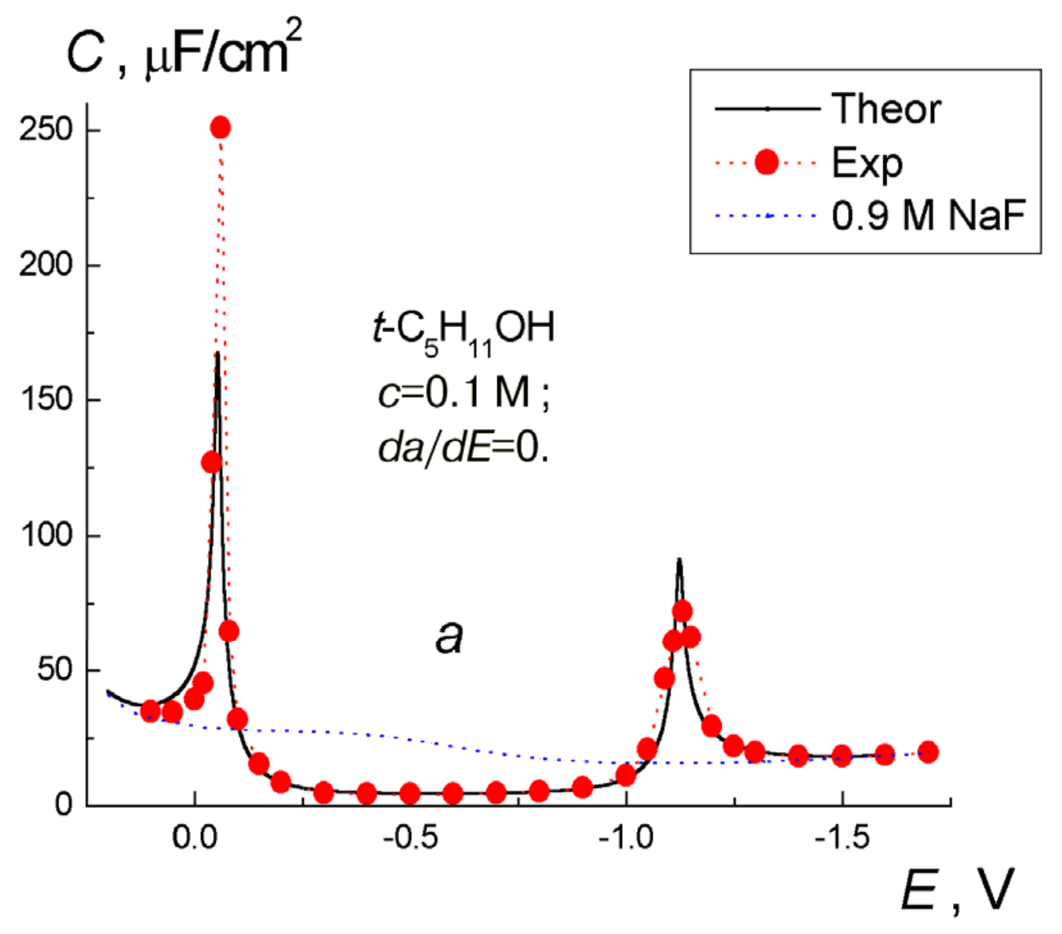


Experimental data

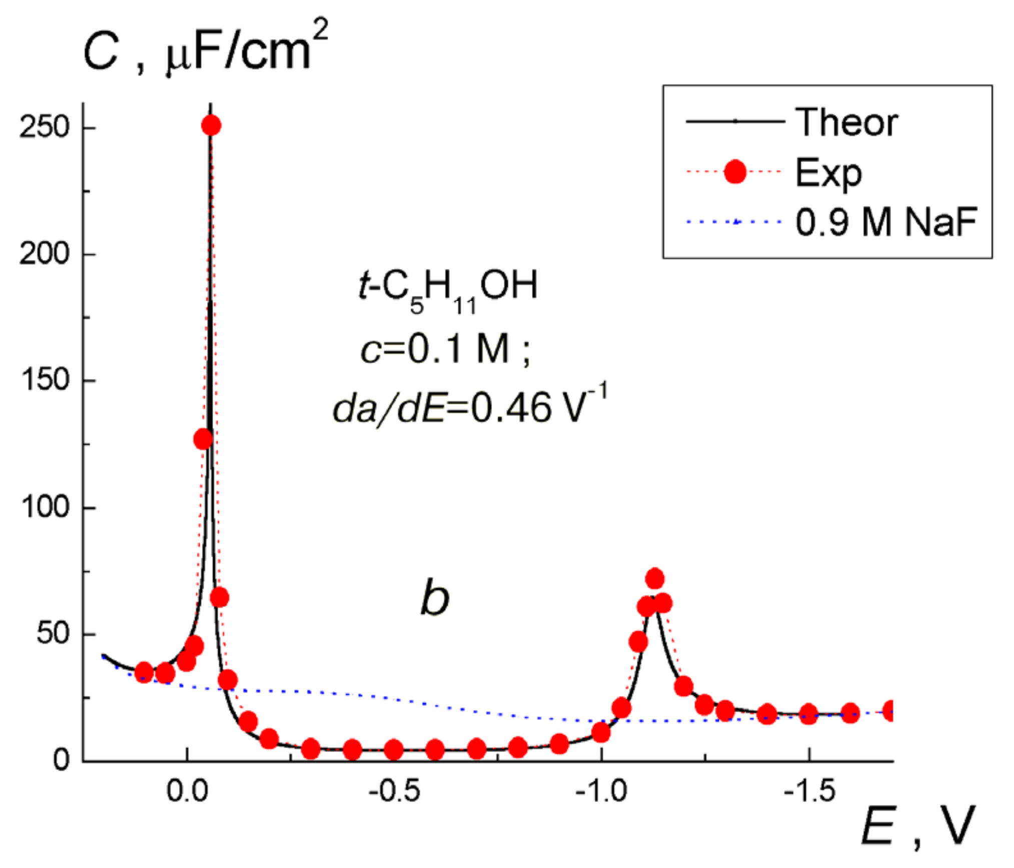
Calculated


5Cl-pentanol-1
Δσ, мН/м
0
5
10
15
20
25
30
35
40
0.0433
0.01718
0.00567
0.002325
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
E0 , В

Experimental and simulated differential capacity curves, a=const



Experimental and simulated differential capacity curves: linear a, E - dependence

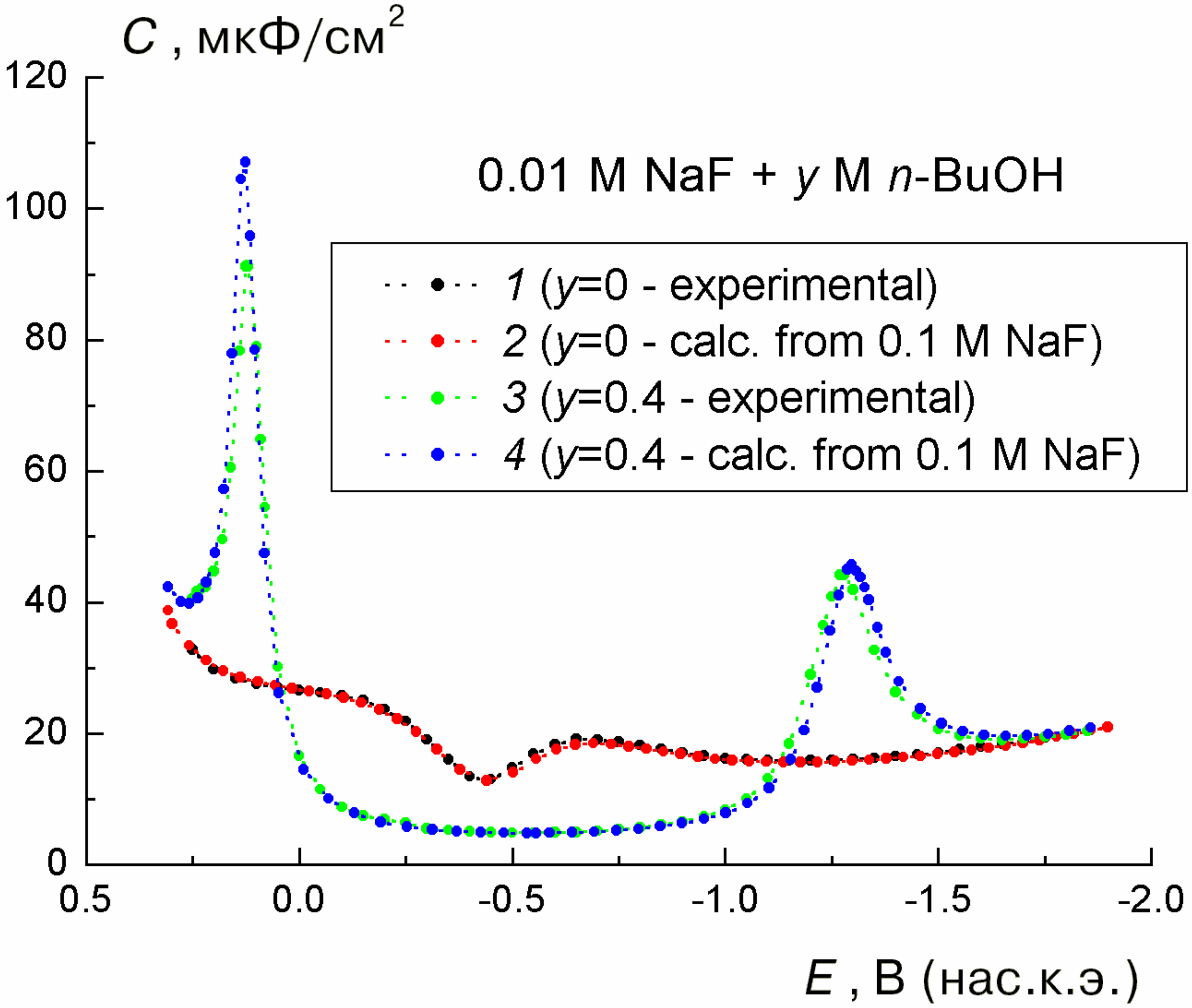


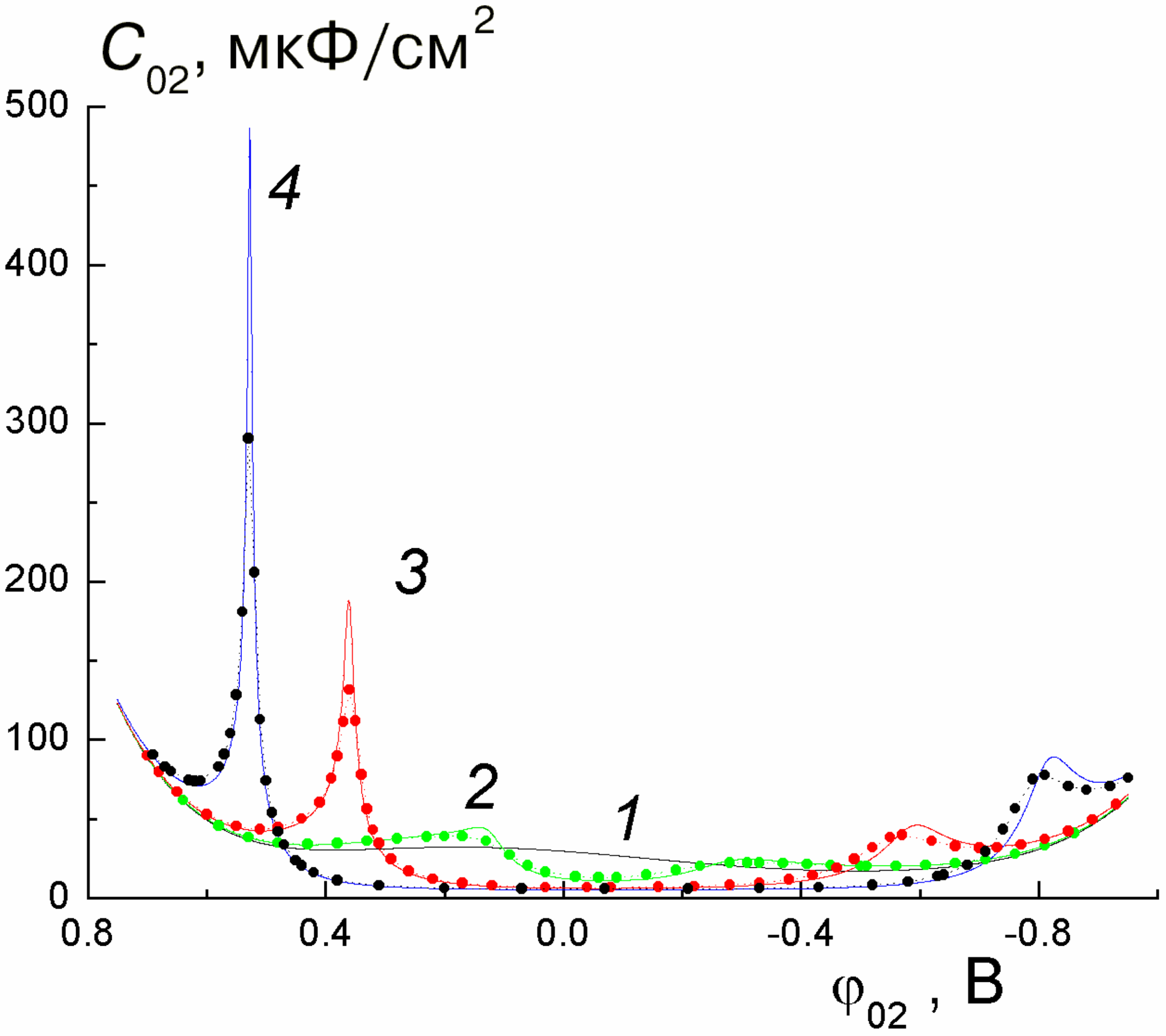
$$1/C = 1/C_{02} + 1/C_2$$

$$\varphi = \varphi_{02} + \varphi_2$$

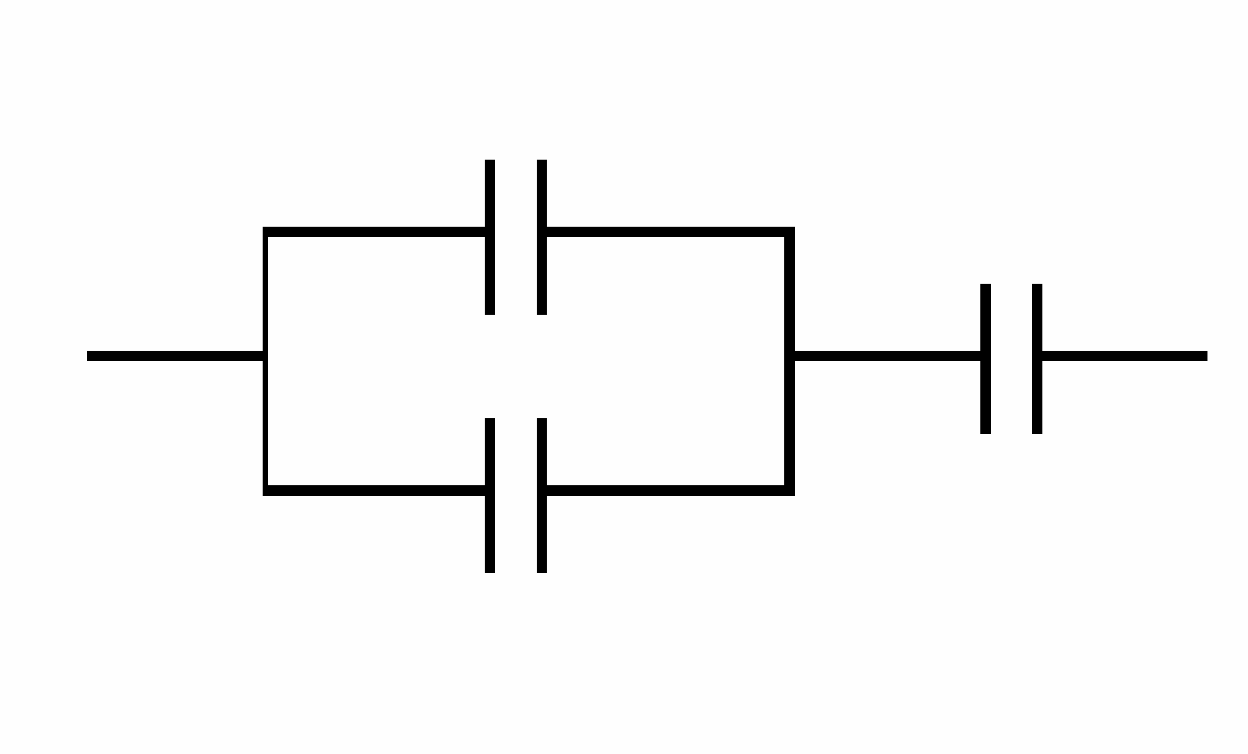
$$C_2 = (F/2RT)\sqrt{4A_\mathrm{d}^2 x + q^2}$$

$$\varphi_2 = \frac{2RT}{F}\,\mathrm{arcsh}\left(\frac{q}{2A_\mathrm{d}\sqrt{x}}\right)$$


C , мкФ/см^2
120
100
80
60
40
20
0
0.01 M NaF + y M n-BuOH
1 (y=0 - experimental)
2 (y=0 - calc. from 0.1 M NaF)
3 (y=0.4 - experimental)
4 (y=0.4 - calc. from 0.1 M NaF)
0.5
0.0
-0.5
-1.0
-1.5
-2.0
E , В (нас.к.э.)


C_{02}, мкФ/см^2
500
400
300
200
100
0
0.8
0.4
0.0
-0.4
-0.8
φ_{02} , В
1
2
3
4

Models of two parallel capacitors taking into account diffuse part of the electrical double layer



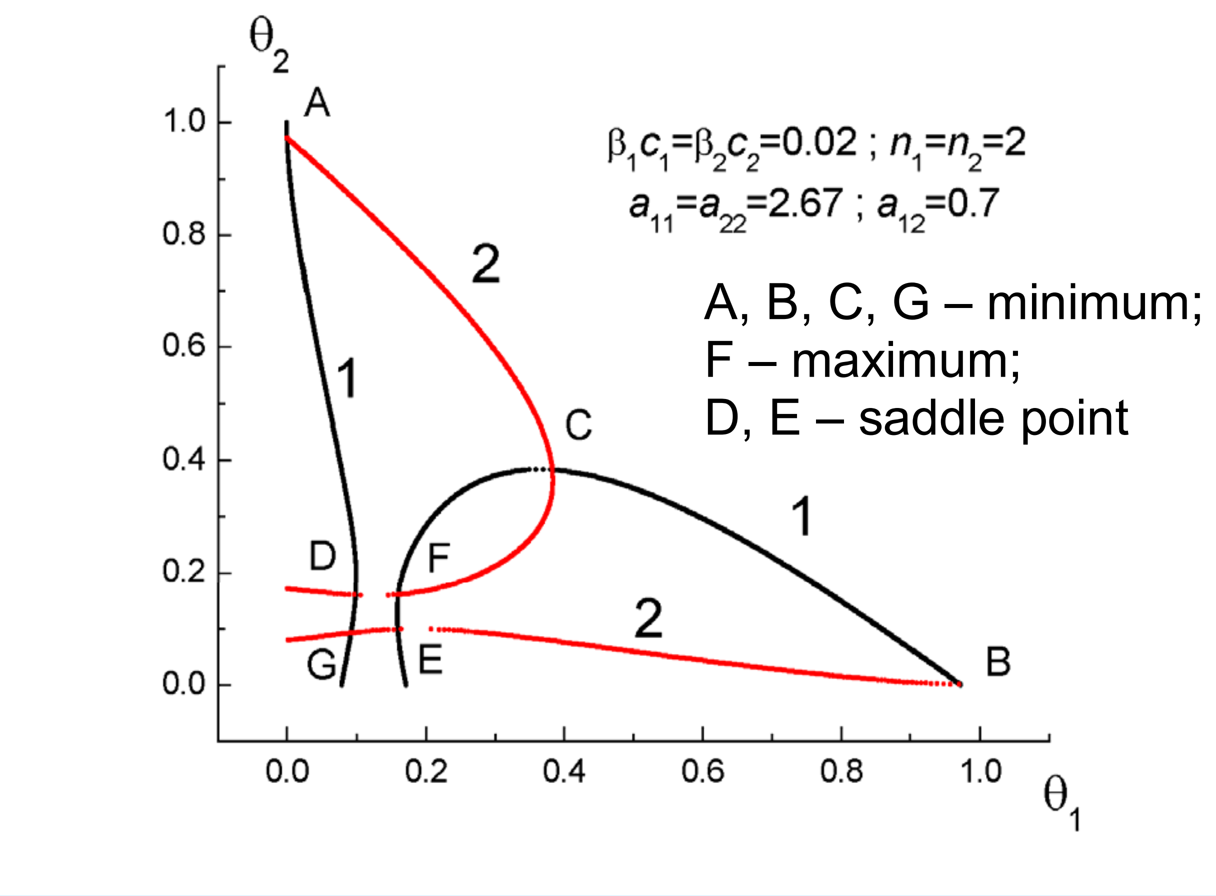
Coadsorption of two solution components. Combination of two mixed Frumkin isotherms

$$\sigma = \sigma_0(1-\theta_1-\theta_2) + C_1\theta_1(E_0 - E_{N1}) + C_2\theta_2(E_0 - E_{N2})$$

$$\beta_1 c_1 = \frac{\theta_1}{n_1\left(1-\theta_1-\theta_2\right)^{n_1}} \exp\left(-2n_1 a_{11}\theta_1 - 2n_1 a_{12}\theta_2\right)$$

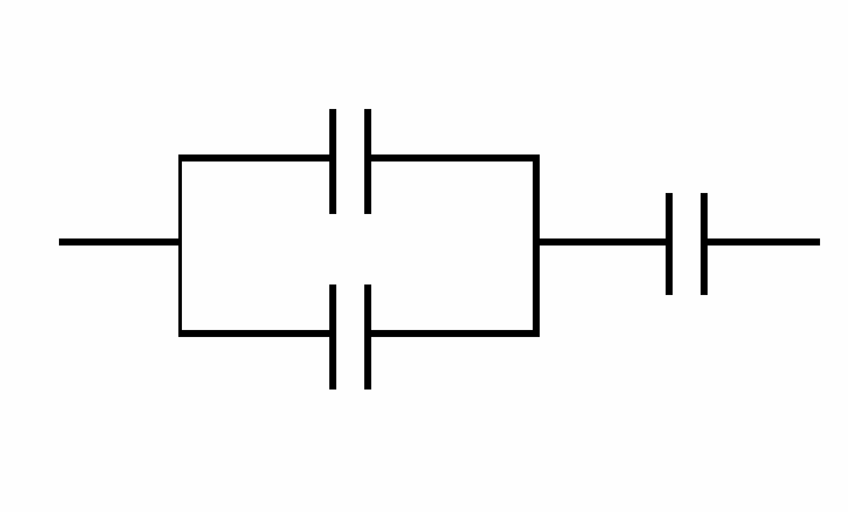
$$\beta_2 c_2 = \frac{\theta_2}{n_2\left(1-\theta_1-\theta_2\right)^{n_2}} \exp\left(-2n_2 a_{22}\theta_2 - 2n_2 a_{12}\theta_1\right)$$

θ_2, θ_1 relartionships corresponding to two equations of mixed Frumkin isotherms

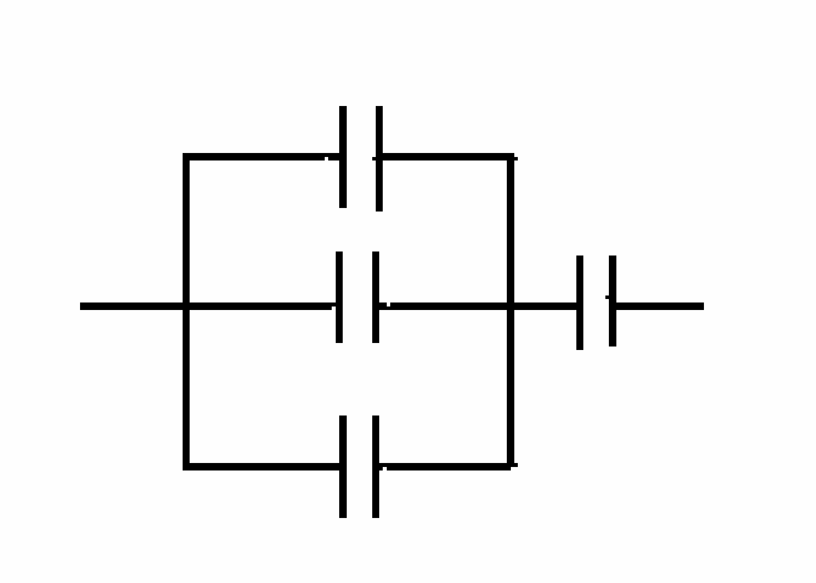


A, B, C, G – minimum;
F – maximum;
D, E – saddle point

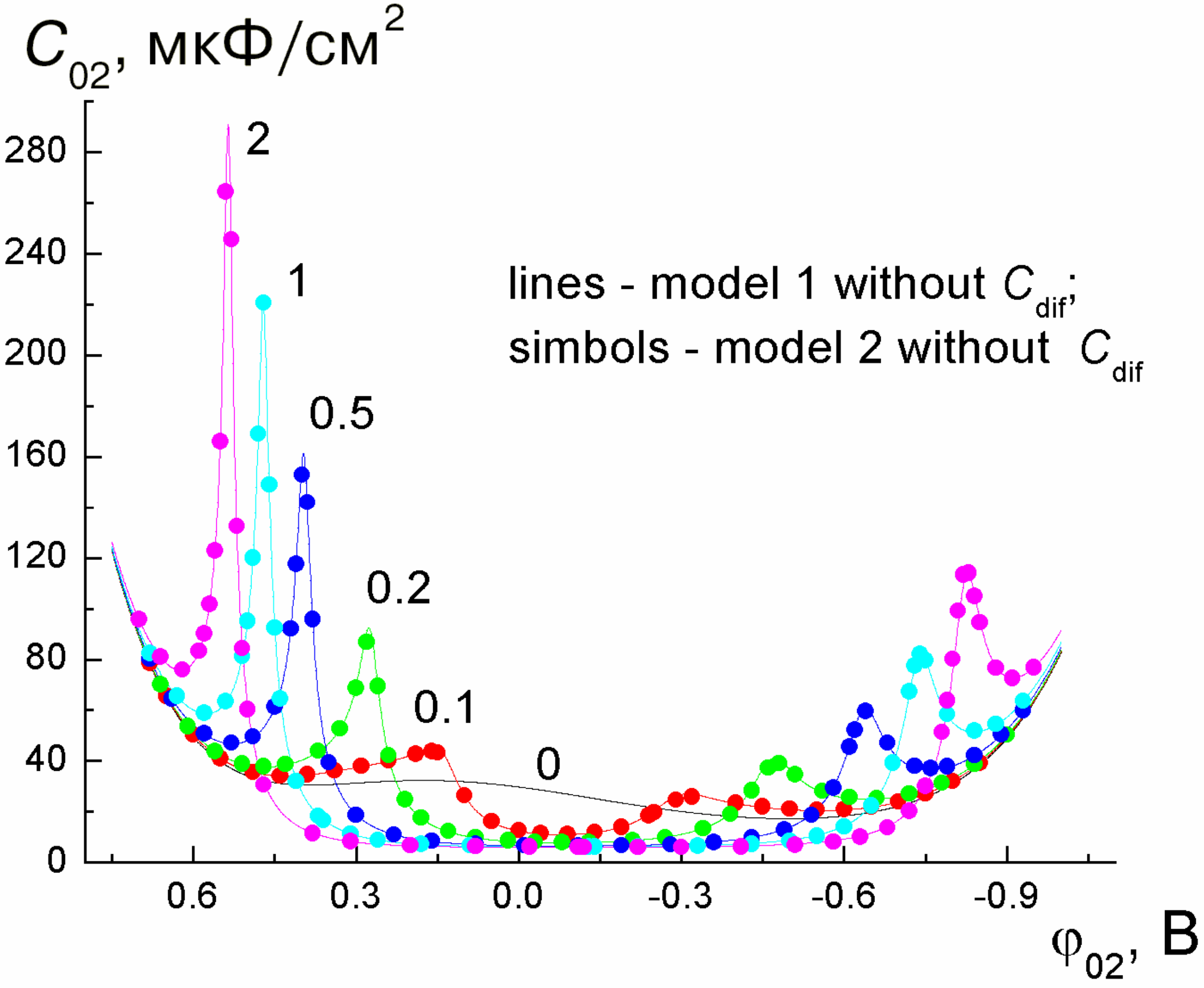
Models of two and three parallel capacitors taking into account diffuse part of the electrical double layer

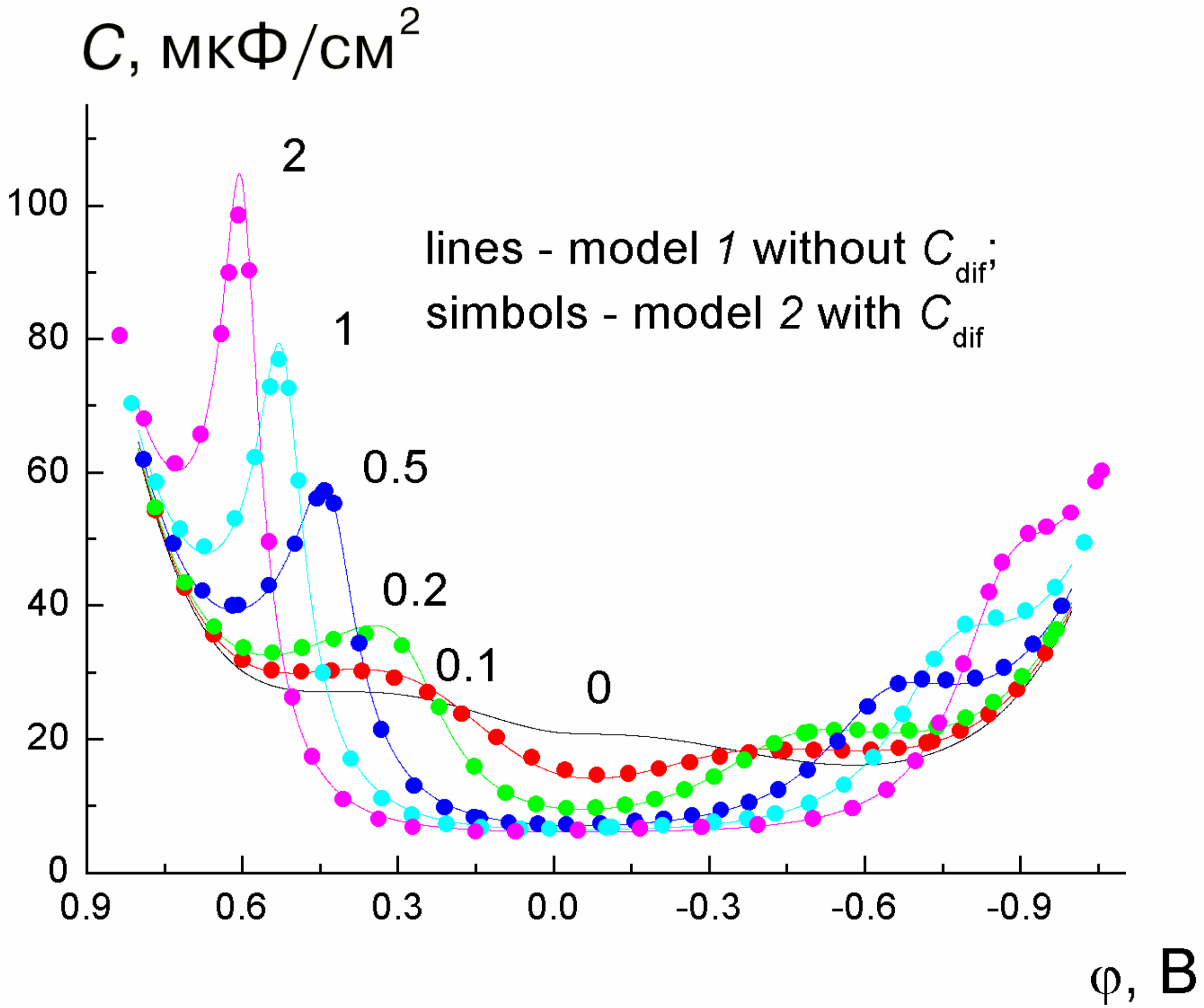


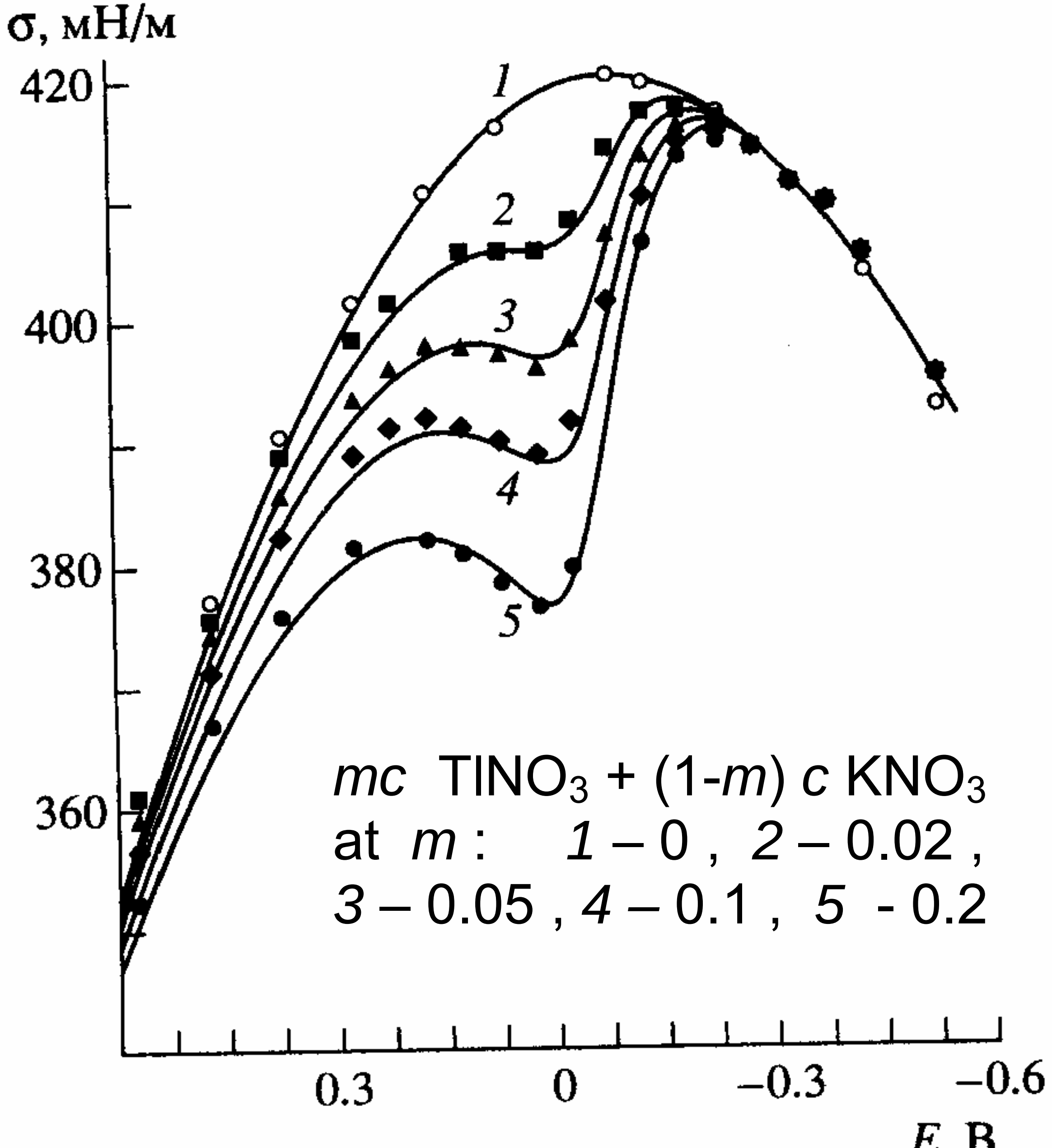
1



2

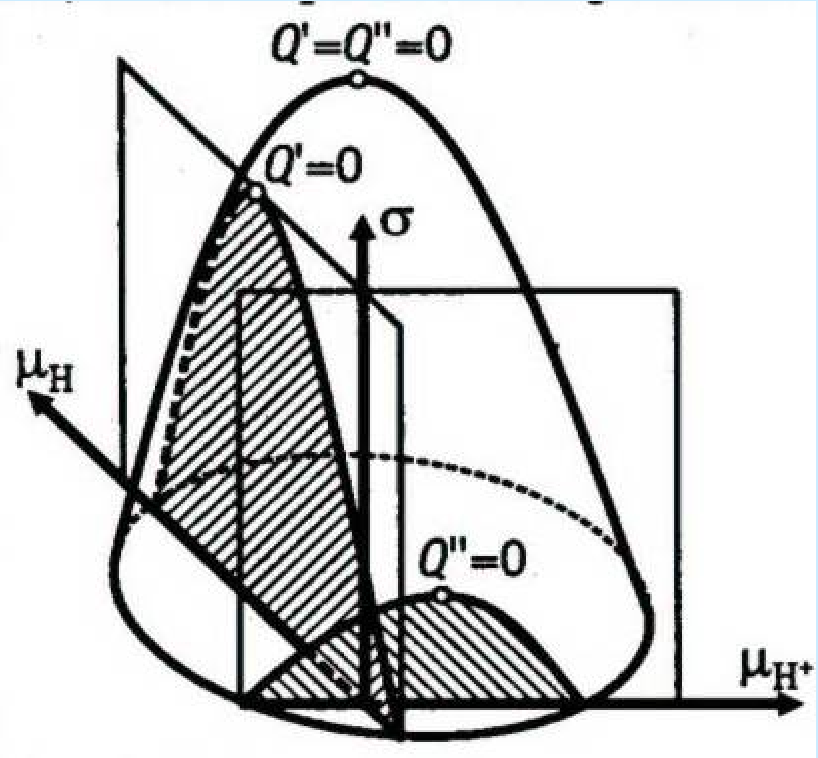

C02, мкФ/см2
280
240
200
160
120
80
40
0
2
1
0.5
0.2
0.1
0
lines - model 1 without Cdif;
simbols - model 2 without Cdif
0.6
0.3
0.0
-0.3
-0.6
-0.9
φ02, B

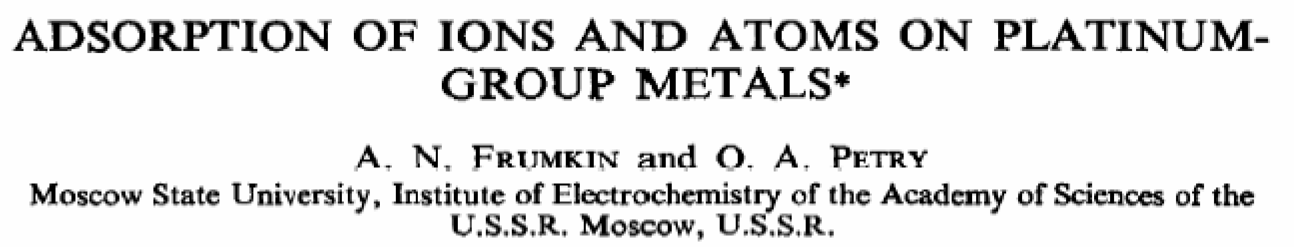

C, мкФ/см^2
100
80
60
40
20
0
0.9
0.6
0.3
0.0
-0.3
-0.6
-0.9
φ, В
2
1
0.5
0.2
0.1
0
lines - model *1* without C_{dif};
simbols - model *2* with C_{dif}



mc $TlNO_3$ + (1-*m*) *c* KNO_3
at *m* : *1* – 0 , *2* – 0.02 ,
3 – 0.05 , *4* – 0.1 , *5* - 0.2

Теромодинамика поверхности электродов, адсорбирующих водород и кислород





ADSORPTION OF IONS AND ATOMS ON PLATINUM-GROUP METALS*

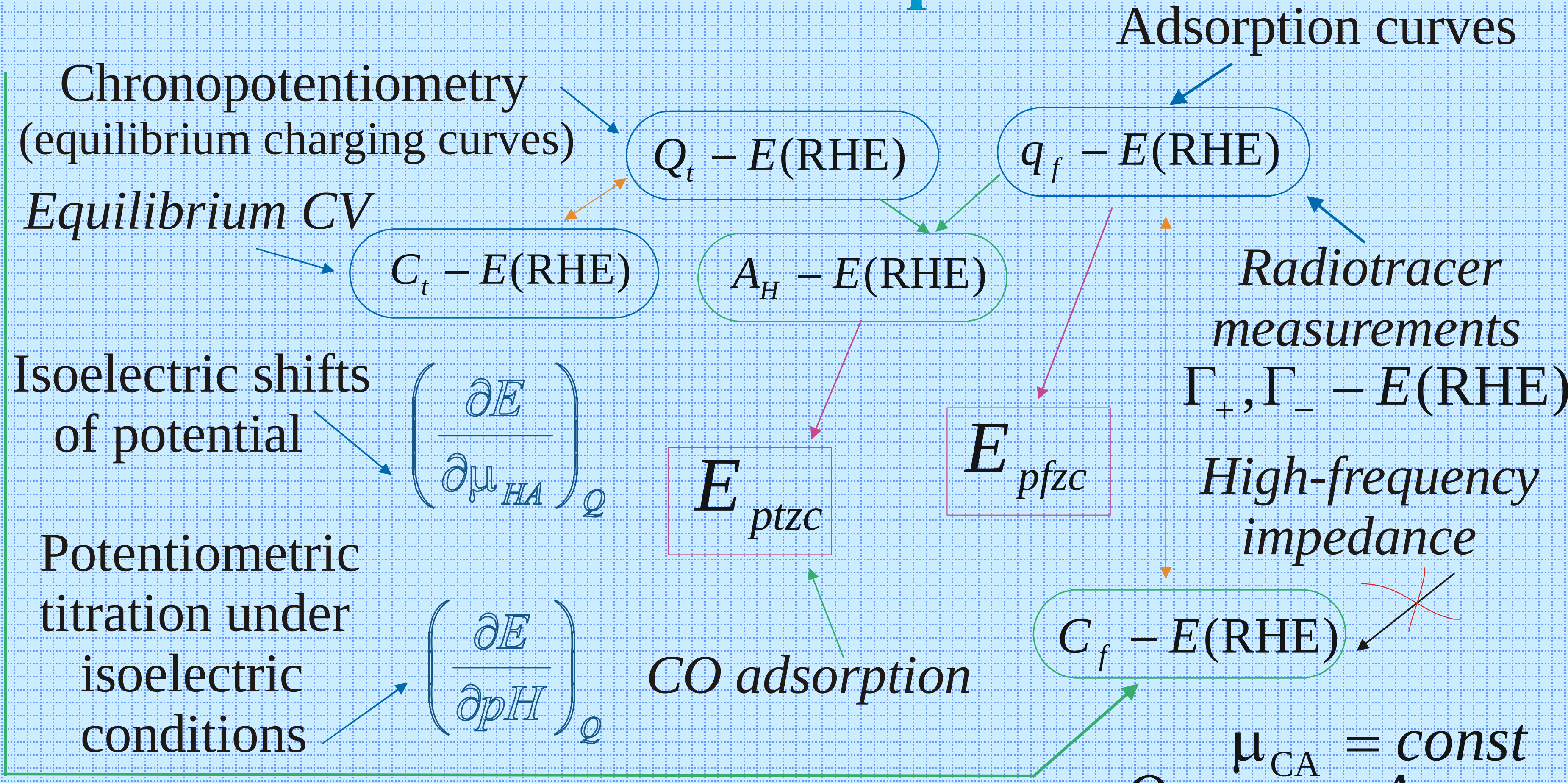
A. N. Frumkin and O. A. Petry
Moscow State University, Institute of Electrochemistry of the Academy of Sciences of the U.S.S.R. Moscow, U.S.S.R.

$$d\sigma = -Q\,dE_{\mathrm{r}} - \frac{q}{F}\,d\mu_{\mathrm{H}^+}$$

$$C_{\mathrm{d.l.}} = -FC\left(\frac{\partial E_{\mathrm{r}}}{\partial \mu_{\mathrm{H}^+}}\right)_Q = \frac{C}{0.058}\left(\frac{\partial E_{\mathrm{r}}}{\partial \mathrm{pH}}\right)_Q,$$

$$C_{\mathrm{d.l.}} = \left(\frac{\partial q}{\partial E_{\mathrm{r}}}\right)_{\mu_i,\mu_{\mathrm{H}^+}};\,C = \left(\frac{\partial Q}{\partial E_{\mathrm{r}}}\right)_{\mu_i,\mu_{\mathrm{H}^+}}.$$

A set of combined techniques



Adsorption curves

Chronopotentiometry
(equilibrium charging curves)

$Q_t - E(\text{RHE})$

$q_f - E(\text{RHE})$

Equilibrium CV

$C_t - E(\text{RHE})$

$A_H - E(\text{RHE})$

Radiotracer measurements

$\Gamma_+, \Gamma_- - E(\text{RHE})$

Isoelectric shifts
of potential

$$\left(\frac{\partial E}{\partial \mu_{HA}}\right)_Q$$

E_{ptzc}

E_{pfzc}

High-frequency impedance

Potentiometric
titration under
isoelectric
conditions

$$\left(\frac{\partial E}{\partial pH}\right)_Q$$

CO adsorption

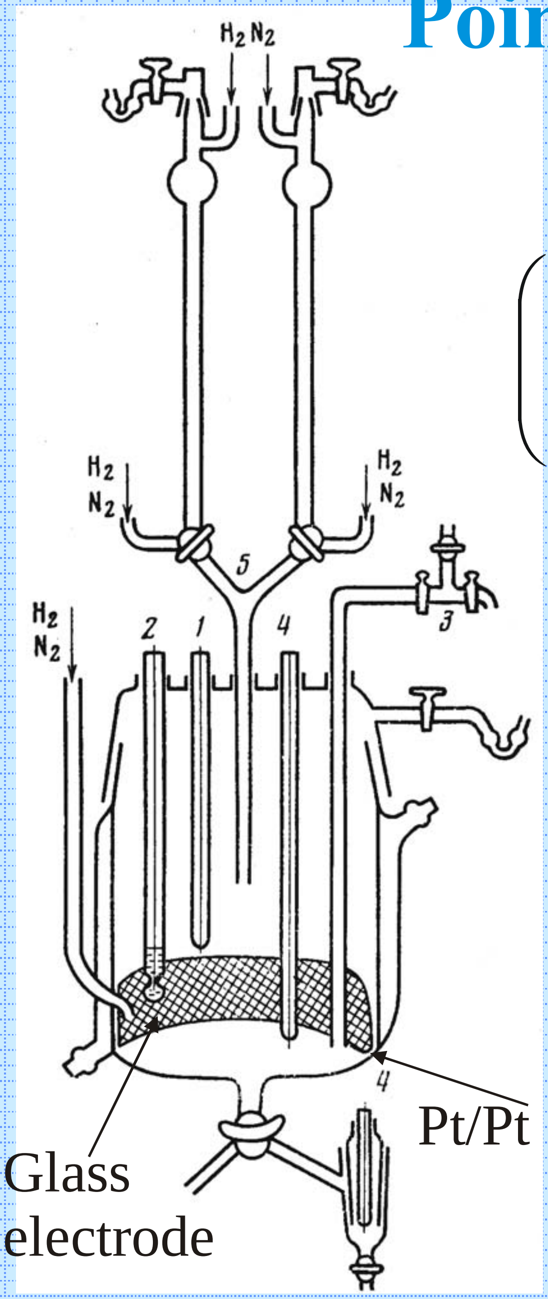
$C_f - E(\text{RHE})$

$$\mu_{\text{CA}} = const$$

$$Q_t = q_f - A_H$$

$$C_t = \left(\frac{\partial Q_t}{\partial E(\text{RHE})}\right)_{\mu_{\text{H}^+}} \qquad C_f = \left(\frac{\partial q_f}{\partial E(\text{RHE})}\right)_{\mu_{\text{H}^+}} = \left(\frac{\partial E(\text{RHE})}{\partial \mu_{\text{H}^+}}\right)_{\mu_{\text{CA}}} * C_t$$

Points of zero charge - pH dependence



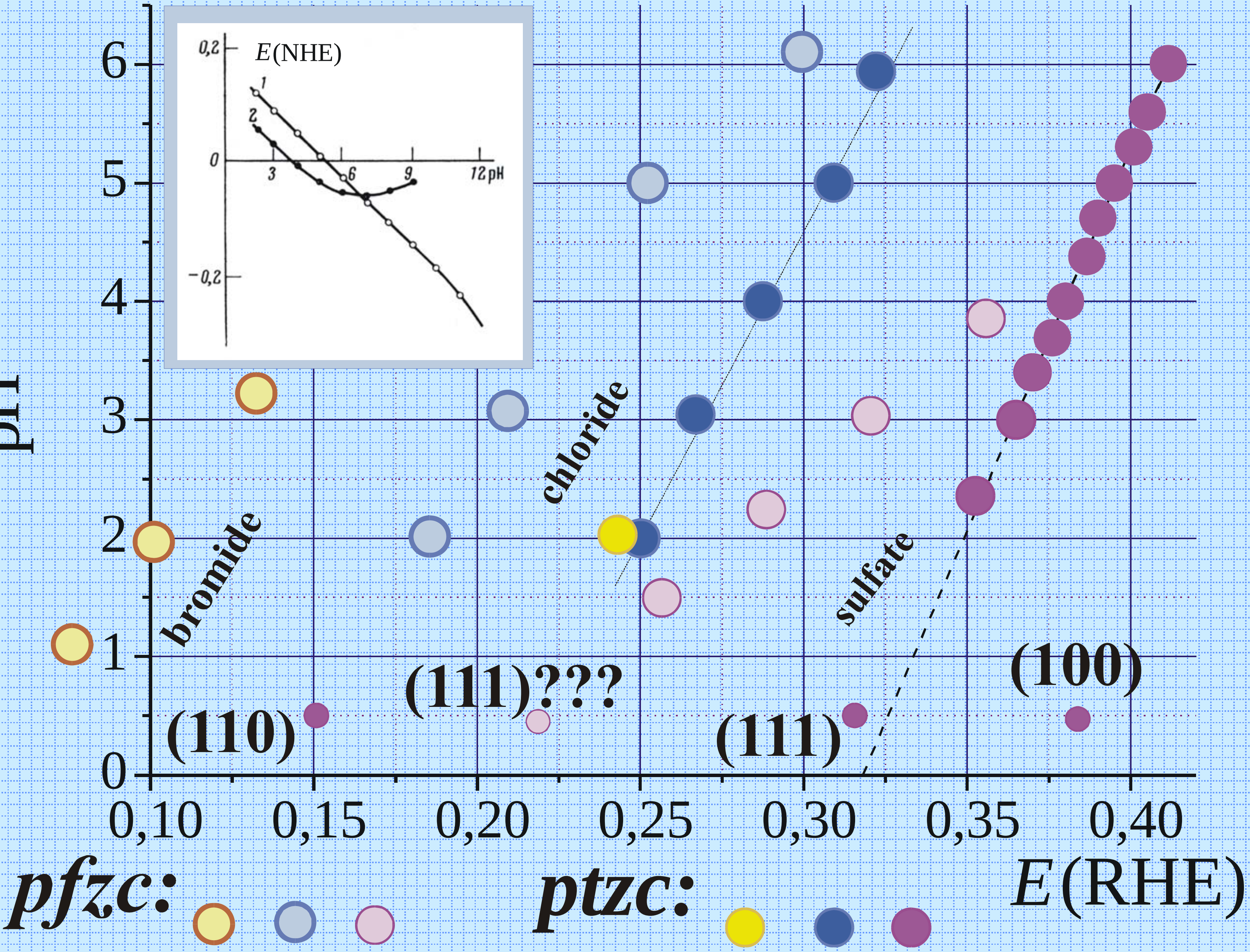
$$E_{pfzc}$$

$$\left(\frac{\partial E}{\partial \mu_{H^+}}\right)_{q_f=0} = \frac{1}{1-\left(\partial q_f/\partial A_H\right)_{E(RHE)}}$$

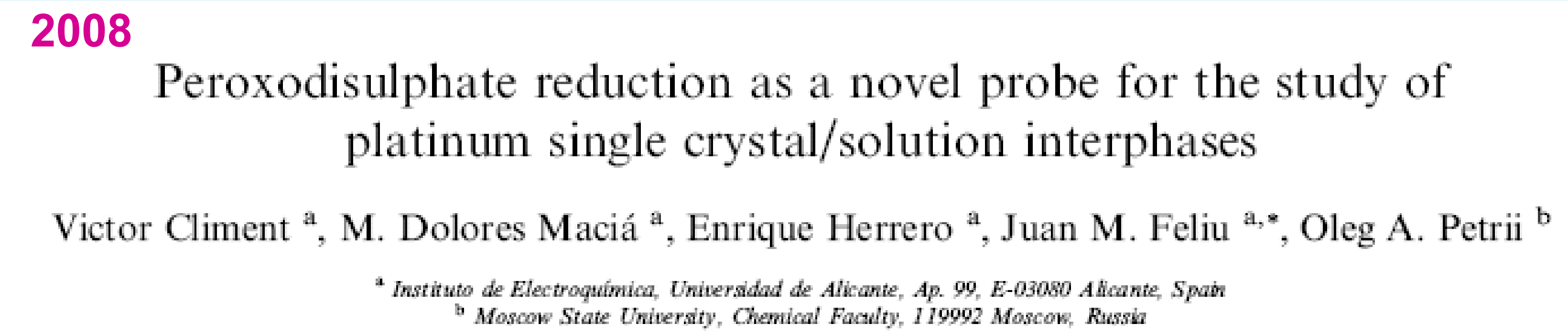
$$E_{ptzc}$$

$$\left(\frac{\partial E}{\partial \mu_{H^+}}\right)_{Q_t=0} = \frac{1}{1-\left(\partial q_f/\partial A_H\right)_{\mu_{H^+}}}$$

Potentiometric titration under isoelectric conditions, 1974


E(NHE)
0,2
0
−0,2
1
2
3
6
9
12 pH
pH
6
5
4
3
2
1
0
0,10
0,15
0,20
0,25
0,30
0,35
0,40
E(RHE)
bromide
chloride
sulfate
(110)
(111)???
(111)
(100)
pfzc:
ptzc:

2008

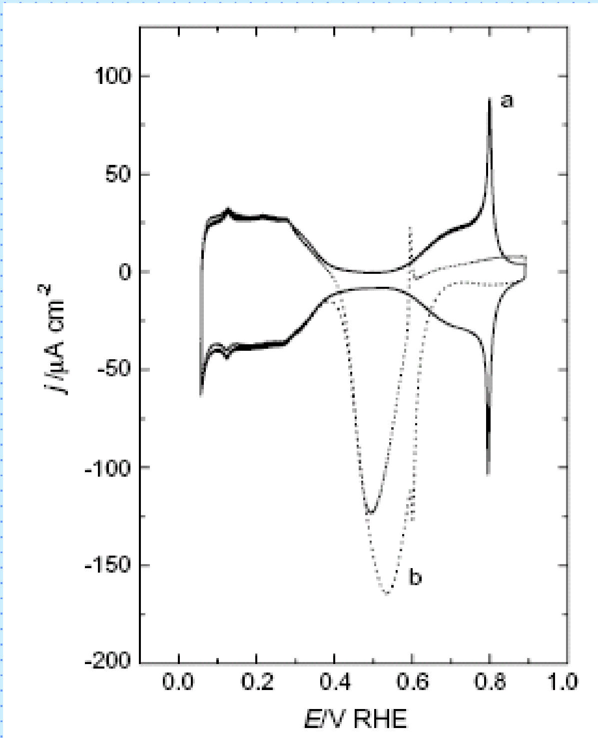


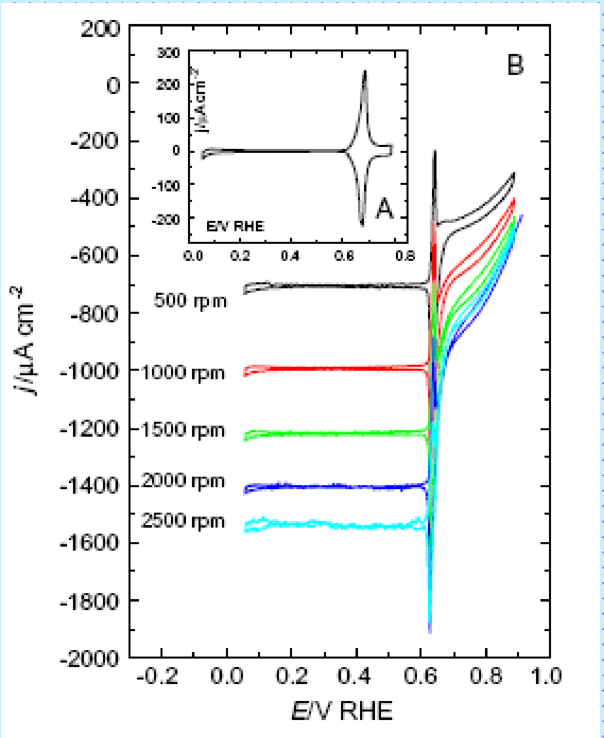
Peroxodisulphate reduction as a novel probe for the study of platinum single crystal/solution interphases

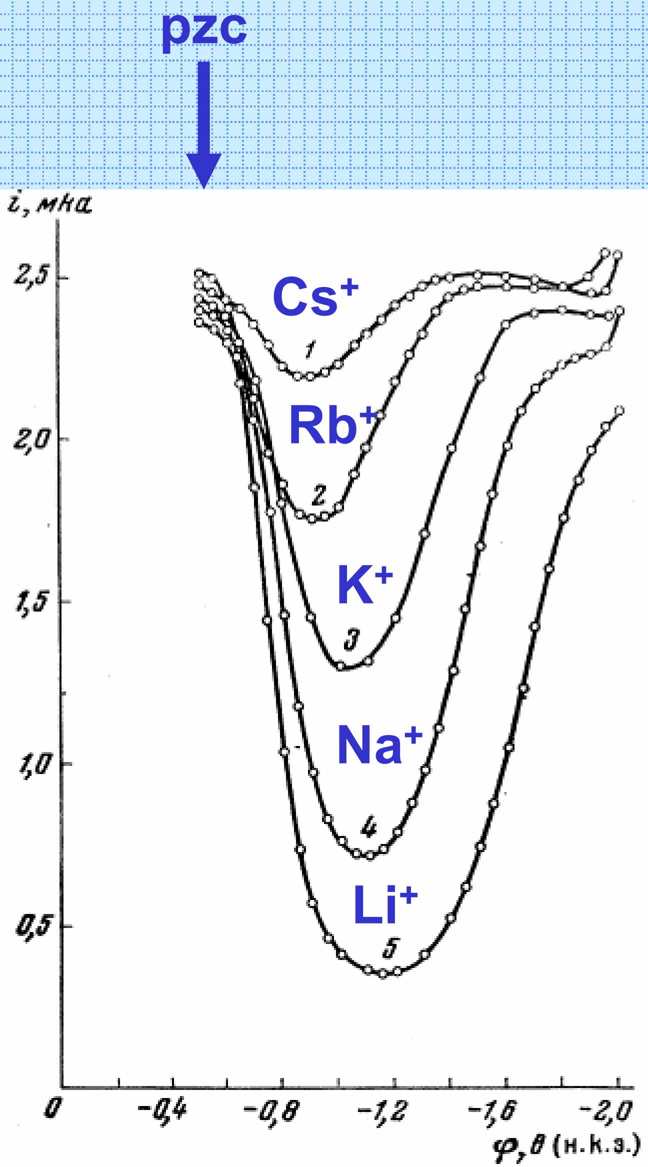
Victor Climent [a], M. Dolores Maciá [a], Enrique Herrero [a], Juan M. Feliu [a,*], Oleg A. Petrii [b]

[a] *Instituto de Electroquímica, Universidad de Alicante, Ap. 99, E-03080 Alicante, Spain*
[b] *Moscow State University, Chemical Faculty, 119992 Moscow, Russia*

Срастание двух тематик: стерта грань между ртутью и платиной!





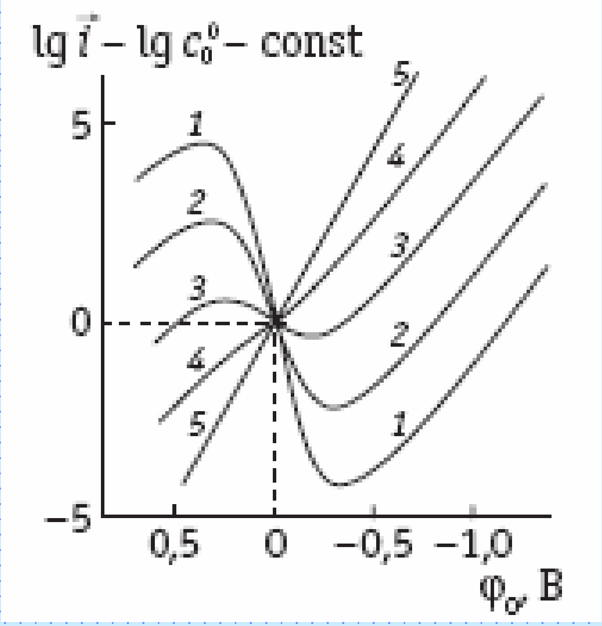


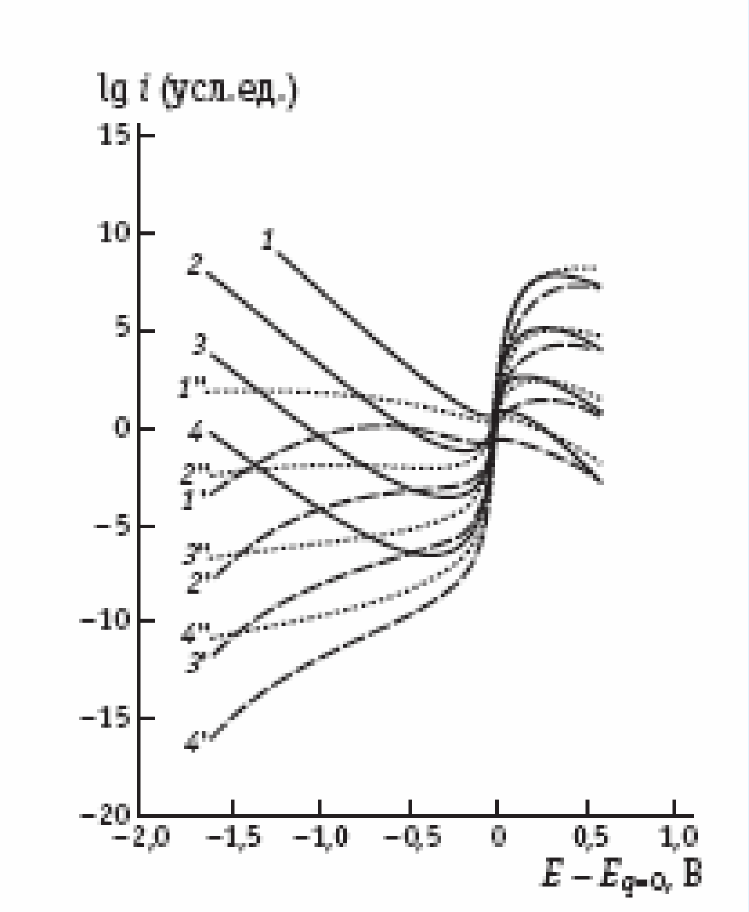
. 1. Поляризационные кривые 10^{-3} N $K_2S_2O_8$ в присутствии:
N CsCl; 2—10^{-2} N RbCl; 3—10^{-2} N KCl; 4—10^{-2} N NaCl; 5 — 10^{-2} N LiCl.

$$S_2O_8^{2-} + 2e^- = 2SO_4^{2-}$$

1953

Восстановление анионов – новый виток



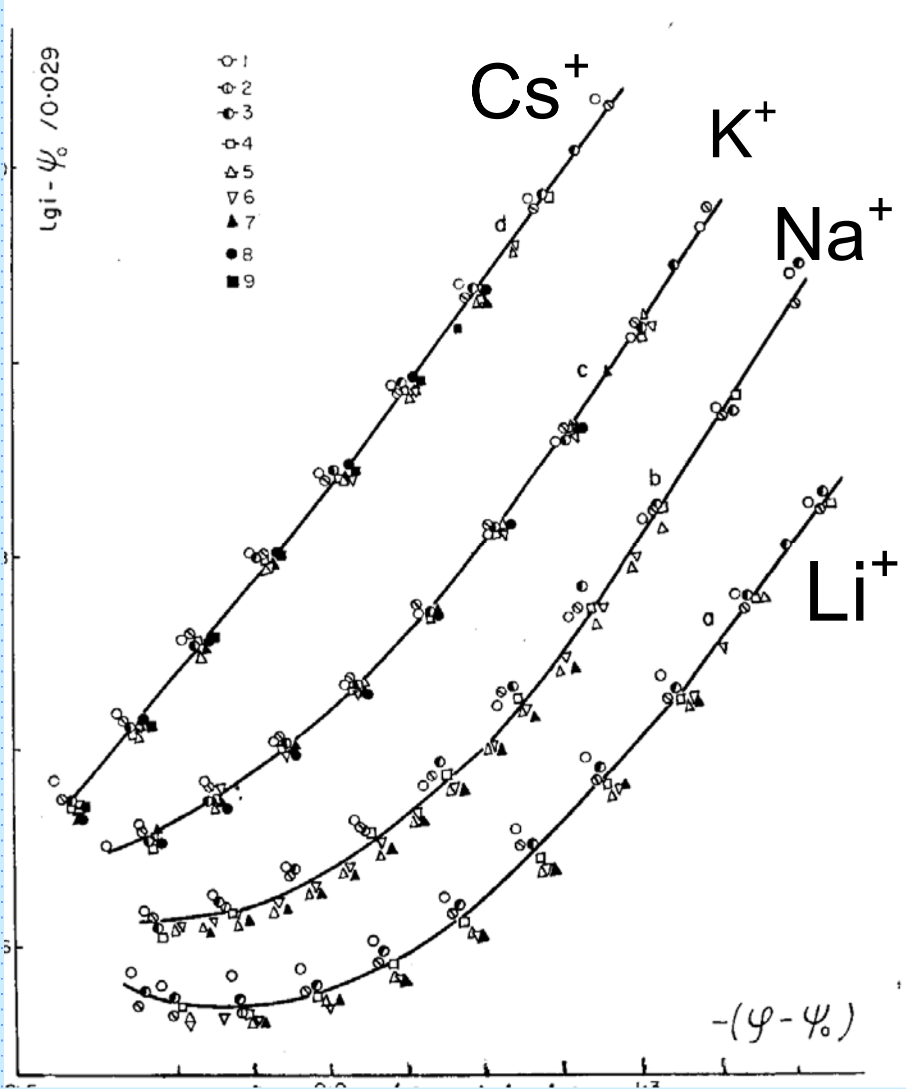


$$\sqrt{RT(\ln\chi - \ln i) - z_0F\psi_1} = \frac{F(\eta - \psi_1)}{2\sqrt{\lambda}} + \frac{\lambda}{2};$$

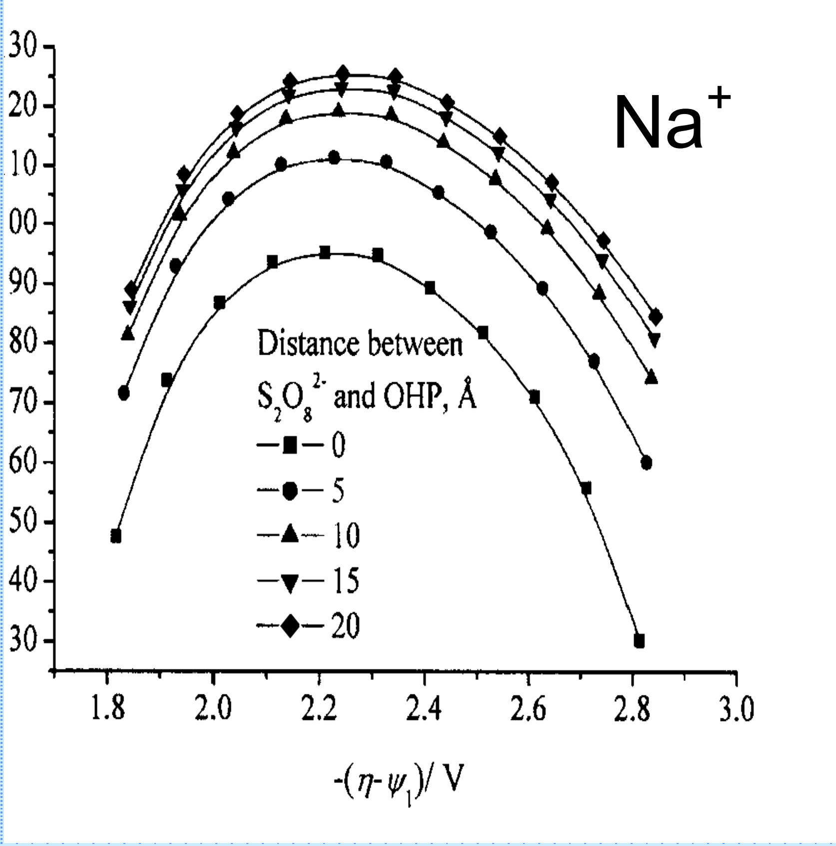
$\sqrt{RT(\ln\chi - \ln i) - z_0F\psi_1}$ versus $\eta - \psi_1$

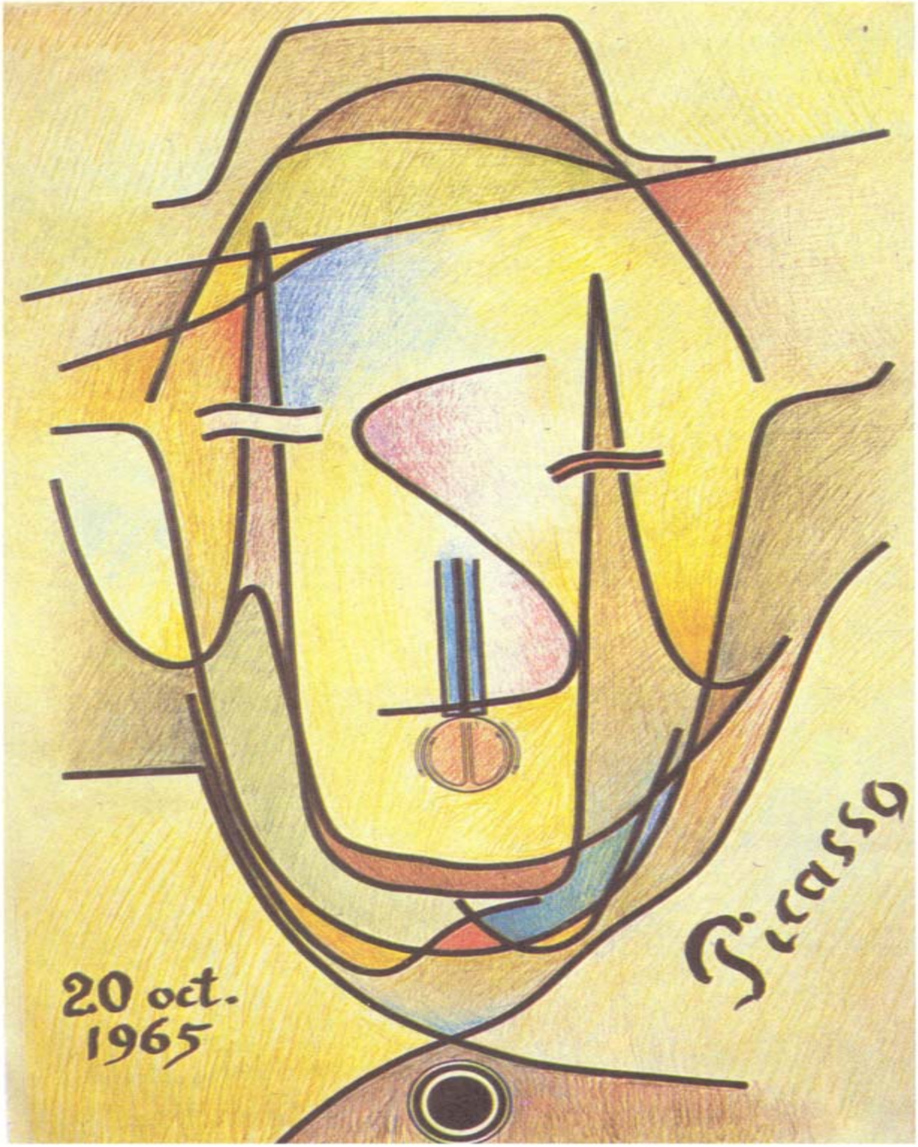
$[H_2CeW_{10}O_{36}]^{6-}$

CTP (1963)



CMP (2006)





Здесь вместо носа появилась изотерма