# RETURNING TO EARLY UKSHE-BUKUN WORKS, WHICH TEACH US THE LESSONS

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## Ionics, key word starting from 1950s:

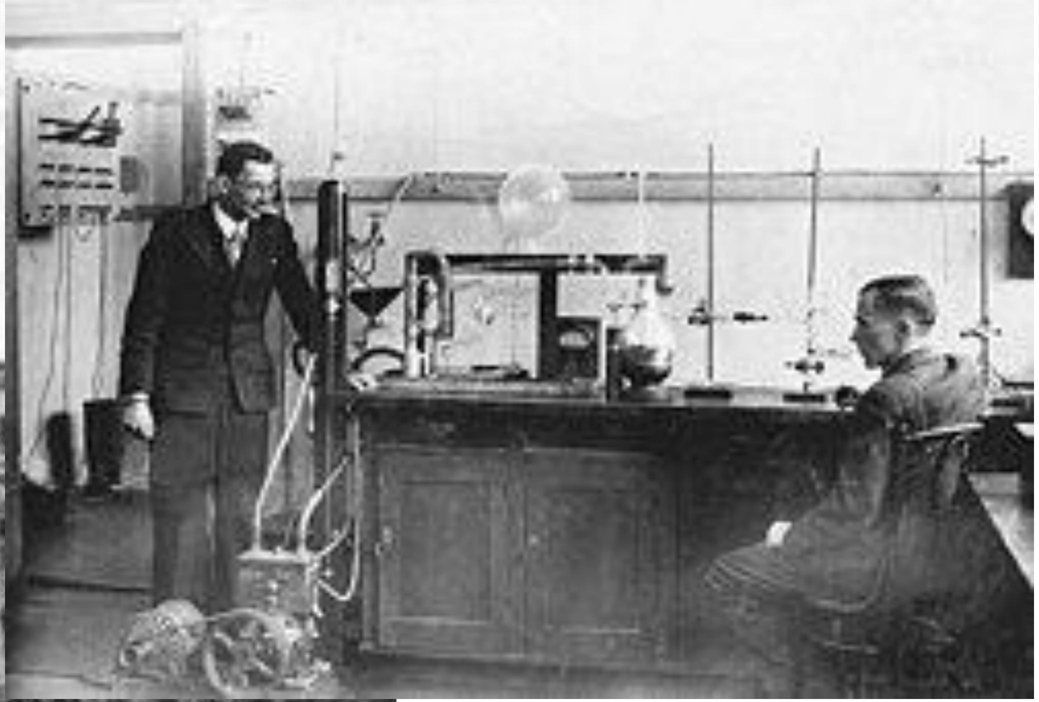
- ionic speciation in aqueous solutions, but not only (Ukshe's PhD period)
- metals dissolution in molten salts (Berezniki period)
- 'double layer' in molten salts (Berezniki + early Chernogolovka periods)
- Impedance: not a topic, but a tool

Presented online at FIPPT-2026, Chernogolovka, June 22, 2026

## Ural Polytech:

- Dept of Technical Electrochemistry, started in 1923
- Dept of Theoretical Electrochemistry, started in 1938

**Merged in 1944: Dept of Electrochemical Engineering (“кафедра ТЭП»)**



*Lab of molten salt electrolysis*

# Ural electrochemistry, very important persons

**Ivan Grigorievich Shcherbakov (1891-1953)**

**Oleg Alekseyevich Esin (1904-1979)**

**Sergey Vasilievich Karpachev (1906-1987)**

**Aron Iosipovich Levin (1907-1999)**

**Aqueous electrodeposition → melt electrochemistry**

**The effects of various factors on copper electrodeposition from complex solutions, PhD thesis. Sverdlovsk, 1953**

Аспирант Е. А. УКШЕ

ИССЛЕДОВАНИЕ ВЛИЯНИЯ РАЗЛИЧНЫХ ФАКТОРОВ НА ЭЛЕКТРООСАЖДЕНИЕ МЕДИ ИЗ КОМПЛЕКСНЫХ РАСТВОРОВ

Автореферат диссертации на соискание ученой степени кандидата технических наук

Таким образом задачи настоящего исследования сводились:

1. К изучению свойств комплексных электролитов, роли комплексообразователя и других факторов.

2. К определению состава комплексных электролитов, наиболее подходящих для целей гальванического меднения, а также к установлению оптимальных концентраций их компонентов.

3. К изучению механизма и кинетики электродных процессов, сопровождающих электролиз комплексных растворов.

4. К изучению особенностей электрокристаллизации при электролизе комплексных растворов.

5. К поискам новых технических возможностей в области замены цианистых ванн и интенсификации гальванического меднения.

Работа выполнена на кафедре технологии электрохимических производств Уральского политехнического института имени С. М. Кирова.

**Study of complex electrolytes, the ligand role.**

**Optimization of bath for Cu deposition.**

**Kinetics of accompanying electrode processes.**

**Specific features of electrocrystallization.**

**Search for technology based on cyanide-free electrolytes**

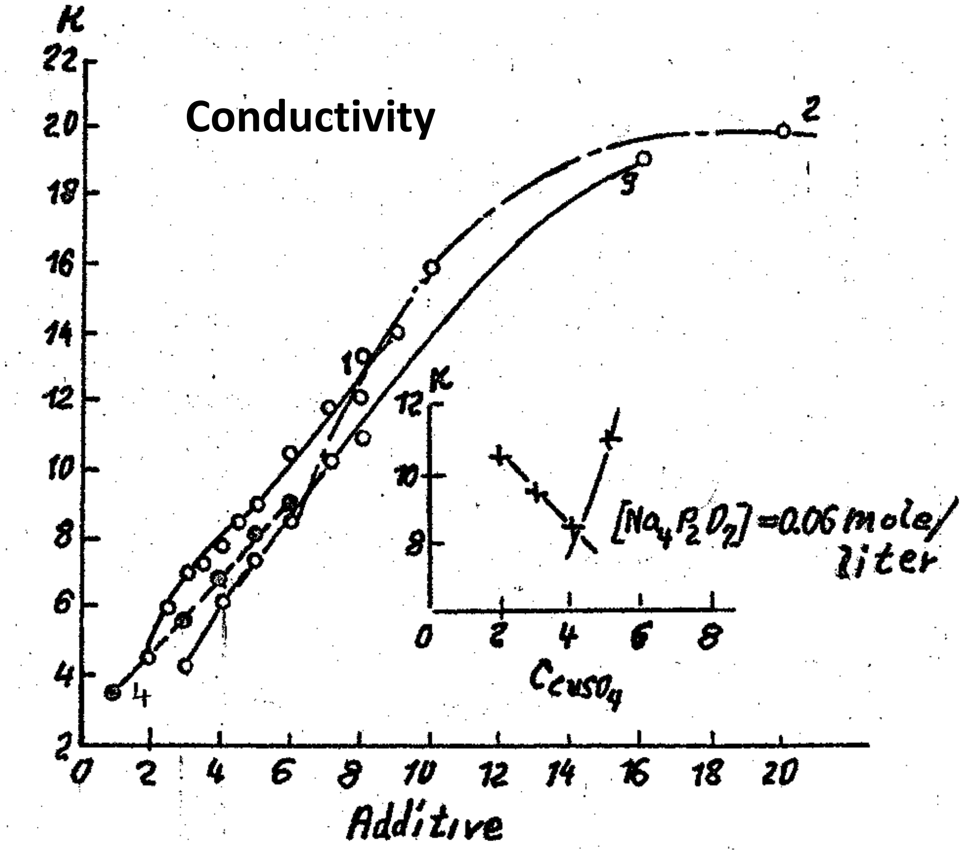
***Ligands: pyrophosphate, oxalate***

# Discussion on pyrophosphate complexes in Russ. J. General Chemistry (Zhurnal Obshei Khimii)

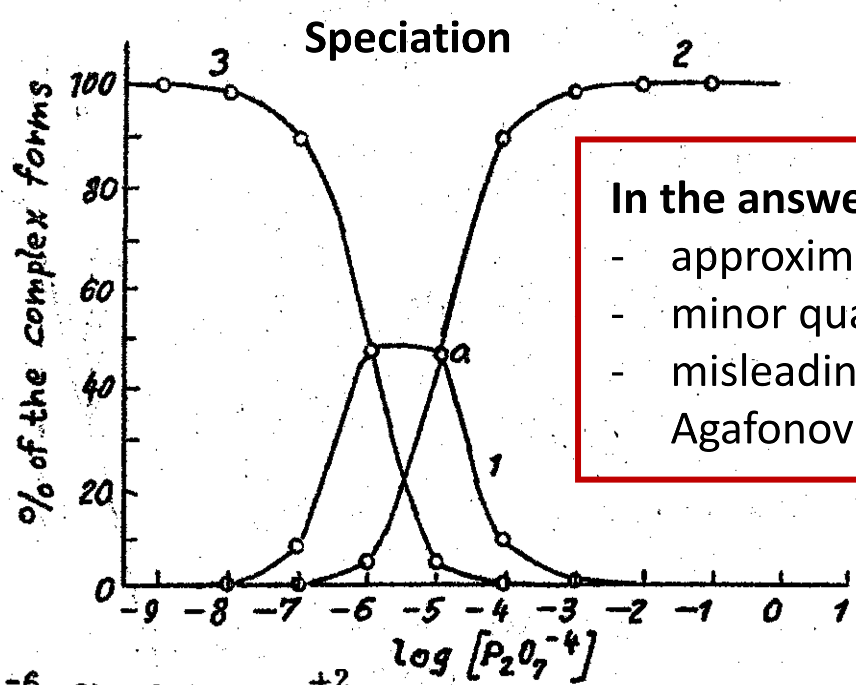
ON THE COMPOSITION AND PROPERTIES OF THE COMPLEX ELECTROLYTE OF THE COPPER-PYROPHOSPHATE BATH

**24 (1954) 781-784**

E. A. Ukshe and A. I. Levin




**Criticized by K. B. Yatsimirskyi, 25 (1955) 1181-1182 and I.L. Agafonov, 25 (1955) 1179-1180**

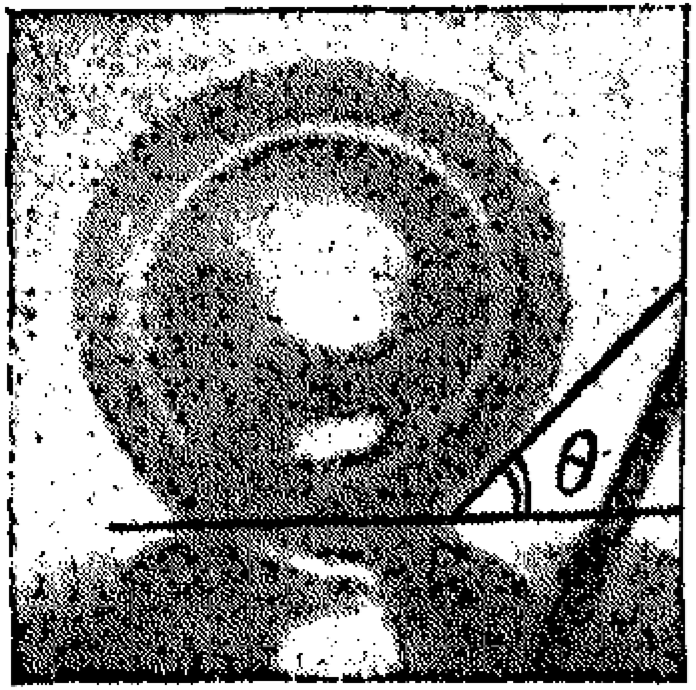



**In the answer, 26 (1956) 2963-2965**,

- approximations are thoroughly listed,
- minor quantitative mistakes are admitted,
- misleading statements and strains in Agafonov's comments are identified

1) $[Cu(P_2O_7)]^{-2}$, 2) $[Cu(P_2O_7)_2]^{-6}$, 3) $Cu(H_2O)_n^{+2}$

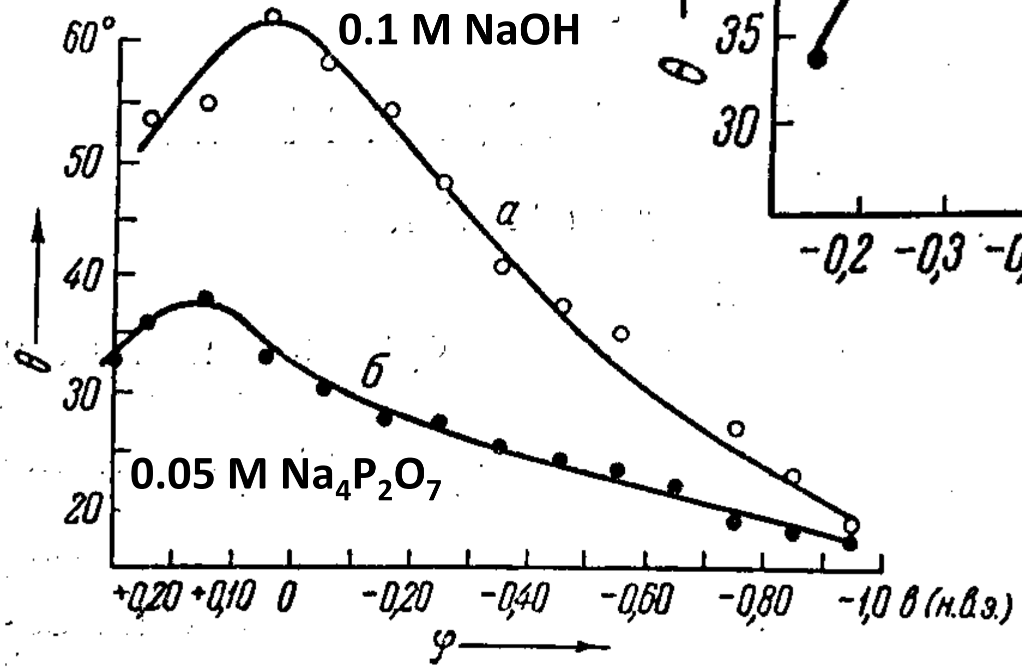
# Zero charge potentials

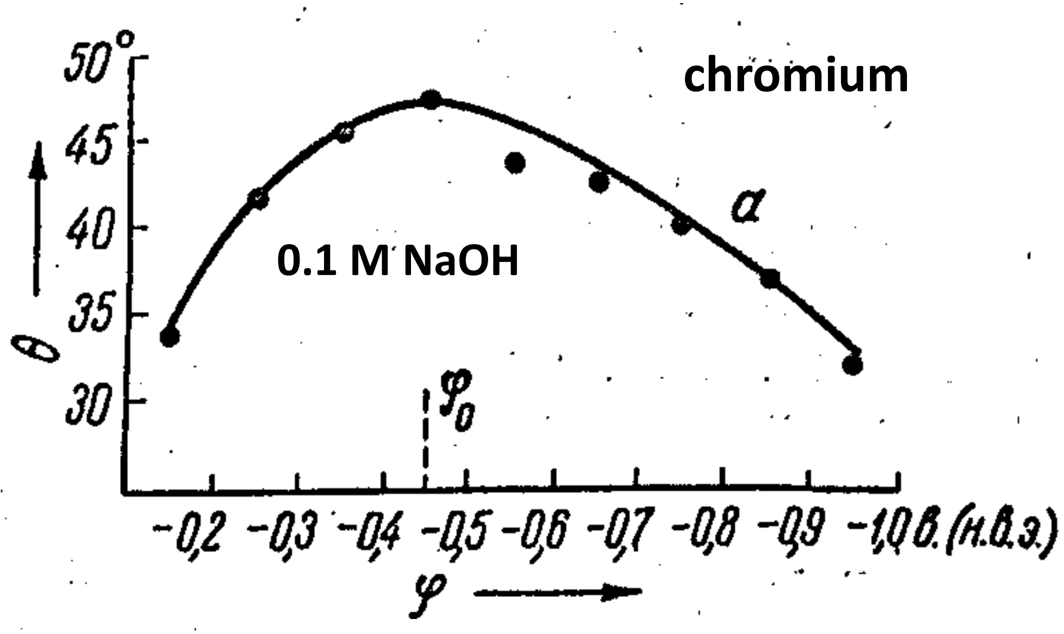



Bubbles: air or hydrogen

Drops: toluene

copper



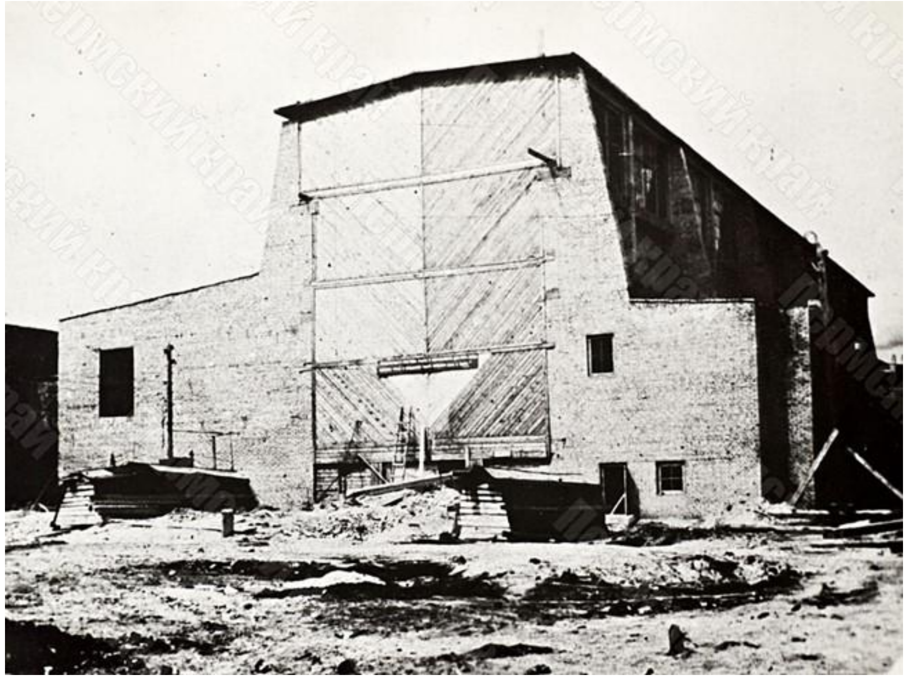




**Discussion of Kanevskyi potential and pzc *vs* work function dependence**

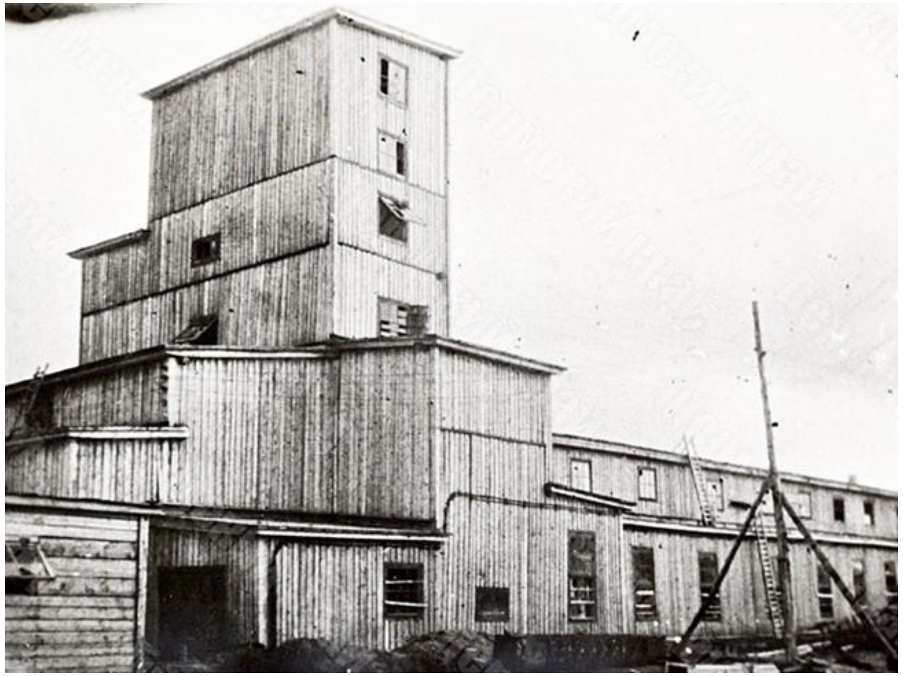
Ukshe, Levin, Doklady AN SSSR 105 (1955) 119-122

Ukshe, Levin, Zhurnal Fizicheskoi Khimii 29 (1955) 219-224

Novakovskyi, Ukshe, Levin Zhurnal Fizicheskoi Khimii 29 (1955) 1847-1853



**Berezniki (Perm region), magnesium production started during WWII**

**Berezniki rapidly developed in 1950s, magnesium plant was totally reconstructed, division of Al-Mg Institute was started in 1956**



CONTENTS



**Early joint Ukshe-Bukun topic:**

# THE DISSOLUTION OF METALS IN FUSED HALIDES

Russian Chemical Reviews 30 (1961) 90-107

E.A. Ukshe and N.G. Bukun

**Starting Refs (!!!) :**

1. H.Davy, Phil.Trans., 98, 336 (1808).
2. H.Davy, Phil.Trans., 97, 1 (1807).

Comparison of the properties of solutions of metals in fused salts and in solid crystals (*F*-centres) suggests their close similarity. In systems containing normal metal ions and sub-ions, the excess electrons are evidently not localised on definite atoms but move freely from one to another. Dimerisation of the sub-ions hinders this process by deepening the potential box for the electron. Nevertheless, it may be assumed that electronic conductivity is shown by solutions of metals, although the conductivity should be not metallic but semiconducting in character. Thus a given solution at relatively low temperatures close to the melting point of the salt can be regarded as a system containing chiefly normal ions and sub-ions, while the same solution at high temperatures can be regarded as a solution of excess electrons

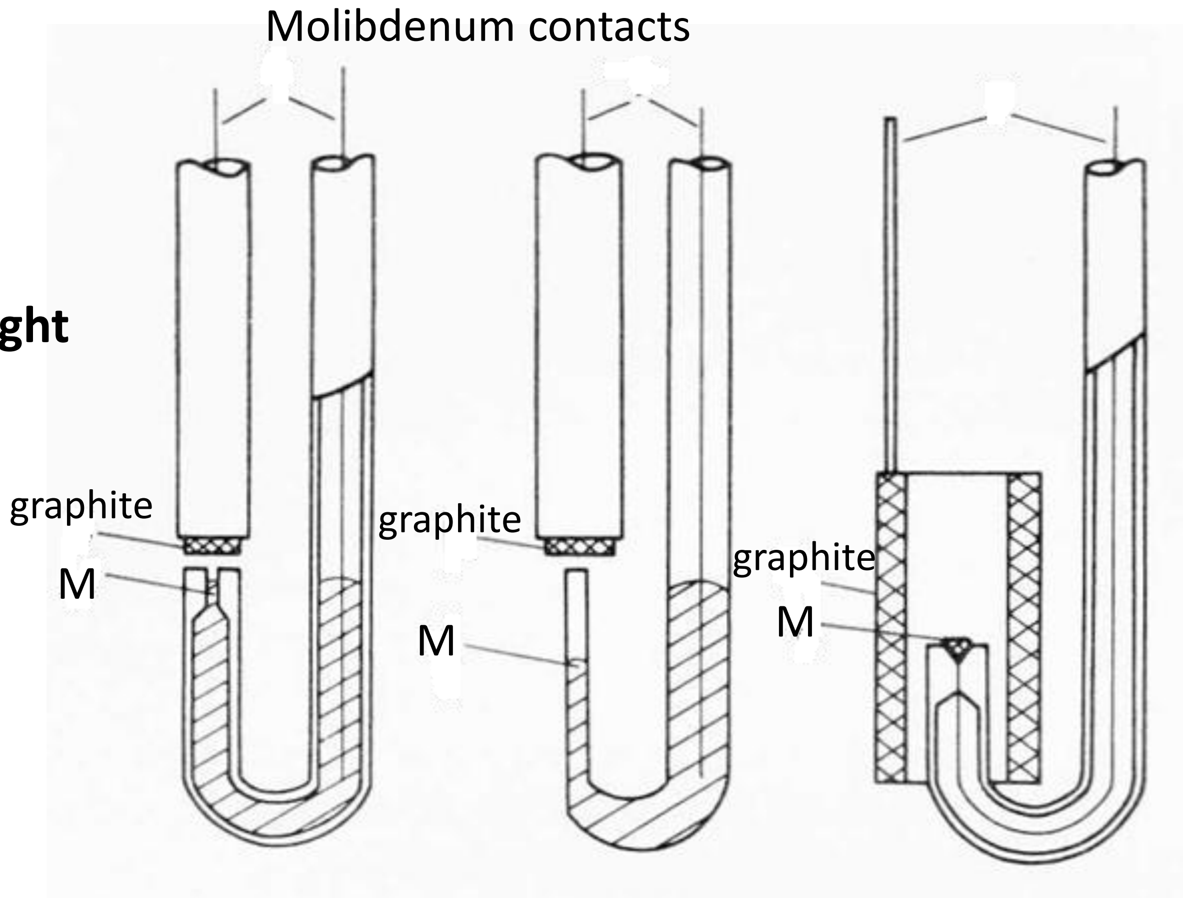
# Capacitance in molten salts, jointly with Frumkin Inst

Dina Iosifovna Leikis (1921-?)
1944 graduate of Ural Univ

**Quartz; capillary of ca. 0.5 mm diam.**

**C at 15-20 kHz, after the fight with frequency dispersion**

**Compared with directly measured electrocapillary curves**

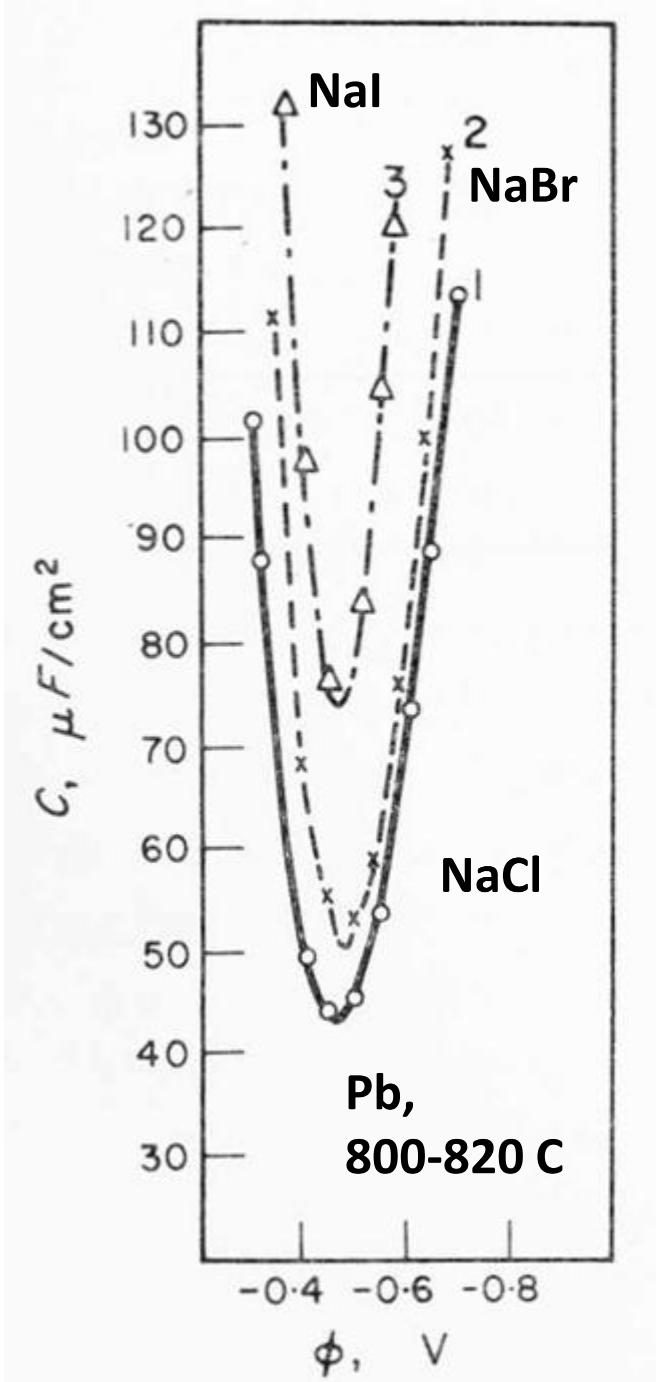


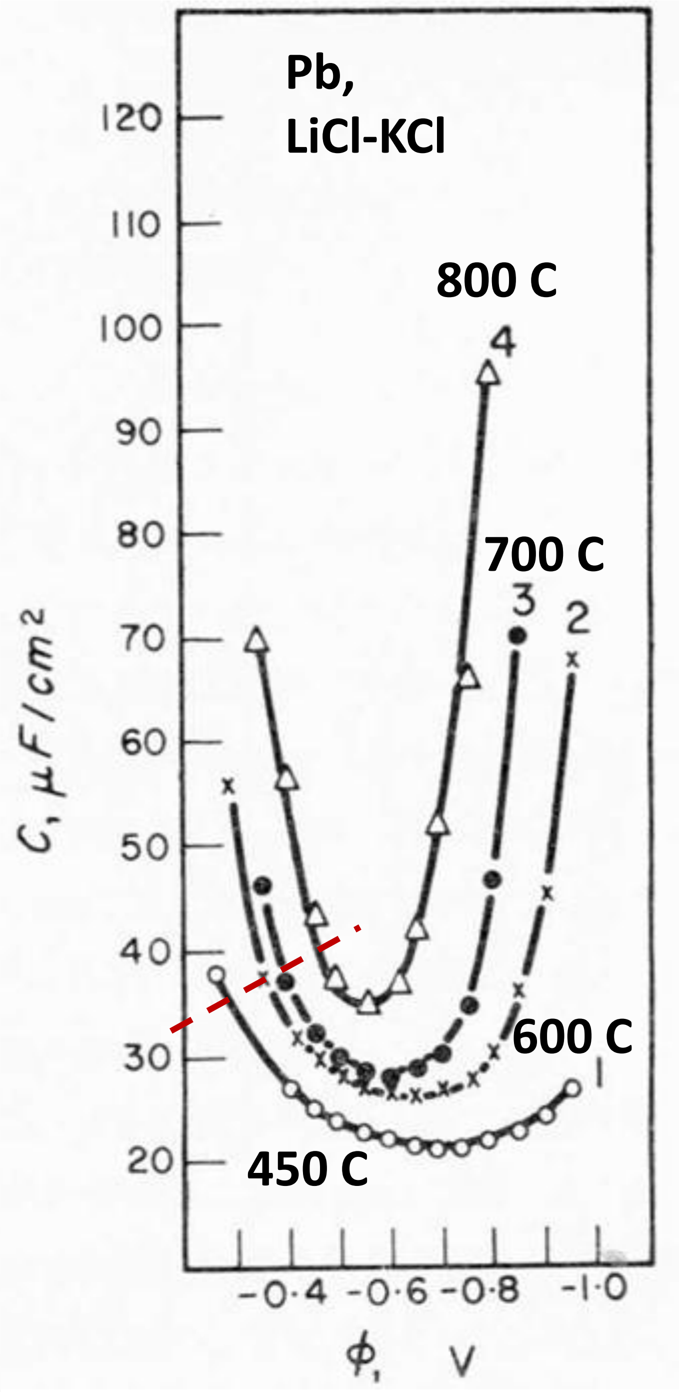

**Liquid metal M had to be renewable and to keep constant and measurable surface area.**

Ukshe, Bukun, Leikis, Doklady Physical Chemistry 135 (1960) 1173-1175 (Doklady Akademii Nauk SSSR 135 (1960) 1183-1186)

……………….

Ukshe, Bukun, Leikis, Frumkin, Electrochim. Acta 9 (1964) 431-439




**REVIEW**
J. Electroanal. Chem. 25 (1970) 349-356; 357-372

THE ELECTRICAL DOUBLE LAYER IN MOLTEN SALTS

PART 1. THE POTENTIAL OF ZERO CHARGE

PART 2. THE DOUBLE-LAYER CAPACITANCE

A. D. GRAVES

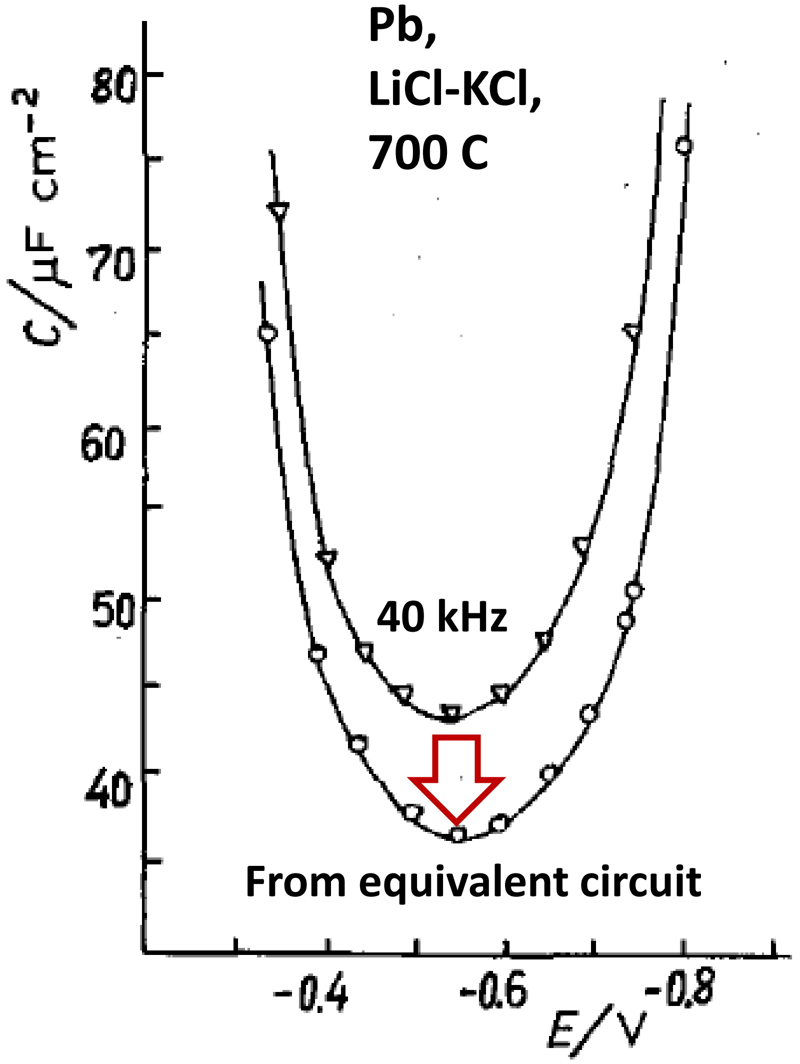
**Key aspects:**

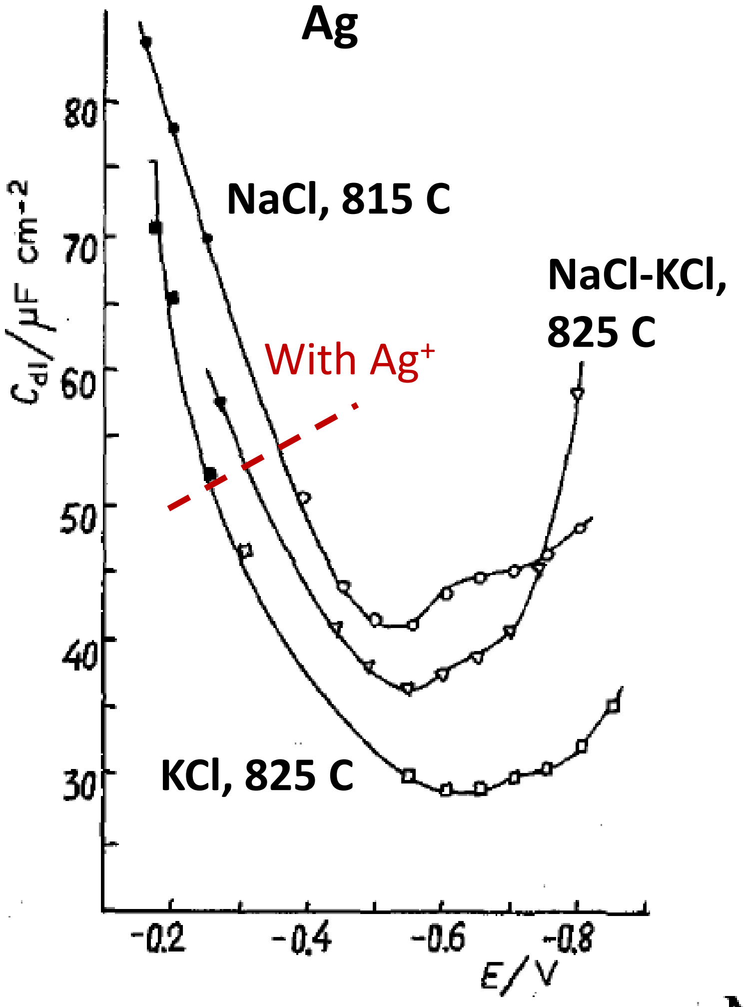
- **Difference of the 'double layers' in melts and solutions**
- **Correlation of pzc in melts and work functions**

**Key problem: Faradaic contribution, which disturbs the ideal polarizability (Graves ; Bek and Lifshits, 1967-1968)**

# Inevitability of the impedance

* It should be noted here that an analogous recalculation of the data of Beck and Lifshits[18] concerning $C_{min}$ for the system $\boxed{Pb/NaCl\text{–}KCl \text{ gives } 37 \pm 7\ \mu F\ cm^{-2} \text{ instead of } 25 \pm 5\ \mu F\ cm^{-2}.}$




Key aspects nowadays:

- Difference of the 'double layers' in molten salts and room temperature ionic liquids
- Compact layer (if any) in molten salts
- Development of molecular-level models

Equivalent circuit accounting for metal dissolution and for intercalation:

$$M^{n+} + n\varepsilon \rightleftharpoons M$$

$$Na^{+} + \varepsilon + xM \rightleftharpoons Na \cdot xM \text{ and so on.}$$

Ukshe, Bukun, J. Electroanal. Chem. 32 (1971) 283-291

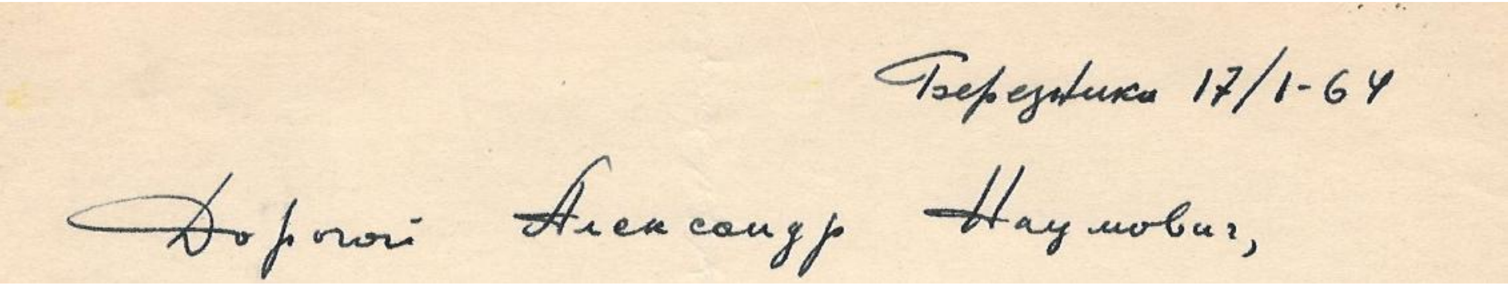
In conclusion, it is necessary to point out an inaccuracy in Graves' article[1]. This author claimed that Frumkin had discovered the "empirical" dependence between the p.z.c. of a metal in contact with electrolyte ($E_{q=0}$) and the work function of electrons ($w$)

$$E'_{q=0} - E''_{q=0} = w' - w''$$

where indexes $'$ and $''$ denote different metals. This dependence is actually not empirical. It was derived by Frumkin from the fact that the e.m.f. of a cell made from two metals at their p.z.c. can differ from zero only owing to potential differences which are localized in the surface layers of metals at their contact with each other and with a solvent. Apparently, the presence of the solvent is not necessary for the existence of such potential difference, and if one neglects the fact that adsorption of the solvent dipole molecules can vary, the e.m.f. in question must be equal[33] to contact potential difference between the two metals, *i.e.* $w' - w''$. The work of Novakovsky *et al.*[34] referred to by Graves may be considered rather as the mathematical interpretation of Frumkin's idea.

Ukshe, Bukun, J. Electroanal. Chem. 32 (1971) 283-291

## Ukshe's letter to Frumkin, January 1964



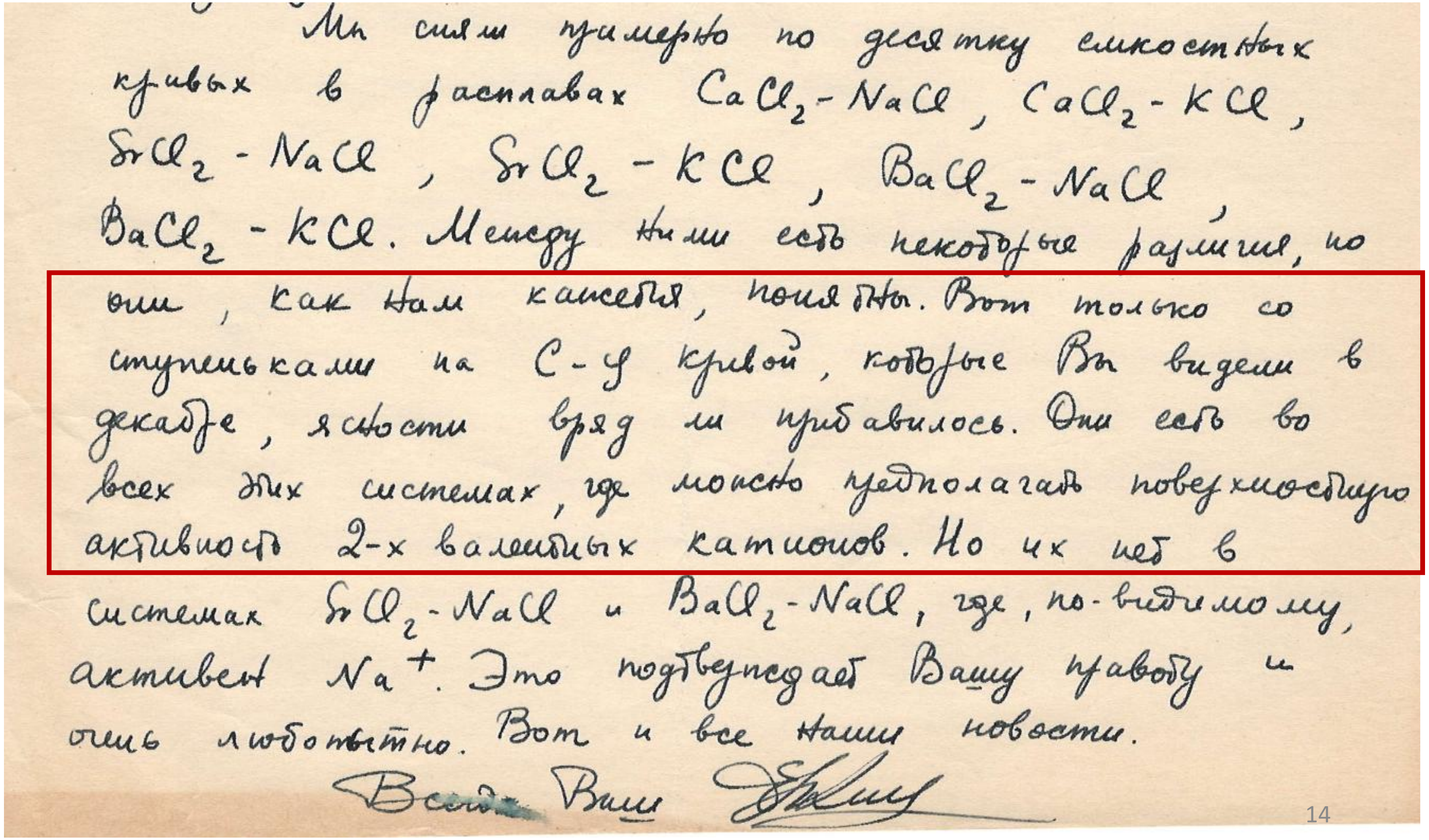
Березники 17/1-64

Дорогой Александр Наумович,

Steps at capacitance vs potential curves appear in certain binary systems, where two cations are expected to be surface-active.

It seems that we still do not know the answer.

Actually, the steps became less mysterious when impedance was started instead of capacitance at constant frequency.



Мы сняли примерно по десятку емкостных кривых в расплавах $CaCl_2$ - $NaCl$, $CaCl_2$ - $KCl$, $SrCl_2$ - $NaCl$, $SrCl_2$ - $KCl$, $BaCl_2$ - $NaCl$, $BaCl_2$ - $KCl$. Между ними есть некоторые различия, но они, как нам кажется, понятны. Вот только со ступеньками на C-φ кривой, которые Вы видели в декабре, ясности вряд ли прибавилось. Они есть во всех этих системах, где можно предполагать поверхностную активность 2-х валентных катионов. Но их нет в системах $SrCl_2$ - $NaCl$ и $BaCl_2$ - $NaCl$, где, по-видимому, активен $Na^+$. Это подтверждает Вашу правоту и очень любопытно. Вот и все наши новости.

Всего Вам

# THE LESSONS

Applied electrochemistry is not something very different from fundamental electrochemistry. Contrary, applied = fundamental + practical result.

Not the object of research (solution, melt, crystal, etc.), and not the technique (impedance, etc.) specify the purpose of the study, but  the phenomenon.

However, all tiny details of both object and technique must be understood, despite of their not a superior role. Nothing can be of secondary importance in research.

Do not look for “descriptors”, look for physically grounded models.

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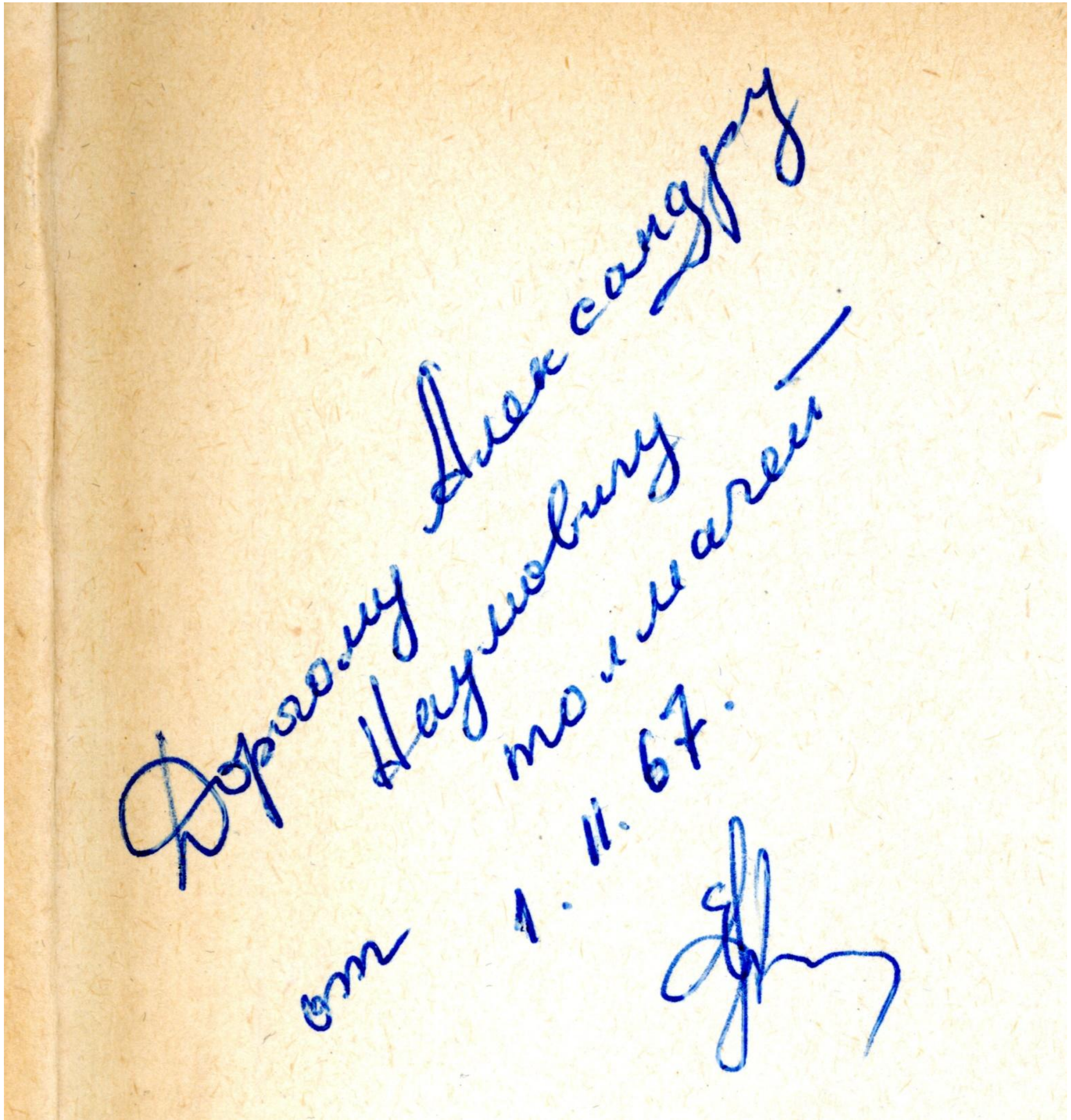
Belonging to scientific school or to the team of like-minded colleagues does not oppose individual achievements. Contrary, it highlights scientific personalities.




# Cannot be translated properly….

**To Dear Aleksandr Naumovich <Frumkin> from “tolmachs”**

“tolmach” is outdated Russian word,
its approximate meaning is “oral translator and interpreter”

**«Строение расплавленных солей»,**

**Перевод Н.Г. Букун, Ю.М. Рябухина и Ю.А. Чизмаджева,**

**под редакцией Е.А. Укше**

**М., Мир, 1966**

**Structure of molten salts,**
**Translated by Bukun, Ryabukhin, and Chizmadzhev, Edited by Ukshe, 1966**