

# История электрохимии. 6. Ионная ассоциация

От аномальной электропроводности – к формулировкам представлений о ионных парах. Разделение с эффектами вязкости.

Дипольные моменты – вероятно, первая физическая характеристика.

Тройники и комплексные ионы

Модели для константы ассоциации (диссоциации)

Учет ионных пар в уравнении для зависимости электропроводности от концентрации

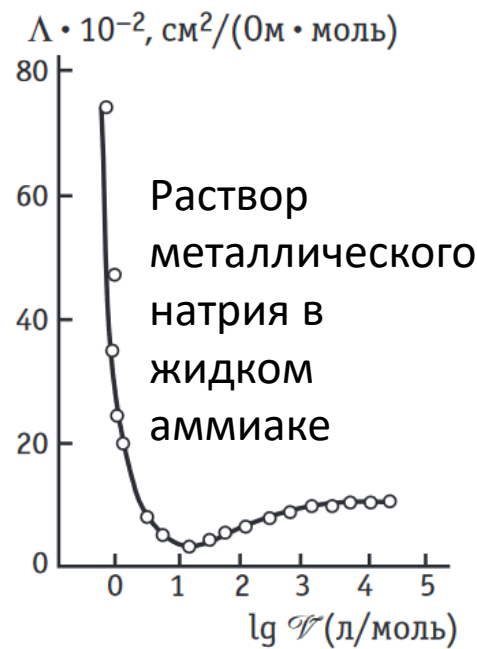
Важная литература

TABLE SHOWING THE COMPARATIVE IONIZING POWER OF AMMONIA  
AND WATER.

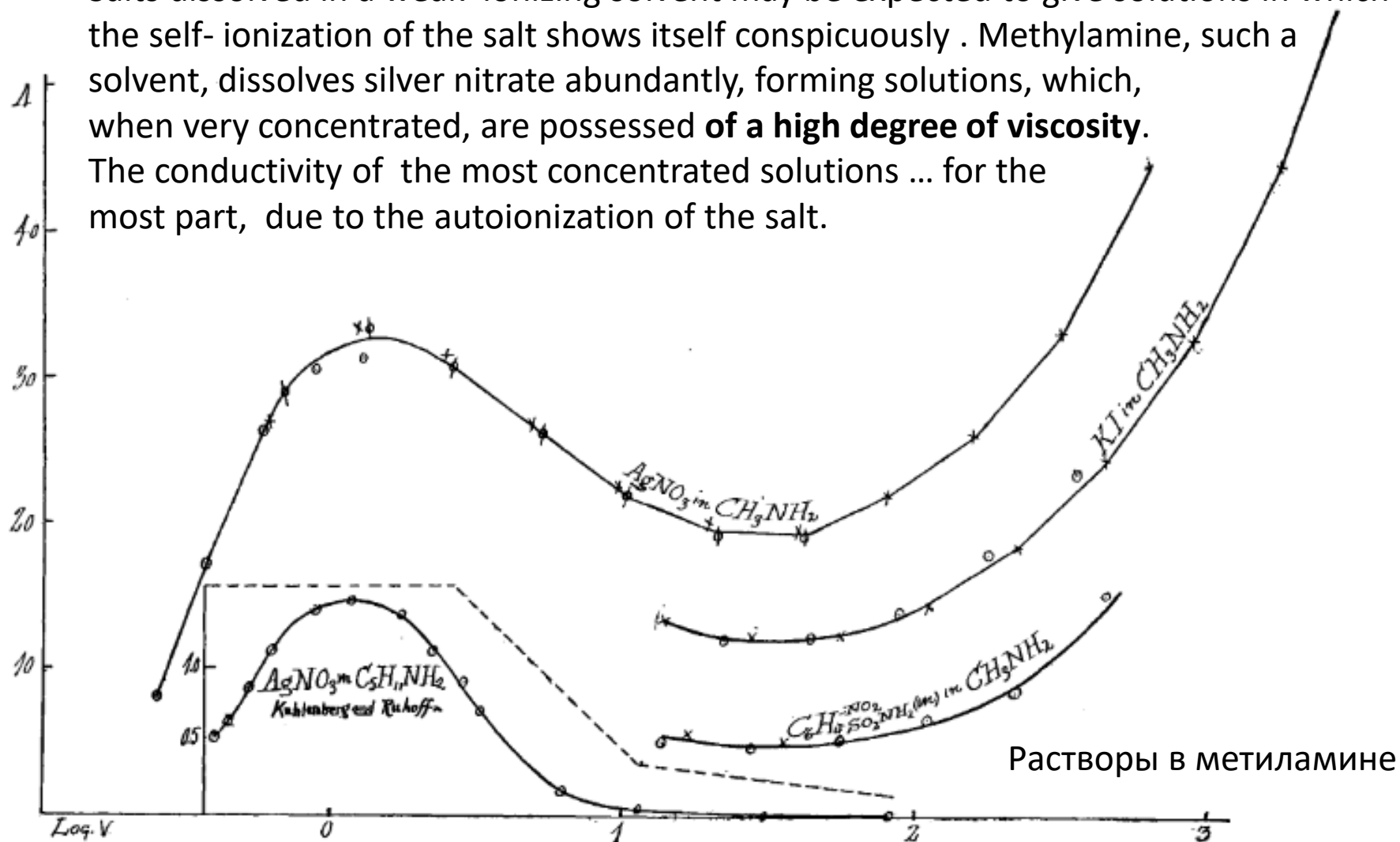
Разведение $\psi/1000$	$\alpha^1$ in ammonia at $-33^\circ$ .				$\alpha$ in water at $8^\circ$ .			
	3.	10.	100.	1000.	0.5.	3.3	10.	100.
KNO <sub>3</sub> .....	0.23	0.26	0.41	0.73	0.55	0.76	0.83	0.95 <sup>2</sup>
					.....	0.73	0.83	0.97 <sup>3</sup>
KCl.....	.....	.....	.....	.....	0.71	0.81	0.86	0.94 <sup>2</sup>
KBr.....	.....	.....	0.47	0.77	0.76	0.81	0.83	..... <sup>4</sup>
					.....	0.79	0.84	0.94 <sup>3</sup>
					.....	.....	.....	0.95 <sup>5</sup>
KI.....	.....	.....	.....	.....	0.77	0.83	0.87	0.95 <sup>2</sup>
C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> )SO <sub>2</sub> OK( <i>m</i> ).....	.....	.....	0.43	0.71	.....	.....	.....	.....
NaNO <sub>3</sub> .....	0.30	0.34	0.52	0.79	0.52	0.77	0.84	0.94 <sup>2</sup>
					0.53 <sup>6</sup>	0.70	0.79	0.95 <sup>3</sup>
NaCl.....	.....	.....	0.44	0.75	0.59	0.77	0.84	0.94 <sup>2</sup>
NaBr.....	0.30	0.34	0.52	0.81	.....	.....	.....	0.92 <sup>5</sup>
					0.71	0.88	0.92	..... <sup>7</sup>
NaI.....	.....	(0.40)	0.60	0.82	.....	.....	.....	0.92 <sup>5</sup>
					0.73	0.86	0.92	..... <sup>7</sup>
NH <sub>4</sub> NO <sub>3</sub> .....	.....	.....	0.56	0.85	0.65 <sup>6</sup>	0.75	0.82	0.90 <sup>8</sup>
HNO <sub>3</sub> .....	.....	.....	.....	.....	0.68	0.89	0.93	0.97 <sup>2</sup>
NH <sub>4</sub> Cl.....	.....	0.23	0.39	0.67	0.71	0.80	0.85	0.94 <sup>2</sup>
HCl.....	.....	.....	.....	.....	0.67	0.89	0.93	0.97 <sup>2</sup>
NH <sub>4</sub> Br.....	.....	.....	0.52	0.78	.....	.....	.....	.....
NH <sub>4</sub> I.....	.....	.....	0.64	.....	.....	.....	.....	.....
LiNO <sub>3</sub> .....	.....	.....	0.53	0.78	.....	.....	.....	0.95 <sup>5</sup>
TiNO <sub>3</sub> .....	.....	.....	0.47	0.76	.....	.....	.....	0.95 <sup>5</sup>
AgNO <sub>3</sub> .....	.....	.....	0.54	0.82	0.48	0.71	0.81	0.94 <sup>2</sup>
AgI.....	.....	.....	0.18	0.43	.....	.....	.....	.....

E.C. Franklin,  
C.A. Kraus,  
J. Amer. Chem. Soc.  
27 (1905) 191-222

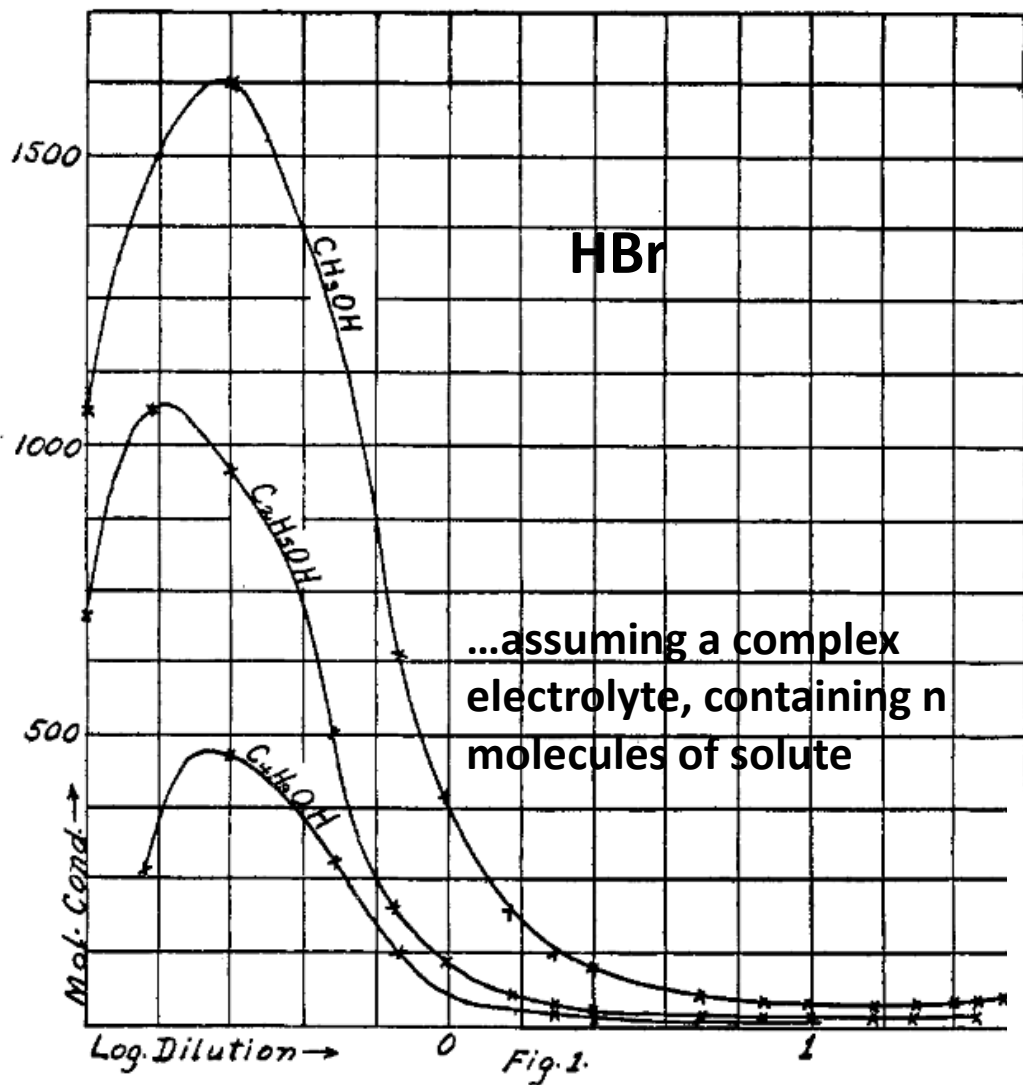
Степень диссоциации  
- из сравнения с  
предельной электро-  
проводностью



Salts dissolved in a weak ionizing solvent may be expected to give solutions in which the self-ionization of the salt shows itself conspicuously. Methylamine, such a solvent, dissolves silver nitrate abundantly, forming solutions, which, when very concentrated, are possessed of a high degree of viscosity. The conductivity of the most concentrated solutions ... for the most part, due to the autoionization of the salt.

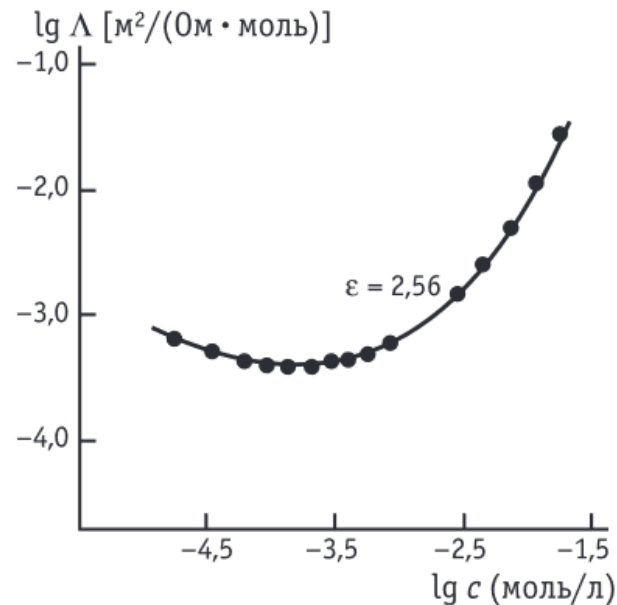


E. C. Franklin, H. D. Gibbs, J. Amer. Chem. Soc. 29 (1907) 1385 - 1396



Log(разведение  $1/c$ )

E. H. Archibald,  
 J. Amer. Chem. Soc. 34 (1912) 584-592



Зависимость эквивалентной электропроводности  $\Lambda$  раствора нитрата тетраизоамиламмония в водно-диоксановой смеси от концентрации  $c$

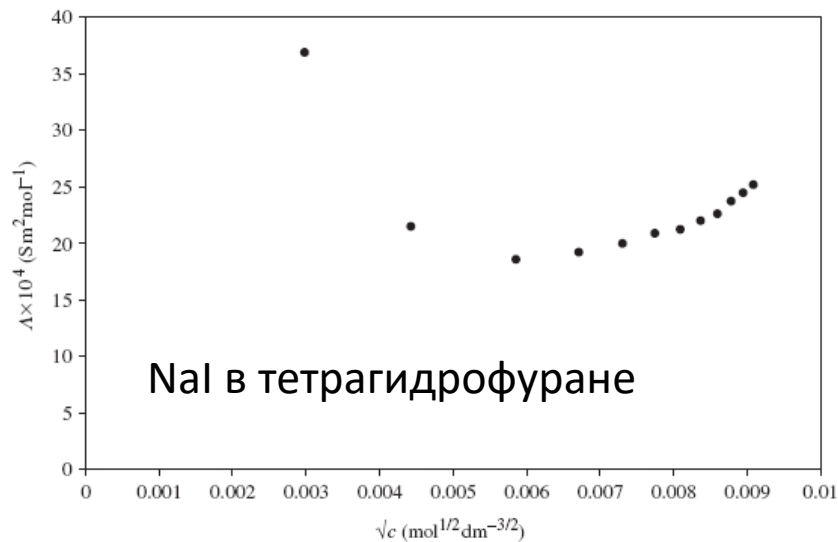


Figure 3. Plot of  $\Lambda$  vs.  $\sqrt{c}$  of NaI in pure THF at 298.15 K.

## LITERATURE CONCERNING THE ABNORMAL DISSOCIATION

Steele, MacIntosh and Archibald: *Zeit. phys. Chem.*, **55**, 129 (1906).

Archibald: *Jour. Am. Chem. Soc.*, **29**, 665, 1416 (1907); **34**, 584 (1912).

Franklin and Kraus: *Ibid.*, **27**, 216 (1905); **29**, 1395 (1907).

Franklin: *Jour. Phys. Chem.*, **15**, 675 (1911).

Lewis and Wheeler: *Zeit. phys. Chem.*, **56**, 190 (1906).

Foote and Martin: *Am. Chem. Jour.*, **41**, 451 (1909).

Sakhanov: *Jour. Russ. Chem. Soc.*, **42**, 683 (1910); **42**, 1363 (1910);  
**43**, 526 (1911); **44**, 324, 1794 (1912); *Zeit. phys. Chem.*, **80**, 13 (1912);  
**83**, 129 (1913); *Zeit. Elektrochemie*, **20**, 529 (1914).

Sakhanov and Prscheborovsky: *Zeit. Elektrochemie*, **20**, 39 (1914);  
*Jour. Russ. Chem. Soc.*, **47**, 879 (1915).

Sakhanov and Rabinowitch: *Jour. Russ. Chem. Soc.*, **47**, 859 (1915).

Sakhanov and Grinbaum: *Ibid.*, 1769 (1915); second paper is printed.

Plotnikov: *Ber. deutsch. chem. Ges.*, **39**, 1794 (1906); **42**, 1154 (1909).

Walden: *Bull. Imper. Akad. Sci. Petersb.*, **1913**, 922, 987, 1100; **1915**, 789.  $D \cdot \sqrt[3]{V_m} = \text{const}$

Hopfgartner: *Wien. Akad. Ber.*, **120**, IIC, 1 (1911); **122**, IIC, 603 (1913).

Fitzgerald: *Jour. Phys. Chem.*, **16**, 621 (1912).

Pearce: *Ibid.*, **19**, 14 (1915).

Anderson: *Ibid.*, **19** (1915).

Fischler: *Zeit. Elektrochemie*, **19**, 126 (1913).

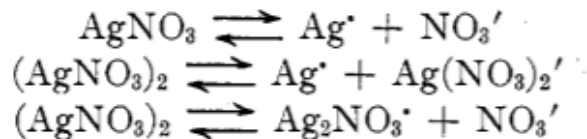
Beckmann: *Zeit. anorg. Chem.*, **77**, 280 (1912).

Beckmann and Waentig: *Ibid.*, **67**, 36 (1910).

Kraus and Bray: *Jour. Am. Chem. Soc.*, **35**, 1315 (1912).

Для минимума  
 электропроводности  
 ( $D$  – диэлектричес-  
 кая проницаемость,  
 $V$  – разведение).

Thus as a general case electrolytic dissociation of associated molecules gives complex anions as well as cations. For example, the electrolytic dissociation of silver nitrate in any of the solvents leads as a general case to the following processes:



These phenomena may be complicated on the one hand by solvation and on the other hand by the formation of still more highly polymerized molecules than double, as is the case with solutions in chloroform.

A.H. Саханов,  
J. Phys. Chem.  
21 (1917) 169–189

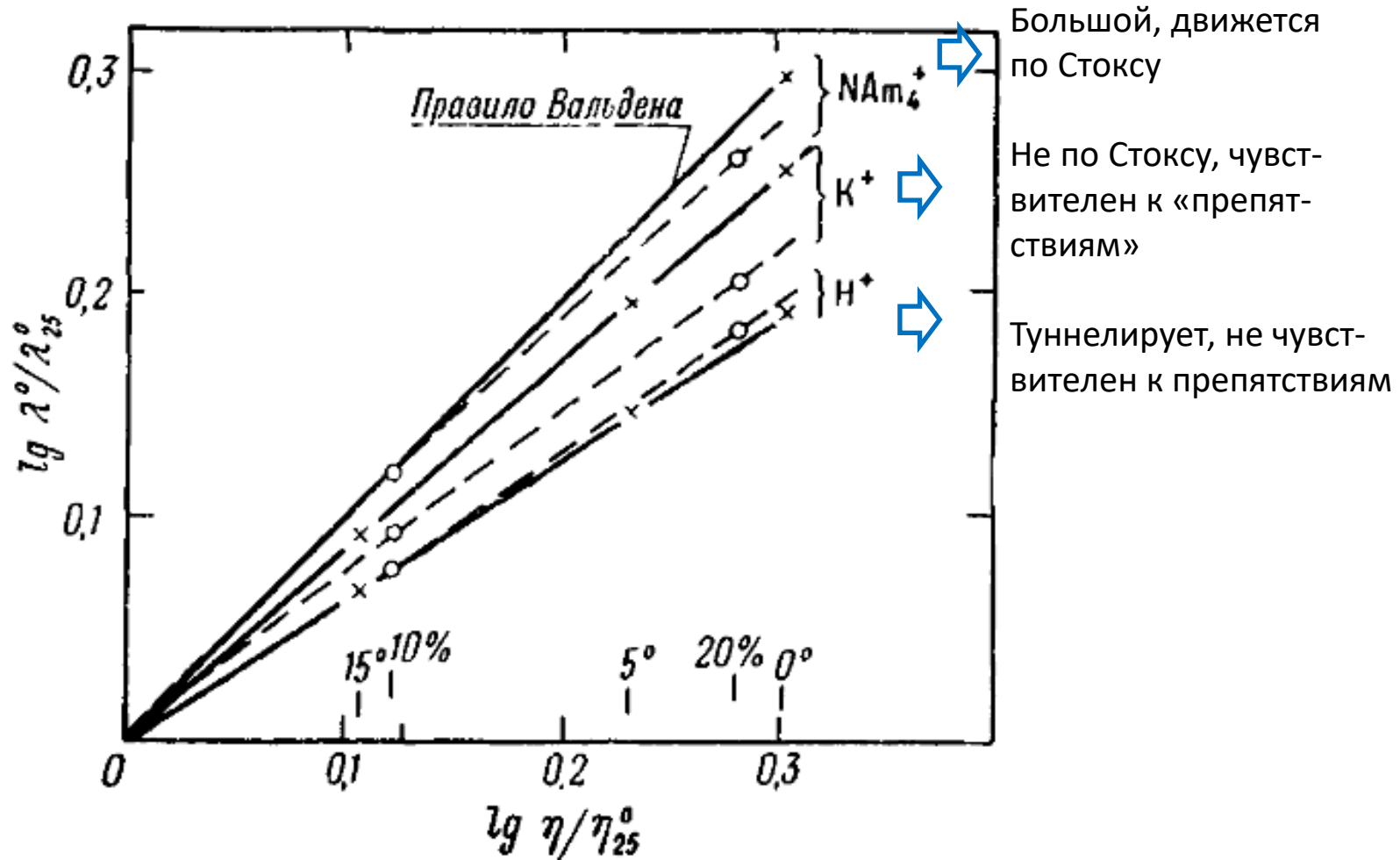
### Conductivity and Viscosity of Solutions

#### I. Silver Nitrate in Aniline

Dilution in lit. Разведение $\frac{v}{c}$	Mol. conduct. $\lambda$	Ratio <sup>1</sup> $\eta : \eta_0$	Corr. mol. cond. $L$
186.6	0.37	1.00	0.37
112.9	0.33	1.00	0.33
52.4	0.32 (Minim.)	1.02	0.33 (Minim.)
32.6	0.34	1.03	0.35
26.38	0.36	1.04	0.37
18.35	0.39	1.06	0.41
10.41	0.64	1.10	0.70
6.76	0.85	1.19	1.01
3.24	1.54	1.46	2.25
1.560	1.96 (Maxim.)	2.33	4.57
0.911	1.57	—	—
0.570	0.76	—	—
0.543	0.62	—	—

$$L = \lambda \cdot \frac{\eta}{\eta_0}$$

## Поправки на вязкость: гораздо лучше работают для крупных ионов



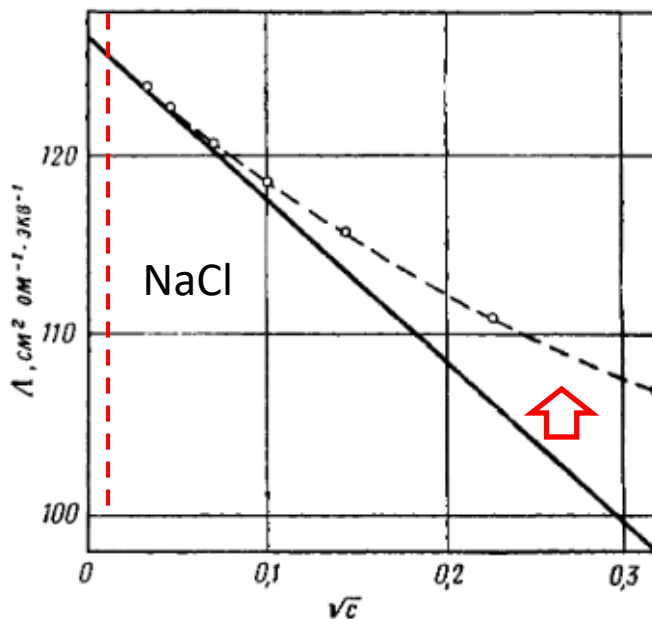
Влияние повышения вязкости, вызванного добавлением сахарозы (кружки) или понижением температуры (крестики), на различные ионы.

Вязкость и эквивалентная электропроводность выражены в долях соответствующих величин для воды при 25°.

Electric moments of ion dipoles in benzene

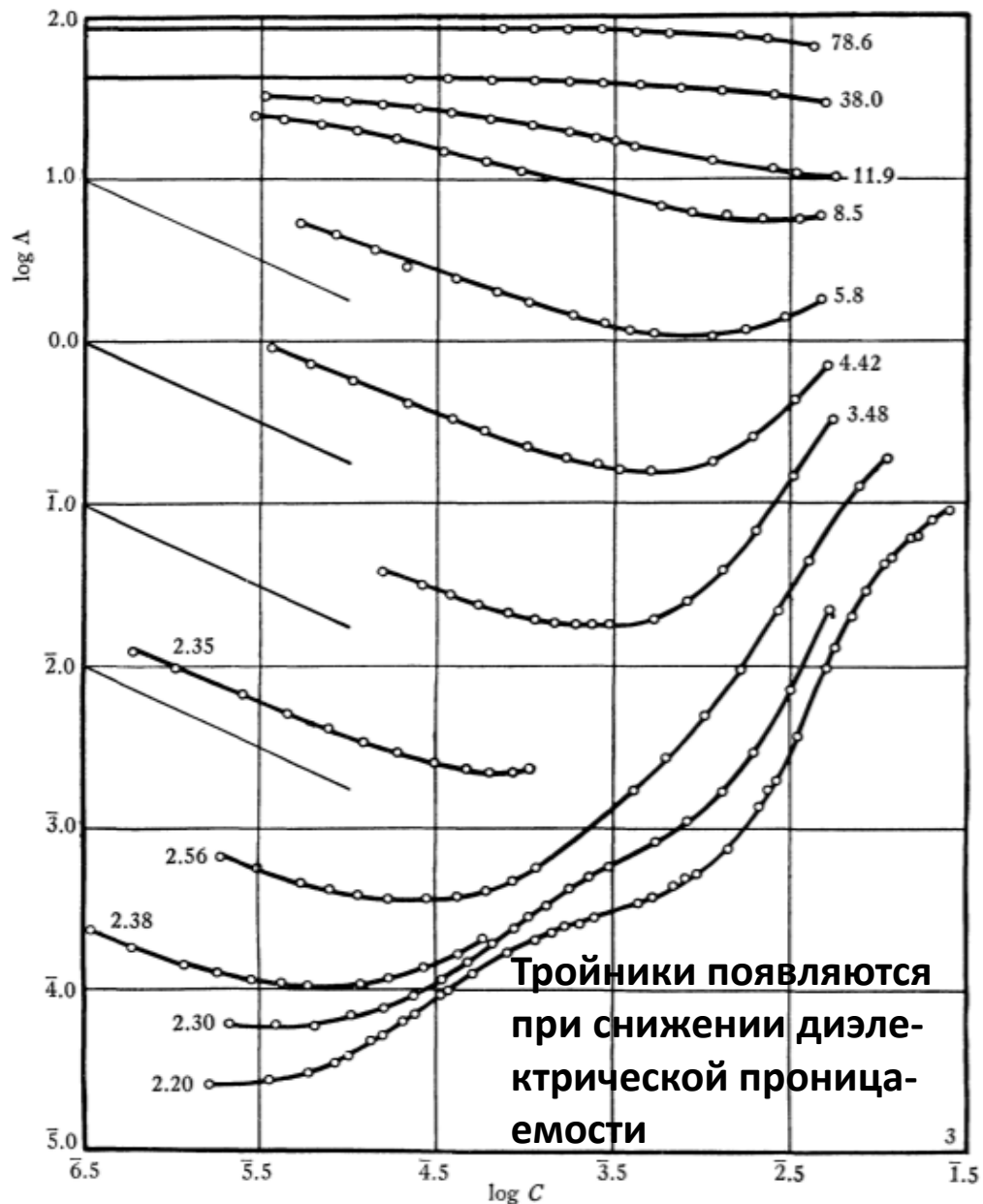
Salt	Polarization	Moment $\times 10^{18}$	$a \times 10^8$
Bu <sub>4</sub> N · Ac	2690	11.2	2.34
Bu <sub>4</sub> N · Br	3250	12.3	2.58
Bu <sub>3</sub> NH · Pi	3770	13.2	2.78
Am <sub>3</sub> NH · Pi	3830	13.3	2.80
Am <sub>4</sub> N · SCN	5050	15.4	3.23
Bu <sub>4</sub> N · Pi	6740	17.8	3.74
Am <sub>4</sub> N · Pi	7090	18.3	3.83
Am <sub>4</sub> N · HOBPh <sub>3</sub>	8200	19.6	4.12

Bu = butyl, Am = amyl, Ph = phenyl, Ac = acetate, Pi = picrate.



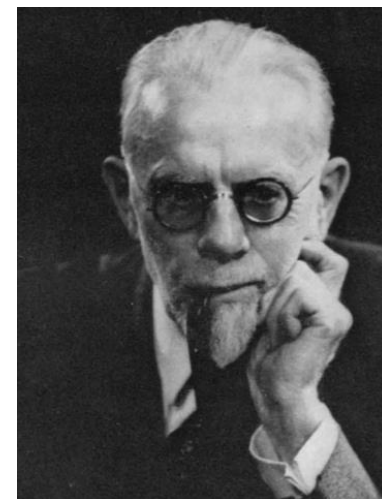
Отклонения от уравнения Онзагера





Смеси вода-диоксан, tetraisoamylammonium nitrate

**Charles August Kraus**  
(1875 – 1967)



**Raymond Matthew Fuoss**  
(1905 – 1987)

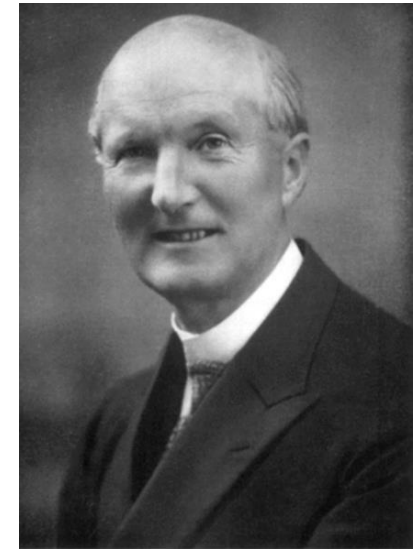
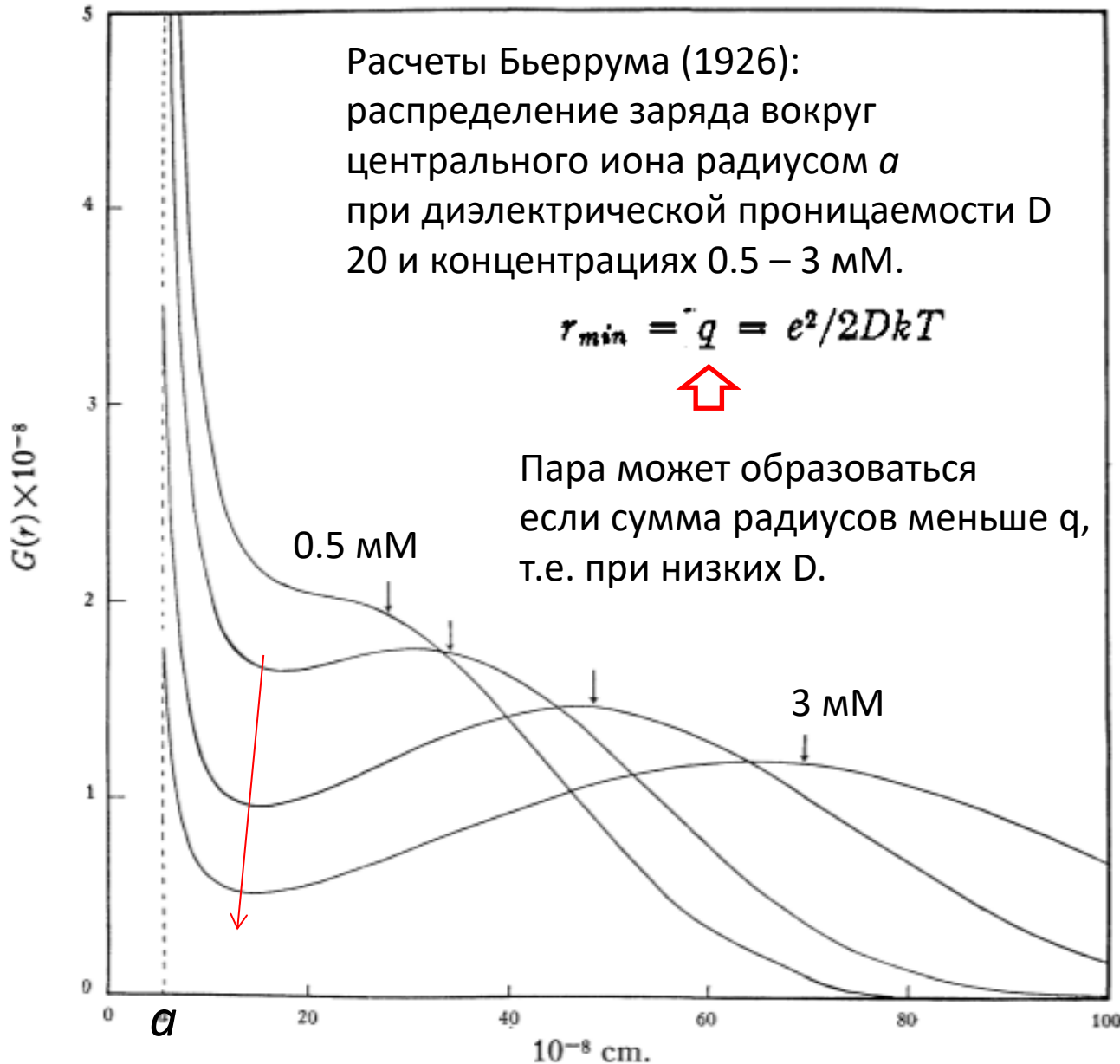
C. A. Kraus, R. M. Fuoss,  
J. Amer. Soc., 55(1933)21

Расчеты Бьеррума (1926):  
распределение заряда вокруг  
центрального иона радиусом  $a$   
при диэлектрической проницаемости  $D$   
20 и концентрациях 0.5 – 3 мМ.

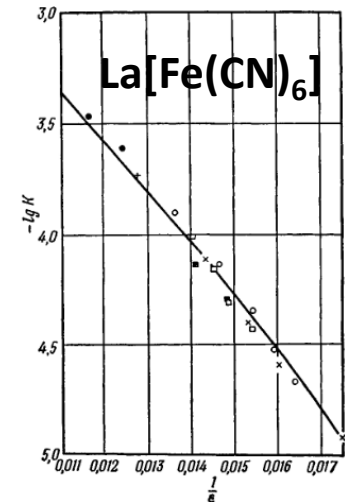
$$r_{min} = \bar{r} = \frac{e^2}{2DkT}$$



Пара может образоваться  
если сумма радиусов меньше  $\bar{r}$ ,  
т.е. при низких  $D$ .



**Niels Janniksen Bjerrum**  
(1879 – 1958)



Константа диссоциации феррицианида лантана как функция диэлектрической постоянной растворителя; сравнение экспериментальных величин с уравнением Бьеррума.

● глицин – вода; × диоксан – вода; ○ ацетон – вода; □ глицерол – вода; ■ этанол – вода; + чистая вода; — теоретическая кривая.

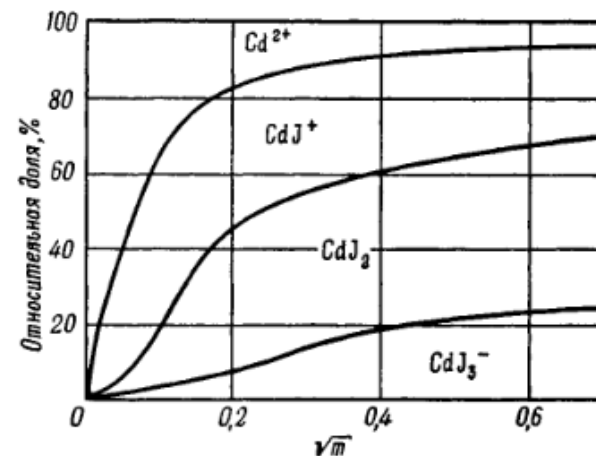
Числа переноса катионов в водных растворах  
2-1-электролитов при 25°; эффект образования  
аутокомплексов в галогенидах цинка

$m^a$	$Zn(ClO_4)_2^b$	$ZnJ_2^c$	$ZnBr_2^r$	$ZnCl_2^s$
0	(0,440)	(0,408 <sub>5</sub> )	(0,404 <sub>1</sub> )	(0,409 <sub>7</sub> )
0,05	—	0,382	0,366	0,365
0,1	0,409	0,363	0,349	0,350
0,2	0,389	0,345	0,331	0,335
0,5	0,361	0,320	0,306	0,331
1,0	0,335	0,291	0,286	0,171
2,0	0,303	0,178	0,181	0,000
3,0	0,281	0,056	—0,059	—0,137
4,0	0,271	—0,050	—0,151	—0,256
5,0	—	—0,190	—0,233	—0,364
8,0	—	—0,444	—0,445	—0,562
10,0	—	—0,550	—0,563	—0,559

R.A. Robinson, H.S. Harned,  
**Some Aspects of the Thermo-  
dynamics of Strong Electrolytes  
from Electromotive Force and  
Vapor Pressure Measurements,**  
Chem. Rev. 28 (1941) 419–476



Аналоги ионной ассоциации:  
комплексообразование,  
гидролиз (тоже изменяются  
число ионов и их заряды с  
концентрацией):



To summarize briefly, we recognize three types of 1-1 electrolytes:  
(a) Those with an anion of the noble-gas type, including all the hydrogen and alkali halides with the exception of the fluorides. The behavior of these electrolytes can be represented by a single family of curves, described by equation 57, with  $\bar{a}$  values which do not permit appreciable ionic association; the thiocyanates also are probably included in this category.  
(b) Those which exhibit reversal of the order of the activity coefficient curves, including the hydroxides, formates, acetates, and fluorides; the interpretation of their behavior is based on an hypothesis of “localized hydrolysis” leading to ionic association, not of the Bjerrum type, but by means of a water molecule as intermediary. (c) Those characterized by appreciable ionic association of the Bjerrum type due to the small “effective” size of the ions; this category is exemplified by most of the alkali nitrates and by the thallos salts.

By RAYMOND M. FUOSS AND CHARLES A. KRAUS

$$1/K \approx \frac{4\pi N}{1000} a^3 \frac{aDkT}{e^2} \exp\left(\frac{1}{a} \frac{e^2}{DkT}\right)$$

Упрощенный вариант уравнения Фуосса для константы диссоциации.



$$\Lambda = \Lambda_0 - \alpha \sqrt{c} - (\Lambda_0/K) c$$



Для обработки данных по электропроводности нужно учесть зависимость двух слагаемых от параметра  $a$

CONSTANTS FOR TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE-WATER MIXTURES

% Water	$D$	$-\log K$	$K$	$E, \text{ cal.}$	$\alpha \times 10^3$
0.60	2.38	15.7	$2 \times 10^{-16}$	21,400	6.01
1.24	2.56	14.0	$1 \times 10^{-14}$	19,100	6.23
2.35	2.90	12.0	$1 \times 10^{-12}$	16,400	6.36
4.01	3.48	9.6	$2.5 \times 10^{-10}$	13,100	6.57
6.37	4.42	7.53	$3.0 \times 10^{-8}$	10,300	6.65
9.50	5.84	5.78	$1.65 \times 10^{-6}$	7,900	6.45
14.95	8.5	4.00	$1.00 \times 10^{-4}$	5,450	6.50
20.2	11.9	3.05	$9.0 \times 10^{-4}$	4,150	6.70
53.0	38.0	0.60	0.25	820	6.15

### CONSTANTS FOR SILVER NITRATE IN DIFFERENT SOLVENTS

Solvent	$\Delta_0$	$-\log K$	$\alpha \times 10^3$	$D$	$\mu \times 10^{18}$
Benzonitrile	55.2	3.495	1.62	25.2	3.91
Acetonitrile	186	1.775	1.90	36	3.11
Ammonia	291	2.314	5.78	22	1.49

### CONSTANTS FOR THE ALKALI METAL NITRATES IN AMMONIA AT $-40^\circ$

Salt	$\Delta_0$	$K \times 10^4$	$\alpha \times 10^3$	Ion	$\Delta_0$ (ion)	$r^* \times 10^3$
$\text{LiNO}_3$	277	36.5	5.04	$\text{Li}^+$	112	0.28
$\text{NaNO}_3$	295.1	28.84	4.46	$\text{Na}^+$	130.1	0.41
$\text{KNO}_3$	329.0	14.71	3.57	$\text{K}^+$	164.0	0.82
$\text{RbNO}_3$	341.8	11.41	3.34	$\text{Rb}^+$	176.8	1.20
$\text{CsNO}_3$	333.5	9.66	3.21	$\text{Cs}^+$	168.5	1.48

Далее Фуосс уточнял описание константы диссоциации и электропроводности, J. Amer. Chem. Soc. 80 (1958) 5059-5061 .... с Онзагером J. Phys. Chem. 69 (1965) 2581–2594.

Нобелевская лекция Онзагера «The motion of ions: principles and concept», Science 166 (1969) 1359 – 1364.

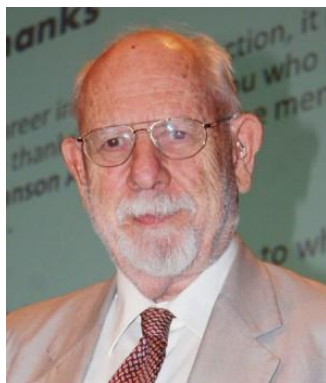
**R.M. Fuoss, Review of the Theory of Electrolytic Conductance,**  
J. Solution Chem. 7 (1978) 771 - 782



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**Книга «Электрохимия растворов» (1959)**

**Yizhak Marcus**



**Ions in solution and their solvation (2015)**

**R. Buchner, What can be learnt from dielectric relaxation spectroscopy about ion solvation and association?**  
Appl. Chem. 80 (2008) 1239–1252

## ELECTROLYTE SOLUTIONS

The Measurement and Interpretation  
of Conductance, Chemical Potential  
and Diffusion in Solutions of Simple  
Electrolytes

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