On the Adsorption of Strong Electrolytes.

By

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Of adsorption of strong electrolytes by solid substances, only few facts are definitely known, as may be seen from the following quotation from H. Freundlich's excellent work " Kapillarchemie,"[1]

" Es ist nicht verwunderlich, dass über die Adsorption stark dissoziierter Stoffe an festen Grenzflächen zur Zeit wenig Sicheres zu sagen ist. Man hat es ja in der Lösung mit verwickelten Gleichgewichten zwischen mehrere Stoffen zu tun, muss also eine Adsorption aus einem Gemisch mehrerer Stoffe in Rücksicht ziehen; dazu kommen noch kapllarelektrische Einflüsse. Die Angaben über die Adsorption von Salzen sind daher nochrecht widerspruchsvoll und schwer zu deuten.

" Allein schon die Frage nach dem Vorzeichen der Adsorption ist nicht eindeutig zu beantwoiten. Lagergren arbeitete mit Kohle und Kaolin als Adsorbentien in ziemlich konzentrierten (ca. 1-molar) Salzlösungen; er beobachtete eine sehr geringe, aber positive Adsorption bei den Nitraten des Natriums, Kaliums, Ammoniums und Baryums. Bei den Chloriden derselben Metalle (ausserdem noch bei Magnesium) war die Konzentration in der Lösung nach der Adsorption grösser als vorher: es war also eine negative Adsorption eingetreten; negativ adsorbiert wurde auch Bromammonium. Bei den Sulfaten war die Adsorption überhaupt gering, sie schien in einigen Fällen positiv, in anderen negativ zu sein..."

It has usually been assumed that the quantity of the solvent adsorbed by the adsorbent may be neglected, as the amount of the adsorbent used is small.[2] But in the case of strong electrolytes, since the adsorption is very slight, the negligence of that of water is not

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[1] p. 165.
[2] Freundlich, *Loc. cit.* 166.

admissible and may have been the cause of irregularity ef adsorption in some cases.

Because of such a consideration the author has undertaken the study of the adsorption of some strong electrolytes by blood charcoal and the results so far obtained are here communicated.

The blood charcoal used was C. Kahlbaum's preparation. It was digested in dilute hydrochloric acid for a few days, then washed by decantation with hot distilled water once or twice a day for about two months, and finally washed on a filter and dried at about 120° to a constant weight. It was preserved in a desiccator over sulphuric acid. It was quite free from chloride, but when shaken with water, it gave traces of extract, which was quantitatively determined, as was necessary for the present method of experiment, as may be seen later.

The salts used were purified in the usual way by recrystallisation, except the potassium bromide and iodide (Pharm. Jap.) which was directly used.

The experiments were carried out in the following way : A small Erlenmeyer flask of about 50 cc. capacity with a paraffined cork stopper was weighed, some refined blood charcoal was put in it and the whole was weighed again. About 50 cc. of a salt solution of an approximately known concentration was added to the flask which was weighed again. The cork stopper was fastened to the neck of the flask with copper wire and was made perfectly water-tight by paraffin. The flask was made to rotate in a thermostat at 25·0° for at least two days, then let stand still in the same thermostat for a day. About 10 cc. of the clear solution was taken out by a pipette, with a glass tube attached, filled with refined cotton previously washed with the same solution, and transferred into a weighed wide glass tube, drawn up at both ends, a so-called duck-tube,[1] and weighed. It was evaporated over a very small flame to dryness and then heated in an air-bath at about 120° to a constant weight. About 10 cc. of the original solution was also taken in a weighed duck-tube and treated in the same way.

As the contents of the solution were thus estimated by direct weighing of the residue, it was necessary to estimate the extract from the blood charcoal, though it was very slight. For this purpose, blood charcoal was treated with distilled water in the same way as with solutions. As the result of 10 experiments, a residue of 0·0003 grm.

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[1] Ostuald-Luthur Physiko-chemische Messungen, 3 ed., p. 264.

was obtained for 10 cc. of water, snd therefore 0·0003 grm. was sub-
tracted from the weight of the residue from a solution treated with
blood charcoal, variations of the amount of charcoal used being dis-
regarded as influential merely within the sphere of experimental error.

The method of calculation, being somewhat complicated, one case
of potassium iodide will be given in detail, as illustration.

1. Solution before Adsorption.

	(1)	(2)
Solution taken in a duck-tube	11·109	11·097
Residue after drying up	1·6352	1·6342
Salt in 10 grm. of the solution	1·4720	1·4727
The same corrected for bouyancy in air	1·4724	1·4731

Mean : 1·4728

2. Solution after Adsorption.

	(1)	(2)
Solution taken in a duck-tube	10·928	11·084
Residue after drying up	1·5732	1·5962
Residue from 10 grm. of the solution	1·4399	1·4400
Extract from blood charcoal	0·0003	0.0003
Salt in 10 grm. of the solution	1·4396	1·4397
The same corrected for bouyancy in air	1·4400	1·4401

Mean : 1·4401

The results of such calculations are as follows :

TABLE I.

No.	Salt in grm. in 10 grm. solution					
	before adsorption.			after adsorption.		
	(1)	(2)	Mean	(1)	(2)	Mean
			Sodium chloride.			
1	0·5629	0·5629	0·5629	0·5639	0 5636	0 5638
2	0·5078	0·5081	0 5080	0·5080	0 5082	0 5081
3	0·3974	0·3979	0·3977	0·3978	0·3976	0·3977
4	0 3422	9·3418	0·3420	0·3422	0·3424	0·3423

No.	Salt in grm. in 10 grm. solution					
	before adsorption.			after adsorption.		
	(1)	(2)	Mena	(1)	(2)	Mean

Sodium nitrate.

1	0·8014	0·8013	0·8014	0·7913	0·7917	0·7915
2	0·6773	0·6763	0·6768	0·6660	0 6659	0·6660
3	0·5437	0·5433	0·5435	0·5331	0·5333	0·5332
4	0·4100	0·4108	0·4104	0·4020	0·4021	0·4021

Sodium sulphate.

1	0 8050	0·8052	0·8051	0 8132	0·8131	0·8132
2	0·6965	0 6967	0 6966	0·7026	0 7034	0·7030
3	0·5558	0·5561	0·5560	0·5607	0·5610	0·5609
4	0·4254	0·4252	0·4253	0·4288	0·4285	0·4287

Potassium chloride.

1	0·9150	0·9152	0·9151	0 9191	0·9197	0·9194
2	0·7332	0·7337	0·7335	0·7384	0·7382	0 7383
3	0·4538	0 4548	0·4543	0·4541	0·4537	0·4539
4	0 3647	0·3642	0 3645	0·3646	0·3640	0·3643

Potassium bromide.

1	1·0527	1·0528	1·0528	1 0437	1 0443	1·0440
2	0·7630	0·7628	0·7629	0·7557	0 7557	0·7557
3	0·5525	0 5533	0·5529	0·5453	0 5454	0·5454

Potassium iodide.

1	1·4724	1·4731	1·4728	1·4400	1·4401	1·4401
2	1·2901	1·2897	1·2899	1·2592	1·2599	1·2596
3	0 9912	0·9919	0·9916	0·9622	0 9629	0 9626
4	0·7583	0·7589	0·7586	0·7304	0·7304	0 7304

Potassium nitrate.

1	0 9499	0·9507	0 9503	0·9352	0·9360	0·9356
2	0 8003	0·8009	0 8006	0·7898	0·7892	0 7895
3	0 6499	0·6505	0 6502	0·6370	0·6376	0 6373
4	0·4952	0 4950	0·4951	0·4842	0·4834	0 4838

No.	Salt in grm. in 10 grm. solution					
	before adsorption.			after adsorption.		
	(1)	(2)	Mean	(1)	(2)	Mean

Potassium sulphate.

No.	(1)	(2)	Mean	(1)	(2)	Mean
1	0·8204	0 8208	0 8206	0 8263	0 8265	0 8264
2	0·6838	0·6840	0 6839	0·6879	0 6879	0·6879
3	0·5596	0 5596	0 5596	0·5629	0·5627	0·5628
4	0 4285	0 4282	0·4283	0·4304	0 4306	0·4305

As seen from the table, sodium nitrate, potassium bromide, potassium iodide and potassium nitrate are positively adsorbed and sodium chloride, sodium sulphate and potassium sulphate are negatively adsorbed, apparently. As to the solution of potassium chloride, when concentration is comparatively high, it is positively adsorbed and when comparatively low, negatively adsorbed, apparently. These distinct forms of adsorption may easily be explained by the fact that the adsorption of the solute is in some cases greater than that of the solvent and in others it is less.

In order to determine the quantity of salt adsorbed, we must determine the total amount of the salt in the solution, before and after adsorption. The former is given in Table 2. The apparent density of the solution and its true weight, deduced by means of it, are also given in the same table for subsequent use.

TABLE 2.

No.	Density.	Solution taken.		Salt in 10 grm. (apparent) solution.	Salt in the solution taken.
		Apparent wght.	Corrected wght.		

Sodium chloride

No.	Density.	Apparent wght.	Corrected wght.	Salt in 10 grm. (apparent) solution.	Salt in the solution taken.
1	1 0366	51·858	51·910	0·5629	2·9191
2	1·0328	51·630	51·682	0·5080	2·6228
3	1·0251	51·256	51·309	0·3977	2·0385
4	1·0208	51·025	51·077	0·3420	1·7450

No.	Density.	Solution taken.		Salt in 10 grm. (apparent) solution.	Salt in the solution taken.
		Apparent wght.	Corrected wght.		

Sodium nitrate.

No.	Density.	Apparent wght.	Corrected wght.	Salt in 10 grm.	Salt in solution
1	1·0512	52·610	52·662	0 8014	4·2161
2	1·0421	52·146	52·198	0 6768	3·5292
3	1·0327	51·665	51·716	0·5435	2·8080
4	1·0242	51·275	51·326	0·4104	2·1043

Sodium sulphate.

No.	Density.	Apparent wght.	Corrected wght.	Salt in 10 grm.	Salt in solution
1	1·0702	53·506	53·558	0 8051	4·3078
2	1·0603	53·028	53 080	0 6966	3·6938
3	1 0475	52·383	52·435	0·5560	2·9125
4	1·0354	51 698	51·750	0·4253	2·1985

Potassium chloride.

No.	Density.	Apparent wght.	Corrected wght.	Salt in 10 grm.	Salt in solution
1	1·0553	52·654	52·707	0 9151	4·8184
2	1·0437	52·020	52·072	0·7335	3·8157
3	1·0250	51·253	51·306	0·4543	2·3284
4	1·0194	50·999	51·051	0·3645	1·8589

Potassium bromide.

No.	Density.	Apparent wght.	Corrected wght.	Salt in 10 grm.	Salt in solution
1	1·0762	53·664	53·716	1·0528	5·6497
2	1·0534	52·504	52·556	0·7629	4·0055
3	1·0369	5·1781	51·833	0·5529	2·8630

Potassium iodide.

No.	Density.	Apparent wght.	Corrected wght.	Salt in 10 grm.	Salt in solution
1	1·1149	55·689	55·740	1·4728	8·2019
2	1·0988	54·836	54 887	1·2899	7·0733
3	1·0733	53·626	53·678	0 9916	5·3176
4	1·0545	52·659	52.711	0 7586	3·9936

Potassium nitrate.

No.	Density.	Apparent wght.	Corrected wght.	Salt in 10 grm.	Salt in solution
1	1·0563	52·868	52·920	0·9503	5·0240
2	1·0474	52·376	52·428	0·8006	4·1932
3	1·0374	51·883	51 935	0·6502	3·3734
4	1 0273	51·387	51·439	0 4951	2·5442

No.	Density.	Solution taken.		Salt in 10 grm. (apparent) solution.	Salt in the solution taken.
		Apparent wght.	Corrected wght		

Potassium sulphate.

No.	Density.	Apparent wght.	Corrected wght	Salt in 10 grm. (apparent) solution.	Salt in the solution taken.
1	1·0638	53·108	53·161	0·8206	4·3580
2	1·0520	52·618	52·671	0·6839	3·5985
3	1·0419	52 049	52·102	0·5596	2·9124
4	1·0305	51·575	51·628	0·4283	2·2090

Since .the amount of salt in a given quantity of solution has been determined, the total amount of salt remaining in solution after adsorption may easily be found, if the total amount of solution after adsorption or that of water in it be known. In order to obtain the amount of water remaining in solution after adsorption, that adsorbed by charcoal must be estimated, but as there is no direct means for its determination, the following procedure was taken. Some water was put in the bottom of a small glass vessel of desiccator form about 9 cm. high, a small glass basin with a given quantity of blood charcoal was placed over it and the cover was water-tightly sealed with *picetin.* The whole apparatus was completely dipped into a thermostat at 25·0° and the basin with charcoal was weighed at intervals of about a week, until it became constant in weight, being kept during the weighing between a pair of watch-glasses. This required about one month; and, as a mean of 5 determinations, it was ascertained that animal charcoal, treated as above stated, adsorbed water to 85 per cent of its weight. As the solutions used in the experiments were about 1 normal or less, it was assumed that the amount of water adsorbed by blood charcoal from solution does not much differ from that adsorbed from pure water.

The total amount of water in the solution after adsorption was obtained as the difference of the quantity of the solution taken and the quantities of the salt and of the water adsorbed by the charcoal. Then the total amount of the salt remaining in the solution after adsorption was found from the composition of the final solution and the total amount of water remaining in the solution. The results are given in Table 3.

TABLE 3.

No.	Blood charcoal.	Water adsorbed by charcoal.	Water in the solution after adsorption.	Salt in 10 grm. (app.) solution after adsorption.	In 10 grm. (corr.) solution after adsorption.		Total salt in the solution after adsorption.
					Salt.	Water.	

Sodium chloride.

1	1·505	1·275	47·716	0·5638	0·5632	9·437	2·8477
2	1·259	1·071	47 988	0·5081	0 5076	9·492	2 5662
3	1·568	1·335	47·935	0·3977	0·3973	9·603	1·9832
4	1·495	1·275	48 057	0·3423	0·3420	9·658	1·7017

Sodium nitratc.

1	1·304	1·109	47 337	0·7915	0·7907	9·209	4·0644
2	1·291	1·097	47·570	0 6660	0·6653	9·335	3 3903
3	1·412	1·200	47·708	0 5332	0·5327	9·467	2 6847
4	1·298	1·102	48·120	0·4021	0 4017	9·598	2·0139

Sodium sulphate.

1	1·365	1·160	48·090	0 8132	0·8124	9·198	4·2525
2	1·362	1·157	48·229	0·7030	0·7023	9 298	3·6429
3	1·458	1·240	48·282	0·5609	0·5604	9·440	2·8660
4	1·442	1·226	48·325	0·4287	0·4282	9·572	2·1617

Potassium chloride.

1	1·447	1·230	46·659	0·9194	0·9185	9·081	4·7191
2	1·596	1·357	46·899	0·7383	0·7376	9·268	3·7347
3	1·315	1·118	47·860	0·4539	0·4535	9·546	2·2735
4	1·386	1·179	48 019	0·3643	0·3638	9.636	1·8129

Potassium bromide.

1	1·463	1·244	46·822	1·0440	1·0430	8·967	5·4461
2	1·431	1·216	47·334	0·7557	0·7549	9·245	3·8651
2	1·545	1·313	47·657	0·5454	0·5448	9·455	2·7460

Potassium iodide.

1	1·573	1·337	46·201	1·4401	1·4388	8·561	7·7647
2	1·487	1·264	46·550	1·2596	1·2583	8·742	6·7003
3	1·491	1·267	47·093	0 9626	0·9613	9·039	5·0084
4	1·573	1·337	47·380	0 7304	0·7297	9·270	3·7296

No.	Blood charcoal.	Water adsorbed by charcoal.	Water in the solution after adsorption.	Salt in 10 grm. (app.) solution after adsorption.	In 10 grm. (corr.) solution after adsorption.		Total salt in the solution after adsorption.
					Salt.	Water.	

Potassium nitrate.

1	1·334	1·142	46 754	0 9356	0·9347	9·065	4·8208
2	1·103	0·937	47·298	0·7895	0·7887	9·211	4·0499
3	1·296	1·102	47·460	0·6373	0·6367	9·363	3·2273
4	1·309	1·113	47·782	0 4838	0 4833	9·517	2·4294

Potassium sulphate.

1	1·360	1·156	47·647	0 8264	0·8256	9·174	4·2883
2	1·294	1·096	47·976	0·6879	0·6872	9·313	3·5401
3	1·277	1·089	48·100	0 5628	0·5622	9·438	2·8652
4	1·394	1·181	48·238	0·4305	0 4301	9·569	2·1681

Now, the total amount of salt, before and after adsorption, have been found and the quantity of salt adsorbed may easily be calculated. The normality of solution was obtained from its density before adsorption and its composition under the admissible assumption that the density does not change practically by adsorption. The results of calculation are represented in Table 4.

TABLE 4.

No.	Total salt in solution.		Salt adsorbed.	Blood charcoal.	Salt adsorbed by 1 grm. charcoal.		Normality of the solution.
	Before adsorption.	After adsorption.			grm.	Milligram equivalent.	

Sodium chloride.

1	2·9191	2·8477	0 0714	1·505	0 0474	0 81	0·998
2	2·6228	2·5662	0·0566	1·259	0·0449	0·77	0 896
3	2·0385	1·9832	0·0553	1·568	0·0353	0·60	0·697
4	1·7450	1·7017	0·0433	1·495	0·0290	0·49	0·597

Sodium nitrate.

1	4·2161	4·0644	0·1517	1·304	0·1517	1·37	0·978
2	3·5292	3·3903	0·1389	1·291	0·1389	1·27	0·816
3	2·8080	2·6847	0·1233	1·241	0·1233	1·03	0·647
4	2·1043	2·0139	0·0904	1·298	0 0904	0 82	0·484

No.	Total salt in solution.		Salt adsorbed.	Blood charcoal.	Salt adsorbed by		Normality of the solution.
	Before adsorption.	After adsorption.			grm.	Milligram equivalent.	

Sodium sulphate.

No.	Before	After	Salt adsorbed	Blood charcoal	grm.	Milligram equiv.	Normality
1	4·3078	4·2525	0·0553	1·365	0·0405	0·57	1·068
2	4·6938	3·6429	0 0509	1·362	0·0374	0·53	0 933
3	2·9125	2·8660	0 0465	1·458	0 0319	0·45	0 753
4	2·1985	2·1617	0 0368	1·442	0 0255	0·36	0·583

Potassium chloride.

No.	Before	After	Salt adsorbed	Blood charcoal	grm.	Milligram equiv.	Normality
1	4·8184	4·7191	0·0993	1·447	0 0686	0·92	0·966
2	3 8157	3·7347	0 0810	1·596	0·0508	0·68	0 765
3	2·3284	2·2735	0 0549	1·315	0 0418	0·56	0·562
4	1·8589	1·8129	0 0460	1·386	0 0332	0·45	0·479

Potassium bromide.

No.	Before	After	Salt adsorbed	Blood charcoal	grm.	Milligram equiv.	Normality
1	5·6497	5·4461	0 2036	1·463	0·1392	1·17	0·970
2	4·0055	3·8651	0·1404	1·431	0 0981	0·82	0·717
3	2·8630	2·7460	0·1170	1·545	0 0757	0·64	0·526

Potassium iodide.

No.	Before	After	Salt adsorbed	Blood charcoal	grm.	Milligram equiv.	Normality
1	8·2019	7·7647	0·4372	1·573	0·2779	1·67	0·967
2	7·0733	6·7003	0·3730	1·487	0·2508	1·51	0·833
3	5·3176	5 0084	0·3092	1·491	0·2074	1·25	0·622
4	3·9936	3·7296	0·2640	1·573	0 1678	1·01	0·464

Potassinm nitrate.

No.	Before	After	Salt adsorbed	Blood charcoal	grm.	Milligram equiv.	Normality
1	5·0240	4·8208	0 2032	1·344	0·1512	1·50	0 977
2	4·1932	4 0499	0·1433	1·103	0·1299	1·28	0·817
3	3·3734	3·2273	0 1461	1·296	0 1127	1·11	0 654
4	2·5442	2·4294	0 1148	1·309	0·0877	0 87	0·491

Potassium sulphate.

| No.	Before	After	Salt adsorbed	Blood charcoal	grm.	Milligram equiv.	Normality
1	4·3580	4·2883	0 0697	1·360	0·0514	0·59	1·010
2	3·5985	3·5401	0·0584	1·294	0 0451	0·52	0·830
3	2·9124	2·8652	0 0472	1·277	0·0370	0·42	0·673
4	2·2090	2·1681	0 0409	1·394	0·0293	0·34	0·509

Normality of salt solution.
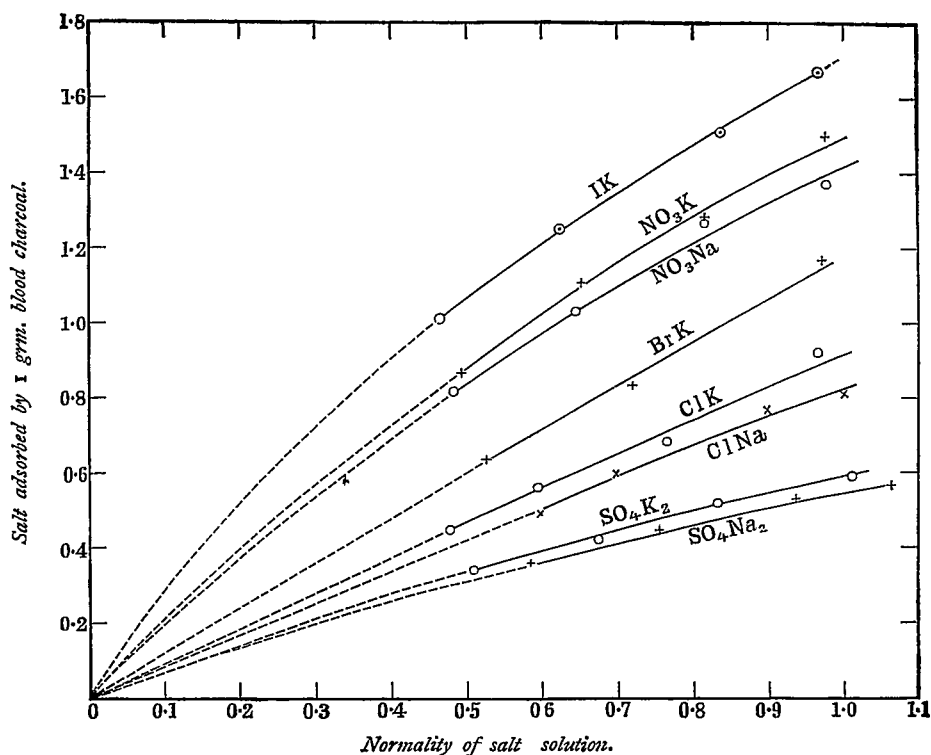
The relation between the normality of the solution and the quantity of the salt adsorbed in milligram-equivalents is graphically represented in Fig. 1.

From the figure it is seen that potassium salts are more adsorbep than the corresponding sodium salts, and this is a generally known fact. With salts of the same base, the degrees of adsorption are in the following order:

$$I > NO_3 > Br > Cl > SO_4.$$
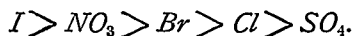
The so-called Hofmeister's series of the precipitating power of anions for alkaline sols is as follows;

$$CNS < I < Br < NO_3 < Cl < C_2H_3O_2 < HPO_3 < SO_4.$$
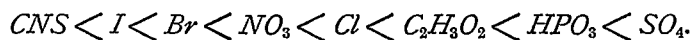
Then W. Pauli, S. Posternak and R. Höber have found that the series is reversed for sols of acid reaction.[1]

The reverse of Hofmeister's series and the series have found for

[1] *cf.* Cassuto, Die Kolloide Zustand der Materie, p. 96 (1913).

adsorption agree except in the case of bromide and nitrate which are reversed.

The following quotation from H. Bechhold's work will not be without interest in connection with the author's result.[1]

" Anorganische Salze erhöhen meist die Oberflächenspannung von Wasser, und zwar ergibt sich nach einer Tabelle von W. K. Röntgen und J. Schneider folgende Reihe für die Erhöhnng der Oberflächen-spannung durch jodalkalien:

$$Na > K > Li > NH_4$$
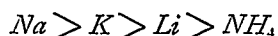
bei den Anionen sämtlicher Alkalien:

$$CO_2 > SO_4 > Cl > NO_3 > J.$$
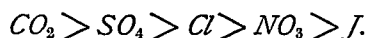
" In ähnlicher Reihenfolge wird durch Neutralsalze die Kompressi-bilität, die Löslichkeitsbeeinflussung und Zähigkeit des Wassers verän-dert. Aber die Beziehung ist noch weit ausgedehnter: die Neutralsalze können katalitische Wirkungen beschleunigen und verlangsamen: die Inversion des Rohrzuckers, die Esterverseifung, die Umwandlung von Azeton in Diazetonalkohol, und zwar ist die Wirkung in saurer Lösung meist umgekehrt wie die in alkalischer, worauf R. Höher hinge-wiesen hat. Im sauren Medium ist die Beschleunigung durch die Kationen:

$$Li > Na > K > Rb > Cs$$
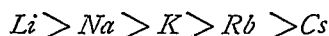
im alkalischen Medium:

$$Cs > Rb > K > Na > Li$$
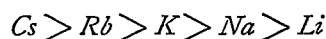
für die Anionen gilt in sauren Lösung die Reihe:

$$J > NO_3 > Br > Cl > CH_3CO_2 > SO_4$$
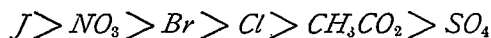
in alkalischer Lösung die umgekehrte."

As may be seen, the series of cations in acid solutions and that of anions in alkaline solutions are in perfect agreement with the author's series. Since the adsorption of salt is intimately connected with the precipitation of a sol and also with its influence on the surface ten-sion of water, this agreement is not a mere accident.

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[1] Die Kolloide in Biologie und Medizin, p. 74 (1912). See also J. Traube, J. Phys. Chem., 14, 452 (1910).