THE SOLUBILITIES OF SOME SPARINGLY SOLUBLE SALTS IN AQUEOUS SOLUTIONS OF UREA AND DIOXANE

BY

KAI JULIUS PEDERSEN

The purpose of this paper is to give a contribution to the discussion of the question whether the influence of a non-electrolyte on the solubility of a salt in water may be accounted for by the change of the dielectric constant caused by the addition of the non-electrolyte. For this purpose the solubilities of some sparingly soluble salts of different valency types have been determined in water and aqueous solutions of urea and dioxane.

Experimental Procedure. Materials.

The saturated solutions of the salts were prepared in glass-stoppered bottles whose necks were covered with ground-on glass bells. The bottles were rotated in an electrically regulated water thermostat. Samples of the solutions were analyzed after different times of rotation in order to make sure that saturation was attained. The samples were sucked from the bottle, which was not taken from the thermostat, through a porous glass filter into a pipet.

A list of the salts examined is given in table 1. The methods used for the analysis of the salts and the saturated solutions are given in the second column of the table. In the next two columns, the molecular weights found by analysis and those calculated from the formulae are enumerated. Then follow the solubilities in pure water at

1*

Table 1.

Salt	Method of analysis[1]	Molecular weight		Solubility in water at 18.00°	
		by analysis	calcd.	this paper	other investigators
K hydrogen tartrate.....	A	188.2	188.2	0.02617	0.02616[2]
NH$_4$ hydrogen tartrate ..	A*	..	..	0.1499	..
Tl hydrogen tartrate	A	353.2	353.5	0.02480	..
KIO$_4$	I	230.0	230.0	0.01618	0.0164[3]
TlIO$_3$.................	I	379.2	379.3	0.001417	..
[Co(NH$_3$)$_4$(C$_2$O$_4$)]IO$_3$, H$_2$O	I	407.3	408.0	0.00821	..
[Co(NH$_3$)$_5$Cl](IO$_3$)$_2$	I	529.2	529.4	0.003760	..
[Co(NH$_3$)$_6$](IO$_3$)$_3$, 3 H$_2$O ..	I	736.8	739.9	0.003890	..
Ca(IO$_3$)$_2$, 6 H$_2$O	I	498.4	498.0	0.005702	0.00569[4]
Ba(IO$_3$)$_2$, H$_2$O	I	504.6	505.2	0.0006706	..
PbCl$_2$..................	V	278.2	278.1	0.03360	{ 0.03358[5] 0.03376[6]
[Co(NH$_3$)$_5$Cl]Cl$_2$	V*	251.3	250.5	0.01697	0.01692[7]
Na$_2$C$_2$O$_4$	{ P A*	.. ..	.. ..	0.2467 0.2466	0.2474[6] ..
[Co(NH$_3$)$_5$Cl]C$_2$O$_4$	P*	270.8	267.6	0.000745	..

[1] A: Acidimetry. I: Iodometry. V: Volhard titration. P: Permanganate titration. An asterisk (*) denotes that the method has been modified as described in the text.   [2] Carpenter and Mack (1). Data interpolated to 18°.   [3] Hill (2). Data interpolated to 18°. The specific weight 1.0014 has been used.   [4] Kilde (3).   [5] International Critical Tables (4).   [6] Flöttmann (5). Data interpolated to 18°.   [7] Lamb and Simmons (6). Data interpolated to 18°.

18.00° C. The solubilities given here and in the following tables are the average values of at least two, in general of a greater number of determinations which agree among each other within the limit of accuracy of the analytical method. Throughout this paper the concentrations are expressed in moles per liter of solution. The last column of the table contains the solubilities found by other investigators, if such data are available. Further information on the materials used and the experimental method will be given below.

Potassium hydrogen tartrate was purified by re-crystallization.

Ammonium hydrogen tartrate was prepared from ammonium carbonate and tartaric acid, and recrystallized from water. After carbon dioxide had been expelled the saturated solutions were titrated with sodium hydroxide to the end point pH = 7 (bromo-thymol blue indicator, comparison with phosphate buffer). The sodium hydroxide solution was standardized on crystalline ammonium hydrogen tartrate by the same procedure. The normality thus determined was slightly higher (up to 0.3 %) than that found by comparison with standard hydrochloric acid.

Thallous hydrogen tartrate was prepared from thallous carbonate and tartaric acid, and twice recrystallized from water.

Potassium periodate was purified by recrystallization. One ml. of the saturated solution (in the solvent water) weighed *in vacuo* 1.0014 g.

Thallous iodate was prepared from thallous sulphate and potassium iodate.

Oxalotetrammine cobaltic iodate monohydrate was prepared by adding a potassium iodate solution to a 60° warm solution of oxalotetrammine cobaltic nitrate. The nitrate was prepared from carbonatotetrammine cobaltic nitrate and oxalic acid (7).

Chloropentammine cobaltic iodate was precipitated by potassium iodate from a 50° warm solution of chloropentammine cobaltic chloride which had first been purified by the method of SØRENSEN and JØRGENSEN (8). Apparently, the solubility of the salt increased slowly with increasing time of rotation, with about 0.1 % per hour in

all the solvents examined. The increase is caused by the slow reaction (9)

$$[Co(NH_3)_5Cl]^{++} + H_2O \rightleftarrows [Co(NH_3)_5(H_2O)]^{+++} + Cl^-.$$
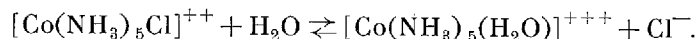
The true solubility was found by extrapolating the data to the time when the experiment was started.

Hexammine cobaltic iodate trihydrate was prepared by addition of potassium iodate to a 60° warm solution of hexammine cobaltic nitrate.

Calcium iodate hexahydrate was prepared from calcium chloride and potassium iodate.

Barium iodate monohydrate was prepared from barium hydroxide and iodic acid.

Lead chloride was prepared from lead nitrate and hydrochloric acid. It was recrystallized from water and dried at 120°.

Chloropentammine cobaltic chloride was purified applying the method of Sørensen and Jørgensen (8). The salt and the saturated solutions were analyzed in the following way. 40 ml. of the saturated solution, or the corresponding amount of the solid salt dissolved in water, were heated almost to the boiling-point with 2 ml. of molar sodium hydroxide solution. The mixture was left for a short time in order to secure complete decomposition of the complex, was then cooled under the water tap and, when quite cold, acidified with 2 ml. of 4 molar nitric acid. A small excess of 0.05 molar silver nitrate was added. The precipitate was filtered from the solution and washed with water. More nitric acid was added to the filtrate and washing water, and the Volhard titration was finished in the usual way.

Due to the slow formation of aquopentammine cobaltic ions, the chloride content of the saturated solution increased

with increasing time of rotation. The increase amounted, however, to only 0.04 % per hour, and it was easy to find the true solubility by extrapolation to the time of the start of the experiment.

Sodium oxalate (Kahlbaum, "nach Sørensen") was used without further purification. The solutions containing urea were titrated with permanganate. Those containing dioxane were evaporated to dryness in a platinum crucible on the water bath. The residue was ignited. The sodium carbonate formed was dissolved in hydrochloric acid. The carbon dioxide was expelled, and the excess of acid was titrated with sodium hydroxide.

Chloropentammine cobaltic oxalate was prepared in the following way. To a solution of 10 g. of purified chloropentammine cobaltic chloride in 2500 ml. of water was added a solution of 6 g. of ammonium oxalate in 200 ml. of water. Five hours later, the crystals were separated, washed with water and alcohol, and dried in the air.

The solubility of this salt was measured in water and in solutions of urea, only. The salt and the saturated solutions were analyzed in the following way. To 100 ml. of the saturated solution, or to the corresponding amount of the salt dissolved in water, at room temperature, 20 ml. of 1 molar sulphuric acid, a little manganous sulphate and, with a calibrated pipet, 2 ml. of 0.1 normal potassium permanganate were added. The mixture was left for two minutes to complete the oxidation of the oxalate. The excess of permanganate was then titrated with 0.01 normal thiosulphate after the addition of potassium iodide. For every new solvent the method was standardized on 100 ml. of $7.50 \cdot 10^{-4}$ molar sodium oxalate in the same solvent.

Urea (Kahlbaum, "für wissenschaftliche Zwecke") was

used without purification. It contained traces of calcium which could not be removed by recrystallization from alcohol (10). 1 to 3 mg. of ash and 1 to $2 \cdot 10^{-5}$ moles of calcium were found per mole of urea. This impurity is without any importance for the measurements described in the present paper.

Dioxane (Haardt u. Co., "Exluan 05") was further purified in the following way. It was left for two days over solid sodium hydroxide, refluxed with sodium for several hours and, finally, distilled in an all-glass apparatus fitted with a column containing glass beads. The main fraction, which was used for the measurements, had the freezing-point 11.65°, compared with 11.80° for pure dioxane (11, 12). It is reported (13) that the freezing-point of dioxane decreases while it is stored; it is stable only when oxygen is excluded (12). Although the dioxane used in the present work was stored in an ordinary glass-stoppered bottle practically the same freezing-point, 11.6°, was found 5 months after the distillation, when the measurements were finished.

The Solubilities of the Salts in Solutions of Urea and Dioxane.

The results of the measurements are given in tables 2 and 3. The name of the salt and the temperature are given in the first column. Then follow the concentration of the solvent, c moles of urea or dioxane per liter solution, the solubility s, and the ratio $\frac{s}{s_0}$, where s_0 is the solubility in pure water. In the fifth column, $\alpha = \frac{1}{c} \ln \frac{s}{s_0}$ has been computed for all the solvents containing urea or dioxane. For a given salt α does not vary much with c. By an easy

Table 2.

The Solubilities of Salts in Aqueous Solutions of Urea.

s is the solubility of the salt in c molar urea.

s_0 is the solubility of the salt in pure water.

f is the activity coefficient of the salt in s molar solution in the solvent water.

$$\alpha = \frac{1}{c}\ln\frac{s}{s_0} \quad \text{and} \quad \alpha' = \frac{1}{c}\ln\frac{fs}{f_0 s_0}.$$

	c	$s \cdot 10^3$	$\dfrac{s}{s_0}$	α	$\dfrac{fs}{f_0 s_0}$	α'
Potassium hydrogen tartrate (17.85°)	0.000	26.00	1.0000	(0.071)	1.0000	(0.066)
	0.250	26.46	1.0177	0.070	1.0165	0.065
	0.500	26.88	1.0339	0.067	1.0315	0.062
	0.750	27.34	1.0516	0.067	1.0479	0.063
	1.000	27.72	1.0663	0.064	1.0615	0.060
Ammonium hydrogen tartrate (17.85°)	0.000	149.4	1.0000	(0.087)	1.0000	(0.077)
	0.250	152.7	1.0221	0.087	1.0195	0.077
	0.500	155.8	1.0428	0.084	1.0377	0.074
	0.750	159.0	1.0643	0.083	1.0566	0.073
	1.000	162.1	1.0850	0.082	1.0747	0.072
Thallous hydrogen tartrate (17.85°)	0.000	24.71	1.0000	(0.174)	1.0000	(0.162)
	0.250	25.80	1.0441	0.173	1.0410	0.161
	0.500	26.93	1.0898	0.172	1.0834	0.160
	0.750	28.09	1.1368	0.171	1.1268	0.159
	1.000	29.27	1.1845	0.169	1.1706	0.158
Potassium periodate (17.85°)	0.000	16.05	1.0000	(0.093)	1.0000	(0.088)
	0.250	16.42	1.0231	0.091	1.0218	0.086
	0.500	16.79	1.0461	0.090	1.0434	0.085
	0.750	17.15	1.0685	0.088	1.0644	0.083
	1.000	17.51	1.0910	0.087	1.0855	0.082
Thallous iodate (17.85°)	0.000	1.410	1.0000	(0.159)	1.0000	(0.156)
	0.250	1.467	1.0404	0.158	1.0396	0.155
	0.500	1.526	1.0823	0.158	1.0806	0.155
	0.750	1.586	1.1248	0.157	1.1221	0.154
	1.000	1.644	1.1660	0.154	1.1623	0.150

Table 2 (continued).

	c	$s \cdot 10^3$	$\dfrac{s}{s_0}$	α	$\dfrac{fs}{f_0 s_0}$	α'
Oxalotetrammine cobaltic iodate monohydrate (18.0°)	0.000	8.215	1.0000	(0.192)	1.0000	(0.184)
	0.500	9.02	1.0980	0.187	1.0934	0.179
	1.000	9.86	1.2002	0.183	1.1904	0.174
Chloropentammine cobaltic iodate (18.0°)	0.000	3.79	1.000	(0.199)	1.000	(0.179)
	0.200	3.94	1.040	0.194	1.036	0.175
	0.400	4.10	1.082	0.197	1.073	0.177
	0.600	4.26	1.124	0.195	1.111	0.175
	0.800	4.42	1.166	0.192	1.148	0.173
	1.000	4.59	1.211	0.192	1.187	0.172
Hexammine cobaltic iodate trihydrate (18.0°)	0.000	3.880	1.0000	(0.257)	1.0000	(0.207)
	0.250	4.133	1.0653	0.253	1.0520	0.203
	0.500	4.394	1.1326	0.249	1.1046	0.199
	0.750	4.662	1.2015	0.245	1.1573	0.195
	1.000	4.934	1.2717	0.240	1.2102	0.191
Calcium iodate hexahydrate (17.9°)	0.000	5.686	1.0000	(0.234)	1.0000	(0.206)
	0.100	5.821	1.0237	0.234	1.0209	0.207
	0.200	5.957	1.0477	0.233	1.0419	0.205
	0.400	6.233	1.0962	0.230	1.0843	0.202
	0.600	6.512	1.1453	0.226	1.1268	0.199
	0.800	6.805	1.1968	0.225	1.1710	0.197
	1.000	7.103	1.2492	0.223	1.2155	0.195
	2.000	8.689	1.5281	0.212	1.4480	0.185
	4.000	12.58	2.212	0.198	..	..
	6.000	17.67	3.108	0.189	..	..
	8.000	24.96	4.390	0.185	..	..
Barium iodate monohydrate (17.9°)	0.000	0.6694	1.0000	(0.202)	1.0000	(0.193)
	0.200	0.6965	1.0404	0.198	1.0384	0.188
	0.400	0.7240	1.0816	0.196	1.0776	0.187
	0.600	0.7510	1.1219	0.192	1.1157	0.182
	0.800	0.7787	1.1633	0.189	1.1548	0.180
	1.000	0.8059	1.2039	0.186	1.1930	0.176
Lead chloride (18.0°)	0.000	33.67	1.0000	(0.204)	1.0000	(0.139)
	0.250	35.42	1.0520	0.203	1.0354	0.139
	0.500	37.28	1.1072	0.204	1.0719	0.139
	0.750	39.22	1.1648	0.203	1.1101	0.139
	1.000	41.20	1.2236	0.202	1.1482	0.138

Table 2 (continued).

	c	$s \cdot 10^3$	$\dfrac{s}{s_0}$	α	$\dfrac{fs}{f_0 s_0}$	α'
Chloropentammine cobaltic chloride (18.0°)	0.000	16.97	1.0000	(0.134)	1.0000	(0.111)
	0.333	17.72	1.0442	0.130	1.0364	0.107
	0.667	18.50	1.0902	0.129	1.0739	0.107
	1.000	19.21	1.1320	0.124	1.1076	0.102
Sodium oxalate (18.00°)	0.000	246.7	1.0000	(—0.059)	..	..
	0.500	239.2	0.9696	—0.061	..	..
	1.000	231.2	0.9372	—0.063	..	..
Chloropentammine cobaltic oxalate (18.0°)	0.000	0.745	1.000	(0.21)	1.000	(0.19)
	0.300	0.795	1.067	0.22	1.059	0.19
	0.600	0.852	1.144	0.22	1.126	0.20
	1.000	0.941	1.263	0.24	1.228	0.21

Table 3.

The Solubilities of Salts in Aqueous Solutions of Dioxane.

s is the solubility of the salt in c molar dioxane.

s_0 is the solubility of the salt in pure water.

f is the activity coefficient of the salt in s molar
   solution in the solvent water.

$$\alpha = \frac{1}{c} \ln \frac{s}{s_0} \quad \text{and} \quad \alpha' = \frac{1}{c} \ln \frac{fs}{f_0 s_0}.$$

	c	$s \cdot 10^3$	$\dfrac{s}{s_0}$	$-\alpha$	$\dfrac{fs}{f_0 s_0}$	$-\alpha'$
Potassium hydrogen tartrate (18.00°)	0.000	26.17	1.0000	(0.315)	1.0000	(0.292)
	0.250	24.17	0.9236	0.318	0.9286	0.296
	0.500	22.27	0.8510	0.323	0.8602	0.301
	0.750	20.52	0.7841	0.324	0.7968	0.303
	1.000	18.83	0.7195	0.329	0.7350	0.308
Ammonium hydrogen tartrate (18.00°)	0.000	149.9	1.0000	(0.261)	1.0000	(0.230)
	0.250	140.3	0.9360	0.265	0.9431	0.234
	0.500	131.0	0.8739	0.270	0.8874	0.239
	0.750	122.3	0.8159	0.271	0.8348	0.241

Table 3 (continued).

	c	$s \cdot 10^3$	$\dfrac{s}{s_0}$	$-\alpha$	$\dfrac{fs}{f_0 s_0}$	$-\alpha'$
Thallous hydrogen tartrate (18.00°)	0.000	24.80	1.0000	(0.248)	1.0000	(0.232)
	0.200	23.57	0.9504	0.254	0.9536	0.237
	0.400	22.33	0.9004	0.262	0.9067	0.245
	0.600	21.14	0.8524	0.266	0.8614	0.249
	0.800	20.01	0.8069	0.268	0.8182	0.251
Potassium periodate (18.00°)	0.000	16.18	1.0000	(0.086)	1.0000	(0.082)
	0.200	15.93	0.9845	0.078	0.9854	0.074
	0.400	15.73	0.9719	0.071	0.9734	0.067
	0.600	15.55	0.9612	0.066	0.9633	0.062
	0.800	15.40	0.9521	0.061	0.9548	0.058
	1.000	15.25	0.9426	0.059	0.9458	0.056
Thallous iodate (18.00°)	0.000	1.417	1.0000	(0.293)	1.0000	(0.288)
	0.250	1.315	0.9276	0.300	0.9290	0.295
	0.500	1.213	0.8552	0.313	0.8577	0.307
	0.750	1.117	0.7873	0.319	0.7909	0.313
Chloropentammine cobaltic iodate (18.00°)	0.000	3.760	1.0000	(0.401)	1.0000	(0.360)
	0.250	3.400	0.9043	0.403	0.9131	0.363
	0.500	3.070	0.8165	0.405	0.8325	0.367
	0.750	2.772	0.7372	0.406	0.7585	0.368
	1.000	2.467	0.6561	0.421	0.6819	0.383
Hexammine cobaltic iodate trihydrate (18.00°)	0.000	3.889	1.0000	(0.510)	1.0000	(0.408)
	0.200	3.509	0.9022	0.515	0.9204	0.415
	0.400	3.161	0.8128	0.518	0.8456	0.419
	0.600	2.836	0.7292	0.526	0.7736	0.428
	0.800	2.538	0.6526	0.534	0.7056	0.436
	1.000	2.272	0.5842	0.537	0.6418	0.443
Calcium iodate hexahydrate (18.00°)	0.000	5.702	1.0000	(0.401)	1.0000	(0.355)
	0.125	5.423	0.9511	0.401	0.9566	0.355
	0.250	5.159	0.9047	0.400	0.9152	0.355
	0.375	4.904	0.8601	0.402	0.8750	0.356
	0.500	4.652	0.8159	0.407	0.8348	0.361
	0.750	4.194	0.7355	0.410	0.7608	0.365
	1.000	3.771	0.6614	0.413	0.6916	0.369
Barium iodate monohydrate (25.00°)[1]	0.000	0.8145	1.0000	(0.439)	1.0000	(0.416)
	1.138	0.4742	0.5821	0.475	0.5969	0.453
	2.292	0.2526	0.3101	0.511	0.3250	0.490
	3.470	0.1217	0.1494	0.548	0.1595	0.529
	4.660	0.0553	0.0679	0.577	0.0735	0.560

[1] Measurements taken from a paper by Davis and Ricci (14).

Table 3 (continued).

	c	$s \cdot 10^3$	$\dfrac{s}{s_0}$	$-\alpha$	$\dfrac{fs}{f_0 s_0}$	$-\alpha'$
Lead chloride (18.00°)	0.000	33.60	1.0000	(0.226)	1.0000	(0.154)
	0.167	32.32	0.9619	0.233	0.9738	0.159
	0.333	31.13	0.9265	0.229	0.9491	0.157
	0.500	29.92	0.8905	0.232	0.9235	0.159
	0.667	28.75	0.8556	0.234	0.8987	0.160
	1.000	26.47	0.7878	0.238	0.8487	0.164
Chloropentammine cobaltic chloride (18.00°)	0.000	16.97	1.0000	(0.234)	1.0000	(0.194)
	0.333	15.66	0.9228	0.241	0.9354	0.200
	0.667	14.38	0.8474	0.248	0.8711	0.207
	1.000	13.15	0.7749	0.255	0.8082	0.213
Sodium oxalate (18.00°)	0.000	246.6	1.0000	(0.488)	. .	. .
	0.333	209.5	0.8496	0.489	. .	. .
	0.667	177.7	0.7206	0.492	. .	. .
	1.000	149.0	0.6042	0.504	. .	. .

extrapolation to infinite dilution with respect to the non-electrolyte, we find

$$\alpha_0 = \lim_{c=0} \frac{1}{c} \ln \frac{s}{s_0} = \lim_{c=0} \frac{s-s_0}{cs_0}. \tag{1}$$

α_0, which is a measure of the effect of small concentrations of the non-electrolyte upon the solubility of the salt, is given in parenthesis in the fifth column of the tables. The last two columns will be explained later. Table 3 includes measurements of the solubility of barium iodate at 25.00° in solutions of dioxane; the values are taken from a paper by Davis and Ricci (14).

Theory and Discussion.

The theory of the dependence of the solubility of a salt on the dielectric constant of the medium is based upon an expression deduced by Born (15), according to which the electrostatic energy of a sphere of radius r and electric

charge ze, e being the charge of the electron, in a medium with the dielectric constant ε, is $\dfrac{z^2 e^2}{2\,r}\,\varepsilon^{-1}$.

Let us consider three solutions, I, II, and III, of the same salt and at the same temperature. The solvents I and II are identical, while the dielectric constant of the solvent III differs infinitesimally from that of the solvents I and II. The concentrations of the salt and the reciprocals of the dielectric constants are, for solution I: s and ε^{-1}, for solution II: $s + ds$ and ε^{-1}, and for solution III: $s + ds$ and $\varepsilon^{-1} + d\left(\varepsilon^{-1}\right)$. Solutions I and III are saturated with respect to the salt. We assume that the salt is completely dissociated into ions which, as a first approximation, may be treated as undeformable spheres. r_+ and r_- are the radii, z_+ and z_- the valencies of the cation and the anion, respectively. The total work required for a reversible transfer of z_- cations and z_+ anions from solution I, *via* solution II, to solution III is zero, solutions I and III being saturated. This fact is expressed in the following equation

$$(z_+ + z_-)\,kT\,d\ln fs + \left(\frac{z_-\,z_+^2\,e^2}{2\,r_+} + \frac{z_+\,z_-^2\,e^2}{2\,r_-}\right) d\left(\varepsilon^{-1}\right) = 0,$$

where k is Boltzmann's constant, T is the absolute temperature, and f is the activity coefficient of the salt in the medium with a dielectric constant ε. If we introduce the mean radius r_m defined by the expression

$$\frac{z_+ + z_-}{r_m} = \frac{z_+}{r_+} + \frac{z_-}{r_-},$$

and assume that the change of the dielectric constant has been caused by an infinitesimal increase of the concentration c of a non-electrolyte, the equation may be written as

$$\frac{d \ln fs}{dc} = -\frac{z_+ z_- e^2}{2\, kTr_m} \frac{d\left(\varepsilon^{-1}\right)}{dc}.$$

We shall apply this expression only to aqueous solutions extremely dilute with respect to the added non-electrolyte, urea or dioxane. If we refer to the solvent pure water by the subscript $_0$, we may write

$$\left(\frac{d \ln fs}{dc}\right)_0 = -\frac{z_+ z_- e^2}{2\, kTr_m}\left(\frac{d\left(\varepsilon^{-1}\right)}{dc}\right)_0. \qquad (2)$$

In order to check this expression we shall, for all solubility determinations, compute $\dfrac{fs}{f_0 s_0}$, where f is the activity coefficient of the salt in s molar solution in the solvent pure water. We use the approximate expression (at $18°$ C.)

$$-\log f = 0.498\, z_+ z_- \frac{\sqrt{\mu}}{1+\sqrt{\mu}}, \qquad (3)$$

where μ is the ionic strength. By means of this expression, we get

$$\log \frac{fs}{f_0 s_0} = \log \frac{s}{s_0} - 0.498\, z_+ z_- \left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - \frac{\sqrt{\mu_0}}{1+\sqrt{\mu_0}}\right),$$

from which formula we compute

$$\frac{fs}{f_0 s_0} \quad \text{and} \quad \alpha' = \frac{1}{c}\ln\frac{fs}{f_0 s_0}.$$

By extrapolation of α' to $c = 0$ we find

$$\alpha'_0 = \lim_{c=0}\frac{1}{c}\ln\frac{fs}{f_0 s_0} = \left(\frac{d \ln fs}{dc}\right)_0. \qquad (4)$$

The results of the computation are given in the last two columns of tables 2 and 3. The values found for α'_0 are given in parenthesis in the last column.

The computation is, of course, rather rough, since it is based upon the approximate formula 3. The error will be greater the greater the solubilities of the salt and the higher the valencies of its ions. In the case of lead chloride which has a relatively great solubility, the values given in the last two columns of the tables have been computed not from formula 3 but from activity coefficients deduced from electrometric measurements by GÜNTELBERG (16), partly by extrapolating his data to supersaturated solutions. It makes a rather great difference whether we use formula 3 or Güntelberg's measurements. This can be seen from the following values of α'_0 found in these two ways

	α_0	α'_0 (form. 3)	α'_0 (Güntelberg)
Urea...........	0.204	0.160	0.139
Dioxane........	—0.226	—0.179	—0.154.

From the equations 2 and 4 we obtain

$$\alpha'_0 = -\frac{z_+ z_- e^2}{2\,kT r_m}\left(\frac{d\left(\varepsilon^{-1}\right)}{dc}\right)_0.$$

If the values of e, k, and T are introduced, we get

$$\alpha'_0 = -287\left(\frac{d\left(\varepsilon^{-1}\right)}{dc}\right)_0 \frac{z_+ z_-}{r_m} \tag{5}$$

at 18° C., where r_m is expressed in Ångström units.

The dielectric constant of aqueous solutions of urea, from 0.5 to 3.0 molar, has been measured by HARRINGTON (17). We may express his measurements by the formula

$$\varepsilon^{-1} = 0.012684 - 0.000448\,c + 0.0000292\,c^2$$

from which we find $\left(\dfrac{d\left(\varepsilon^{-1}\right)}{dc}\right)_0 = -0.00045$. $\left(\dfrac{d\left(\varepsilon^{-1}\right)}{dc}\right)_0$ for dioxane is computed from the measurements of Åkerlöf and Short (18). At 10° C. and 20° C. we find 0.00102 and 0.00112, respectively, and, by interpolation, 0.00110 at 18° C.

If we introduce the values of $\left(\dfrac{d\left(\varepsilon^{-1}\right)}{dc}\right)_0$ into equation 5, we obtain for solutions of urea

$$\alpha'_0 = 0.129 \frac{z_+ z_-}{r_m}, \qquad (6)$$

for solutions of dioxane

$$\alpha'_0 = -0.316 \frac{z_+ z_-}{r_m}, \qquad (7)$$

and the ratio of α'_0 for solutions of dioxane and urea
$$\beta = \frac{0.00110}{-0.00045} = -2.5 \text{ for all the salts.}$$

We shall now examine how these consequences of the theory agree with the experimental results summarized in table 4. We notice at once that the direction of the effect is in agreement with the theory. The solubilities increase when urea is added, and they decrease when dioxane is added. Among the salts examined, there is only one exception: the solubility of sodium oxalate is smaller in solutions of urea than in pure water.

As an attempt to test the theory, we shall calculate r_m from the equations 6 and 7 and examine whether the values obtained are reasonable. r_m found in this way is given in the 6th and 9th columns of table 4 for the addition of urea and dioxane, respectively. The values are of the right order of magnitude, but it is of no use to compare them with the ionic radii of the salts found in other ways. The figures indicate that r_m of one and the same salt in

Table 4.

The Effect of Small Concentrations of Urea and Dioxane on the Solubility of Salts in Water.

α_0, defined by equation 1, is a measure of the effect of the non-electrolyte. α_0', defined by equation 4, is a measure of this effect after correction for the interionic forces. r_m is the average radius of the ions in Å., calculated from equations 6 and 7. β is the ratio of the values of α_0' for dioxane and urea. According to the theory, β should have the value -2.5 for all salts.

Salt	z_+	z_-	Urea			Dioxane			$-\beta$
			α_0	α_0'	r_m	$-\alpha_0$	$-\alpha_0'$	r_m	
K hydrogen tartrate.....	1	1	0.071	0.066	2.0	0.315	0.292	1.1	4.4
NH$_4$ hydrogen tartrate ..	1	1	0.087	0.077	1.7	0.261	0.230	1.4	3.0
Tl hydrogen tartrate	1	1	0.174	0.162	0.8	0.248	0.232	1.4	1.4
KIO$_4$	1	1	0.093	0.088	1.5	0.086	0.082	3.9	0.9
TlIO$_3$....................	1	1	0.159	0.156	0.8	0.293	0.288	1.1	1.8
[Co (NH$_3$)$_4$ (C$_2$O$_4$)] IO$_3$, H$_2$O	1	1	0.192	0.184	0.7				
[Co (NH$_3$)$_5$ Cl] (IO$_3$)$_2$	2	1	0.199	0.179	1.4	0.401	0.360	1.8	2.0
[Co (NH$_3$)$_6$] (IO$_3$)$_3$, 3H$_2$O ...	3	1	0.257	0.207	1.9	0.510	0.408	2.3	2.0
Ca (IO$_3$)$_2$, 6H$_2$O	2	1	0.234	0.206	1.2	0.401	0.355	1.8	1.7
Ba (IO$_3$)$_2$, H$_2$O...........	2	1	0.202	0.193	1.3	0.439[1]	0.416[1]	1.5	2.2
PbCl$_2$......	2	1	0.204	0.139	1.9	0.226	0.154	4.1	1.1
[Co (NH$_3$)$_5$ Cl] Cl$_2$	2	1	0.134	0.111	2.3	0.234	0.194	3.3	1.8
Na$_2$C$_2$O$_4$	1	2	$-$0.059	.		0.488			
CaC$_2$O$_4$, H$_2$O [2]	2	2	0.19	0.19	2.7				
[Co (NH$_3$)$_5$ Cl] C$_2$O$_4$	2	2	0.21	0.19	2.7				

[1] Calculated from the solubility measurements of Davis and Ricci (14). Temperature 25°.

[2] From solubility measurements at 25° (10).

general is far from being the same for the two solvents. For some salts the greatest r_m is found for urea solutions, for other salts r_m is greatest for dioxane solutions. The same discrepancy from the theory is seen more directly

from the last column of the table, where β, the ratio be-
tween α_0' of the two solvents, is given. According to the
theory, β should be equal to -2.5 for all the salts, but
actually it varies from -0.9 to -4.4. However, the average
of β of the 11 salts examined is -2.0, which is not so
very different from the theoretical value of -2.5.

From the examination we may conclude that the theory
gives the right order of magnitude of the effect of small
concentrations of urea and dioxane on the solubility of
salts in water; however, the theory fails to give a quanti-
tative account of the effect. This result is not surprising.
Firstly, the effect of the dielectric constant is not given
quantitatively by the theory because too rough approx-
imations have been made, *viz.* the ions have been treated as
spheres of constant radii in a uniform medium. Secondly,
even if the effect of the dielectric constant were that pre-
dicted by the theory, other effects of the non-electrolyte
may participate in determining the solubility. The ions may
attract the non-electrolyte molecules more, or less, than
they do attract the water molecules, and this effect may
produce an uneven distribution which affects the solubility.
In the extreme case, a complex formation between the ion
and the non-electrolyte may take place. Also the hydration
of the salt may have some influence on the effect of the
non-electrolyte, *viz.* if $n \neq p$, where n is the number of
crystal water molecules in one molecule of the salt, and p
is the total number of molecules of hydrate water in the
ions formed by one molecule of the salt. Due to this in-
fluence, the solubility will fall proportionally with a^{p-n},
where a is the activity of the water. For a dilute c molar
solution of a non-electrolyte the activity of the water is
$1 - 0.018\,c$, if it is 1 before the addition of the non-elec-

trolyte. If the hydration effect were the only influence, the solubility in a c molar solution of a non-electrolyte would be $s_0 (1 - 0.018\, c)^{p-n}$. If we introduce this expression into equation 1 we find that α_0 decreases $0.018\,(p-n)$ owing to the hydration. Since we know very little about the hydration of the ions in solution no correction has been applied for this effect.

In recent years, the influence of the dielectric constant of the medium upon the solubility of salts or, in general, upon the activity coefficients of the ions in the medium, has been discussed in numerous papers, and experimental data have been compared with the theory based upon Born's equation. The conclusions of the present paper are consistent with the general impression we get from the literature. The theory is often found to agree roughly with the experiments, but it is not unusual that it fails to give even the right order of magnitude. We shall mention some of the papers, but no complete list of the literature will be given.

In a paper on the interaction of electrolytes with non-electrolytes Scatchard (19) has developed the theory on the basis of Born's equation. He has tested the theory on e. m. f., freezing-point, and solubility data. The agreement is often surprisingly good. La Mer and Goldman (20) measured the solubility of thallous iodate in ethyl alcohol-water mixtures, and Lynch and La Mer (21) determined acid dissociation constants in water-dioxane mixtures. In both cases, the authors consider the agreement with the theory to be satisfactory. Failey (22) studied the solubility of thallous iodate and thallous chloride in the presence of amino acids and found fairly good agreement. Dunning and Shutt (23) found that the solubilities of lead chloride

and silver chloride in aqueous solutions of urea and glycine qualitatively obey Born's equation. OWEN (24) and NEUMAN (25) determined, independently of each other, the solubility of silver bromate in mixtures of water and different alcohols. Both conclude that Born's formula is inadequate. Recently, DAVIS and RICCI (14, 26) studied the solubilities of barium iodate, silver acetate, and silver sulphate in dioxane-water mixtures. They find that Born's equation fails to account for the course of the solubility, especially in more concentrated dioxane solutions, where expectation and observation disagree even in the order of magnitude.

Appendix.

The Solubilities of Calcium Iodate and Hexammine Cobaltic Iodate in Homoionic Solvents.

Before ending this paper, we shall give the results of some solubility measurements carried out with calcium iodate in aqueous solutions of (a molar) magnesium iodate, and with hexammine cobaltic iodate in aqueous solutions of (a molar) hexammine cobaltic chloride. The analyses of the saturated solutions were carried out by iodometry. In the first series of measurements, the solubility s was found by subtracting a from the total concentration $(s + a)$ of calcium and magnesium iodate.

Magnesium iodate tetrahydrate was prepared by adding 4.6 g. of basic magnesium carbonate to a solution of 18 g. of iodic acid at 50° C. The solution was evaporated slowly at 50° C. (27). The large crystals formed were separated and analyzed by iodometry. The molecular weight found was 445.6 (calcd. 446.3).

Hexammine cobaltic chloride. An old preparation

was reprecipitated with concentrated hydrochloric acid. The molecular weight 267.7 (calcd. 267.5) was found by means of a Volhard titration after decomposition of the complex in the same way as for chloropentammine cobaltic chloride.

The solubilities observed are given in the second column of tables 5 and 6. It is of interest to note that the solubility of hexammine cobaltic iodate, when hexammine cobaltic ions are added, decreases first, but soon passes a minimum, and increases afterwards. We shall examine to which extent the observed solubilities may be expressed by the formulae based upon well known expressions for the activity coefficients. The formulae used are given on top of tables 5 and 6. Formulae 6 and 8, which have been deduced from formula 3, contain but one empirical constant each, while formulae 7, 9, and 10 involve two empirical constants each. It is seen from table 5 that s calculated from either of the formulae 6 or 7 agrees excellently with the observed value. The difference between the observed and the calculated value never exceeds 0.1 % of $(s + a)$, the concentration determined directly by analysis. Table 6 shows that the values of s calculated from either of the two formulae 9 or 10 agree excellently, while s calculated from formula 8 agrees only moderately with the value observed. The difference between the observed values of s and those calculated from formulae 9 or 10 never exceeds 0.1 % of s.

From formulae 6 and 9 which both agree well with the observed solubilities we may, according to the Debye-Hückel theory, calculate the average ionic diameters or the distances of closest approach. For calcium iodate in magnesium iodate solution, we find the average diameter to be $1/0.326 = 3.1$ Å. This value is in fairly good agreement with the values of the mean radius for calcium iodate, 1.2

Table 5.

The Solubility of Calcium Iodate Hexahydrate in
Aqueous Solutions of Magnesium Iodate (a molar) at 17.9°.

$$-\frac{1}{3}\log s\,(s+a)^2 = 2.3600 - 0.996\,\frac{\sqrt{\mu}}{1+\sqrt{\mu}} \qquad (6)$$

$$-\frac{1}{3}\log s\,(s+a)^2 = 2.3626 - 0.996\,\sqrt{\mu} + 0.76\,\mu \qquad (7)$$

$a \cdot 10^3$	$s \cdot 10^3$ (obsd.)	μ	$s \cdot 10^3$ (calcd. form. 6)	$s \cdot 10^3$ (calcd. form. 7)
0.000	5.686	0.0171	5.689	5.688
1.009	5.087	0.0183	5.084	5.086
2.011	4.528	0.0196	4.529	4.531
3.012	4.029	0.0211	4.023	4.026
5.000	3.174	0.0245	3.163	3.172
10.00	1.771	0.0353	1.780	1.788

Table 6.

The Solubility of Hexammine Cobaltic Iodate Trihydrate in
Aqueous Solutions of Hexammine Cobaltic Chloride
(a molar) at 18.0°.

$$-\frac{1}{4}\log\,(s+a)\,s^3 = 2.6090 - 1.494\,\frac{\sqrt{\mu}}{1+\sqrt{\mu}} \qquad (8)$$

$$-\frac{1}{4}\log\,(s+a)\,s^3 = 2.6193 - 1.494\,\frac{\sqrt{\mu}}{1+0.622\,\sqrt{\mu}} \qquad (9)$$

$$-\frac{1}{4}\log\,(s+a)\,s^3 = 2.6209 - 1.494\,\sqrt{\mu} + 0.784\,\mu \qquad (10)$$

$a \cdot 10^3$	$s \cdot 10^3$ (obsd.)	μ	$s \cdot 10^3$ (calcd. form. 8)	$s \cdot 10^3$ (calcd. form. 9)	$s \cdot 10^3$ (calcd. form. 10)
0.000	3.880	0.0233	3.880	3.881	3.880
1.250	3.855	0.0306	3.827	3.855	3.856
2.500	3.863	0.0382	3.805	3.862	3.863
3.750	3.889	0.0458	3.801	3.886	3.887
5.000	3.923	0.0535	3.807	3.924	3.923

and 1.8 Å., found in table 4. For hexammine cobaltic iodate in solutions of hexammine cobaltic chloride, we find from formula 9 an average diameter of $0.622/0.326 = 1.9$ Å. This value is not in agreement with the values of the mean radius, 1.9 and 2.3 Å., found in table 4.

I wish to express my thanks to the head of the laboratory, Professor Niels Bjerrum, for his kind interest in my work.

Summary.

The solubilities of 14 sparingly soluble salts have been determined in water (table 1) and in aqueous solutions of urea (table 2).

The solubilities of 11 of the salts have furthermore been determined in aqueous solutions of dioxane (table 3).

It has been examined whether the effect of urea and dioxane on the solubilities of the salts in water may be explained from the change of the dielectric constant according to the Born expression. The theory can explain only the order of magnitude of the effect. Table 4 gives a summary of the measurements and of the computations necessary for a comparison with the theory.

In an appendix to the paper, some measurements of the solubility of calcium iodate in aqueous solutions of magnesium iodate (table 5) and of hexammine cobaltic iodate in aqueous solutions of hexammine cobaltic chloride (table 6) are described.

From the Chemical
Laboratory of the Royal Veterinary and
Agricultural College.
Copenhagen, Denmark.

References.

(1) D. C. CARPENTER and G. L. MACK, J. Amer. Chem. Soc., **56** (1934) 311.

(2) A. E. HILL, J. Amer. Chem. Soc., **50** (1928) 2678.

(3) G. KILDE, Z. anorg. Chem., **218** (1934) 113.

(4) International Critical Tables, **VII** (1930) 314.

(5) F. FLÖTTMANN, Z. anal. Chem., 73 (1927) 1.

(6) A. B. LAMB and J. P. SIMMONS, J. Amer. Chem. Soc., **43** (1921) 2197.

(7) W. SCHRAMM, Z. anorg. Chem., **180** (1929) 161.

(8) S. P. L. SØRENSEN and S. M. JØRGENSEN, Z. anorg. Chem., **19** (1899) 79.

(9) A. B. LAMB and J. W. MARDEN, J. Amer. Chem. Soc., **33** (1911) 1873.

(10) K. J. PEDERSEN, J. Amer. Chem. Soc., **61** (1939) 334.

(11) M. J. TIMMERMANS and HENNAUT-ROLAND, J. Chim. Physique, **34** (1937) 724.

(12) K. HESS and H. FRAHM, Ber. d. Deutschen Chem. Ges., **71** (1938) 2627.

(13) W. A. ROTH and I. MEYER, Z. Elektrochem., **41** (1935) 229.

(14) T. W. DAVIS and J. E. RICCI, with C. G. SAUTER, J. Amer. Chem. Soc., **61** (1939) 3274.

(15) M. BORN, Z. Physik, **1** (1920) 45.

(16) E. GÜNTELBERG, Studier over Elektrolyt-Aktiviteter i vandige Opløsninger, Dissertation, Copenhagen 1938.

(17) E. A. HARRINGTON, Physical Rev., **8** (1916) 581.

(18) G. ÅKERLÖF and O. A. SHORT, J. Amer. Chem. Soc., **58** (1936) 1241.

(19) G. SCATCHARD, Chem. Rev., **3** (1927) 383.

(20) V. K. LA MER and F. H. GOLDMAN, J. Amer. Chem. Soc., **53** (1931) 473.

(21) C. C. LYNCH and V. K. LA MER, J. Amer. Chem. Soc., **60** (1938) 1252.

(22) C. F. FAILEY, J. Amer. Chem. Soc., **55** (1933) 4374.

(23) W. J. DUNNING and W. J. SHUTT, Trans. Faraday Soc., **34** (1938) 1192.

(24) B. B. OWEN, J. Amer. Chem. Soc., **55** (1933) 1922.

(25) E. W. NEUMAN, J. Amer. Chem. Soc., **56** (1934) 28.

(26) J. E. RICCI and T. W. DAVIS, J. Amer. Chem. Soc., **62** (1940) 407.

(27) A. E. HILL and S. MOSKOWITZ, J. Amer. Chem. Soc., **53** (1931) 941.