605. *The Influence of Mixed Solvents on the Solubilities of Salts.*

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The solubilities of several sparingly soluble iodates have been measured in various mixed solvents. The results indicate that the chemical character of the solvent is of major importance in influencing the decrease in solubility with decreasing dielectic constant of the solution.

In general, the solubility of a salt at a given temperature is related to the dielectric constant of the solvent, but there is no doubt that the chemical nature of the solvent also has a decided influence. For mixed solvents one of the best illustrations is provided by silver bromate, which has received detailed consideration by Owen (*J. Amer. Chem. Soc.*, 1933, **55**, 1922) and Neuman (*ibid.*, 1934, **28**, 56). Using the expression given in the preceding paper, we may write, for these solutions :

$$\log S_0 = \log [Ag^+][BrO_3^-] - F'(I)$$

Table I.

Silver bromate solubilities (Concns., × 10^{-3}).

Organic solvent, %	Methanol[a]			Ethanol[a]			*n*-Propanol[a]		
	S	D	$-\log S_0$	S	D	$-\log S_0$	S	D	$-\log S_0$
0	8·12	78·5	4·263	—	—	—	—	—	—
10	5·51	74·1	4·592	5·53	72·8	4·592	5·80	71·8	4·553
20	3·79	69·2	4·912	3·86	67·0	4·900	4·36	64·9	4·803
30	2·65	64·3	5·220	2·78	61·1	5·184	3·31	57·7	5·046
40	1·82	59·6	5·541	1·97	55·0	5·483	2·41	50·3	5·326
50	1·24	54·9	5·871	1·36	49·0	5·805	1·63	43·0	5·671
60	0·83	50·1	6·216	—	—	—	—	—	—
70	—	—	—	—	—	—	—	—	—
80	—	—	—	—	—	—	—	—	—

Organic solvent, %	Mannitol[a]			Organic solvent, %	*iso*Propanol[b]			Organic solvent, %	Dioxan[c]		
	S	D	$-\log S_0$		S	D	$-\log S_0$		S	D	$-\log S_0$
5	8·24	77·8	4·251	11·12	5·29	70·6	4·631	10	6·24	69·7	4·496
10	8·38	77·1	4·238	22·90	3·60	62·4	4·966	20	4·76	60·8	4·739
15	8·51	76·3	4·227	31·16	2·81	56·0	5·185				
				39·77	2·10	49·7	5·442				

Organic solvent, %	Acetone[a]			Ethylene glycol[a]			Glycerol[a]		
	S	D	$-\log S_0$	S	D	$-\log S_0$	S	D	$-\log S_0$
0	—	—	—	—	—	—	—	—	—
10	5·92	73·0	4·534	7·26	75·6	4·361	7·80	75·5	4·300
20	4·29	67·0	4·812	6·50	72·8	4·456	7·49	72·9	4·338
30	3·00	61·0	5·121	5·85	69·8	4·549	7·15	70·0	4·382
40	2·03	54·6	5·459	5·26	66·6	4·643	6·84	67·1	4·425
50	—	—	—	4·70	63·2	4·743	6·48	64·0	4·476
60	—	—	—	—	—	—	6·08	60·0	4·539
70	—	—	—	3·61	54·7	4·981	5·59	55·6	4·620
80	—	—	—	—	—	—	4·94	50·6	4·738

[a] Owen, *loc. cit.* [b] Neuman, *loc. cit.* [c] Present work.

Strictly, allowance should be made for undissociated silver bromate (see preceding paper), but little error is introduced by not doing so, and the figures given in Table I are thereby obtained. The characteristic variations in the solubilities as the type of solvent is changed is shown clearly on plotting $-\log S_0$ against D (see Fig. 1).

As an extension of this work, the solubilities of calcium, barium, and lanthanum iodates have been determined in some mixed solvents. These salts were chosen since they are reasonably strong electrolytes; the dissociation constant of $Ca(IO_3)^+$ in water is 0·13 (Wise and Davies, *J.*, 1938, 273), that of $Ba(IO_3)^+$ is 0·09 (Macdougall and Davies, *J.*, 1935, 1416), and while that of $La(IO_3)^{2+}$ is unknown, the dissociation is probably quite large as the corresponding chloride appears to be fully ionised (James and Monk, *Trans. Faraday Soc.*, 1950, **46**, 1041). Accordingly no serious errors are involved in regarding these three iodates as being completely dissociated.

EXPERIMENTAL.

Calcium iodate crystals were prepared by Wise and Davies's method (*loc. cit.*), and barium iodate by allowing dilute solutions of potassium iodate and of barium chloride to drip slowly into hot water. Crystals of lanthanum iodate were formed by LaMer and Goldman's method (*J. Amer. Chem. Soc.*, 1929, **51**, 2632) by using lanthanum chloride prepared from "Spec-pure" lanthanum oxide; these crystals were too fine for use, but larger ones of suitable size were obtained by dissolution in water followed by evaporation.

FIG. 1.

Silver bromate.

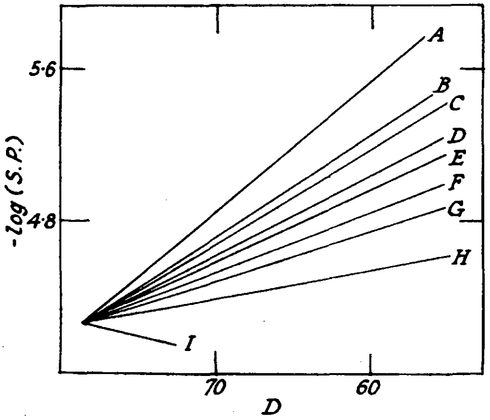
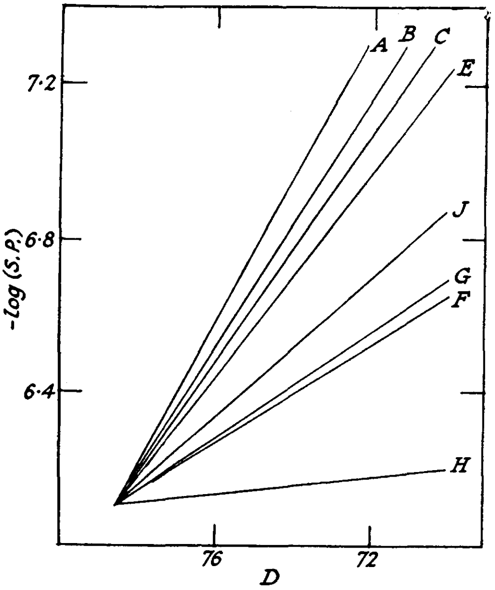


FIG. 2.

Calcium iodate.



Key to Figs. *A* methanol, *B* ethanol, *C* acetone, *D* *iso*propanol, *E* *n*-propanol, *F* glycol, *G* dioxan, *H* glycerol, *I* mannitol, and *J* ethyl acetate.

The organic solvents used were of laboratory grade, except in the cases of acetone and dioxan (AnalaR). Ethyl acetate was purified by shaking it with aqueous sodium carbonate, followed by fractional distillation.

The types of saturators used, and the experimental procedure of determining the solubilities (at 25° ± 0·03°) have been described previously (Monk, *Trans. Faraday Soc.*, 1951, **47**, 285). The saturated solutions containing dioxan were corrected for peroxides by blank titrations. Each solvent mixture was made by dilution of a stock solution, the density of which was determined. From these densities, the composition of each solution was calculated from available data, *viz.*, Owen, *loc. cit.* (methanol), Int. Crit. Tables, Vol. III, pp. 114, 117 (ethanol, *n*-propanol, ethyl acetate), Squibb, *J. Amer. Chem. Soc.*, 1895, **17**, 187 (acetone), Knight, Massi, and Roesel, *ibid.*, 1946, **68**, 641 (glycol), Davis, Ricci, and Sauter, *ibid.*, 1939, **61**, 3274 (dioxan), and Bosart and Snoddy, *J. Ind. Eng. Chem.*, 1927, **19**, 506 (glycerol). Dielectric constants were obtained by interpolation from the data given by Harned and Owen ("The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, 1943, p. 118) except in the case of ethyl acetate (Albright and Williams, *Trans. Faraday Soc.*, 1937, **33**, 247).

The results are recorded in Table II, where the concentrations are given in millimols. per l. D represents the dielectric constants of the solvents, and {S.P.} the activity solubility products; these have been calculated from the equations

$$\log\{\text{S.P.}\} = \log[M^{2+}][IO_3^-]^2 - 3F'(I) \quad (M = \text{Ca, Ba})$$

and

$$\log\{\text{S.P.}\} = \log[La^{3+}][IO_3^-]^3 - 6F'(I)$$

DISCUSSION.

The results given in Table II are plotted as $-\log\{S.P\}$ against D in Figs. 2, 3, and 4. These plots are more linear than when plotted against $1/D$ (Owen, *loc. cit.*). Comparison of Figs. 1, 2, 3, and 4 shows that, apart from minor deviations, the slopes lie in the same order with each salt. In the previous paper, reference was made to the Born–Scatchard solubility expression.

FIG. 3.

Barium iodate.

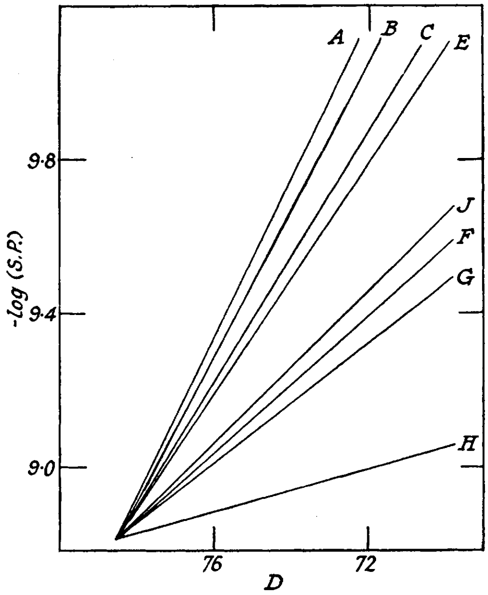


FIG. 4.

Lanthanum iodate.

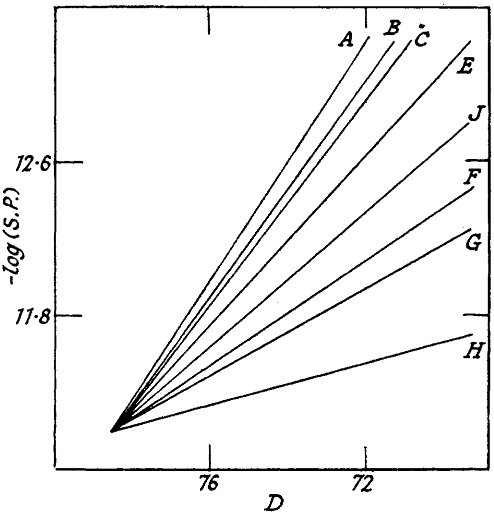


TABLE II.

Calcium, barium, and lanthanum iodate solubilities.

Solvent.	%.	*D*.	$Ca(10_3)_2$, $\times 10^{-3}$.	$-\log\{S.P.\}$.	$Ba(10_3)_2$, $\times 10^{-4}$.	$-\log\{S.P.\}$.	$La(10_3)_3$, $\times 10^{-4}$.	$-\log\{S.P.\}$.
Water	100	78·5	7·84	6·100	8·12	8·809	8·83	11·186
Methanol	4·72	76·5	4·88	6·501	5·71	9·252	5·78	11·867
	9·53	74·3	4·02	6·900	4·05	9·686	3·99	12·469
	14·43	72·1	2·94	7·280	2·84	10·136	2·70	13·109
Ethanol	3·82	76·4	5·83	6·463	5·80	9·232	5·95	11·821
	7·67	74·1	4·33	6·818	4·18	9·644	4·20	12·387
	11·59	72·1	3·23	7·170	3·02	10·058	2·89	12·999
Acetone	4·09	76·3	5·91	6·446	5·99	9·195	6·01	11·805
	8·25	73·9	4·46	6·787	4·46	9·566	4·28	12·356
	12·46	71·7	3·32	7·145	3·27	9·959	3·01	13·065
n-Propanol	4·16	75·8	5·72	6·482	5·78	9·238	5·92	11·833
	8·40	72·9	4·20	6·862	4·13	9·664	4·08	12·441
	12·71	70·0	3·07	7·243	2·94	10·096	2·84	13·039
Ethyl acetate	3·8	75·6	6·26	6·378	6·42	9·108	6·55	11·673
	6·1	73·8	5·50	6·541	5·59	9·284	5·59	11·936
Dioxan	2·2	76·6	7·04	6·239	7·15	8·972	7·69	11·416
	4·7	74·4	6·26	6·388	6·04	9·145	6·63	11·663
	9·4	70·2	4·93	6·694	4·72	9·504	4·88	12·175
	10·0	69·7	—	—	4·74	9·500	—	—
Glycol	5·62	76·9	7·16	6·216	7·18	8·966	7·50	11·452
	11·24	75·3	6·60	6·321	6·40	9·113	6·69	11·641
	16·85	73·7	6·12	6·420	5·73	9·253	5·91	11·847
Glycerol	6·31	76·6	7·75	6·118	7·81	8·859	8·22	11·316
	12·44	74·8	7·70	6·147	7·52	8·914	7·89	11·387
	18·43	73·3	7·70	6·161	7·28	8·958	7·61	11·456

For the two types of salts under discussion the appropriate expressions are, for calcium and barium iodates :

$$\ln (\{S.P._1\}/\{S.P._2\}) = (3e^2)/(rkT)(1/D_2 - 1/D_1)$$

and for lanthanum iodate :

$$\ln \{S.P._1\}/\{S.P_2\} = (6e^2)/(rkT)(1/D_2 - 1/D_1)$$

The resulting values of *r* for these three salts and for silver bromate are given in Table III.

TABLE III.

Calculated values of r (Å).

	Silver bromate	Calcium iodate	Barium iodate	Lanthanum iodate
Methanol	0·78	0·68	0·66	0·87
Ethanol	0·98	0·82	0·71	0·90
Acetone	1·05	0·90	0·82	1·03
*iso*Propanol	1·23	—	—	—
n-Propanol	1·35	1·0	0·89	1·2
Ethyl acetate	—	1·4	1·4	1·5
Glycol	1·63	2·1	1·2	1·9
Dioxan	2·0	2·2	1·7	2·3
Glycerol	3·5	14·0	6·0	5·0

The figures being taken as a whole, it is evident that *r* is characteristic of the organic constituent of the solvent rather than of the salt. The outstanding exception is calcium iodate in glycerol solutions, which may be the result of a specific cation–glycerol interaction. So far as minor deviations are concerned, the slightly smaller values of *r* with barium iodate may be related to the smaller effective radius of the hydrated barium ion as compared with those of calcium and lanthanum. A comparison of the slopes of the curves in the Figs. with those for the dissociation constants of silver acetate in the preceding paper shows some general features, namely, that in both instances glycerol has the less effect, and the group acetone, ethanol, and methanol has the most influence, whilst glycol and dioxan are intermediate.

It would appear then that further theoretical treatment lies in a consideration of the solvent properties. As the dielectric constant is varied the composition of the solvent alters also, and this is attended by specific energy changes. Accordingly, the organic solvent–water, organic solvent–ion, and water–ion interactions are all dependent on the proportions and nature of the organic constituent.

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