The Ternary Systems KI–K₂SO₄–H₂O and NaI–Na₂SO₄–H₂O

BY JOHN E. RICCI

In addition to the purpose of obtaining solubility data for the salt pairs KI–K₂SO₄ and NaI–Na₂SO₄ in water, this brief investigation also had as its object the question of the formation of solid solutions of the alkali iodides in the corresponding sulfates. The crystals of sodium sulfate offer a considerable number of instances of the formation of solid solutions with other salts (as, with Na₂CO₃, Na₂CrO₄, Na₂S, Na₂SO₃, Na₂S₂O₃, Ag₂-SO₄,[1] and NaBrO₃[2]). As to the iodides in particular, sodium sulfate has been reported[3] to form crystals of Na₂SO₄·10H₂O containing varying quantities of NaI, KI, NH₄I and LiI, held in the form of solid solution; these results, however, are based on non-equilibrium studies, in which the decahydrate was allowed to crystallize slowly from solutions of varying concentrations of the iodides, at a roughly constant temperature near room temperature. Although the fact that such crystals contain iodide (from 0.4% in the case of NaI, to 0.65% for LiI) may well be the result of simple occlusion due to lack of equilibrium, the crystals are reported to be solid solutions ("mixed crystals") on the strength of their clearness and transparency. Since on the basis of such work there seemed to be some doubt as to the actual existence of such solid solutions as stable phases in the systems, it was thought desirable to make an equilibrium study of the particular system NaI–Na₂SO₄–H₂O.

In the present work both the system KI–K₂SO₄–H₂O and the system NaI–Na₂SO₄–H₂O were studied, from the point of view of the phase rule, the first at 25°, the second at 15, 25 and 45°. The results, which represent equilibrium in the systems, show no solid solutions to be formed in either case, within the limits of the rather small experimental error of this type of work. The only solid phases encountered are the pure anhydrous or hydrated salts themselves.

Experimental Method

The experimental procedure for the solubility measurements has already been described in pre- vious similar publications.[4] The temperature was maintained constant to within ±0.02°. The time allowed for the attainment of equilibrium varied from three days in the case of the potassium salts, to as long as fourteen days in the case of the sodium salts; the latter system was found by experiment to require from ten to fourteen days to reach equilibrium in all complexes which involved the formation of Na₂SO₄·10H₂O as solid phase. The densities reported for the potassium salt system and for some solutions of the sodium salt system, were obtained by means of volumetric pipets calibrated for delivery. For the analysis of the solutions, the iodide was determined volumetrically by titration with 0.2 N silver nitrate using dichlorofluorescein as indicator, the total solid was determined by evaporation to dryness, and the sulfate was then calculated by difference. In some cases of the KI–K₂SO₄–H₂O system the sulfate was determined directly by the gravimetric method, and the iodide then calculated by difference. The results of the two methods being in sufficiently close agreement, the more rapid method (titration of the iodide) was used in general. The solid phases were in each case verified by the method of algebraic extrapolation of tie-lines,[5] the average error of the extrapolations, for both systems, being 0.18%.

Results

The experimental data for the system KI–K₂SO₄–H₂O at 25° are given in Table I and Fig. 1;

TABLE I
KI–K₂SO₄–H₂O AT 25°

Original complex, wt. %		Saturated solution, wt. %			
K₂SO₄	KI	K₂SO₄	KI	Density	Solid phase
. . .	0.00	10.76	0.00	1.083	K₂SO₄
23.01	7.53	6.57	9.13	1.127	K₂SO₄
22.02	15.01	3.57	18.57	1.185	K₂SO₄
21.47	23.02	1.70	28.81	1.273	K₂SO₄
21.01	31.49	0.69	39.57	1.399	K₂SO₄
20.74	40.04	.25	50.35	1.553	K₂SO₄
19.99	47.03	.10	58.70	1.701	K₂SO₄
19.98	48.19	.08	59.69	1.724	K₂SO₄ + KI
12.05	57.91	.08	59.70	1.724	K₂SO₄ + KI
3.00	66.05	.08	59.67	1.720	K₂SO₄ + KI
0.59	67.98	.08	59.68	1.721	K₂SO₄ + KI
Av. (of 4) . . .		.08	59.69	1.722	K₂SO₄ + KI
0.00	. . .	.00	59.76	1.718	KI

(1) "International Critical Tables," Vol. IV, 1928.

(2) Ricci, THIS JOURNAL, 57, 805 (1935).

(3) Fabris, Ann. chim. applicata, 17, 321 (1927); 18, 115, 326 (1928).

(4) Ricci THIS JOURNAL, 56, 290 (1934).

(5) Hill and Ricci, ibid., 53, 4305 (1931).

the solubility curve consists of two simple branches, one for solutions in equilibrium with potassium sulfate, the other, extremely short, for solutions saturated with KI.
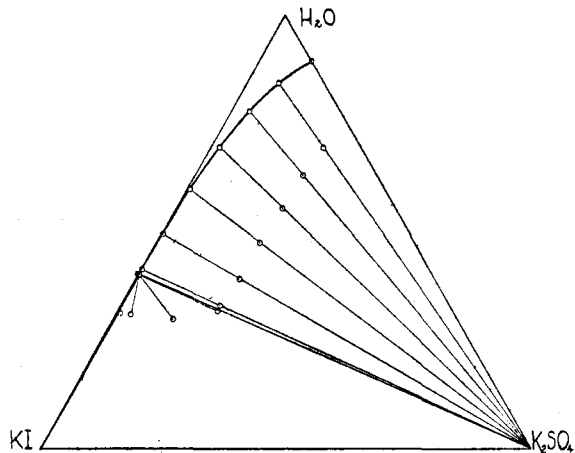

Fig. 1.—25° Isotherm: KI-K₂SO₄-H₂O.

The results for the system NaI–Na₂SO₄–H₂O, at 15, 25 and 45°, are presented in Table II, the

TABLE II

NaI–Na₂SO₄–H₂O

15°

Original complex, wt. %		Saturated solution, wt. %			
Na₂SO₄	NaI	Na₂SO₄	NaI	Density	Solid phase
...	0.00	11.60	0.00	1.106	Na₂SO₄·10H₂O
9.01	27.98	2.51	33.16	1.367	Na₂SO₄·10H₂O
5.95	36.09	2.15	39.67	1.460	Na₂SO₄·10H₂O
8.00	35.95	2.10	41.78	1.490	Na₂SO₄·10H₂O
8.01	37.99	2.13	44.07	1.532	Na₂SO₄·10H₂O
13.05	33.57	2.23	44.79	1.543	Na₂SO₄·10H₂O + Na₂SO₄
5.97	41.85	2.19	44.85	1.543	Na₂SO₄·10H₂O + Na₂SO₄
15.02	37.41	2.22	44.84	1.540	Na₂SO₄·10H₂O + Na₂SO₄
Av. (of 3)		2.21	44.83	1.542	Na₂SO₄·10H₂O + Na₂SO₄
15.09	42.99	0.93	50.15	1.613	Na₂SO₄
15.04	48.43	.15	56.92	1.733	Na₂SO₄
15.00	53.52	.02	62.89	1.875	Na₂SO₄
15.08	54.59	.01	63.33	1.881	Na₂SO₄ + NaI·2H₂O
4.99	64.90	.05	63.31	1.882	Na₂SO₄ + NaI·2H₂O
Av. (of 2)		.03	63.32	1.881	Na₂SO₄ + NaI·2H₂O
0.00	...	.00	63.35	1.881	NaI·2H₂O

25°[a]

...	0.00	21.78	0.00		Na₂SO₄·10H₂O
23.91	5.15	17.54	6.77		Na₂SO₄·10H₂O
23.58	8.10	14.87	11.50		Na₂SO₄·10H₂O
20.09	13.94	11.83	18.46		Na₂SO₄·10H₂O
15.52	17.42	10.81	20.30		Na₂SO₄·10H₂O

13.11	22.20	9.37	24.81	Na₂SO₄·10H₂O
13.05	23.56	8.70	26.84	Na₂SO₄·10H₂O
14.03	25.00	7.94	30.05	Na₂SO₄·10H₂O
13.49	27.02	7.61	31.77	Na₂SO₄·10H₂O + Na₂SO₄
18.05	26.02	7.66	31.74	Na₂SO₄·10H₂O + Na₂SO₄
12.48	29.31	7.64	31.76	Na₂SO₄·10H₂O + Na₂SO₄
Av. (of 5)		7.63	31.77	Na₂SO₄·10H₂O + Na₂SO₄
...	0.00	33.97	0.00	Na₂SO₄ (m)[b]
36.74	6.57	26.65	7.60	Na₂SO₄ (m)
20.01	19.97	14.91	21.22	Na₂SO₄ (m)
20.13	27.11	7.97	31.21	Na₂SO₄ (m)
20.00	32.16	4.09	38.58	Na₂SO₄
20.16	36.77	2.06	45.01	Na₂SO₄
20.27	41.72	0.70	51.91	Na₂SO₄
19.94	45.45	.30	56.54	Na₂SO₄
20.06	49.73	.14	62.05	Na₂SO₄
19.96	54.55	.02	64.76	Na₂SO₄ + NaI·2H₂O
4.02	64.97	.07	64.76	Na₂SO₄ + NaI·2H₂O
2.98	72.00	.07	64.75	Na₂SO₄ + NaI·2H₂O
Av. (of 4)		.06	64.75	Na₂SO₄ + NaI·2H₂O
0.00	...	.00	64.79	NaI·2H₂O

45°[a]

...	0.00	32.09	0.00	Na₂SO₄
35.01	12.98	17.19	16.52	Na₂SO₄
29.87	23.88	6.73	31.73	Na₂SO₄
25.01	32.89	2.22	42.85	Na₂SO₄
20.07	41.98	0.51	52.27	Na₂SO₄
17.78	43.54	.43	52.75	Na₂SO₄
20.16	54.22	.04	67.85	Na₂SO₄
6.02	64.78	.04	68.29	Na₂SO₄ + NaI·2H₂O
6.00	67.92	.02	68.22	Na₂SO₄ + NaI·2H₂O
2.04	70.48	.06	68.25	Na₂SO₄ + NaI·2H₂O
Av. (of 3)		.04	68.25	Na₂SO₄ + NaI·2H₂O
0.00	...	.00	68.32	NaI·2H₂O

[a] The data for the 45°, and for part of the 25°, isotherms were obtained by Dr. Nicholas S. Yanick, formerly of this Department. [b] m = metastable solid phase.

three isotherms being shown graphically in Figs. 2, 3 and 4. As may be seen from the diagrams the
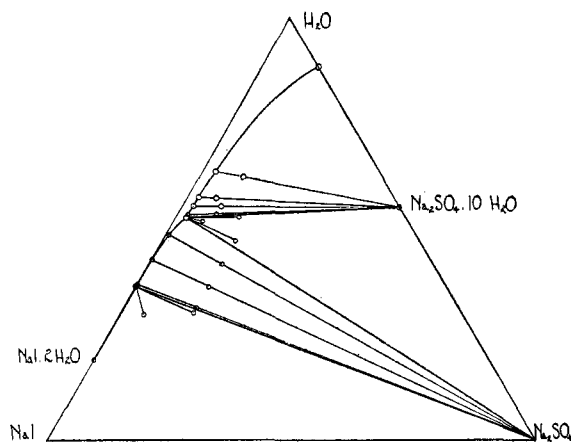

Fig. 2.—15° Isotherm: NaI–Na₂SO₄–H₂O.

only stable phases existing in the system at 45° are anhydrous Na₂SO₄ and NaI·2H₂O, while at

15 and 25°, Na$_2$SO$_4$·10H$_2$O appears, giving three stable phases. In Fig. 3, for the 25° isotherm, the curve a-b represents the solubility of Na$_2$SO$_4$·10H$_2$O as stable phase in the ternary system;
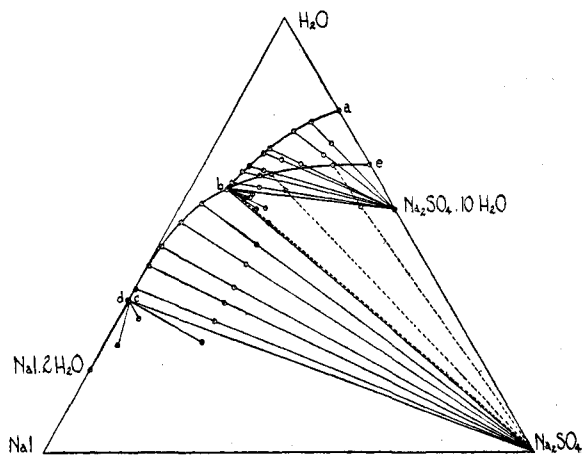
Fig. 3.—25° Isotherm: NaI–Na$_2$SO$_4$–H$_2$O.

point b, an isothermally invariant solution in equilibrium with both hydrated and anhydrous Na$_2$SO$_4$; the curve b-c, solutions in equilibrium with anhydrous Na$_2$SO$_4$ as solid phase; point c, the isothermally invariant solution for the two solid phases Na$_2$SO$_4$ and NaI·2H$_2$O; and the very short curve c-d, the solubility curve of NaI·2H$_2$O. The curve b-e is the metastable extension of the solubility curve b-c, of Na$_2$SO$_4$, point e being

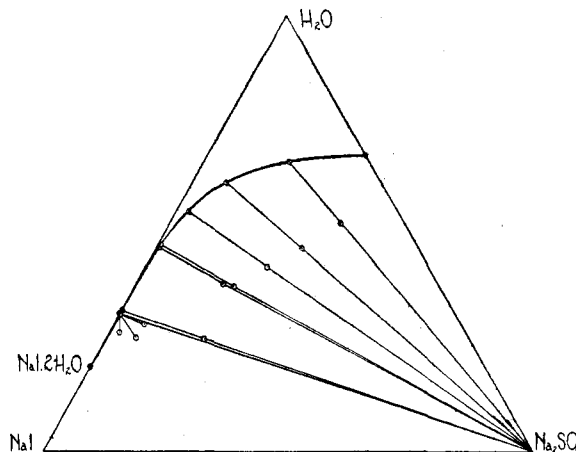the metastable solubility of anhydrous Na$_2$SO$_4$ in water at 25°.

Fig. 4.—45° Isotherm: NaI–Na$_2$SO$_4$–H$_2$O.

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Summary

Solubility measurements are given for the systems KI–K$_2$SO$_4$–H$_2$O (at 25°) and NaI–Na$_2$SO$_4$–H$_2$O (at 15, 25 and 45°); these salt pairs form neither double salts nor solid solutions at the temperatures reported.

Phenyl Urethan Anesthetics. II

BY E. S. COOK AND T. H. RIDER

The value of phenyl urethans as local anesthetics has been pointed out by Rider.[1] The present paper continues work in this field and deals largely with phenyl urethans of γ-dialkylaminopropanols (R$_2$NCH$_2$CH$_2$CH$_2$OH). Two esters of dialkylaminoisopropyl alcohols (R$_2$NCH$_2$CH-OHCH$_3$) and the phenyl urethan of β-diethylaminoethanol are included.

These compounds are of particular interest because they are isomeric with the p-aminobenzoates, several of which have found considerable use as local anesthetics. The p-aminobenzoate homologs of compounds 4 and 9 (see Table I) are

marketed as butyn and procaine, respectively, and the p-aminobenzoate homologs of compounds 2, 3,[2] and 6[3] have been prepared and found to possess local anesthetic activity.

Experimental Part

Amino Alcohols.—Beta-diethylaminoethanol, γ-diethylaminopropanol, and γ-di-n-butylaminopropanol were obtained from the Eastman Kodak Company and redistilled. The other γ-dialkylaminopropanols (dimethylamino-, di-n-propylamino-, piperidino- and methylphenethylamino-) were prepared by condensing the proper secondary amine with trimethylene bromohydrin in the absence of a solvent.

(1) T. H. Rider, (a) THIS JOURNAL, **52**, 2115 (1930); (b) ibid., **52**, 2583 (1930); (c) J. Pharmacol., **39**, 457 (1930); (d) ibid., **47**, 255 (1933).

(2) O. Kamm, R. Adams and E. H. Volwiler, U. S. Patents 1,358,-750 and 1,358,751; E. H. Volwiler, Science, **53**, 145 (1921); H. L. Schmitz and A. S. Loevenhart, J. Pharmacol., **24**, 159 (1924).

(3) A. C. Cope and S. M. McElvain, THIS JOURNAL, **53**, 1587 (1931).