Results and Discussion

Table I gives the results of the analyses performed on the alkali fluoroplatinates. Only the cations were determined since the presence of the anion was confirmed by its characteristic absorption spectrum.

TABLE I

ANALYTICAL DATA

Compound	Alkali, % Calcd.	Alkali, % Found
Na_2PtF_6	12.95	12.9
$(NH_4)_2PtF_6$	10.45	10.4
K_2PtF_6	20.18	20.2
Rb_2PtF_6	35.60	35.5
Cs_2PtF_6	46.23	46.2

The solubilities and densities of the compounds at 25 ± 0.5° are presented in Table II.

TABLE II

Compound	Solubility, g./100 ml. of soln.	Density
Na_2PtF_6	20.49	4.21
$(NH_4)_2PtF_6$	7.32	3.59
K_2PtF_6	0.750	4.83
Rb_2PtF_6	0.278	6.00
Cs_2PtF_6	0.484	5.39

The solubility of the ammonium salt is to be noted and contrasted with the appreciably smaller solubilities of the ammonium and potassium chloroplatinates. Cox and Sharpe[5] have mentioned the general tendency of the ammonium salts of fluoro complexes to be appreciably more soluble than the corresponding chloro complexes. This fact coupled with the smaller solubility of the potassium fluoroplatinate suggests that the gravimetric determination of potassium using fluoroplatinic acid as the precipitating reagent may be better than that with chloroplatinic acid.

Schlesinger and Tapley[2] reported that very dilute solutions of potassium fluoroplatinate obeyed Beer's law. This was confirmed by measuring the 275 mμ peak at various concentrations of potassium, rubidium and cesium fluoroplatinates. These solutions, however, are relatively dilute even when saturated. Therefore, the more concentrated solutions of the sodium and ammonium salts were used for a further study.

Ammonium fluoroplatinate solutions up to 0.05 *M* were measured and found to obey Beer's law within experimental error. However, the extinction coefficients of this salt differed slightly from those obtained for comparable concentrations of the potassium, rubidium and cesium salts. This may be attributed to the hydrolysis of the ammonium salt.

The results of the study with the sodium salt reveal a small but definite departure from Beer's law. When the concentration was plotted against optical density, a slight curve was obtained which did not pass through the origin.

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[5] B. Cox and A. G. Sharpe, *J. Chem. Soc.*, 1798 (1954).

The System Na_2SO_4–Li_2SO_4–H_2O at 0°[1]

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The determination of the 0° isotherm of the system Na_2SO_4–Li_2SO_4–H_2O was necessary in connection with a study of the system Na_2SO_4–Li_2SO_4–$Al_2(SO_4)_3$–H_2O at 0°. Although Spielrein[2] reported, without presenting the supporting experimental data, a variety of double salts as stable solid phases ($Na_2SO_4 \cdot Li_2SO_4 \cdot 5.5H_2O$ at 0 to 16°; $3Na_2SO_4 \cdot Li_2SO_4 \cdot 12H_2O$, 16 to 24°; $Na_2SO_4 \cdot 4Li_2SO_4 \cdot 5H_2O$, 24 to 32°; $Na_2SO_4 \cdot Li_2SO_4 \cdot 3H_2O$, 32 to 100°), the only double salts found in the recent study of two isotherms by Cavalca and Nardelli[3] are $3Na_2SO_4 \cdot Li_2SO_4 \cdot 12H_2O$ at 27° and both $3Na_2SO_4 \cdot Li_2SO_4 \cdot 12H_2O$ and $Na_2SO_4 \cdot Li_2SO_4$ at 45.6°. The results presented here confirm the latter report in that the 0° isotherm is found to be similar, except for numerical relations, to that at 27°. The sole solid phases are $Na_2SO_4 \cdot 10H_2O$, $3Na_2SO_4 \cdot Li_2SO_4 \cdot 12H_2O$ and $Li_2SO_4 \cdot H_2O$. It is likely therefore that the only stable double salt solid phases of the system are those reported by Cavalca and Nardelli, who also described their crystallographic characteristics.

Experimental Procedure

The anhydrous simple salts were employed in the preparation of mixtures of known composition. $Li_2SO_4 \cdot H_2O$, a J. T. Baker reagent product, was dehydrated without further purification. It was heated in platinum at 550–600° after a preliminary dehydration at 110°. Anhydrous Na_2SO_4, also a J. T. Baker reagent product, was similarly treated without the preliminary step. The sodium content of the dried Li_2SO_4 was estimated by flame photometry and corrections applied in the calculation of the compositions of the mixtures.

The apparatus and procedure was the same as that described in a previous paper by the present authors[4] dealing with another ternary system involving Li_2SO_4. All complexes were seeded with a small crystal of $Na_2SO_4 \cdot 10H_2O$. This was necessary to produce a solid phase in those mixtures which were relatively rich in Na_2SO_4. Changes were also observed in most of the mixtures where a solid phase was already present. The complexes were mixed 24 hours before seeding and at least 14 days before final analysis. Constancy of composition was used as a criterion of attainment of equilibrium.

The filtered saturated solutions were analyzed for combined sulfates and for lithium, the sodium being obtained by difference. A given sample was evaporated to dryness at 100° and the residue heated to constant weight at 180°. An ion-exchange chromatographic procedure,[5,6] with slight modifications, was then applied to the determination of the lithium in this residue. In the procedure, both sodium and lithium were adsorbed on Colloidal Dowex 50 resin, the

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[1] This work was begun under a grant from the National Science Foundation. The major portion was completed with the assistance of a summer research grant from St. John's University to the principal author.

[2] C. Spielrein, *Compt. rend.*, **157**, 46 (1913).

[3] L. Cavalca and M. Nardelli, *Gazz. chim. ital.*, **82**, 394 (1952).

[4] J. A. Skarulis, H. A. Horan, *et al.*, THIS JOURNAL, **76**, 3096 (1954).

[5] J. Beukenkamp and W. Rieman, *Anal. Chem.*, **22**, 582 (1950).

[6] R. C. Sweet, W. Rieman and J. Beukenkamp, *ibid.*, **24**, 952 (1952).

lithium then eluted with 0.70 *M* HCl. The eluate was evaporated to LiCl and the lithium estimated by the Mohr titration of the chloride, after a small correction for free HCl retained by the residue.

The analytical procedure was tested with mixtures of known composition, the materials being the same as those used in the complexes. In these runs the sodium was also determined in the same manner as the lithium. The lithium values were reproducible with good precision but the sodium values obtained by direct measurement were in general unsatisfactory. Duplicate samples when passed through different columns yielded lithium values which seldom differed by more than 3 parts per 1000. The lithium values were consistently high by 5 ± 1 parts per 1000. The sodium values on the other hand were 10 to 20 parts per 1000 high. It was noted that the lithium values were not as good when the total number of equivalents in the sample was low. For this reason, the weights of saturated solutions taken for analysis were such that the aliquots introduced into the columns contained at least 1 me. of lithium.

All analyses were run in duplicate on separate samples of saturated solution. The results are tabulated in Table I and plotted in the usual manner in Fig. 1.

TABLE I

THE SYSTEM Na_2SO_4–Li_2SO_4–H_2O AT 0°

A = Na_2SO_4, B = Li_2SO_4, W = H_2O.

	Complex		Solution		
	A, %	B, %	A, %	B, %	Solid
1	13.01	2.46	4.40	3.17	A·10W
2	16.06	6.48	4.83	9.09	A·10W
3	15.08	9.99	4.95	13.58	A·10W
4	10.07	13.97	5.25	16.01	A·10W
5	9.57	17.97	5.73	20.02	A·10W
6	9.05	21.91	6.22	23.31	A·10W + 3A·B·12W
7	14.95	20.90	6.30	23.23	A·10W + 3A·B·12W
8	19.84	20.96	6.17	23.41	3A·B·12W
9	18.01	21.33	6.23	23.37	3A·B·12W
10	18.00	21.56	6.10	23.72	3A·B·12W
11	21.43	20.96	6.04	23.80	3A·B·12W
12	18.35	25.88	5.87	24.12	3A·B·12W + B·W
13	18.00	25.93	5.81	24.16	3A·B·12W + B·W
14	16.91	35.45	5.87	24.15	3A·B·12W + B·W
15	13.26	29.60	5.84	24.14	3A·B·12W + B·W
16	11.06	28.86	5.83	24.14	3A·B·12W + B·W
17	9.24	32.21	5.87	24.12	3A·B·12W + B·W
18	5.05	33.86	5.99	24.03	B·W
19	2.10	34.86	2.36	25.52	B·W

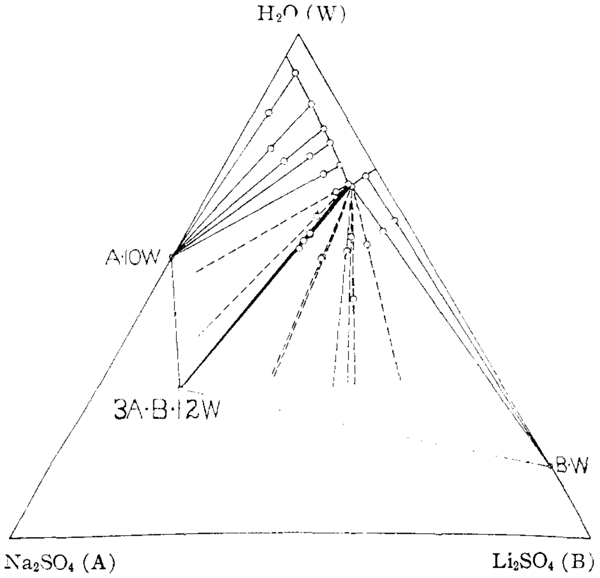

Fig. 1.—The system Na_2SO_4–Li_2SO_4–H_2O at 0°.

Discussion of Results

Algebraic extrapolation[7] of the data indicates three solid phases at 0°: $Na_2SO_4 \cdot 10H_2O$, $3Na_2SO_4 \cdot Li_2SO_4 \cdot 12H_2O$ and $Li_2SO_4 \cdot H_2O$. Extrapolation of the tie-lines of complexes 1–5 inclusive to % Li_2SO_4 at 44.09% Na_2SO_4, the theoretical % Na_2SO_4 in the decahydrate, gives values of −0.10, −0.03, −0.29, −0.43 and −0.46, respectively. The tie-lines of complexes 8–11 inclusive when extrapolated to % Li_2SO_4 at 56.65% Na_2SO_4, the theoretical % Na_2SO_4 in the double salt, yield the values 14.36, 14.64, 14.54 and 14.56, respectively, as compared to a theoretical value of 14.61. The solid phases of these four complexes were centrifuged and analyzed for water content. The nearly free-flowing crystalline material contained 30% H_2O as compared with the theoretical value 28.74. Extrapolation of complexes 18–19 to % Na_2SO_4 at 85.93% Li_2SO_4, the theoretical % Li_2SO_4 in the monohydrate, gives values of +0.07 and +0.68, respectively. In general, the above extrapolations deviate in the direction expected because the lithium analyses of the saturated solutions are slightly high, as indicated in a preceding paragraph. No attempt was made to correct these analyses.

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[7] A. E. Hill and J. E. Ricci, THIS JOURNAL, **53**, 4306 (1931).