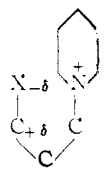
that neither static inductive effects nor direct resonance will explain the results.

There is some evidence that the inductive effect of an electronegative group can be transmitted directly through space, field effect,[25] instead of being transmitted through a chain of electronic linkages. This inductive field effect is a polarization phenomenon. By working with molecular models, it is clearly seen that the substituent group in the β- or γ-position can approach the nitrogen atom in the ring. It thus seems reasonable that a large field effect might well influence the present dissociation constant results. The direction of the group moment[26] of the substituent group in the β- or γ-position as a result of the particular spatial relationship might well determine the influence of the substituent on the dissociation process. Without knowing the exact geometric configuration of the various atoms in the salts, it is not possible to predict absolutely why the β-substituted salts are all stronger than the unsubstituted *n*-propyl while the γ-substituted salts are all weaker. It is seen that the γ-substituted salts could cyclize into a five-membered ring



which would be stabilized by the fractional resonance charges defined usually as $-\delta$ and $+\delta$. The somewhat restricted rotation of the substituted propyl side chain should then allow the picrate ion to move in closer; thus accounting for the lower K's in the case of the γ-substituted salts. Cyclic structures like these would block approach of the solvent on one side, in agreement with the higher Λ_0's observed for the γ-isomers.

Acknowledgment.—The partial support of this work by the Research Corporation is acknowledged with appreciation. Through the kind efforts of Drs. R. M. Fuoss and D. Edelson, complete details were provided to us for constructing the shielded conductance bridge, considerably in advance of their publication[20] of the specifications. Many helpful suggestions in interpretation were furnished by Dr. E. Grunwald.

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[26] G. E. K. Branch and M. Calvin, "Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 142.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY]

Some Aqueous Systems Involving Sulfamates

BY JOHN E. RICCI AND BERNARD SELIKSON

The solubility isotherms at 25° of a few ternary aqueous systems containing a sulfamate and the corresponding halide were found to be simple, with the pure salts as sole solid phases. The systems ammonium sulfamate–ammonium sulfate–water and potassium sulfamate–potassium sulfate–water were also found to be simple at 25°, with no solid solution between the corresponding sulfamate and sulfate. The aqueous system of the sulfamates of ammonium and potassium, however, studied at 9, 25 and 45°, forms extensive solid solution with a miscibility gap. The distribution relations are those of Type V of Roozeboom's classification. The 25° isotherm of the reciprocal quaternary system of water and the salt pair ammonium sulfamate–potassium sulfate was also determined, involving continuous solid solution of the sulfates and the two series of solid solutions of the sulfamates as its three solid phases. The isothermally invariant quaternary solution saturated with all three solids is of the transition type, being incongruently saturated with respect to the sulfamate solid solution rich in potassium sulfamate. The determination of ammonium in presence of the amine sulfonate, and of the total nitrogen of the solution, was made by an adaptation of the procedure of Marcali and Rieman for organic nitrogen, which uses Kolthoff's titration of the ammonium salt of a strong acid in presence of formaldehyde.

Since the review of the chemistry of sulfanic acid and related compounds by Audrieth, Sveda, Sisler and Butler in 1940,[1] the literature on the sulfamates has been expanding, with the need for further information accompanying the growing applications[2] of these substances. In the further studies of properties of sulfamic acid and the sulfamates, investigations of solubility equilibria have been rather limited[3] and the only phase studies reported are those on the binary systems $NaSO_3NH_2$–H_2O,[4,5] $NH_4SO_3NH_2$–NH_4NO_3,[6] $NH_3SO_3NH_2$–$NaSO_3NH_2$ and $NaSO_3NH_2$–$NaNO_3$,[7] and on the ternary system sulfamic acid–ammonium sulfamate–water.[4]

This is a report of further observations on some of the sulfamates, in respect to solubility equilibria in aqueous solutions. The isotherms at 25° of the four ternary aqueous systems of a sulfamate and a halide with common cation were found to be simple, with the pure salts as solid phases. The quaternary aqueous system of the reciprocal salt pair $NH_4SO_3NH_2$–K_2SO_4 was also studied at 25°, together with its constituent ternary systems $NH_4SO_3NH_2$–$(NH_4)_2SO_4$–H_2O, KSO_3NH_2–K_2SO_4–H_2O, and $NH_4SO_3NH_2$–KSO_3NH_2–H_2O, the fourth, or $(NH_4)_2SO_4$–K_2SO_4–H_2O, being available from the literature. The analysis of the quaternary solutions involved indirect calculations based on the determination of ammonium in presence of sulfamate and of the total nitrogen of the solution, together with determination of total solid. The only three solid

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[1] L. F. Audrieth, M. Sveda, H. H. Sisler and M. J. Butler, *Chem. Revs.*, **26**, 49 (1940).

[2] For review of industrial applications, see M. E. Cupery and W. E. Gordon, *Ind. Eng. Chem.*, **34**, 792 (1942).

[3] G. B. King and J. F. Hooper, *J. Phys. Colloid Chem.*, **45**, 938 (1941); F. Oberhauser B and H. E. Urbina C, *Anales facultad filosóf. y educación, Univ. Chile Sección quím.*, **3**, 109, 119 (1946), from *C. A.*, **41**, 1944 (1947).

[4] J. E. Ricci and B. Selikson, THIS JOURNAL, **69**, 995 (1947).

[5] S. H. Laning and P. A. van der Meulen, *ibid.*, **69**, 1828 (1947).

[6] J. A. Thelin and P. A. van der Meulen, *ibid.*, **70**, 1796 (1948).

[7] S. H. Laning and P. A. van der Meulen, *ibid.*, **70**, 1799 (1948).

phases of the quaternary isotherm are the two solid solutions of the sulfamates and the known continuous solid solution of the sulfates.

The general procedure was that used in similar phase studies. Complexes of known composition, prepared from the pure components, and totaling ~35 g. for the ternary and ~55 g. for the quaternary mixtures, were rotated in glass tubes containing marbles for internal agitation, and the filtered saturated solution was analyzed at equilibrium. Solutions were sampled through filter paper into pipets, specific gravity pipets being used for the density measurements. The composition of the solid phase was calculated by algebraic extrapolation of tie-lines fixed by the compositions of total complex and liquid solution, with wet residues being used in a few cases. Equilibrium was verified by reanalysis of the solution after further stirring. In the simple systems equilibrium was reached in several hours, while a few days, possibly only one day, sufficed in those involving solid solution. No hydrolysis was detected in any case, on the basis of a test for sulfate,[4] except for a negligible positive test in the case of saturated solutions at 45° in the system $NH_4SO_3NH_2$–KSO_3NH_2–H_2O after one week's stirring. The solids settled well except for the light, long fibrous crystals of $NaSO_3NH_2 \cdot H_2O$, the unusual properties of which have already been described,[4] and for the fine powder of K_2SO_4 requiring several hours to settle.

Materials.—Ammonium sulfamate, prepared as previously described,[4] crystallized in large rectangular plates which could be split into thinner crystals, suggesting a sheet-like structure. Like all the sulfamates handled, including $NaSO_3NH_2 \cdot H_2O$, it showed parallel extinction. The crystals were several mm. to 1 cm. long, even in rotating solubility tubes. Its solubility is high (62.26, 68.90 and 76.54% at 9, 25 and 45°, respectively), and it deliquesces rapidly on warm humid days. Its saturated solution has a slippery feel and does not wet glass, an effect also noticeable, to a smaller degree, for saturated solutions of KSO_3NH_2 and of $NaSO_3NH_2$. For this reason densities had to be determined with specific gravity pipets rather than with delivery pipets. The solution is easily supercooled when evaporated at 80–90°, giving a persisting glassy state, and the crystals are not readily obtained on cooling in a desiccator at room temperature, even though the final residue is anhydrous.[8] When disturbed, the clear mass becomes opaque, and the appearance of striations is accompanied with cracking sounds. Hydrolysis in the saturated solution at 25° is extremely slow, the test for sulfate being negative even after 1.5 years of stirring.[9]

Potassium sulfamate was obtained pure (99.9+% on the basis of nitrogen determination) by several recrystallizations of technical grade material or of the product of reaction of purified sulfamic acid and either KOH or K_2CO_3. It forms white square (but not cubic) crystals. Its solubility is 31.44, 43.72 and 56.40% at 9, 25 and 45°, respectively. It is not deliquescent.

Anhydrous sodium sulfamate was prepared from pure sulfamic acid neutralized with $Na_2CO_3 \cdot 10H_2O$, by precipitation, as suggested by Laning and van der Meulen,[5] with methanol. It was noted that addition of ethanol, isopropyl alcohol, dioxane or acetone to a concentrated solution of the salt caused formation of two liquid layers.

Other materials used were C.P. or reagent grade substances believed to be of dependable purity.

Analytical Methods.—Total solid was determined by evaporation at 80°, first overnight in an open drying oven and again overnight in a vacuum oven; tests proved that this treatment involved only negligible error. Only the solutions containing sodium sulfamate were dried at 95° and brought to constant weight at 110°.

Chloride was determined by the Volhard method with filtration of the AgCl. Iodide was titrated with silver nitrate to the clear-point, with eosin as a preliminary indicator; tests showed that sulfamate did not interfere.

For ammonia, and for total nitrogen after hydrolysis of the sulfamate to ammonium and sulfate, a few of the determinations were made by the Kjeldahl method, with titration of the ammonia after distillation into boric acid. Most of the determinations, however, were done with a faster method[10] (Kolthoff) based on the titration of the ammonium salt of strong acid in a solution adjusted to the methyl red end-point, after reaction with formaldehyde to form hexamethylenetetramine, which is negligibly weak as a base ($K_b = 8 + 10^{-10}$). The procedure followed was essentially that described by Marcali and Rieman for organic nitrogen.[11] It was found necessary, however, to have the solution at ~50° for the reaction with formaldehyde to be completed rapidly enough to give a permanent end-point directly. At room temperature the first apparent end-point (pink of phenolphthalein) occurs early and fades, hours being required for a permanent end-point.

The formaldehyde was used in ~18% solution, prepared from reagent grade 37% formaldehyde. With 0.3 to 0.4 ml. of 1% phenolphthalein per 10 ml., this solution was adjusted to a pale pink with NaOH, and it was freshly prepared as required.

For ammonium salt in absence of sulfamate, the sample, in 50 ml. volume, was adjusted with HCl and NaOH to the methyl red end-point, and treated with 10 ml. of the formaldehyde solution per 8 milliequivalents of ammonia. After first turning yellow, the mixture became red in a second or so. It was titrated rapidly with standard NaOH to a distinct pink, whereupon the flask was stoppered and heated at 50° for 5+ minutes, the solution turning yellow again. It was then finally titrated hot (50°) to the sharpest color change of the phenolphthalein, a point approximately 5 drops of 0.2 *N* NaOH beyond the first appearance of pink. This end-point, permanent in the stoppered flask for as long as a week, could be reached more rapidly by comparison, therefore, with a titrated sample of pure $(NH_2)_2SO_4$ as reference color for each batch of titrations. With less formaldehyde the end-point faded, while more caused no error. Tests on 2, 4, 6, 8 milliequivalents revealed no internal blank. Back titration with HCl gave no error if performed immediately, high results being otherwise obtained.

For ammonium salt in presence of sulfamate, this procedure gives high results, increasing with the amount of formaldehyde used, apparently independent of the amount of sulfamate present, and increasing with the room temperature. The following fixed procedure was therefore established and followed. Formaldehyde solution (15 ml.) was added to the sample, adjusted to methyl red, in a volume of 60 ml. at 35°. The solution was then titrated as rapidly as possible, the end-point being fixed within 60–70 seconds after addition of the formaldehyde.

For total nitrogen, or ammonium + sulfamate, the sample was first hydrolyzed in acid solution. Complete hydrolysis was obtained by treatment of the sample (~8 milliequivalents) in 15–20 ml. volume, with 1–2 ml. of concd. H_2SO_4, heating for 1 hour on a hot-plate, and finally to fumes of SO_3 for several minutes. The diluted residue, cooled in ice, was almost neutralized (methyl red) with 30% NaOH, and then neutralized with 1 *N* NaOH, with care not to lose ammonia by making it alkaline. It was then just acidified with HCl and boiled to expel CO_2. After cooling and readjustment with NaOH, it was treated as first described for ammonium salt in absence of sulfamate.

Tests showed these procedures to be accurate within 0.1%.

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[8] The supercooling, and perhaps also the splitting of the crystals, observed both for this salt and for the monohydrate of the sodium salt, suggests a crystal structure involving hydrogen bonding. Although sulfamic acid itself does not seem to behave in this manner, the recent study of its crystal structure by F. A. Kanda and A. J. King, THIS JOURNAL, **73**, 2315 (1951), shows considerable hydrogen bonding.

[9] This agrees with G. J. Doyle and N. Davidson, *ibid.*, **71**, 3491 (1949); see also S. H. Maron and A. R. Berens, *ibid.*, **72**, 3571 (1950),

[10] I. M. Kolthoff, *Pharm. Weekblad*, **58**, 1463 (1921); see also I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1947, p. 158.

[11] K. Marcali and W. Rieman, III, *Anal. Chem.*, **18**, 709 (1946).

System $NaSO_3NH_2$–NaCl–H_2O at 25°.—The solution was analyzed for chloride and for total solid, with results as listed in Table I. The only solid phases are apparently pure NaCl and pure $NaSO_3NH_2 \cdot H_2O$. The tie-lines deviate, when extrapolated, by 0.3, 0.9 and 1.3% X at 100% Y, for the three complexes with Y as solid phase, and by 0.1 and 0.2% Y at 86.86%X, theoretical for $X \cdot H_2O$, where this is the solid phase. One complex had the anhydrous sulfamate as metastable solid phase, persisting through two successive samplings (total of 6 days of stirring) before it changed. Because of the difficulties involved in preparing and handling saturated solutions of the monohydrate $NaSO_3NH_2 \cdot H_2O$,[4] complexes with this compound as a solid phase were made up to have very little excess of solid. An excess of the hydrate tended to immobilize the whole mixture, and when the complex was heated (~30°) to make it flow, it persisted in supersaturation when cooled again to 25°, often requiring reseeding. A mobile mixture with excess of solid could be obtained only with repeated very slow warming and cooling through the desired temperature of 25°, and with vigorous shaking throughout, the process often requiring a whole day's attention for one complex. When a satisfactory mixture was thus prepared, several weeks of stirring at 25° gave crystals which were quite uniform, small and needle-like, settling well. After several months of stirring of the pure saturated solution, the solid became more translucent, with a density apparently close to that of the saturated solution. The complex in line 2 of the table was prepared by addition of NaCl to the clear saturated solution of the monohydrate, so that very little solid was present. Nevertheless it became immobile, and had to be broken up several times with a glass rod.

TABLE I

SYSTEM $NaSO_3NH_2$(X)–NaCl(Y)–H_2O AT 25°

m, metastable; r, wet residue

Complex X, %	Complex Y, %	Solution X, %	Solution Y, %	Density	Solid phase
...	0.00	55.25	0.00	1.427	$X \cdot H_2O$
		52.14	2.75		$X \cdot H_2O$
52.02	4.11	49.99	4.34	1.459	$X \cdot H_2O$
(71.02	1.92)r				
48.75	7.29	46.24	7.79	1.452	$X \cdot H_2O$
(69.43	3.33)r				
48.00	9.63	47.69	9.68	1.495	X(m)
52.5	10.0	43.03	11.21	1.459	$X \cdot H_2O$ + Y
50.5	13.5	43.02	11.22	1.458	$X \cdot H_2O$ + Y
31.31	26.85	37.26	13.09	1.412	Y
20.69	31.57	25.21	17.27	1.336	Y
9.79	36.14	12.24	21.97	1.260	Y
0.00	...	0.00	26.47	1.196	Y

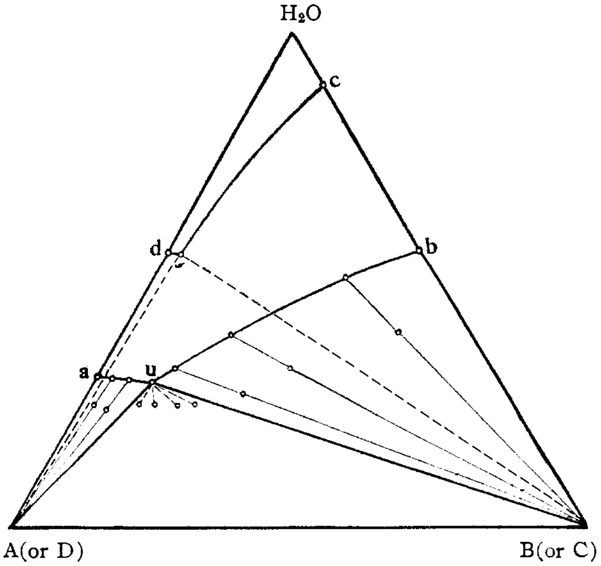

Fig. 1.—Systems $NH_4SO_3NH_2$(A)–$(NH_4)_2SO_4$(B)–H_2O and KSO_3NH_2(D)–K_2SO_4(C)–H_2O (solubility curve alone, **dwc**) at 25°.

Systems $NH_4SO_3NH_2$–NH_4Cl–H_2O, KSO_3NH_2–KCl–H_2O and KSO_3NH_2–KI–H_2O, at 25°.—Each of these systems is simple, with the separate salts as the only solid phases. The complete data, on compositions of complexes and saturated solutions, with densities, are not presented, but are available on microfilm.[12] The isothermally invariant solutions saturated with two solids have, respectively, the following compositions for each of the three systems: 60.06% $NH_4SO_3NH_2$, 9.26% NH_4Cl, density 1.372; 29.11% KSO_3NH_2, 17.51% KCl, density 1.353; and 15.01% KSO_3NH_2, 50.67% KI, density 1.777. For the ammonium salt system the saturated solution was analyzed for chloride and for total ammonium (not including the amine sulfonate) by the Kjeldahl method. For the others the analysis consisted of titration of halide and evaporation for total solid. The tie-lines in all these cases indicate that the only solid phases are the pure anhydrous salts, with small errors of extrapolation of the tie-lines.

For the following ternary systems and their composite quaternary system, the components and the solid phases are represented by the following symbols: A, $NH_4SO_3NH_2$; B, $(NH_4)_2SO_4$; C, K_2SO_4; D, KSO_3NH_2; BC, solid solution of B and C; AD_1, solid solution of D in A with x as limit; AD_2, solid solution of A in D with y as limit.

System $NH_4SO_3NH_2$–$(NH_4)_2SO_4$–H_2O at 25°.—The formaldehyde method was used for determination of *a*, the number of equivalents of ammonium per g. solution, and of *b*, the total number of equivalents of nitrogen (both ammonium and sulfamate) per g. solution. The number of equivalents of $NH_4SO_3NH_2$ (A) per g. is then $b - a$, and the number of equivalents of $(NH_4)_2SO_4$ (B) per g. is $2a - b$. In most cases the weight percentage of total solid, or % (A + B), was also determined directly by evaporation, the results showing in general very close agreement with the total obtained by the two titrations. The compositions of the invariant points of the isotherm are listed in Table II in terms of weight percentage, and the full results are plotted in the same units in Fig. 1. The complete numerical data for the isotherm are available on microfilm.[12] Despite the indirectness of the analysis, causing some multiplication of the experimental errors in the calculation, the extrapolation of the tie-lines through total complex and saturated solution shows clearly that the solid phases are the pure salts, the average absolute deviation from the corners of the diagram, by extrapolation, being 0.5%, with maximum of 1.0%.

TABLE II

SYSTEM $NH_4SO_3NH_2$(A)–$(NH_4)_2SO_4$(B)–H_2O AT 25°

Point	A, %	B, %	Density	Solids
a	68.90	0.00	1.391	A
u	60.00	10.14	1.401	A + B
b	0.00	43.43	1.244	B

System KSO_3NH_2–K_2SO_4–H_2O at 25°.—The solutions were analyzed for total solid and for sulfamate by hydrolysis and titration of the ammonium salt formed. Some of the titrations were made by the Kjeldahl method and some by Kolthoff's formaldehyde method. The solubility curve is shown in Fig. 1 and the numerical values for the points of the isotherm are listed in Table III; the complete data are avail-

TABLE III

SYSTEM KSO_3NH_2(D)–K_2SO_4(C)–H_2O AT 25°

Point	D, %	C, %	Density	Solids
d	43.72	0.00	1.327	D
w	42.03	2.17	1.335	D + C
c	0.00	10.75	1.084	C

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(12) For complete data for these isotherms order Document 3414 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

able on microfilm.[12] The tie-lines show that the solid phases are the pure salts, the average absolute error of their extrapolation to the corners being 0.4%, with 1.0% as maximum.

System $NH_4SO_3NH_2$–KSO_3NH_2–H_2O.—The complexes for this system, forming extensive solid solution, were rotated for a minimum of 3 days and for as long as 7 months in the experiments at 25°, and all complexes (except three points at 45°) were reanalyzed after further stirring to verify equilibrium. At 9° the samples were rotated for 3–8 weeks, and at 45° for 2–7 days. The formaldehyde method was used throughout to determine the number of equivalents of ammonium (*a*) and of total nitrogen (*b*) per g. solution. Then *a* is the number of equivalents of $NH_4SO_3NH_2$ and $b - 2a$ of KSO_3NH_2 per g. solution. Some of the results are listed in Table IV, in weight percentage. The complete data for the 9 and 45° isotherms are available on microfilm.[12] Total solid, determined directly for several points of the 25° and all those of the 0° isotherm, agreed well with the sum calculated from the titrations, the average deviation being 0.07% with 0.19% as maximum.

TABLE IV

SYSTEM $NH_4SO_3NH_2(A)$–$KSO_3NH_2(D)$–H_2O AT 25°

Complex A, %	Complex D, %	Solution A, %	Solution D, %	Solution Density	D in solid,[a] %	Solid phase
			Temperature, 9°			
...	0.00	62.26	0.00	1.347	0	A
52.93	10.07	(52.63	9.82	1.375)m[b]	27.9	AD_1
Average (v)		45.60	15.64	1.380		x + y
0.00	...	0.00	31.44	1.222	100	D
			Temperature, 25°			
Point **a**		68.90	0.00	1.391	0	A
71.73	4.21	65.76	3.55	1.403	6.6	AD_1
64.62	7.24	62.69	6.77	1.414	12.8	AD_1
63.05	11.73	(59.82	9.95	1.422)m[b]	20.7	AD_1
56.36	15.72	55.37	14.08	1.435	33.1	AD_1
54.29	19.76	53.07	16.37	1.439	38.8	AD_1
50.91	21.01	50.59	18.52	1.443	45.9	AD_1
48.97	26.00	49.00	19.79	1.447	51.2	AD_1
48.10	25.02	48.20	20.46	1.447	52.5	x + y
46.98	26.01	48.32	20.18	1.447	61.1	x + y
45.72	26.80	48.13	20.75	1.447	72.5	x + y
44.95	26.99	48.29	20.42	1.445	84.1	x + y
43.87	28.04	48.09	20.49	1.445	91.7	x + y
Average (v)		48.20	20.46	1.446		x + y
40.96	31.97	47.00	20.76	1.442	90.9	AD_2
42.43	28.84	46.69	21.25	1.439	94.6	AD_2
39.99	30.03	44.24	22.09	1.432	94.5	AD_2
29.81	31.37	31.61	27.07	1.388	99.1	AD_2
23.03	39.28	26.63	29.22	1.375	97.9	AD_2
18.72	39.96	21.15	31.85	1.360	99.0	AD_2
12.01	47.20	14.88	35.25	1.347	100.9	AD_2
8.99	47.06	10.59	37.52	1.340	99.8	AD_2
Point d		0.00	43.72	1.338	100	D
			Temperature, 45°			
...	0.00	76.54	0.00		0	A
		(57	20)m[b]		40	AD_1
Average (v)		50.56	26.24			x + y
0.00	...	0.00	56.40		100	D

[a] By tie-line extrapolation. [b] m, region of minimum water content.

The results for 25° are plotted in Fig. 2, the two other isotherms being very similar to this. The salts form two series of solid solutions, with a high limiting concentration of B in A, point **x**, and a low solubility of A in B, point **y**. When the mole fraction of A in the dissolved salts is plotted against its mole fraction in the solid solution, the relations may be analyzed further on the basis of the Roozeboom distribution diagram of Fig. 3, in which the miscibility gap is seen to decrease with rising temperature. The horizontal section of this curve represents in height the composition of the isothermally invariant liquid solution (point v of Fig. 2), and its intersections with the adjacent curves give the compositions of the two saturating limiting solid solutions **x** and **y**. The related compositions, in weight percentage, are the following:

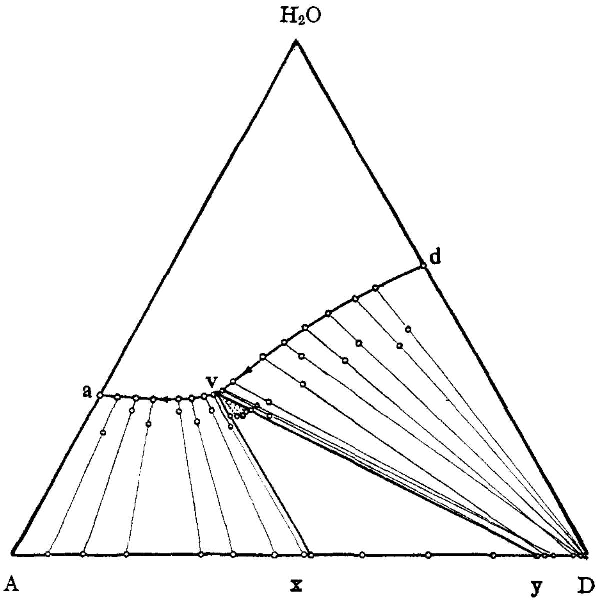

Fig. 2.—System $NH_4SO_4NH_2(A)$–$KSO_3NH_2(D)$ at 25°.

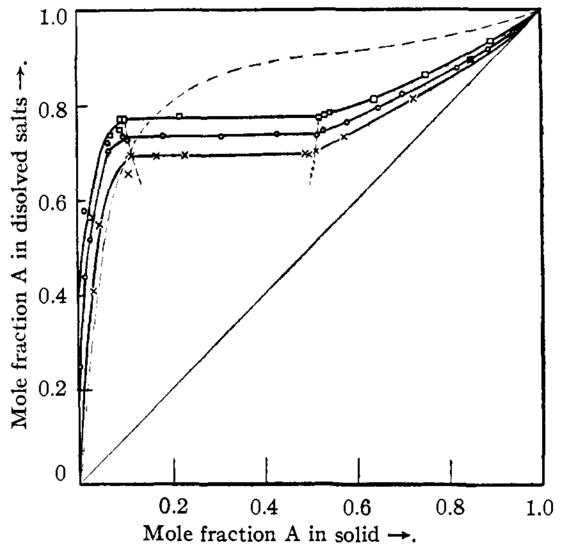

Fig. 3.—Distribution in system $NH_4SO_3NH_2(A)$–$KSO_3NH_2(D)$–H_2O; □, at 9°; ○, at 25°; ×, at 45°; dashed curve represents system $(NH_4)_2SO_4$–K_2SO_4–H_2O at 25°.

Temp., °C.	Liquid y A, %	Liquid y D, %	Solid x D, %	Solid y A, %
9	45.60	15.64	52.0	8.3
25	48.20	20.46	52.5	8.8
45	50.56	26.24	53.2	9.9

With the mole fraction of A in the dissolved salts always greater than its mole fraction in the solid phase, the distribution relations are those of Type

V of Roozeboom's classification.[13] Other examples of this type (not frequent) are the systems $CuCl_2 \cdot 2NH_4Cl$–$CuCl_2 \cdot 2KCl$–H_2O at 17°.[14] $NaClO_3$–$AgClO_3$–H_2O at 25°,[15] and $NaBrO_3$–$AgBrO_3$–H_2O (5–50°),[16] the last system involving furthermore the definite compound $NaBrO_3 \cdot AgBrO_3$ as the limiting solid solution **y**. The general shape of the solubility curve, moreover, is quite similar to that of the system $NaClO_3$–$NaBrO_3$–H_2O at 25 and 50°,[17] in which, however, the solid solution is continuous.

With all the tie-lines passing, on extension, to the left of the H_2O corner, the course of isothermal evaporation of the saturated solution is always in the direction **d** → **v** → **a**, so that **a** and not **v** is the vapor pressure minimum of the solubility curve. At the same time the analytical water content, as weight percentage of water, passes through a slight minimum on the curve **v** → **a**. Still greater discrepancies between vapor pressure and water content minima, as also discrepancies between such maxima, have been discussed in connection with aqueous systems involving thallous sulfate and other sulfates.[18]

The phase reaction for isothermal evaporation of the incongruently saturated solution **v** is of the transition type: liquid **v** + solid solution **y** → solid solution **x** + $H_2O\nearrow$. The general relations in equilibrium evaporation are as indicated for the system $NaClO_3$–$AgClO_3$–H_2O.[15]

System $(NH_4)_2SO_4$–K_2SO_4–H_2O.—The 25° isotherm of this system is available from the work of Weston[19] and of Hill and Loucks.[20] The system is a familiar example of Roozeboom's Type I, continuous solid solution with the proportion of $(NH_4)_2SO_4$ always greater in the dissolved salts than in the solid solution. The triangular diagram is shown in Fig. 4, for orientation in connection with the subsequent quaternary system, and the distribution curve is added, as a light dotted line, on Fig. 3. The composition of saturated solution moves always in the direction **c** → **b** in isothermal evaporation, the solubility curve having neither a minimum of vapor pressure nor one of water content between points **c** and **b**. Two new points, found to fall on the curve of the literature data, were determined, verifying that one day would be sufficient for equilibrium, this information being required in the quaternary work. The compositions of the two points were: 39.52% B, 2.62% C in the liquid, 80.4% B in the anhydrous solid solution, and 38.18% B, 3.38% C in the liquid, with 67.7% B in the solid.

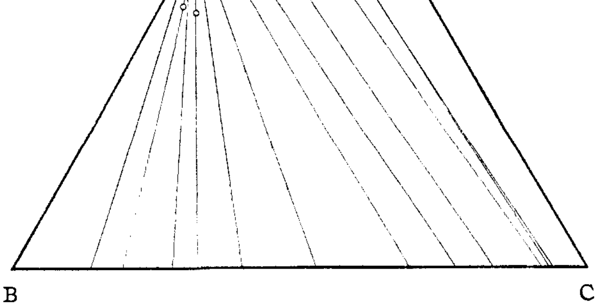

Fig. 4.—System $(NH_4)_2SO_4$(B)–K_2SO_4(C)–H_2O at 25°.

The Quaternary System $NH_4SO_3NH_2$–K_2SO_4–H_2O **at 25°**.—The three solid phases involved are the solid solution of the sulfamates rich in ammonium sulfamate, or AD_1, with its limit **x**, the sulfamate solid solution rich in potassium sulfamate, AD_2, with its limit **y**, and the continuous solid solution of the sulfates, or BC. The only isothermally invariant ternary solutions, saturated with two solids, are the points **u**, **w**, **v** of Figs. 1 and 2, the first two for the pure salts A + B and D + C, respectively, the third for the limiting solid solutions **x** + **y**. Each of these points is the origin of a quaternary curve for solution of twofold saturation: the curve starting at point **u** for saturation with the variable solid solutions AD_1 + BC, and that from point **w** for AD_2 + BC, while that from **v** represents saturation with the fixed solids **x** + **y**, which do not change in composition as sulfate is added to the liquid solution at constant temperature. These three quaternary curves divide the quaternary liquidus into three saturation surfaces, one for each of the three solids AD_1, AD_2 and BC. The curves meet at an isothermally invariant quaternary solution Q, which is saturated with three solids, namely **x** and **y** (sulfamate solid solutions) and a particular sulfate solid solution, BC, the composition of which will be represented as point **z**.

The salt proportions in the saturated solutions are shown in the Jänecke diagram, Fig. 5, in which the number of equivalents of potassium per equivalent of salt, or N_+ is plotted from left to right, and the number of equivalents of sulfamate per equivalent of salt, or N_-, is plotted upward from the base. The continuous solid solution of the sulfates is represented by the base of the square, and the two series of solid solutions of the sulfamates are at the top, AD_1 from A to **x** and AD_2 from **y** to D.

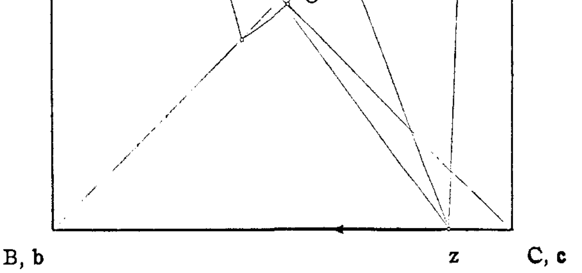

Fig. 5.—System $NH_4SO_3NH_2$–K_2SO_4–H_2O at 25°, Jänecke diagram; set of light curves around Q′ represents the orthogonal diagram.

The compositions may also be expressed, by recalculation, in terms of the percentage, in equivalents, of water and each of three of the actual salts as the four components, permitting if necessary a negative percentage for one of the salts. The isotherm then takes the form of a regular pyramid with H_2O at its apex and with the square of Fig. 5

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(13) H. W. B. Roozeboom, *Z. physik. Chem.*, **8**, 521 (1891).

(14) A. Fock, *ibid.*, **12**, 658 (1893).

(15) J. E. Ricci and J. Offenbach, THIS JOURNAL, **73**, 1597 (1951).

(16) J. E. Ricci and J. J. Aleshnick, *ibid.*, **66**, 980 (1940).

(17) T. Swenson and J. E. Ricci, *ibid.*, **61**, 1974 (1939).

(18) J. E. Ricci and J. Fischer, *ibid.*, **74**, 1443 (1952).

(19) A. Weston, *J. Chem. Soc.*, **121**, 1223 (1922).

(20) A. E. Hill and C. M. Loucks, THIS JOURNAL, **59**, 2094 (1937).

as its base.[21] If the quaternary curves of twofold saturation are projected radially or perspectively from the H_2O apex upon this base, the result is the "Jänecke diagram" already presented as Fig. 5, while if they are projected orthogonally on the base, we have the relations shown in light curves at the center of the same figure; Q now appears as Q′. This "orthogonal diagram" may be plotted directly by measuring the "equivalent percentage" of the salt D in excess of that of its reciprocal salt B on the half diagonal OD, and then the equivalent percentage of the salt A parallel to OA toward A. The relation between the two diagrams is such that the distance Q′Q, for example, divided by OQ is the equivalent fraction of water in the quaternary composition.[22]

The composition of the saturated solution was calculated from three analytical measurements, all per g. solution: *a*, the number of equivalents of ammonium, *b*, the number of equivalents of total nitrogen (both determined by the formaldehyde method), and *c*, the number of grams of total solid. Then $d = b - a$ = number of equivalents of sulfamate, e = number of equivalents of potassium and f = number of equivalent of sulfate. With $N_+ = e/(e + a)$, $N_- = d(e + a)$, $a + e = d + f$, and $a(\mathrm{NH_4}) + e(\mathrm{K}) + d(\mathrm{SO_3NH_2}) + f(\mathrm{SO_4}/2) = c$, we have

$$\begin{aligned} N_+ &= [c - b(\mathrm{SO_3NH_2} - \mathrm{SO_4}/2) - a(\mathrm{SO_4} + \\ &\qquad \mathrm{NH_4} - \mathrm{SO_3NH_2})]Z \\ &= [c - b(48.04) - a(18.00)]/Z, \\ N_- &= (b - a)(\mathrm{K_2SO_4}/2)/Z = (b - a)(87.13)/Z, \end{aligned}$$

with

$$\begin{aligned} Z &= c - b(\mathrm{SO_3NH_2} - \mathrm{SO_4}/2) + \\ &\qquad a[\mathrm{KSO_3NH_2} - (\mathrm{NH_4})_2\mathrm{SO_4}/2] \\ &= c - b(48.04) + a(69.12). \end{aligned}$$

The data and the calculated results for N_+ and N_- are listed in Table V.

A few of the points on the curves **u**Q and **w**Q were obtained with complexes prepared individually directly from the components and brought to equilibrium before analysis. Most were obtained by addition of a mixture of the necessary salts to the ternary points (**u**, **w**). The ternary invariant was first brought to equilibrium, and checked by determination of density and total solid, sometimes by complete analysis. In some cases a further addition of salts was made either to the residual liquid or to the mixture of liquid and solids, to obtain further points on the same curve, toward Q. The point on the short curve **v**Q was obtained from two complexes differing only in the weight of KSO_3NH_2-(D) used, and hence both falling on one plane passing through the edge AD. The two liquids should therefore have the same composition if they fall on the curve **v**Q. This was the case, as seen in Table V. Addition of the sulfates to each mixture then gave the first two determinations of the invariant Q listed. The third determination of Q was obtained by addition of KSO_3NH_2 to the nearest point on the curve **u**Q.

TABLE V

SYSTEM $NH_4SO_3NH_2$–K_2SO_4–H_2O AT 25°

Compositions of saturated solutions

Equivalents ($\times 10^3$) per gram		Wt. %	Equivalents per equivalent of salt		
NH_4^+ (*a*)	Σ (*N*) (*b*)	H_2O, 100 *c*	K^+ (N_+)	$SO_3NH_2^-$ (N_-)	Density
	Curve **w** → Q.		Solids AD_2 + BC		
0	3.108	55.80	1.00	0.925	1.335
0.191	3.365	55.04	0.945	.919	1.338
.297	3.527	54.41	.915	.918	1.340
.405	3.642	54.15	.887	.906	1.343
.487	3.772	53.81	.865	.910	1.344
.710	4.079	52.86	.809	.905	1.346
.915	4.365	52.01	.761	.901	1.350
1.156	4.689	50.82	.709	.889	1.351
1.430	5.078	49.76	.651	.890	1.358
1.579	5.296	48.90	.624	.885	1.360
1.855	5.673	47.60	.574	.876	1.368
2.091	6.003	46.26	.537	.866	1.371
2.584	6.699	43.82	.462	.857	1.380
2.872	7.132	42.00	.426	.851	1.392
2.899	7.171	41.90	.422	.852	(1.41)
3.362	7.770	40.13	.359	.841	(1.40)
4.402	9.377	33.53	.260	.836	1.432
	Curve **v** → Q.		Solids **x**(AD_1) + **y**(AD_2)		
4.224	9.961	31.34	0.264	1.00	1.446
4.452	9.938	31.19	.252	0.922	1.448
4.452	9.938	31.10	.253	.920	1.447
	Point Q.		Solids **x**(AD_1) + **y**(AD_2) + **z**(BC)		
4.696	9.936	30.86	0.241	0.847	1.451
4.686	9.959	30.85	.240	.855	1.451
4.677	9.923	30.92	.242	.851	1.452
	Average	30.88	.241	.851	1.451
	Curve Q → **u**.		Solids AD_1 + BC		
4.811	10.046	30.46	0.231	0.837	1.450
5.100	10.341	30.36	.196	.826	1.448
5.206	10.442	30.18	.186	.818	1.446
5.406	10.632	29.75	.167	.806	1.443
5.809	11.030	29.55	.121	.790	1.434
6.306	11.557	29.20	.062	.781	1.419
6.541	11.800	29.42	.035	.776	1.413
6.794	12.051	29.85	0	.772	1.401

The position of point **z**, the composition of the solid solution of the sulfates constituting, with solids **x** and **v**, the third solid saturating the invariant liquid Q, was estimated by analogy with the disposition of the tie-lines of the system $(NH_4)_2SO_4$–K_2SO_4–H_2O in Fig. 4. It is thus located, roughly, at $N^+ \cong 0.86$.

The water content along the curves of twofold saturation is plotted in Fig. 6; the slight minimum of water content noted in the ternary curve **v** → **a** of Fig. 2 apparently persists in the quaternary curve Q → **u**. Nevertheless again this minimum does not correspond to a minimum of vapor pressure of the saturated solution. The direction of isothermal evaporation is always from right to left in the diagram of Fig, 5, as shown by the arrows, which therefore also indicate the direction of falling vapor pressure of the isothermally invariant solutions.

Solutions with original salt proportions (which we shall call P) in the region **y**DC**z** would dry up, in isothermal evaporation with complete equilibrium, to leave two solid solutions, one of the sulfamates

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(21) F. A. H. Schreinemakers, *Z. physik. Chem.*, **69**, 557 (1909).

(22) W. C. Blasdale, "Equilibria in Saturated Salt Solutions," Chemical Catalog Co., (Reinhold Publ. Corp.), New York, N. Y., 1927, pp. 123, 141.

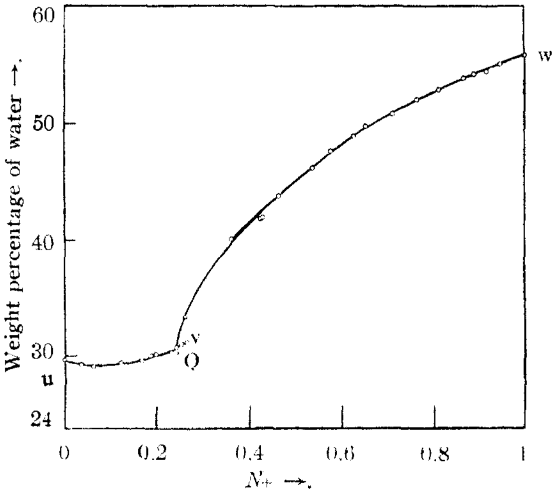

Fig. 6.—Water content for quaternary curves.

on the line **y**D and one of the sulfates on the line **z**C, and the liquid is consumed as it travels on the curve w → Q before it reaches Q. The 3-phase triangle (condensed phases) for this curve therefore starts as the line wDC and ends as Qyz. Similarly, liquids with P in A**xz**B dry up on the curve Q → u to leave AD_1 on the line A**x** and BC on line B**z**, the 3-phase triangle starting as Q**xz** and ending as **u**AB. Those with P in the triangle **xyz** dry up at point Q to leave the three solids **x** + y + **z**. The phase reaction on the curve v → Q is that of the ternary point v, namely, Liquid + y → x + $H_2O\nearrow$, except that the liquid on the curve is quaternary, containing sulfate. The 3-phase triangle starts as **vxy** and ends as Q**xy**. At point Q, which lies outside the triangle of its three saturating solids **xyz** (no matter where the point **z** is estimated to be), the invariant phase reaction is therefore still of the transition type, Liquid (Q) + y → **x** + z + $H_2O\nearrow$. Liquids reaching Q with P in **xyz** lose the liquid phase in the invariant reaction to leave the three solids, while those reaching Q with P in the triangle Q**xz** lose the solid y and proceed, while saturated with AD_1 and BC, to dry up on the curve Q → u.

The transition curve v → Q is crossed by liquids reaching it with original salt proportions P in the special region **vx**Q. These liquids approach the curve, from the right, with solid solution AD_2 as primary crystallization, and, with complete equilibrium, this solid attains the limiting composition y as the liquid reaches the curve v → Q, when solid solution **x** appears as a second solid phase. Before the liquid reaches the invariant point Q, however, all of the solid y is consumed in the reaction Liquid (on vQ) + y → x + $H_2O\nearrow$, and the remaining liquid, now saturated only with solid solution AD_1, leaves the curve to enter upon the saturation surface of AD_1, or AvQu. The liquid finally dries up on the curve Q → **u**, to leave AD_1 + BC on the line Bz.

If, as is practically inevitable, complete solid phase equilibrium is not maintained in isothermal evaporation, then only solutions reaching curve Q → u directly will leave only two solids when they finally dry up (practically at point u), and each solid, moreover, will not be uniform in composition although possibly "homogeneous" in structure. Solutions reaching directly either v → Q or w → Q will stop only momentarily at point Q, and will dry up (also at point **u**) to leave three solids, again each not uniform in composition.

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[Contribution from the Department of Chemistry, University of Manitoba]

The System Aluminum–Indium–Tin

By A. N. Campbell, L. B. Buchanan, J. M. Kuzmak and R. H. Tuxworth

Of the three component binary systems, only the system aluminum-indium is at all in doubt. For this system we have determined the complete equilibrium diagram. An extensive region of partial miscibility, in the liquid state, occurs and for this we find the critical solution temperature and composition to be 875° and 61% indium by weight, respectively. For the ternary system Al–In–Sn, the isotherms have been established for 750, 700, 650 and 450°, using a constant temperature furnace and sampling and analyzing congruent solutions. In this way the critical compositions have been evaluated for the above temperatures. X-Ray diffraction measurements have shown that aluminum does not enter into In–Sn solid solutions to an extent greater than 5%, and probably not at all, since the lines of the diffraction picture were not shifted to any observable extent when aluminum was added to the In–Sn system. The ternary eutectic temperature is 117.1° and the composition 48.83% by weight in tin, 51.03% indium and 0.14% aluminum.

The equilibrium diagram of this ternary system has not been investigated previously; those of the component binary systems have, Al–Sn and In–Sn exhaustively, Al–In not so completely. The literature of the latter system requires some discussion, since the results are incomplete and not in agreement.

Interest in the Al–In system centers around a wide miscibility gap, which exists in the liquid state. According to Raub and Engel[1] the limits of the miscibility gap are 17.3% In up to nearly pure indium: the temperature of the invariant system: solid aluminum–liquid 1–liquid 2, is given in 634°. As far as Raub and Engel could determine, aluminum has no effect on the freezing point of indium and hence the binary eutectic composition must lie very close to that of pure indium, and the eutectic temperature close to the freezing point of pure indium, which is variously given as 155.5–156.4°. These authors also find, by microscopic and X-ray investigation, that the solid solubility of indium in aluminum is very small. According to Valentiner and Puzicka[2] the miscibility gap extends from 13 to 98 weight per cent. indium, at the invariant temperature, which they give as 634°; the eutectic temperature is very close to 156°. Valentiner also

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(1) E. Raub and M. Engel, *Metallforsch.*, **1**, 148 (1946).

(2) S. Valentiner and I. Puzicka, *ibid.*, **2**, 127 (1947).