sible, in part, by a grant from the Defense Research Laboratory, The University of Texas, under the sponsorship of the Bureau of Ordnance, Navy Department, Contract NOrd-9195. The authors express their gratitude.

AUSTIN, TEXAS RECEIVED OCTOBER 9, 1951

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF PORTLAND]

Dissociation Constants of Some Substituted Propylpyridonium Picrates in Ethanol; Correlation with Structural Effects[1]

BY EUGENE L. COLICHMAN, WILLIAM R. VANDERZANDEN[2] AND SHIH KUNG LIU

Previously unreported halogen and hydroxyl substituted propylpyridonium picrates were prepared and used in studying the effect of structure on ion-pair dissociation in ethanol. The Fuoss and Kraus conductance method was employed in evaluating the corresponding dissociation constants. Ethanol proved to be a satisfactory solvent for the study of structural variations. The dissociation constants were correlated with structure.

It has been clearly demonstrated by Kraus[3] and his many co-workers that if structural differences in ions are to be studied, solvents of sufficiently low dielectric constants must be employed. Under these conditions, ion-pair dissociation constant measurements yield information about ionic structure. The most commonly used solvent for these studies has been ethylene chloride[3] ($D = 10.2$ at 25°). Benzene[3] ($D = 2.2$ at 25°) has been used occasionally; however, very low salt solubilities and low conductances enhance random errors. Other non-aqueous solvents, such as for example, liquid ammonia[4,5] ($D = 22.4$ at about -33 to $-40°$) and nitrobenzene[6,7] ($D = 34.5$ at 25°), have been widely used. Previously, very few dissociation constant measurements have been reported in ethanol. Goldschmidt and Dahll[8] determined the dissociation constants of the halogen acids. Hartley and associates[9,10] studied the conductance of uni-univalent inorganic salts in ethyl alcohol. A few conductance measurements on common inorganic salts have been made in ethanol–water mixtures.[11–13] Specific influences and anomalies are seen in these results. Presumably, ethanol has been avoided in previous work because solvation might complicate the conductance studies, and also, the higher dielectric constant ($D = 24.3$ at 25°) might not allow full realization of the influence of structural effects on the dissociation process. Recent results by Bezman and Verhoek[14] using modern techniques and theories show the importance of knowing precisely the water content in conductance work in alcohol–water mixtures. Relatively small changes in water concentration can greatly influence the dissociation process of electrolytes.

As shown previously,[15] isomeric salts are desirable when making a systematic study of the effect of structure on ion-pair dissociation processes. Kraus' results[16] on phenylpyridonium picrate in ethylene chloride showed that unsymmetrically coördinated "onium" salts show unique conductance properties in non-aqueous solutions. Thus, it was anticipated that a series of isomeric pyridonium picrates would show considerable variation in their dissociation constants in ethanol. β- and γ-substituted propylpyridonium picrates (previously unreported) were synthesized and used in the present conductance study.

Experimental

Preparation of Salts.—The *n*-propyl-, *i*-propyl- and γ-hydroxypropylpyridonium halides were prepared by accepted procedure[17,18] using Eastman Kodak Co. White Label chemicals. The γ-chloro-, γ-bromo- and γ-iodo-substituted salts were prepared by heating equimolar quantities of the corresponding 1,3-dihalopropanes (Eastman Kodak Co. White Label) and C.P. pyridine (J. T. Baker Co.) in sealed tubes at 45–50° for one to two days. The γ-bromo- and γ-iodopyridonium halides were obtained in substantially 100% yields. About a 70% yield of the γ-chloro-salt was obtained by freeing the reaction mixture of the unreacted pyridine and trimethylene chloride by several washes with C.P. ethyl acetate.

Equimolar quantities of propylene bromohydrin (Eastman Kodak Co. White Label, purified by vacuum distillation) and C.P. pyridine were heated in a sealed tube as described above to give approximately a 100% yield of β-hydroxypropylpyridonium bromide.

The β-chloropropylpyridonium bromide was prepared by mixing 0.0057 mole of C.P. thionyl chloride (Eastman Kodak Co. White Label) with 0.01 mole of β-hydroxypropylpyridonium bromide and heating at 40° for a period of five hours. The yield of the β-chloro-salt by this procedure was 97.5%. Before deciding upon these conditions, several others were tried and found to be less satisfactory. β-Hydroxypropylpyridonium bromide was maintained at 0.01 mole and various quantities of thionyl chloride were tried.

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(1) Supported in part by a grant-in-aid from the Research Corporation.

(2) Part of the work described herein was included in a thesis submitted by W. R. Vanderzanden to the University of Portland in partial fulfillment of the requirements for the Degree of Master of Science.

(3) For summaries of early results see C. A. Kraus, *Trans. Electrochem. Soc.*, **66**, 179 (1934); *J. Franklin Inst.*, **225**, 687 (1938); *Science*, **90**, 281 (1939). Many later investigations, too numerous to mention, have been published in the last four or five years in THIS JOURNAL.

(4) R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 1019 (1933).

(5) C. A. Kraus, *et al.*, *ibid.*, **55**, 2776, 3542 (1933); **71**, 1565 (1949).

(6) C. A. Kraus, *et al.*, *ibid.*, **69**, 1731, 2472 (1947); **70**, 1707 (1948); **71**, 1455, 2695, 3288 (1949).

(7) R. E. Van Dyke and H. E. Crawford, *ibid.*, **73**, 2018, 2022 (1951).

(8) H. Goldschmidt and P. Dahll, *Z. physik. Chem.*, **114A**, 1 (1925).

(9) M. Barak and H. Hartley, *ibid.*, **165A**, 272 (1933).

(10) E. D. Copley, D. M. Murray-Rust and H. Hartley, *J. Chem. Soc.*, 2492 (1930).

(11) F. Nies, *Z. physik. Chem.*, **138A**, 447 (1928).

(12) L. C. Connell, R. T. Hamilton and J. A. Butler, *Proc. Roy. Soc.* (*London*), **147A**, 418 (1934).

(13) R. L. Bateman, Univ. Microfilms (Ann Arbor, Mich.) Pub. No. 668, p. 73; *Microfilm Abstracts*, **6**, No. 1, 23 (1945).

(14) I. I. Bezman and F. H. Verhoek, THIS JOURNAL, **67**, 1330 (1945).

(15) J. B. Ramsey and E. L. Colichman, *ibid.*, **69**, 3041 (1947).

(16) L. M. Tucker and C. A. Kraus, *ibid.*, **69**, 454 (1947).

(17) F. Krollpfeiffer and E. Braun, *Ber.*, **69B**, 2523 (1936).

(18) O. A. Barnes and R. Adams, THIS JOURNAL, **49**, 1307 (1927).

The thionyl chloride was always added to the pyridonium salt and heated on a water-bath at 40° for varying time intervals. These results can be summarized as follows: 0.005 mole, five hours heating, 88.2% yield; 0.006 mole, five or nine hours heating, 95.0% yield; 0.0057 mole, five hours heating, 97.5% yield; and 0.020 mole, 15 hours heating, 70.0% yield. In the last case a 6 *N* solution of hydrochloric acid in 95% ethanol was used as the source of chlorine rather than thionyl chloride. The results did not justify its further use. Larger quantities of thionyl chloride, approaching a one to one molar ratio of reactants, yielded a product, or mixture of products, containing twice as much substituted chlorine in the molecule as the desired product. The position either in the side chain or on the ring of the extra halogen was not determined since the material was rejected for conductance use.

The β-bromopropylpyridonium bromide was prepared by mixing equimolar amounts of β-hydroxypropylpyridonium bromide and hydrobromic acid and refluxing the mixture at 90° for nine hours. The yield was substantially 100%. The hydrobromic acid was added as an aqueous 48% solution (J. T. Baker Co. C.P. grade), with 44 ml. of absolute ethanol added for each 0.1 mole of hydrobromic acid. It was found that the nine hours reflux time and alcohol addition were necessary for complete reaction.

β-Iodopropylpyridonium bromide was prepared in approximately 100% yields by refluxing equimolar quantities of β-hydroxypropylpyridonium bromide and 58% hydriodic acid solution (Merck Co., Inc., Reagent Grade) for 3.5 hours on a water-bath at 95°. The desired salt was precipitated by cooling the solution in the refrigerator for several days.

In all cases the salts were purified by warming them slightly in a vacuum. This technique was used since the impurities were the excess reactants which are quite volatile. The salts are oily type solids which cannot be recrystallized in the usual fashion. No melting point data are available for these salts since they decompose on heating. The m.ps. of the two unsubstituted propyl salts were reported previously as picrates.[17] The remaining seven salts were characterized by argentometric halide titrations.[19] Determinations were made for both ionizable halogen and total halogen after sodium fusion (see Table I).

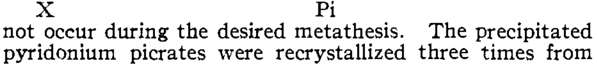
TABLE I

HALOGEN COMPOSITIONS OF PYRIDONIUM SALTS

Salt	Halogen, % Total Theor.	Total Found	Ionizable Theor.	Ionizable Found
n-Propyl bromide	39.6	39.5	39.6	39.5
i-Propyl bromide	39.6	39.4	39.6	39.4
β-OH bromide	36.6	36.8	36.6	36.8
β-Cl bromide	48.8	49.0	33.8	33.7
β-Br bromide	56.9	56.6	28.4	28.5
γ-OH bromide	36.6	36.4	36.6	36.4
γ-Cl chloride	36.9	36.7	18.5	18.6
γ-Br bromide	56.9	57.2	28.4	28.6
γ-I iodide	67.7	67.5	33.8	34.0

Theoretical and experimentally found halogen compositions are in excellent agreement thereby substantiating the structure and purity of the halide salts.

Each of the desired picrates was obtained by metathesizing the corresponding pyridonium halide with a slight excess of dilute alcohol-water solutions of sodium picrate. The picrates so obtained were shown to contain no ionic halides, showing thus that the following type side reaction,



$\mathrm{C{-}\underset{X}{C}{-}C{-}\overset{+}{N}C_5H_5 + \overset{-}{Pi} = C{-}\underset{Pi}{C}{-}C{-}\overset{+}{N}C_5H_5 + \overset{-}{X}}$, did

not occur during the desired metathesis. The precipitated pyridonium picrates were recrystallized three times from ethanol. The picrates after the second and third recrystallization gave the same melting points, thereby substantiating the purity of these salts. It is not generally practical to analyze the finished picrates due to explosion difficulties. All attempts to make β-iodopropylpyridonium picrate from the corresponding halide salt were unsuccessful. Even the use of silver picrate or picric acid followed by careful stepwise precise neutralization with ammonia removed the β-iodo group rather than causing the desired metathesis. This technique was found necessary and was successful with the β-bromo salt.

The melting points found for the pyridonium picrates prepared and used in the conductance study were: *n*-propyl-, 173°, reported[17] 171–172°; *i*-propyl-, 195°, reported[17] 195–196°; β-chloropropyl-, 227°; β-bromopropyl-, 164–165°; β-hydroxypropyl-, 224–225°; γ-chloropropyl-, 174–175°; γ-bromopropyl-, 170–171°; γ-iodopropyl-, 175–176°; and γ-hydroxypropyl-, 267–269° dec.

Conductance Bridge, Equipment and Procedure.—Conductance measurements were made at a frequency of 2500 cycles/sec. with a shielded conductance bridge built in this Laboratory according to specifications provided by Edelson and Fuoss and later published[20] by them. The bridge, amplifier and oscillator units were all mounted on one chassis. It was found necessary, however, to submount the amplifier section on rubber grommets to eliminate microphonics. The temperature of the oil thermostat was maintained constant at 25° within 0.01°. The other equipment and procedure were described previously.[15]

Solvent.—Ethanol "constant-boiling" (95.5% by wt.) from Commercial Solvents Corp. was distilled through a three-foot Vigreux column. Distilled solvent batches checked at random had same density, and also agreed with the original "constant-boiling" ethanol[21] as follows: 0.8008 ± 0.0001, sp. gr. 25°/25°; thereby substantiating the constancy of the alcohol-water content of the solvent used in the conductance study.

Results

The dissociation constants (*K*) and the limiting equivalent conductances (Λ_0) were obtained from conductance measurements by the method of Fuoss and Kraus.[22] Results given were obtained from at least two independent runs with different batches of solvent. In each case, agreement was found within at least 3% in *K* values. These values for the various pyridonium picrates are given in Table II.

TABLE II

DISSOCIATION CONSTANTS AND LIMITING EQUIVALENT CONDUCTANCES IN ETHANOL (95.5% BY WT.) AT 25° OF SUBSTITUTED PYRIDONIUM PICRATES

Salt	$K \times 10^3$	Λ_0
n-Propyl[a]	2.0	53
i-Propyl	3.6	52
β-Hydroxypropyl	3.7	58
β-Bromopropyl	5.7	68
β-Chloropropyl	58	60
γ-Hydroxypropyl	0.96	63
γ-Iodopropyl	.36	76
γ-Bromopropyl	.24	74
γ-Chloropropyl	.41	64

[a] H. L. Pickering and C. A. Kraus, THIS JOURNAL, **71**, 3288 (1949), found the *K* for this salt in ethylene chloride at 25° to be 0.49×10^{-4}.

In deriving these values, the dielectric constant of 95.5% (by weight) ethanol at 25° has been taken as 26.44,[23] and the viscosity at 25° as 0.0127 poise.[24] The F/Λ against $C\Lambda f^2 \pm /F$ graphs for the various pyridonium salts are given in Figs. 1–3.

Discussion

It is interesting that the β-substituted halogen

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[19] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1936, p. 445.

[20] D. Edelson and R. M. Fuoss, *J. Chem. Educ.*, **27**, 610 (1950).

[21] N. A. Lange, "Handbook of Chemistry," 4th ed., Handbook Publishers Inc., Sandusky, Ohio, 1941, p. 1191, reports 0.8008 for sp. gr. 25°/25°.

[22] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476 (1933); R. M. Fuoss, *ibid.*, **57**, 488 (1935).

[23] G. Akerlof, *ibid.*, **54**, 4125 (1932).

[24] E. W. Washburn, "International Critical Tables," Vol. 5, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 22.

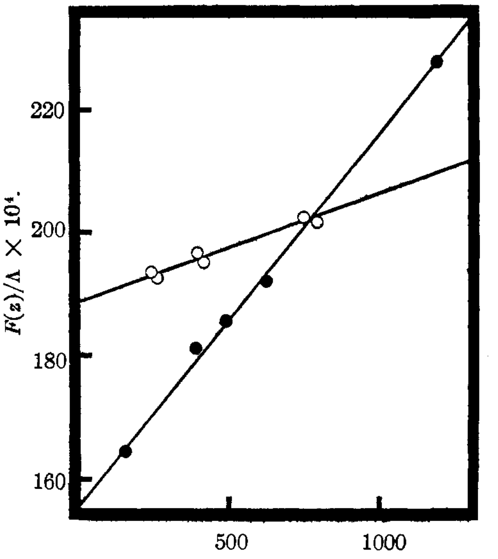


Fig. 1.—Plot for evaluation of dissociation constants and equivalent conductances of substituted propylpyridonium picrates in ethyl alcohol at 25°: ●, γ-chloro; ○, *n*-propyl.

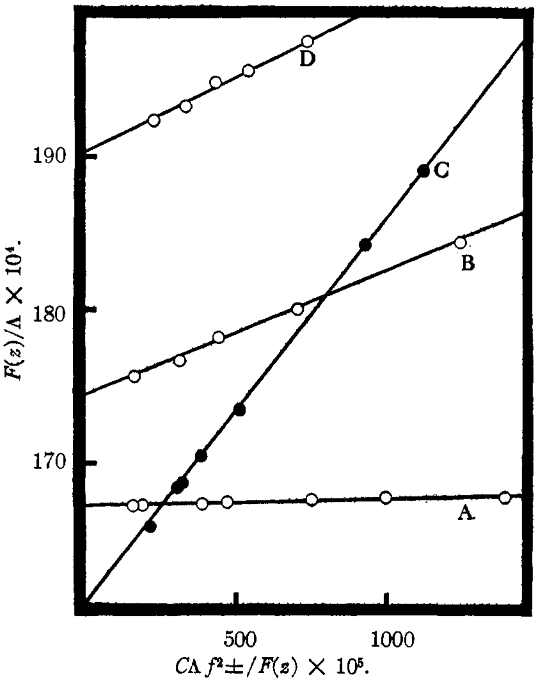
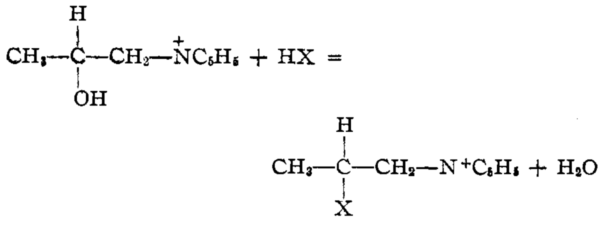


Fig. 2.—Plot for evaluation of dissociation constants and equivalent conductances of substituted propylpyridonium picrates in ethyl alcohol at 25°: A, β-chloro; B, β-hydroxy; C, γ-hydroxy; D, isopropyl.

salts could be prepared in substantially theoretical yields by the substitution reaction


$$\mathrm{CH_3{-}\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}{-}CH_2{-}\overset{+}{N}C_5H_5 + HX = CH_3{-}\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}{-}CH_2{-}N^{+}C_5H_5 + H_2O}$$

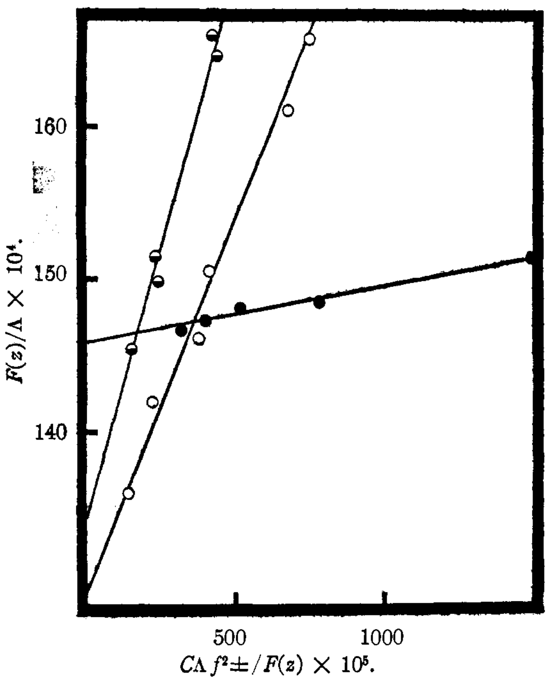
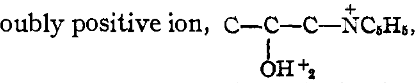


Fig. 3.—Plot for evaluation of dissociation constants and equivalent conductances of substituted propylpyridonium picrates in ethyl alcohol at 25°: ○, γ-iodo; ●, β-bromo; ◒, γ-bromo.

Apparently, the hydroxyl group is much more active when present in β-hydroxypropylpyridonium ion as compared to its activity in isopropyl alcohol. In the usual substitution reactions like these, the desired halide reaction product is obtained in partial yield only after distillation. It is indeed fortunate that the substitution reaction could be carried to completion here when performed under the proper conditions. Any appreciable quantity of unreacted β-hydroxypropylpyridonium salt would have invalidated the method of preparation since the two pyridonium salts could not be separated by fractional recrystallization or distillation. It would seem that the doubly positive ion,  $\mathrm{C{-}\underset{\underset{OH^{+}_{2}}{|}}{C}{-}\overset{+}{N}C_5H_5}$, accelerates and thereby causes the S_N2 substitution to be complete.

All the substituent groups in the β-position cause an increase in dissociation as compared to the unsubstituted *n*-propyl salt. If purely static inductive effects,[25] $-I_s$, were the predominate forces operating in displacing the electrons within the pyridonium ion, the highly electronegative halogen groups should cause the localization of the unit positive charge on the nitrogen to be greater; thereby decreasing the dissociation constants contrary to the increases noted (see Table II). Apparently, static induction is not the primary force functioning in the present system. Furthermore, the substituent groups in the β- and γ-positions are insulated from the nitrogen in the heterocyclic ring, that is, not connected by conjugate double bonds. These groups, therefore, cannot contribute directly to resonance in the ring system. Thus, it is seen

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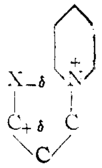
(25) A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, chap. 5.

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.

PORTLAND, OREGON RECEIVED JULY 17, 1951

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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 sulfamic 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 quim.*, **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).