

[CONTRIBUTION NO. 235 FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Determination of the Activity Coefficients of the Methylamine Hydrochlorides from Freezing Point Data¹

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Object of the Investigation

Scatchard and Prentiss³ have shown, in their freezing point depression investigations, that in the familiar "*j*" versus $M^{1/2}$ graphs for ammonium salts, the lines all crossed the limiting law values at concentrations below 0.08 *M*. Since the methylamine hydrochlorides are so closely related, it was decided to determine the activity coefficients of these salts and to ascertain whether their *j*-values also crossed the limiting law values as did those of the ammonium salts. It was thought, furthermore, that any peculiarity associated with the structural symmetry of the amine ions might make itself manifest through a characteristic variation in the values of the activity coefficients.

Experimental

The Cryostat.—The cryostat was an adaptation of the apparatus employed and described by Scatchard, Jones and Prentiss.⁴ It was a differential one consisting of two Dewar flasks of equal capacity, one serving as the fixed hot junction (0°) and the other as the variable cold junction of a multijunction thermocouple. All metal parts of the pump and hand stirrers, etc., were heavily gold-plated. All the usual precautions against heat-leakage, as prescribed for an apparatus for high precision, were taken. A detailed description of the apparatus may be found elsewhere.⁵

The Thermocouple.—The thermocouple built into this apparatus was composed of 48 elements of no. 30 copper and no. 36 constantan wire, double silk covered. The 48 elements were divided into eight units of six elements each, each element having been insulated by means of cellulose acetate; actually, it was found necessary to use only one six-element unit with the circuit employed. The method of assembling and mounting was essentially that of Scatchard, Jones and Prentiss.⁴ The metal sheath which covered the assembled elements was prepared by electroplating a carefully machined form of Wood's metal with copper and finally with gold. After melting the Wood's metal, the cleansed sheath was fitted tightly over the paraffined elements.

(1) Constructed from theses submitted by James Homer Jones and Frank Jacob Spuhler to the Graduate Faculty of the University of Texas in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941, and 1938, respectively. Original manuscript received May 29, 1941.

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(2) Present address: Humble Oil and Refining Co., Baytown, Texas.

(3) Scatchard and Prentiss, *THIS JOURNAL*, **54**, 2696 (1932).

(4) Scatchard, Jones and Prentiss, *ibid.*, **54**, 2676 (1932).

(5) J. H. Jones, Ph.D. Thesis, The University of Texas, June, 1941.

The thermocouple was calibrated against a platinum resistance thermometer (N.B.S. No. 277), using a Mueller bridge. The freezing point depressions of solutions of sodium nitrate were used in the calibration, covering the range from 0 to -5°. For the six-junction unit actually used, the equation relating the freezing point depression, θ , to the electromotive force *E* in microvolts is

$$\theta = 4.4333 \times 10^{-3}E + 4.31 \times 10^{-8}E^2$$

Thermocouple and Potentiometer Circuits.—The voltages of the thermocouple were measured potentiometrically, using a Leeds and Northrup Type K potentiometer and calibrated standard cells. The voltage multiplying circuit is shown in Fig. 1, a circuit recommended by Professor Arnold Romberg of the Physics Department of the University of Texas. The legend beneath the figure serves to describe the circuits; the portion of the circuit in which the 10,000 ohm decade resistor, F, is located is a voltage divider. When the voltages became too low to balance the galvanometer G with 4 volts in the main circuit, the voltage divider was connected into the circuit in place of the battery.

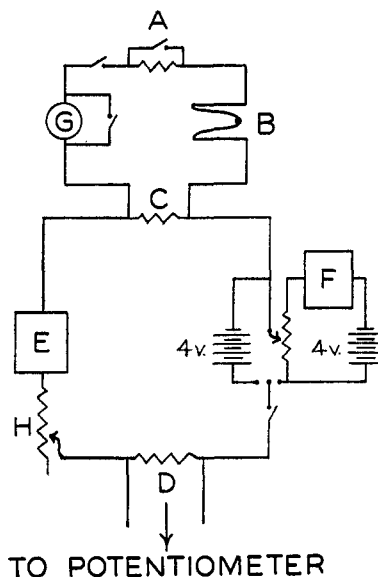


Fig. 1.—A, combination mercury switch and a 500 Ω shunted knife switch; B, multijunction thermocouple; C, one-ohm standard resistor; D, 1000 Ω standard resistor; E and F, 10,000 Ω decade resistors; G, H, S. galvanometer; and H, Kohlrausch slide wire.

Analysis of Equilibrium Solutions.—The solutions in thermal equilibrium with the ice during the freezing point investigation were analyzed conductimetrically. The molar conductances of the amine hydrochlorides had been determined by F. J. Spuhler,⁶ using a completely shielded

(6) F. J. Spuhler, Ph.D. Thesis, The University of Texas, June, 1938.

modification of the Jones and Josephs' bridge, as described by Dike.⁸ The oscillator system consisted of a General Ratio Type 508A oscillator followed by a Type 330E 1000-cycle filter.⁹ A 5000-ohm resistance was introduced in

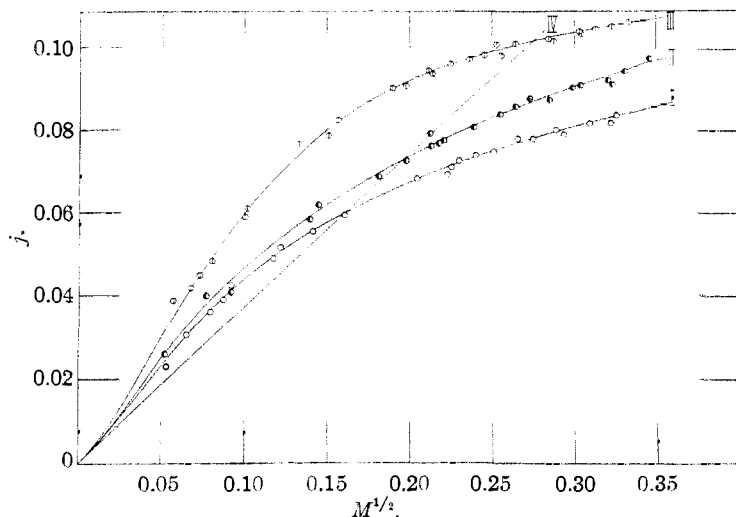


Fig. 2.—I, Monomethylamine hydrochloride; II, dimethylamine hydrochloride; III, trimethylamine hydrochloride; IV, limiting law: $j = 0.3738 M^{1/2}$.

series with the Type 45 oscillator tube, as recommended by Fields.¹⁰ An 85 d. b., three-stage, resistance-capacity coupled amplifier, with tuned filter circuit between the second and third stage (allowing either 1000 or 2000 cycles) together with tunable head phones constituted the detector circuit. All conductivity measurements were made at 25° in a thermostat controlled by means of a photoelectric cell system to $\pm 0.0005^\circ$. The conductivity cells were of modern design, having cell constants of approximately 120, 15, 1.5, and 0.25; the specific conductance data of Jones and Prendergast¹¹ for potassium chloride were used in the calibration. The conductimetric data of Spuhler⁶ were plotted on a very large scale; values at rounded concentrations were read from this molar conductance versus $c^{1/2}$ graph to yield the results given in Table I.

The Materials Used.—C. p. hydrochlorides of Eastman Kodak Co. manufacture were used after careful purification. **Monomethylamine Hydrochloride.**—The dried c. p. salt was purified by the methods of Bertheaume¹² and of François,¹³ which removed di- and trimethylamine hydrochlorides and ammonium chloride. The final dry salt was analyzed to yield 52.49% chlorine (52.51%, theoretical). **Dimethylamine Hydrochloride.**—The chloroform extraction method of Bertheaume¹² separated the soluble dimethylamine hydrochloride from the mono-salt and the ammonium chloride. The solid resulting from the chloro-

form solution was then subjected three times to fractional crystallization, yielding a product, upon thorough drying, which had a chloride content of 43.46% (43.49, theoretical).

Trimethylamine Hydrochloride.—The c. p. salt was again separated from ammonium chloride and monomethylamine hydrochloride by chloroform extraction. The dry salt, obtained by a concentration of the chloroform solution, was recrystallized three times from dry propanol. Its chloride content, upon analysis, was found to be 37.03% (37.09, theoretical); the salt is very difficult to keep dry, which undoubtedly accounts for the slightly lower chloride content. All salts were stored in an evacuated desiccator until used. **Water and Ice.**—All water (and ice) used in this investigation had a specific conductance of 0.9×10^{-6} reciprocal ohms at 25°. **Freezing Point Determinations.**—After thermal equilibrium had been attained, the final readings of the thermocouple voltage were made and a 75 ml. sample of the equilibrium solution was withdrawn by means of a special pipet into a 125-ml. glass-stoppered Erlenmeyer flask. The sample was placed in the thermostat (to attain the bath temperature and to lose dissolved nitrogen which had been used as a partial stirrer), after which they were analyzed conductimetrically.

TABLE I
MOLAR CONDUCTANCES OF THE METHYLAMINE HYDROCHLORIDES AT 25°

A comparison of these data with those recorded in "I.C.T." leads the authors to the conclusion that the previously published values are in error due in part to traces of ammonium chloride and in part to less precise bridge equipment. The values in Table I are most probably precise to 0.05%. They were made as part of a program leading to the precise determination of the ionization constants of aqueous solutions of the methyl- and ethylamines.

c , g. moles per liter	$\mu\text{CH}_3\text{NH}_2\text{Cl}$	$\mu(\text{CH}_3)_2\text{NH}_2\text{Cl}$	$\mu(\text{CH}_3)_3\text{NHCl}$
0.00000	135.07	128.22	123.60
.00025	133.35	126.53	122.03
.0005	132.63	125.89	121.32
.0010	131.72	124.91	120.31
.0025	129.90	123.16	118.51
.005	127.97	121.32	116.62
.010	125.53	118.99	114.33
.025	121.47	114.88	110.24
.050	117.62	110.66	106.03
.100	112.81	105.68	101.06
.250	105.19	97.51	92.03
.500	98.67	90.22	84.09
1.000	91.49	81.71	74.55

The Data and their Treatment

Approximately 50 freezing point determinations were made for each salt at concentrations ranging from approximately 0.0025 to 1.0 molal. The data obtained may be expressed by means of a listing of j -values, defined by

(7) Jones and Josephs, *THIS JOURNAL*, **50**, 1049 (1928).

(8) Dike, *Rev. Sci. Inst.*, **2**, 379 (1931).

(9) General Radio Company, Cambridge, Massachusetts, Cat. H *et seq.*

(10) Fields, *General Radio Exp.*, X, no. 9, 4 (1936).

(11) Jones and Prendergast, *THIS JOURNAL*, **59**, 731 (1937).

(12) Bertheaume, *Compt. rend.*, **150**, 1251 (1910).

(13) François, *ibid.*, **144**, 567 (1907).

$$j = 1 - \frac{\theta}{1.858\nu M}$$

Here θ is the observed freezing point depression; ν is the number of ions from one salt molecule; and M is the molality of the solution. These j -values were calculated for each individual determination, the observed data for which are listed elsewhere.⁵

Large scale graphs of $j/M^{1/2}$ versus $M^{1/2}$ were constructed for each salt, following the procedure of Randall and White¹⁴ and extrapolating the curves to the limit specified by them (*i. e.*, 0.375). From the curves thus constructed, there were calculated values of j at rounded concentrations of M . These values are given in Table III. These j values and some values calculated from the curves below $M = 0.001$ were then

TABLE II
VALUES OF j BELOW 0.05 MOLAL FROM OBSERVED VALUES OF θ

CH ₃ NH ₂ Cl		(CH ₃) ₂ NH ₂ Cl		(CH ₃) ₃ NHCl	
$M^{1/2}$	j	$M^{1/2}$	j	$M^{1/2}$	j
0.0529	0.0230	0.0520	0.0260	0.0572	0.0387
.0650	.0306	.0767	.0399	.0675	.0418
.0793	.0361	.0916	.0408	.0728	.0449
.0871	.0390	.1397	.0584	.0805	.0483
.0919	.0425	.1448	.0618	.1005	.0590
.1110	.0468	.1812	.0688	.1020	.0611
.1174	.0490	.1979	.0726	.1330	.0765
.1219	.0516	.2124	.0792	.1511	.0786
.1418	.0555	.2132	.0761	.1570	.0824
.1571	.0573	.2177	.0768	.1900	.0902
.1610	.0594	.2208	.0776	.1971	.0908
.2047	.0683	.2391	.0808	.2117	.0946
.2231	.0693	.2549	.0840	.2140	.0938
.2255	.0712	.2643	.0859	.2251	.0963

TABLE III
 j -VALUES OF THE METHYLAMINE HYDROCHLORIDES (READ FROM CURVES)

Molality	CH ₃ NH ₂ Cl	(CH ₃) ₂ NH ₂ Cl	(CH ₃) ₃ NHCl
0.001	0.0141	0.0151	0.0171
.002	.0207	.0214	.0265
.005	.0329	.0357	.0436
.010	.0433	.0471	.0606
.020	.0552	.0597	.0779
.050	.0705	.0781	.0957
.100	.0829	.0927	.1049
.200	.0935	.1048	.1165
.300	.0996	.1107	.1244
.400	.1040	.1144	.1286
.500	.1064	.1165	.1311
.600	.1072	.1178	.1326
.700	.1072	.1180	.1328
.800	.1070	.1172	.1338
.900	.1064	.1156	.1336
1.000	.1058	.1145	.1334

(14) Randall and White, *THIS JOURNAL*, **48**, 2514 (1926).

plotted against $M^{1/2}$, as shown in Fig. 2 for concentrations up to about 0.05 M ; in the dilute region the curve asymptotically approaches the limiting law line, $j = 0.3738\sqrt{M}$, as specified by Lange¹⁵ on the basis of the Debye-Hückel theory. In Table II are presented the values of j based upon observed values of θ at concentrations below about 0.05 molal.

Calculation of Activity Coefficients

The values of Table III were used to calculate the activity coefficients. The equation of Scatchard, Jones and Prentiss,⁴ based upon that of Lewis and Randall,¹⁶ was employed

$$-\log \gamma' = 0.4343 (j + CM) + \frac{2A}{B} \log (1 + BM^{1/2}) + \int_0^M \Delta j \, d \log M - 0.000461 \int_0^{\theta} (1 - j) d\theta$$

In this relation, the constants A , B and C are those of a deviation function having the form

$$\Delta j = j - \frac{AM^{1/2}}{1 + BM^{1/2}} - CM$$

A is 0.3738 or 0.3738 times the product of the valence of the ions. The constants B and C were determined to be

	B	C
CH ₃ NH ₂ Cl	1.2	-0.0632
(CH ₃) ₂ NH ₂ Cl	1.0	-0.0724
(CH ₃) ₃ NHCl	1.0	-0.0535

The evaluation of the integrals in the activity coefficient relation followed exactly the procedure outlined by Scatchard, Jones and Prentiss.⁴ For

TABLE IV
PROVISIONAL ACTIVITY COEFFICIENTS OF THE METHYLAMINE HYDROCHLORIDES

Molality	γ' CH ₃ NH ₂ Cl	γ' (CH ₃) ₂ NH ₂ Cl	γ' (CH ₃) ₃ NHCl
0.001	0.961	0.959	0.955
.002	.943	.941	.932
.005	.909	.904	.888
.010	.877	.869	.842
.020	.838	.827	.789
.050	.778	.762	.715
.100	.729	.708	.661
.200	.677	.654	.606
.300	.649	.622	.572
.400	.627	.601	.550
.500	.611	.584	.533
.600	.599	.571	.520
.700	.590	.563	.509
.800	.581	.553	.499
.900	.575	.546	.492
1.000	.569	.542	.486

(15) Lange, *Z. physik. Chem.*, **A168**, 147 (1934); **A177**, 193 (1936).

(16) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, New York, N. Y., 1923, p. 286.

the mono- and dimethylamine hydrochlorides, no value of Δj exceeded 0.02; for the trimethylamine hydrochloride some values rose as high as 0.03.

Discussion of Results

It is difficult to set up an absolute degree of accuracy in the values given. By a consideration of the possibilities of heat leakage, stray electromotive forces, contact electromotive forces, precision of measuring devices, etc., it is estimated that most of the observed freezing point lowerings are accurate to approximately one two-thousandth of the freezing point depression. The method of determining the concentration was, ultimately, a graphical one. The conductance measurements are estimated to be accurate to within one-hundredth of one per cent. and the concentrations to at least that accuracy.

The behavior of the methylamine hydrochlorides is similar to that of the ammonium salts, as found by Scatchard and Prentiss⁸ and to some

of the tetraalkylammonium halides, as described by Jörn Lange.¹⁵ Lange found that the j -values of these halides asymptotically approached the limiting law line from below in some cases and from above in other cases. In the case of tetramethylammonium chloride, the limiting law was approached from below, which is opposite to the approach of the salts of this investigation.

Summary

A differential freezing point apparatus was utilized to determine the freezing point depressions of aqueous solutions of mono-, di- and trimethylamine hydrochlorides over a concentration range 0.0025 to 1.0 molal.

The data are presented in terms of j -values at rounded concentration values.

From these j -values, provisional values for the activity coefficients were calculated.

Conductivity data for the methylamine hydrochlorides are presented.

AUSTIN, TEXAS

RECEIVED JANUARY 13, 1942

[CONTRIBUTION FROM THE INSTITUTO BACTERIOLÓGICO D.N.H., BUENOS AIRES]

Studies on Argentine Plants. III. Alkaloids from *Lycopodium Saururus*¹

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The presence of alkaloids in a plant of the genus *Lycopodiaceae* was first shown by Bödeker,² who isolated *lycopodine* from *L. Complanatum*. Shortly thereafter Arata and Canzoneri³ isolated from *L. saururus* a substance, $C_{15}H_{20}ON_2$, m. p. 64–65°, to which the name *pillijanine* was assigned. More recently Orechoff⁴ has mentioned the presence of alkaloids in *L. annotinum*, and Muszynski⁵ has confirmed this finding, and extended his study to other European species with similar results. From one of the latter, *L. clavatum*, Achmatowicz and Uzieblo⁶ isolated lycopodine, as well as clavatine and clavatoxine.

We have re-studied *L. saururus*, a plant which is widely distributed not only in Argentina, but in other South American countries, and in Africa. From it we have isolated two bases. The first, and most important, substance for which we propose the name *saururine*, was obtained as a sirup,

from which a crystalline picrate, $C_6H_5O_7N_3 \cdot C_{10}H_{19}N$, and methiodide, $C_{10}H_{19}N \cdot CH_3I$, could be obtained. Its nitrogen atom is tertiary, and the base is isomeric with lupinanes. Further, a crystalline levorotatory alkaloid, $C_{17}H_{26}ON_2$, m. p. 198°, was obtained in small amounts. This substance forms a monomethiodide, has one tertiary nitrogen atom, and no methoxyl groups. Although the formula of our substance bears some resemblance to that of pillijanine, obtained from the same plant by Arata and Canzoneri,³ the properties of the two substances differ markedly. For the new alkaloid we propose the name *sauruxine*. We were not able to isolate any substance having the properties of pillijanine, even when employing the method of extraction described by the earlier investigators.

Experimental

Extraction of the Plant.—Seventy-four hundred grams of air-dried *L. saururus* leaves was allowed to stand for two weeks with fifty liters of 2% hydrochloric acid. This operation was repeated twice.

The combined extracts were evaporated to a volume of

- (1) Part II, *J. Chem. Soc.*, 1051 (1940).
- (2) Bödeker, *Ann.*, **208**, 363 (1881).
- (3) Arata and Canzoneri, *Gazz. chim. ital.*, **22**, 146 (1892).
- (4) Orechoff, *Ber. deut. pharm. Ges.*, **272**, 673 (1934).
- (5) Muszynski, *ibid.*, **273**, 452 (1935).
- (6) Achmatowicz and Uzieblo, *Roczniki Chem.*, **18**, 88 (1938).