tassium in the absence of other monovalent cations. Three different acids were used: acid phthalate, *p*-toluenesulfonic and *p*-nitrophenol. Salts of these acids also could be used to determine the effect of a large anion upon the membrane potential. Potassium hydroxide solutions were used to obtain the effect of the hydroxide ion. Use of the membranes in strongly alkaline solutions is restricted due to attack of the alkali on the cement. The results are summarized in Table IV. From these data it may be seen that the anomalous effect due to hydrogen disappears above a *p*H of 4. At *p*H of 4 and above the potentials follow the simple Nernst equation as given provided a_2 is replaced by the sum of the activity of the hydrogen and the potassium. This, of course, is only important when the potassium ion activity is low.

Discussion

The results obtained with electrodialyzed bentonite membranes dried at 490° indicate that potassium ion activities may be determined in absence of other monovalent cations with a precision within 5% at *p*H values above 4. A high degree of reproducibility is possible using commercial Wyoming bentonite from which all particles larger than 200 mμ in equivalent spherical diameter have been removed by supercentrifuging.

The method is at present being used for the study of potassium ion activities in negatively charged colloidal systems and the results will be reported in due course.

Preliminary experiments indicate that these membranes may serve as electrodes for the determination of other monovalent cations. The results with sodium appear promising. Search is being continued for membrane materials which will serve as electrodes for the determination of divalent cations.

Acknowledgment.—The authors are indebted to the Research Council of the University of Missouri for a grant-in-aid which has made this work possible.

Summary

1. The detailed electrochemical behavior toward potassium ions of apophyllite and montmorillonite membranes has been investigated.

2. Apophyllite membranes are difficult to prepare and were found to show a variable behavior with potassium.

3. Montmorillonite membranes dried at 490° gave reproducible results with solutions of several potassium salts; and at concentrations below 0.1 *N*, estimations of potassium ion activities can be made with a precision within 5%.

COLUMBIA, MISSOURI RECEIVED APRIL 18, 1941

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND CO.]

Studies on High Molecular Weight Aliphatic Amines and their Salts. II. Solubilities of Primary Aliphatic Amine Hydrochlorides and Acetates in Ethanol and Benzene

BY H. J. HARWOOD, A. W. RALSTON AND W. M. SELBY

In connection with the investigation of the properties of high molecular weight aliphatic amine salts a series of solubility measurements has been made. Solubilities have been determined for the hydrochlorides of the series decylamine through octadecylamine in 95% ethanol and for the acetates of the series dodecylamine through octadecylamine in 95% ethanol and in anhydrous benzene. A number of interesting peculiarities in the behavior of these salts have become evident as a result of this work.

Experimental Part

The amine salts used were prepared from amines, the preparation of which has been previously described.[1] The hydrochlorides were obtained by treating an ethanol solution of the amine with concentrated hydrochloric acid. The resulting solution was evaporated to dryness under reduced pressure and the salt recrystallized from a mixture of ethanol and ether. The acetates were obtained by adding the calculated amount of glacial acetic acid to an ether solution of the amine. The acetates were recrystallized from a mixture of ethanol and ether until further crystallization failed to raise the melting point of the salt. Constants for the salts used are given in Table I.

The ethanol used was commercial 95% ethanol. The benzene was Baker C. P. thiophene-free grade and was dried over sodium wire.

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[1] Ralston, Selby, Pool and Potts, *Ind. Eng. Chem.*, **32**, 1093 (1940).

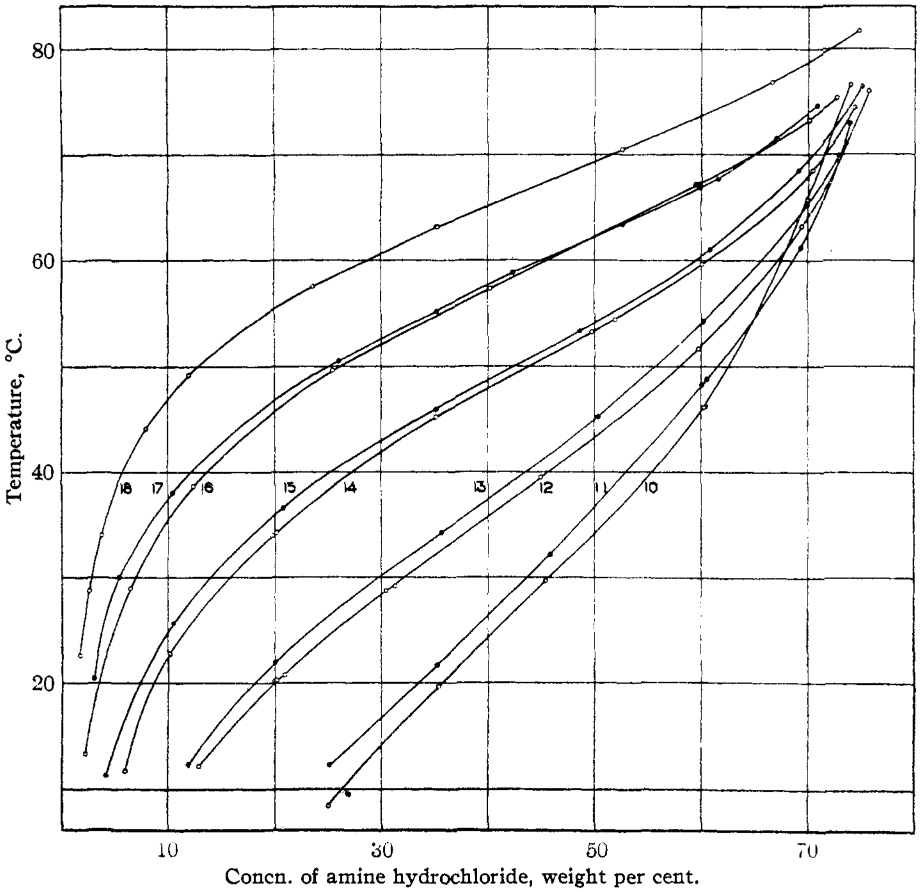

Fig. 1.—Solubilities of amine hydrochlorides in 95% ethanol. Curve numbers refer to number of carbon atoms in the molecule.

TABLE I

CONSTANTS FOR AMINE SALTS

C atoms	% Cl in hydrochlorides[a] Calcd.	Found	M. p. of acetate, °C.
10	18.31	18.35	
11	17.08	17.13	
12	16.00	15.80	68.5–69.5[b]
13	15.04	15.19	66.0–67.5
14	14.20	14.25	74.5–76.0
15	13.44	13.62	75.0–76.5
16	12.77	12.92	80.0–81.5[c]
17	12.15	12.29	81.5–82.5
18	11.60	11.85	84.0–85.0

[a] Parr bomb. [b] Calcd.: C, 68.56; H, 12.74; N, 5.74. Found: C, 68.88; H, 12.36; N, 5.79. [c] Calcd.: C, 71.74; H, 13.05; N, 4.65. Found: C, 72.09; H, 12.72; N, 4.62. Analyses (b) and (c) by T. S. Ma, University of Chicago, Chicago, Illinois.

The solubility determinations were made on synthetic samples prepared in the following manner. A portion of the amine salt was accurately weighed into a thin-walled glass tube. The tube was 8 cm. long and 6 mm. inside diameter and was partially constricted about 1 cm. from the open end. Solvent was then added by means of a capillary dropper, care being taken to wash the amine salt into the tube. After sealing the tube, the total weight of the amine salt plus solvent was determined. No attempt was made to prepare samples of definite concentration, although it was possible to arrive at values within 1% of those desired. The total weight of amine salt plus solvent varied between 0.6 g. and 1.0 g. depending upon the concentration.

The solubility determinations were carried out in a water-bath consisting of a 2-liter beaker heated electrically by means of a coil of "Chromel" wire wound on the outside of the beaker. The temperature was controlled by means of a rheostat in series with the coil. Temperatures were read with an ordinary 100° thermometer which had been calibrated with a National Bureau of Standards calibrated thermometer. The tube containing the sample was held in the bath by means of a clip soldered to the end of a rod. The rod was rotated slowly by an electric motor and was held at an angle of approximately 15° from the perpendicular so that the contents of the tube were thoroughly agitated.

In making a solubility determination the tube containing the sample was warmed with a free flame until the amine salt had dissolved. The tube was then placed in the bath which was at a temperature about 1° below the temperature at which solution would occur. The bath was heated at such a rate as to raise the temperature 0.1° every

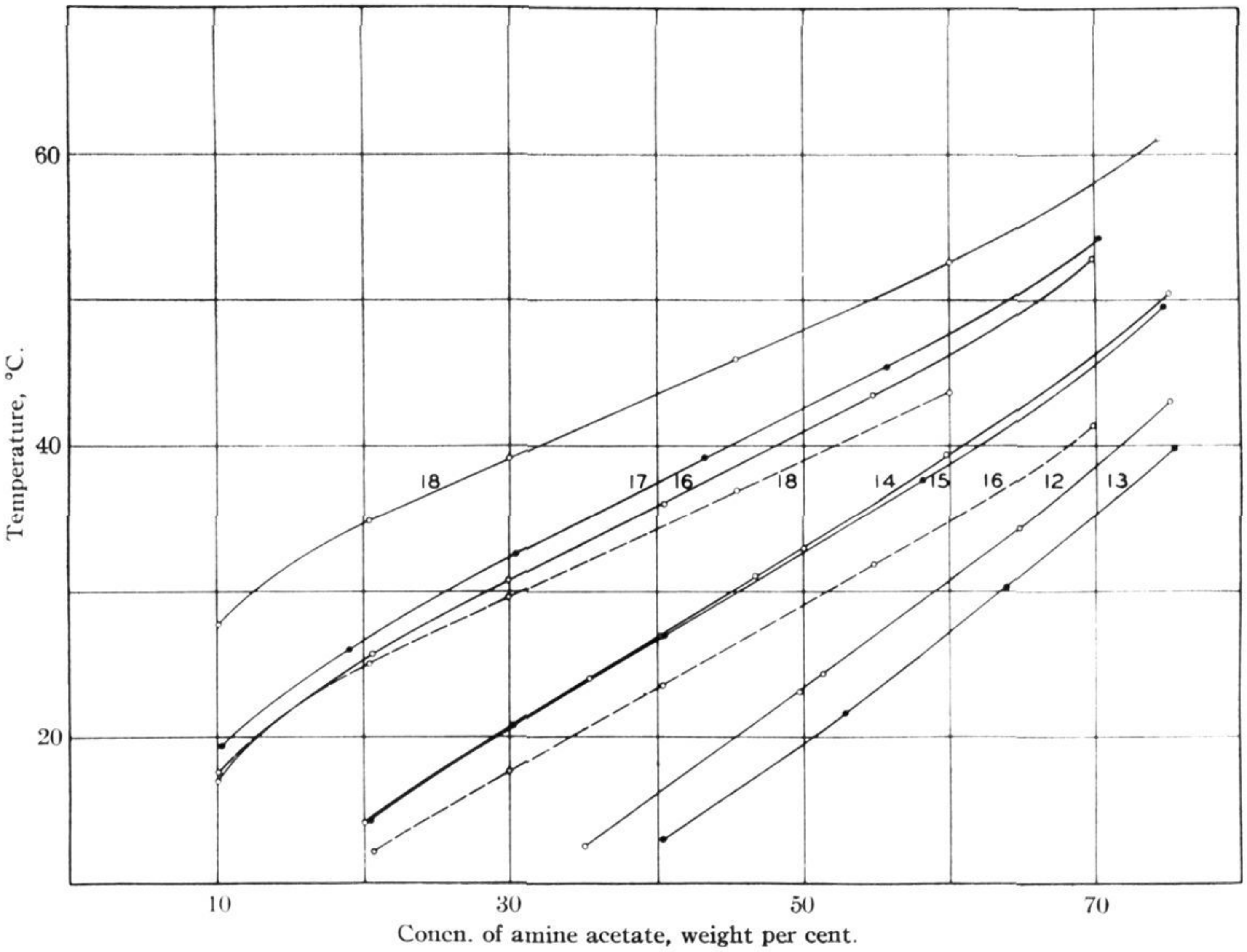

Fig. 2.—Solubilities of amine acetates in 95% ethanol. Curve numbers refer to number of carbon atoms in the amine.

two to three minutes. The tube was removed from the bath and the end placed in cold water or an ice-salt freezing mixture until a few small crystals had precipitated. It was then returned to the bath and the agitation and heating continued. It was easily possible, by stopping the rotation of the tube, to observe the temperature at which all crystals had disappeared. Temperatures were estimated to 0.1° and were considered to be accurate within ±0.2°. The values obtained were reproducible.

Temperature-concentration curves constructed by plotting the values obtained in this work are shown in Figs. 1, 2 and 4.

Fig. 3a.—Octadecylamine acetate in 95% ethanol; unstable form, ×200.

Fig. 3b.—Octadecylamine acetate in 95% ethanol; stable form, ×200.

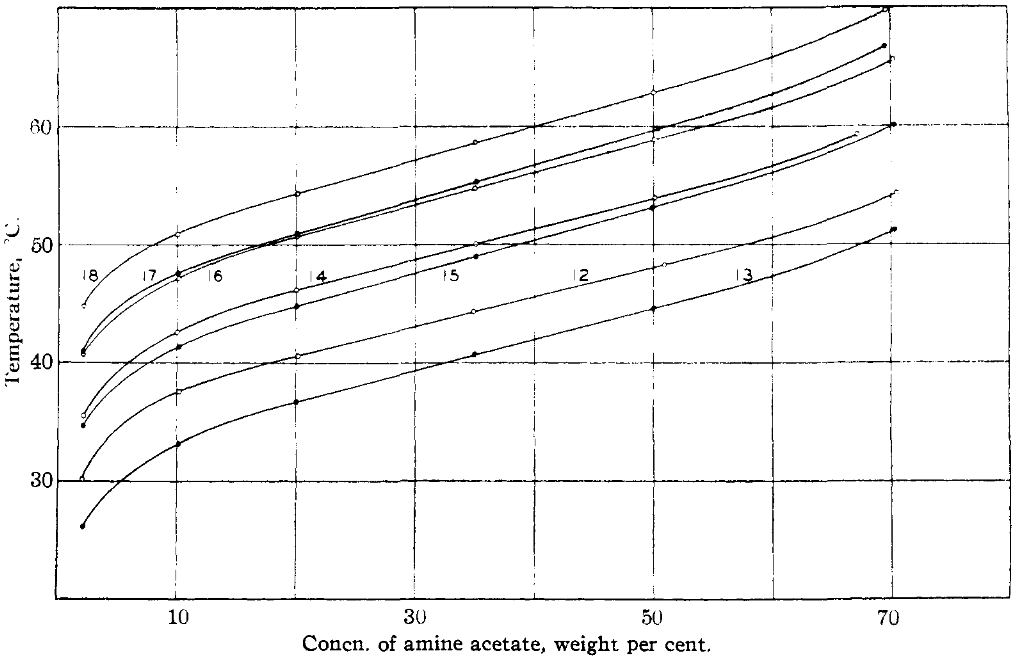

Fig. 4.—Solubilities of amine acetates in anhydrous benzene. Curve numbers refer to number of carbon atoms in the amine.

Results and Discussion

In the set of solubility curves for the amine hydrochlorides in 95% ethanol (Fig. 1) the pairing of the members of the series having an even number of carbon atoms with the next higher member having an odd number of carbon atoms is to be noted. The curve for heptadecylamine hydrochloride crosses that for hexadecylamine hydrochloride in two places. As the temperature increases the solubility of the lower members of the series becomes less than that of the higher members. This results in the curves for the lower members crossing those above.

Pairing also occurs in the case of the solubility curves for the amine acetates in 95% ethanol (Fig. 2). Here, however, the order of the curves is peculiar. Heptadecylamine acetate is less soluble than hexadecylamine acetate while pentadecylamine acetate is more soluble than tetradecylamine acetate and tridecylamine acetate is more soluble than the dodecylamine salt. The salts having an even number of carbon atoms may be considered as one series and those having an odd number as another. The interval between the curves in the first series is less than that in the second, which results in the apparent disorder noted.

Two of the salts, octadecylamine acetate and hexadecylamine acetate, were found to exhibit polymorphism as evidenced by the existence of two solubility curves for these salts in 95% ethanol. In Fig. 2 the solubility curves for the less stable forms are indicated by broken lines. The unstable forms were obtained by chilling the sample tube in the manner previously described. In the samples of low concentration the unstable form could be kept indefinitely. As the concentration was increased it became more difficult to keep the unstable form for more than a few minutes near the temperature at which solution occurred. No attempt was made to determine the transition temperature for the two forms. In both cases it was probably below 10°. Because of the existence of the unstable modification at temperatures considerably above the apparent transition point, these forms are considered to be polymorphs rather than solvates. The latter possibility, however, has not been rigidly excluded by the evidence presented.

The crystalline forms of the polymorphs were quite different. This is shown in the photomicrographs (Figs. 3) of octadecylamine acetate in 95% ethanol. The stable form crystallized in long needles while the unstable form appeared as minute plates. Attempts to filter off the unstable forms were unsuccessful. Examples of polymorphism in high molecular weight normal aliphatic hydrocarbons,[2] alcohols,[2] esters,[3] acids[4] and nitriles[5] are reported in the literature. Polymorphism in triglycerides is well known.

The solubility curves for the amine acetates in anhydrous benzene (Fig. 4) were in the same order as the curves for these salts in 95% ethanol. No indication of polymorphism of octadecylamine acetate and hexadecylamine acetate was found with benzene as the solvent.

Summary

The solubilities of a series of high molecular weight aliphatic primary amine hydrochlorides in 95% ethanol and of a series of high molecular weight aliphatic primary amine acetates in 95% ethanol and in anhydrous benzene have been determined.

Polymorphic modifications of octadecylamine acetate and hexadecylamine acetate are reported.

CHICAGO, ILLINOIS RECEIVED MAY 2, 1941

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(2) Carey and Smith, *J. Chem. Soc.*, 635, 1348 (1933).

(3) Bellinghen, *Bull. soc. chim. Belg.*, **47**, 640 (1938).

(4) Dupré la Tour, *Ann. phys.*, **18**, 199 (1932).

(5) Levene and Taylor, *J. Biol. Chem.*, **59**, 905 (1924).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

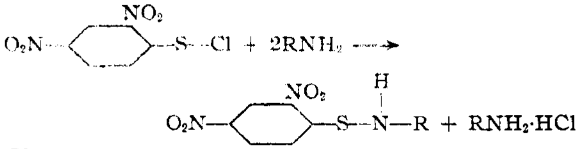
The Formation of Solid Derivatives of Amines. II

BY JOHN H. BILLMAN,[1] JOSEPH GARRISON, R. ANDERSON AND BERNARD WOLNAK

It has been shown[2] that *o*-nitrobenzenesulfenyl chloride can be used advantageously for the identification of amines since the derivatives form readily, are usually solid, and can be decomposed quickly to give nearly quantitative yields of the amine hydrochlorides. However, some low-melting amines give oily or low-melting derivatives and it therefore appeared of interest to test the feasibility of using 2,4-dinitrobenzenesulfenyl chloride for the identification of amines.

2,4-Dinitrobenzenesulfenyl chloride was prepared as a yellow solid (m. p. 94–96°) from 2,2′,4,4′-tetranitrodiphenyl disulfide and chlorine by a method analogous to the one described for the preparation of *o*-nitrobenzenesulfenyl chloride.[3] When removing the nitrobenzene which is used as a solvent for the reaction, care must be taken to keep the temperature below 135°. Vigorous decomposition is likely to occur above this temperature.

The amides (Table I) were prepared readily by the addition of an ethereal solution of the 2,4-dinitrobenzenesulfenyl chloride to an ethereal solution of the amine at room temperature. The reverse procedure worked equally well with aromatic amines.



In the case of an aqueous solution of an amine, enough ether was added to make the mixture homogeneous before reaction. Addition of the reagent was continued until no further precipitation was noticed. The amine hydrochloride was filtered off and washed with ether; the filtrates were combined and evaporated until all of the ether was removed. The resulting material was dissolved in hot 95% alcohol and recrystallized two or three times from this solvent. The addition of pyridine to the ethereal solution of the amine before the addition of the reagent did not in any way aid the reaction. A solution containing 10% alkali failed to dissolve any of the primary amine derivatives.

TABLE I

PROPERTIES OF THE AMINE DERIVATIVES

Amines	M. p.[a] of amides, °C.	Anal. of amides, % N Calcd.	Found
Aniline	142.5–143	14.43	14.33
p-Anisidine	158 –159	13.09	13.06
p-Bromoaniline	180.5–181	11.36	11.17
n-Butylamine	88.5– 89	15.50	15.40
p-Chloroaniline	164 –164.5	12.91	13.11
Cyclohexylamine	109.5–110	14.14	14.06
Ethylamine	66 – 66.5	17.28	17.17
Methylamine	99 – 99.5	18.34	18.23
N-Methylcyclohexylamine	95.5– 96	13.46	13.32
α-Naphthylamine	188.5–189	12.32	12.29
β-Naphthylamine	167 –168	12.32	12.27
n-Propylamine	94 – 94.5	16.34	16.33
o-Toluidine	155 –156	13.77	13.73
p-Toluidine	161 –161.5	18.77	13.63

[a] Melting points are uncorrected.

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(1) Present address: Indiana University, Bloomington, Indiana.

(2) Billman and O'Mahony, THIS JOURNAL, **61**, 2340 (1939).

(3) "Organic Syntheses," Vol. XV, 1935, p. 45.