of magnesium is very marked. The simplest explanation is that, in the case of the aromatics, the anion is sometimes discharged to give an aryl halide instead of the free radicals

$$(R_2MgX_2)^{=} \longrightarrow RX + RMgX + 2e$$

The RX would then diffuse over to the cathode and react with the magnesium deposited there to produce more Grignard reagent, so that the net result of the electrolysis would be zero. The eating away of the magnesium by aryl halide would account for its appearance.

In order to test the above mechanism, phenylmagnesium bromide was electrolyzed in a transference cell where diffusion was avoided. As would be predicted, the magnesium in the cathode portion was gray and unreactive. The anode portion was drained off and found to contain appreciable amounts of bromobenzene. A portion of the Grignard before electrolysis contained no unreacted bromobenzene.

The increased tendency of aryl Grignards to give this secondary reaction, where a halide is formed, may be due to the greater strength of the carbon to halogen bond. It is significant that this reaction is not found in the cases where the Wurtz–Fittig type of reaction occurs

$$RX + RMgX \longrightarrow R—R + MgX_2$$

The observed vigorous attack on hydrogen bearing substances by the aryl radicals is probably related to the fact that the concentration of free radicals at any instant is very low due to the secondary anode reaction outlined above. Both the coupling and disproportionation of phenyl free radicals in the absence of a solvent have been reported.[4] In general, the evidence indicates that the aryl radicals are more difficult to form and once formed, are more reactive than the aliphatic free radicals of simple nature.

Summary

1. The products of electrolysis of phenyl-, *p*-tolyl-, *p*-chlorophenyl- and benzylmagnesium bromides are reported.

2. The alternative discharge of aryl halides as an anode reaction is shown to occur with aromatic Grignard reagents.

3. The behavior of short-lived aryl free radicals in ether solution is discussed and mechanisms advanced for their reactions.

4. The marked difference between aliphatic and aromatic Grignards upon electrolysis is brought out.

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[4] Bachmann and Clarke, THIS JOURNAL, **49**, 2089 (1927).

EVANSTON, ILLINOIS RECEIVED JULY 14, 1941

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

Studies on High Molecular Weight Aliphatic Amines and their Salts. III. Behavior of the Acetates of Dodecylamine and Octadecylamine in Water

BY A. W. RALSTON, CHARLES W. HOERR AND EVERETT J. HOFFMAN

The behavior of the acetates of dodecylamine and octadecylamine in water is qualitatively similar to the behavior of the corresponding hydrochlorides in water.[1]

A study of the cooling curves coupled with visual observations of both the dodecylamine acetate–water system and octadecylamine acetate–water system show that they both exhibit colloidal properties over a wide range of temperature and concentration. Determination of the osmotic coefficient *g* and dew-point data further substantiate the colloidal behavior of these systems. Dodecylamine acetate is more soluble in water than octadecylamine acetate. A metastable region was observed in the case of octadecylamine acetate and water but not in the dodecylamine acetate–water system. This differs from the corresponding hydrochlorides where the metastable region was observed only in the dodecylamine hydrochloride–water system.

Experimental

Preparation of Materials.—Lauronitrile and stearonitrile were prepared by the action of ammonia upon the respective acids.[2] The lauronitrile was purified by fractional distillation *in vacuo*[3] ($n^{25}\text{D}$ 1.4342–1.4344) and the stearonitrile by crystallization from 95% ethanol (m. p. 42.0–43.0°). The nitriles were hydrogenated to the corresponding amines, and the amines were fractionally distilled *in vacuo*.[4] The amines were then converted to the acetates which were then crystallized from the appropriate

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[1] Ralston, Hoffman, Hoerr and Selby, THIS JOURNAL, **63**, 1598 (1941).

[2] Ralston, Harwood and Pool, *ibid.*, **59**, 986 (1937).

[3] Ralston, Selby and Pool, *Ind. Eng. Chem.*, **33**, 682 (1941).

[4] Ralston, Selby, Pool and Potts, *ibid.*, **32**, 1093 (1940).

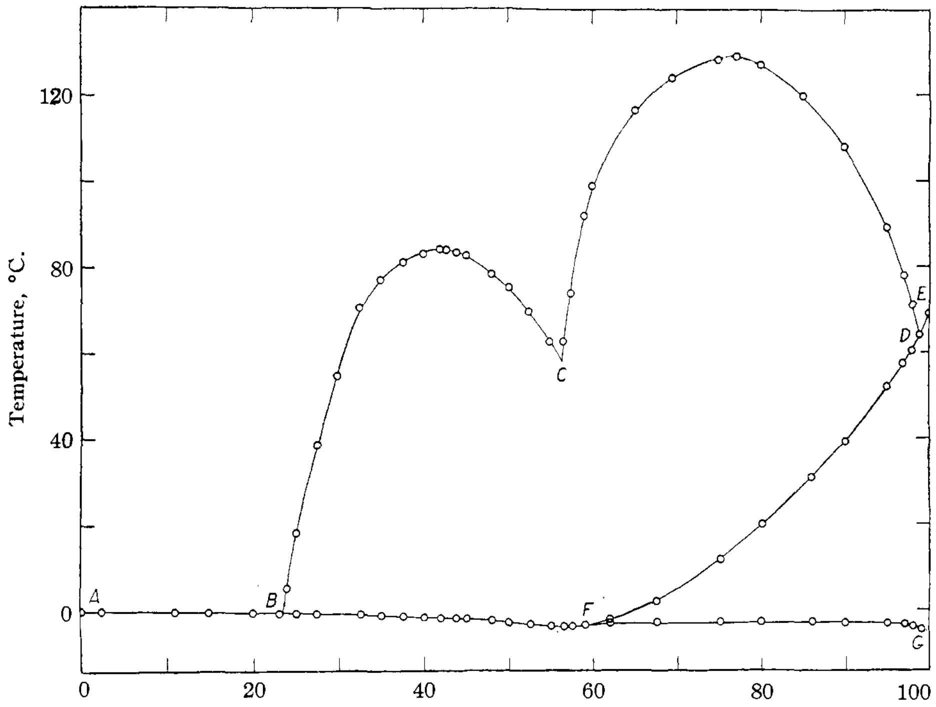

Fig. 1.—Transition temperatures for the system $C_{12}H_{25}NH_2 \cdot CH_3COOH-H_2O$.

solvents to remove any unchanged amine. The procedures used for the preparation of the amine salts from the amines were as follows:

Dodecylamine acetate—dodecylamine (15.6 g.) was dissolved in diethyl ether (U. S. P., 1 liter), and glacial acetic acid (5.6 g.) was added slowly to this solution. The solution was cooled to −25° to effect crystallization. The product was crystallized once from ether and four times from benzene (m. p. 68.5–69.5°).

Octadecylamine acetate—octadecylamine (16.0 g.) was dissolved in diethyl ether (U. S. P., 1 l.), and glacial acetic acid (3.6 g.) was added slowly to the solution. Octadecylamine acetate precipitated immediately, and it was necessary to reflux the mixture in order to dissolve the amine salt. The solution was then allowed to crystallize. The product was recrystallized twice from a mixture of diethyl ether and 95% ethanol and four times from benzene (m. p. 84.5–85.0°).

Water—distilled water was boiled to remove dissolved gases prior to its use.

Procedure

Preliminary visual observations were made by a method similar to that devised by Alexejew[5] for the study of binary liquid systems and corresponding to that employed in our investigations of the amine hydrochloride–water systems.[1] Transition points were determined by a study of the cooling curves of the amine salt–water mixtures over the entire range of concentration. A 15-g. sample was placed in a 100-ml. Dewar flask fitted with a rubber stopper through which were inserted a glass stirrer and a thermocouple well. Iron–constantan thermocouples were employed and the reference junction was immersed in melting ice. The cooling bath was maintained at approximately 10° below the transition points. The freezing point of water in the samples which contained 40% or less of dodecylamine acetate was determined by means of a Beckmann freezing point apparatus. Microscopic investigations were made upon a number of samples at room temperature. Dew point determinations were made in the case of the octadecylamine acetate–water mixtures which contained 50, 75, 95 and 99% amine salt. The apparatus employed was similar to that described by McBain and Salmon[6] with the exception that the silver tube was replaced by a chromium plated brass tube.

Experimental Results

The transition temperatures for the system dodecylamine acetate–water are shown graphically in Fig. 1. Above the curve ABCDE all mixtures are isotropic liquids. The line BCD marks a change to a gel on cooling. Along the line AB the system solidifies to a mixture of crystals, probably ice and amine acetate, and in crossing the line BF a similar change takes place in the gel. Dodecylamine acetate crystallizes along the line FDE to give a mixture of crystals and solution, and this mixture becomes a crystalline mass along the line FG. No evidence of compound formation is exhibited although this possibility has not been rigidly excluded.

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[5] Alexejew, *Wied. Ann.*, **28**, 305 (1880).

[6] McBain and Salmon, THIS JOURNAL, **42**, 426 (1920).

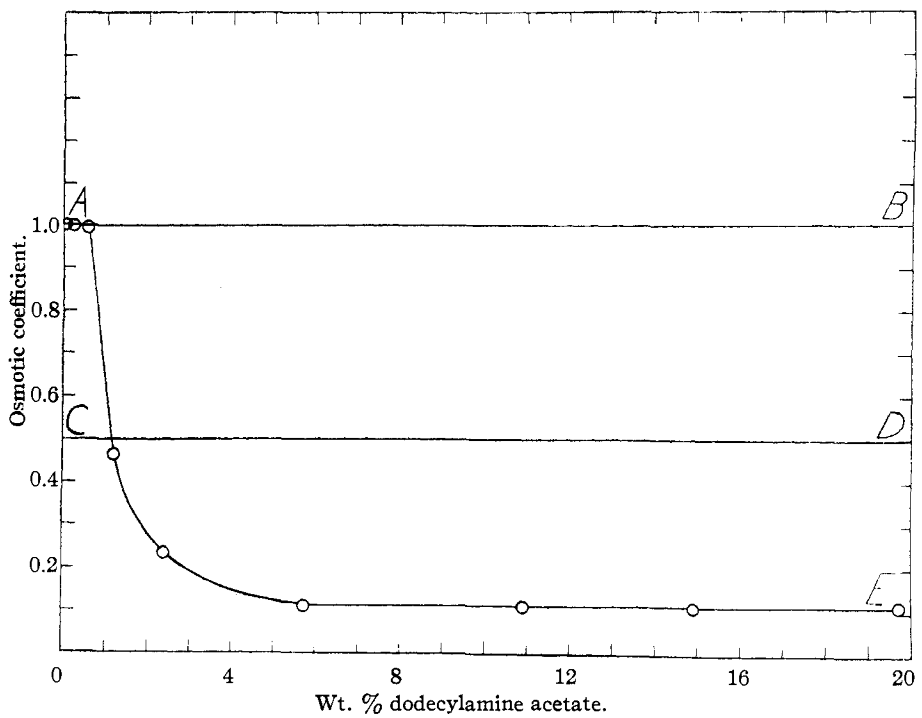

Fig. 2.—Osmotic coefficients for the system $C_{12}H_{25}NH_2\cdot CH_3COOH-H_2O$.

Figure 2 shows the change of the osmotic coefficient *g* with concentration of dodecylamine acetate in the dodecylamine acetate–water system. Line AB is the theoretical value for *g* for the completely dissociated molecule and CD for the undissociated molecule. A study of the curve AE shows that the amine salt is completely dissociated at concentrations below 0.6% and colloidal properties are indicated in solutions containing more than 1.2% amine salt.

Figure 3 shows the transition temperatures for the system octadecylamine acetate–water. Mixtures above the curve AB and to the left of the curve BC are isotropic liquids. This is also true of mixtures above the curve GFH. Observations (not shown) indicate that the lines BC and FH meet at some temperature above 190° but this conclu-

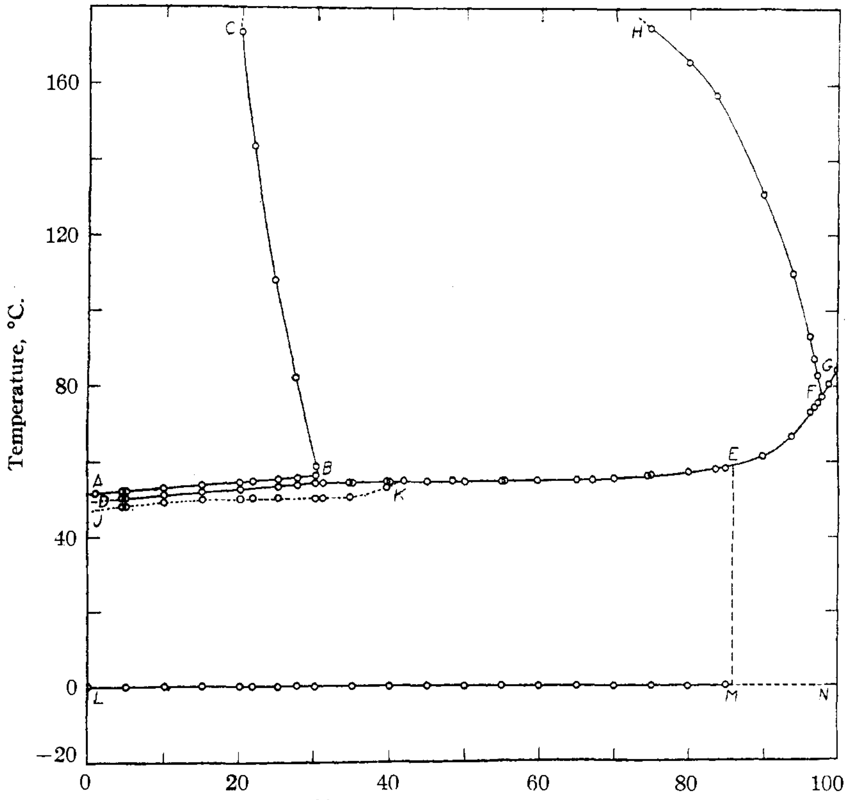

Fig. 3.—Transition temperatures for the system $C_{18}H_{37}NH_2\cdot CH_3COOH-H_2O$.

sion is rendered questionable because of thermal decomposition. Mixtures between the lines DEFH and ABC are emulsions. These mixtures upon cooling become isotropic liquids as they cross the line CB. The slope of the line CB shows that the solubility of the amine salt in water decreases with increased temperature. The emulsion solidifies to a gel as it crosses the line DE. If the emulsion crosses the line EF, the gel assumes a somewhat crystalline appearance. All compositions below the line DEF may differ only in the amount of liquid present. On cooling the isotropic liquid above the line FG, it solidifies to a crystalline mass. All mixtures below the line LMN are crystalline and are probably composed of a mixture of crystals of octadecylamine acetate and ice. The line JK represents a metastable transformation from an emulsion to a gel and transitions along this line occur only if the sample is cooled rapidly and without agitation.

TABLE I

VAPOR PRESSURES OF OCTADECYLAMINE ACETATE–WATER MIXTURES

% C_{18} acetate in water	Temp. of sample, °C.	Dew-point, °C.	Vapor pressure lowering, mm.
50.0	30.0	29.6	0.7
	40.0	39.8	.6
	50.0	49.9	.5
	60.0	59.9	.7
75.0	20.0	19.4	.6
	30.0	29.6	.7
	40.0	39.8	.6
	50.0	49.9	.5
	60.0	59.9	.7
95.0	20.0	19.1	.9
	25.0	24.3	1.0
	30.0	29.4	0.9
	35.0	34.6	.9
	40.0	39.7	.7
	50.0	49.7	1.4
	60.0	59.8	1.4
99.0	30.0	29.2	1.4
	40.0	39.3	2.0
	50.0	49.5	2.3
	60.0	59.8	1.4

Table I shows the lowering of the vapor pressure of water at various temperatures for octadecylamine acetate–water mixtures. These values were determined by the dew-point method previously described. The values obtained indicate a colloidal system.

Summary

1. The systems dodecylamine acetate–water and octadecylamine acetate–water have been investigated.

2. These amine salts show crystalloidal properties in dilute aqueous solutions and colloidal properties in concentrated solutions.

CHICAGO, ILL. RECEIVED MAY 19, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant of Formic Acid in Dioxane–Water Mixtures

BY HERBERT S. HARNED AND ROBERT S. DONE[1]

The ionization constants of acetic acid and water from 0 to 50° in dioxane–water mixtures have been determined from cells without liquid junction by Harned and Kazanjian,[2] and Harned and Fallon.[3,4] By means of the cells

$$H_2 \mid HF(m),\ NaF(m),\ NaCl(m),\ \text{Dioxane}(X),\ \text{Water}(Y) \mid AgCl\text{–}Ag$$

we have extended these investigations to include formic acid represented by HF. From the ionization constant and its temperature coefficient, the free energy, heat content, heat capacity and entropy of ionization have been calculated.

Experimental

The solutions were made by diluting an aqueous stock solution containing formic acid, sodium formate and sodium chloride at the same molality with the proper quantities of dioxane and water. Two kilograms of Eastman Kodak Co. formic acid were redistilled twice from an all-glass column still. The first middle fraction was collected over a temperature range of 0.6° and the second and final middle fraction (800 g.) over a temperature range of 0.2°. About 400 g. of the purified acid was added to two liters of water. This solution was analyzed by weight titration against standard carbon dioxide-free sodium hydroxide solution. The standard buffered solution was made by adding enough sodium hydroxide solution to

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[1] This communication contains material from a dissertation presented by Robert S. Done to the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1941.

[2] Harned and Kazanjian, THIS JOURNAL, **58**, 1912 (1936). Also Harned, *J. Phys. Chem.*, **43**, 275 (1939).

[3] Harned and Fallon, THIS JOURNAL, **61**, 2377 (1939). Acetic acid in 82% by weight dioxane–water solution.

[4] Harned and Fallon, *ibid.*, **61**, 2374 (1939).