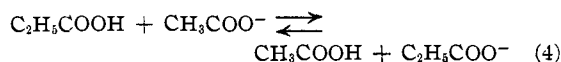


pure solvents, the results may be expressed by the equation

$$\log K_{A_xB_0} = -0.022 - \frac{7.1}{D}$$

and the values thus calculated are given in column five of Table II.

It should be emphasized that the values of $K_{A_xB_0}$ for the experiments reported in this paper are direct determinations of the equilibrium constant for the reaction



and the corresponding reaction for formic acid. The measurements were made in the presence of 0.045 mole per liter of lithium chloride with a 1.0 molar bridge solution of the same salt. For a reaction of the charge type of equation (4), the equilibrium constant would be expected to be independent of ionic strength, for the same solvent salt, and comparable to the thermodynamic equilibrium constant. This is borne out by the results at various ionic strengths given in the following table.

In addition, the value of $K_{A_xB_0}$ calculated from the thermodynamic constants in water given in

TABLE III

THE EFFECT OF IONIC STRENGTH ON THE EQUILIBRIUM CONSTANT OF THE REACTION

$$HCOOH + CH_3COO^- \rightleftharpoons CH_3COOH + HCOO^-$$

Solvent	$K_{A_xB_0}$					
	$\mu = 0.05$	0.10	0.20	0.50	1.00	2.00
Water	..	10.3	10.3	10.3	10.3	10.3
Methyl alcohol	17.3	17.8	17.6			
Ethyl alcohol	19.6	19.5	19.8			

Table I, agrees with the value in 0.095 molar potassium chloride.

The authors would like to take this opportunity to thank the Faculty Research Committee of the University for a grant.

Summary

In dioxane-water mixtures, the logarithm of the acid strength of formic acid relative to acetic, or of propionic relative to acetic, is not a linear function of the reciprocal of the dielectric constant of the medium. In the pure solvents studied—water, ethylene glycol, methyl alcohol and ethyl alcohol—a linear relationship holds. This same phenomenon has been observed in the case of the substituted benzoic acids.

PHILADELPHIA, PENNA.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

Studies on High Molecular Weight Aliphatic Amines and their Salts. VIII. Soluble and Insoluble Films of the Amine Acetates. A. The Surface Tension of Aqueous Solutions of Dodecylamine Acetate

BY EVERETT J. HOFFMAN, G. E. BOYD AND A. W. RALSTON

Introduction

In the fifth paper of this series¹ we reported the results of an investigation of the surface properties of a simple, long chain cationic colloidal electrolyte, namely, dodecylamine hydrochloride. The present paper deals with a study of the surface properties of aqueous solutions of dodecylamine acetate. In this case the time effects of long duration which were observed for dilute solutions of dodecylamine hydrochloride were not found. In the case of $5 \times 10^{-3} N$ solutions at 25°, constant values of the surface tension were obtained within thirty minutes. No time effects were observed at other temperatures for this same solution. With a solution of concentration $7.5 \times 10^{-3} N$ (critical

micelle concentration = $1.2 \times 10^{-2} N$) no time effects were observed at any temperature. In contrast to this behavior, in the case of dodecylamine hydrochloride a steady decrease was observed even after five hours.

The absence of aging effects with unbuffered *n*-alkylamine acetate solutions may not, however, reflect the behavior in general of solutions containing this type of colloidal electrolyte. Preliminary experiments on a $5 \times 10^{-3} N$ solution of dodecylamine acetate in the presence of $10^{-2} N$ acetic acid-sodium acetate revealed an appreciable variation of surface tension with time. It is possible that the surface active species in our experiments consists of free amine in equilibrium with amine acetate in the interior of the solution.

(1) E. J. Hoffman, G. E. Boyd and A. W. Ralston, *THIS JOURNAL*, **64**, 498 (1942).

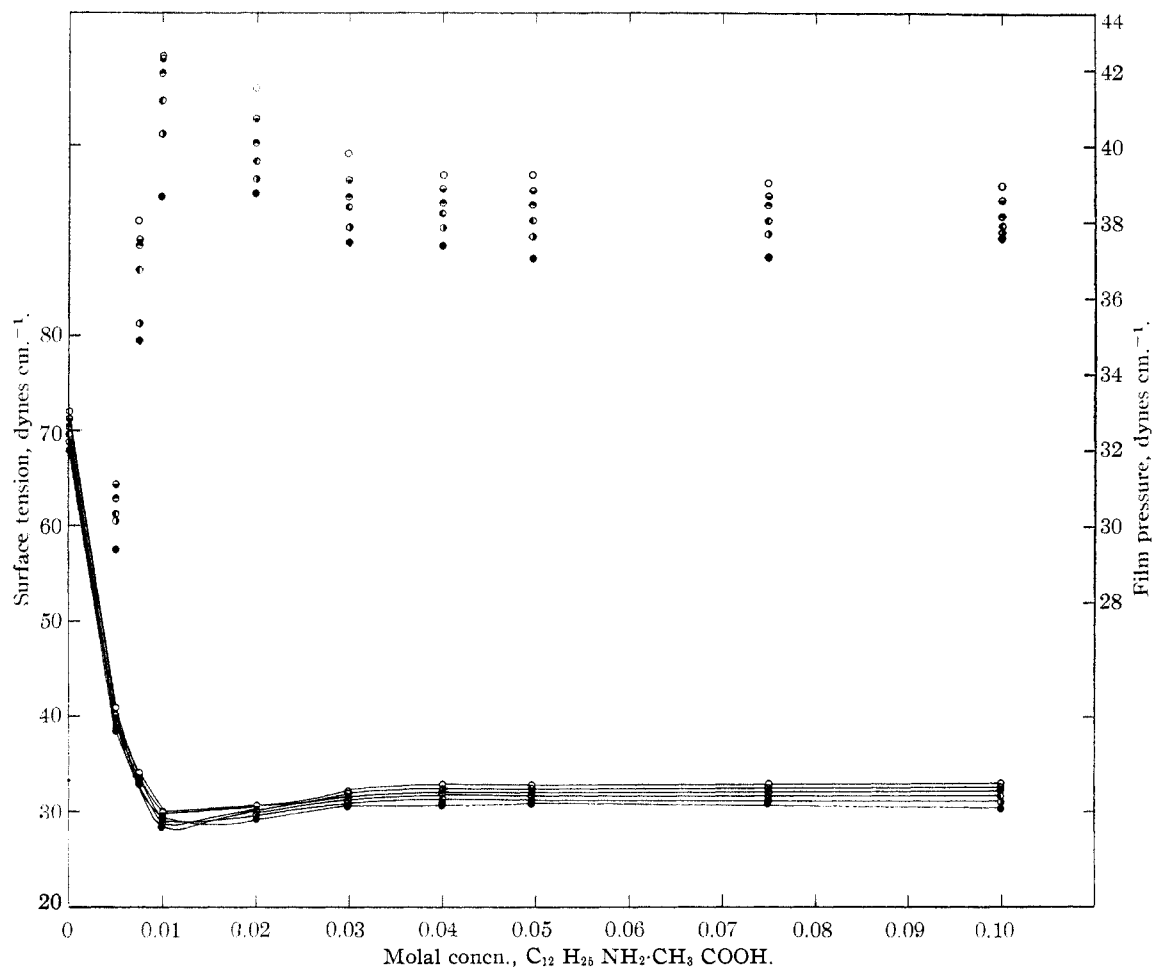


Fig. 1.—(a) Surface tension-concentration curves for aqueous solutions of dodecylamine acetate; (b) film pressure-concentration values for aqueous solutions of dodecylamine acetate: ○, 25°; ◐, 30°; ◑, 35°; ◒, 40°; ◓, 45°; ●, 50°.

Experimental Part

Preparation of Materials. Dodecylamine Acetate.—Dodecylamine acetate was prepared by the method previously described.² Solutions were made with triple distilled water as described in an earlier communication.¹ Densities of the solutions were determined by means of a 25-ml. pycnometer by C. W. Hoerr of the Armour Research Laboratories.

Apparatus and Procedure.—Surface tensions were determined at five degree intervals from 25 to 50° by the ring method with the apparatus used by Harkins and Jordan.³ The ring used was made of platinum-iridium, and its mean radius was 0.6402 cm.; the value of R/r was 45.64, where R is the mean radius of the ring, and r is the mean radius of the wire.

(2) A. W. Ralston, C. W. Hoerr and E. J. Hoffman, *THIS JOURNAL*, **63**, 2576 (1941).

(3) W. D. Harkins and H. F. Jordan, *ibid.*, **52**, 1751 (1930).

Experimental Results

Surface tension-concentration curves at five-degree intervals from 25 to 50° are shown in Fig. 1. A plot of the film pressure, $\pi = -\Delta\gamma = \gamma_0 - \gamma$, where γ_0 is the surface tension of water and γ is the surface tension of the solution, against concentration is also shown. The latter plot has the advantage that the values are separated so that the effect of temperature is more clearly demonstrated.

Discussion

It is evident from an examination of the curves in Fig. 1 that the surface tension of solutions of dodecylamine acetate of concentrations above that exhibiting a minimum value decreases with increasing temperature. At lower concentrations this is true except for the surface tension at 40°. A slightly deeper minimum is obtained at 40° than at any other temperature investigated. A

similar behavior was observed in the study of the surface tension of aqueous solutions of dodecylamine hydrochloride.¹

An examination of the values for the film pressure (Fig. 1) shows that at a given concentration it decreases with increasing temperature and that the value of $-\Delta\pi/\Delta T$ is fairly constant in the range 25 to 50°. The fact that, at a constant concentration, the film pressure decreases with increasing temperature shows that adsorption of dodecylamine acetate in the surface is less at higher temperatures. Between concentrations of approximately 3×10^{-2} and $10^{-1} N$ the film pressure does not change greatly with the concentration although this change is slightly greater at higher temperatures than at 25°.

The surface tension-concentration curves for aqueous solutions of dodecylamine acetate are similar to those obtained by us for dodecylamine hydrochloride¹ and by other investigators for anionic colloidal electrolytes.⁴ A comparison of the concentration for minimum surface tension with that for the break in the conductance curve⁵ shows that they are essentially the same. This is the so-called critical micelle concentration.

B. Pressure-Area Relations of Docosylamine Acetate Monolayers on Acetic Acid

Introduction

In a previous publication¹ we have reported a systematic study of the effect of inorganic anions on insoluble films of long-chain amines. In 1930, N. K. Adam⁶ reported an extensive study of the variation of the character of amine films with *pH* in which the importance of the nature of the anion was noted. A portion of this investigation dealt with the use of an acetate buffer (*pH* 4.0) in which the total acetate concentration was $5 \times 10^{-2} N$. Adam reports that the insoluble films, even of eicosylamine, were gaseous and that that of hexadecylamine was one of the most perfect gaseous films ever found with insoluble substances. This last statement appears to be erroneous on the basis of our results since the film of octadecylamine acetate was so soluble that satisfactory pressure readings could not be obtained. Several trial runs were made by rapid compression of films of octadecylamine acetate to a con-

stant area and observing the change in pressure with time. There was a continuous decline of pressure with time with an approximately constant final value regardless of the initial pressure. Films spread on sub-solutions from which a film from a previous experiment had been removed by sweeping invariably gave higher pressures than the first film spread on $10^{-1} N$ acetic acid. In order to eliminate this difficulty, octadecylamine acetate was replaced by docosylamine acetate. The solubility effect was not observed in this case.

Experimental Part

Preparation of Materials. Docosylamine Acetate.—Docosylamine acetate was prepared by Dr. F. M. Garland of the Armour and Co. Research Laboratories by a method similar to that described for the preparation of octadecylamine acetate.²

Preparation of Sub-solutions.—Sub-solutions were prepared by diluting glacial acetic acid with double distilled water¹ to a concentration of $10^{-1} N$.

Apparatus and Procedure.—The film balance was that described in detail by Nutting and Harkins.⁷ One degree of the divided circle corresponded to 0.0634 dyne cm.^{-1} pressure on the float; the circle was read to 0.2° .

Docosylamine acetate (*ca.* 23 mg.) was weighed by means of a semi-micro analytical balance into a calibrated 25-ml. volumetric flask, dissolved in ethanol (95%, *ca.* 4 ml.), and diluted with purified benzene to 25 ml. This solution was stored in a 50-ml. ground-glass stoppered volumetric flask. Solutions were spread from a pipet (0.0722 ml. capacity) of the type described by Harkins and Anderson.⁸ A period of fifteen minutes after the spreading of the film was permitted before the experiment was started. Pressure readings were made at one-minute intervals on compression to various areas and also, in separate experiments, as rapidly as possible at a much smaller number of areas. Good agreement of results between these two methods was obtained. This indicates that loss due to solubility was negligible.

Experimental Results

Pressure-area isotherms for films of docosylamine acetate on a $10^{-1} N$ acetic acid sub-solution at 14.8, 19.9 and 24.9° are given in Fig. 2. At

(4) J. W. McBain and G. F. Mills, "Reports on Progress in Physics," V. 30 (1939).

(5) A. W. Ralston, C. W. Hoerr and E. J. Hoffman, *THIS JOURNAL*, **64**, 97 (1942).

(6) N. K. Adam, *Proc. Roy. Soc. (London)*, **A126**, 526 (1930).

(7) G. C. Nutting and W. D. Harkins, *THIS JOURNAL*, **61**, 1180 (1939).

(8) W. D. Harkins and T. F. Anderson, *ibid.*, **59**, 2189 (1937).

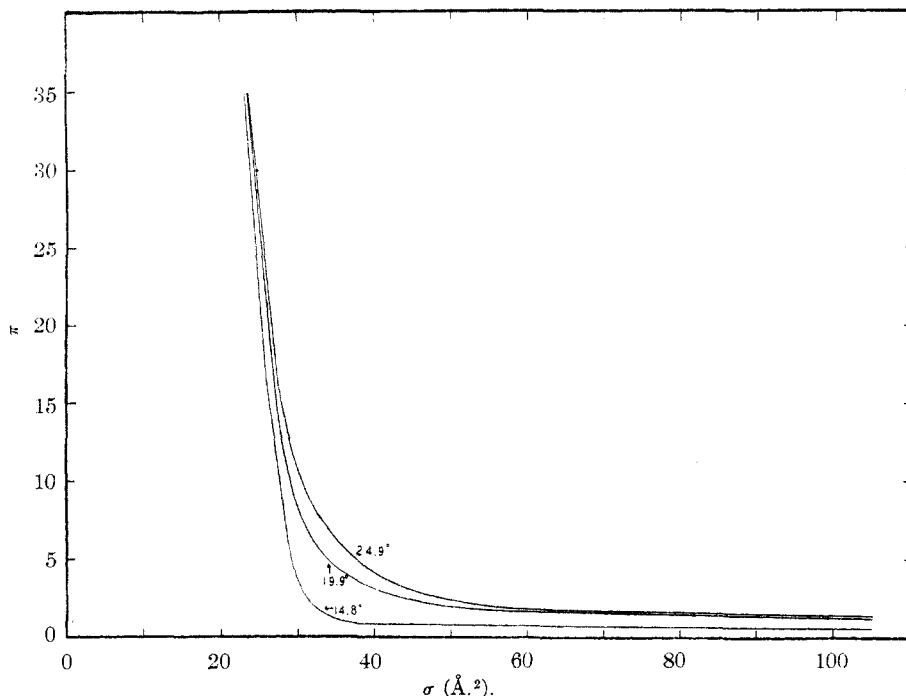


Fig. 2.—Pressure-area isotherms for docosylamine acetate monolayers on 10^{-1} *N* acetic acid.

large areas per molecule the film is vapor expanded in all three cases, but increased pressure produces condensed films.

The extrapolated area per molecule at zero pressure, at 14.8° is 27.9 sq. Å., at 19.9° it is 29.4 sq. Å. and at 24.9° it is 30.4 sq. Å.

The entropy of spreading is defined by the equation⁹

$$s_s = \frac{q_s}{T} = \left(\frac{\partial S}{\partial \sigma} \right)_T = \left(\frac{\partial \pi}{\partial T} \right)_\sigma$$

A plot of π against T for $\sigma = 35$ sq. Å. gives a value of 0.44 erg cm.⁻² deg.⁻¹ for s_s .

The increase of heat content on spreading may be calculated by use of the equation⁹

$$h_s = \left(\frac{\partial H_s}{\partial \sigma} \right)_T = - \left[\frac{\partial(\pi/T)}{\partial(1/T)} \right]_\sigma$$

At $\sigma = 35$ sq. Å., $h_s = 140$ ergs cm.⁻². This value is much lower than that obtained for octadecylamine hydrochloride.¹

Discussion

A comparison of the curves in Fig. 2 shows the effect of temperature on the pressure-area relations of monolayers of docosylamine acetate. They show the normal trend, the film becoming more

expanded with increasing temperature. The change between 14.8 and 19.9° is much greater than that in the range 19.9 to 24.9° . The isotherm at 14.8° much more closely approximates that of a true condensed film than does either one of the others.

Summary

1. The variation of surface tension of solutions of dodecylamine acetate with concentration has been investigated at a series of temperatures by the ring method.

2. A time effect was observed only at 25° in one solution below the critical concentration for micelle formation. This is in sharp contrast to the behavior of dodecylamine hydrochloride solutions previously reported.

3. It has been pointed out that monolayers of octadecylamine acetate are too soluble to permit investigation by means of the film balance.

4. Insoluble monolayers of docosylamine acetate spread on an acetic acid sub-solution have been investigated by means of the film balance.

5. An increase in temperature causes docosylamine acetate films to become more expanded. The heat of spreading at an area of 35 sq. Å. per molecule was estimated to be 140 ergs cm.⁻².

(9) W. D. Harkins, T. F. Young and G. E. Boyd, *J. Chem. Phys.*, **8**, 954 (1940).