

[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. V. Soluble and Insoluble Films of the Amine Hydrochlorides

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

A. The Surface Tension of Aqueous Solutions of Dodecylamine Hydrochloride

Introduction.—Previous investigations of the surface tension of aqueous solutions of paraffin-chain salts¹⁻⁴ have dealt usually with those substances which are colloidal anionic electrolytes. Extremely dilute solutions of these salts have exhibited surface tension-time effects in all cases, and a discussion of the various explanations for this phenomenon has been presented recently by Alexander.⁴ In the work reported in this paper, an examination of the surface properties of a simple, long chain *cationic* colloidal electrolyte was carried out, and a study of the influence of temperature variation on the time effect was made in the hope that a better understanding of this complex sequence might be reached.

Experimental

Preparation of Materials. Dodecylamine Hydrochloride.—Dodecylamine hydrochloride was prepared by the method previously described.⁵

Water.—The water used in this investigation was prepared by distilling ordinary distilled water from a mixture of phosphoric acid and potassium permanganate in a glass still and condensing in block tin condensers. The water thus obtained was redistilled in an all Pyrex glass still equipped with a distilling column. Fresh portions of water were prepared at least once a week.

Preparation of Solutions.—Solutions of various concentrations were prepared in 500-ml. ground-glass stoppered Erlenmeyer flasks by adding water to a weighed quantity of dodecylamine hydrochloride. The water was weighed by means of a large beam balance to a precision of at least one part in forty thousand. Buoyancy corrections were applied. Densities of the solutions were determined by means of a 25-ml. pycnometer by Mr. C. W. Hoerr of the Armour Research Laboratories.

Apparatus and Procedure.—Surface tensions of all solutions were determined at five-degree intervals from 25 to 50° by the ring method with the apparatus used by Harkins and Jordan.⁶ 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. The experimental procedure followed in the study of time effects was that described by Nutting, Long and Harkins.² In the study of the time effects, it was found to be impossible to obtain check results if the filled cup were merely overflowed and this time taken as zero. It was necessary to take the initial time as that when overflow occurred on *first* filling the cup.

Extreme care was taken in cleaning all of the glass apparatus. The flasks in which the solutions were prepared as well as the Pyrex ground-glass stoppered bottle in which the water was stored were cleaned with fresh chromic acid cleaning solution, rinsed repeatedly with distilled water, and steamed for at least thirty minutes prior to use. The surface tension flask was cleaned in a similar manner with the steam jet directed into the cup so that the inlet tube was also thoroughly cleaned. The cup was rinsed twice with the solution to be investigated.

The platinum-iridium ring was rinsed with distilled water and then flamed to redness prior to each experiment.

Results

Surface tension-concentration curves at five-degree intervals from 25 to 50° are shown in Fig. 1a. 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 shown in Fig. 1b. The plot in Fig. 1b has the advantage that the values are separated so that the effect of temperature is more clearly shown. Surface tension-time curves for dodecylamine hydrochloride at various temperatures at a concentration of $5 \times 10^{-3} N$ are shown in Fig. 2. After an initial rapid decrease, which occurs during the first few minutes, the decline becomes much slower and finally the surface tension is practically linear with time. The surface tension of this solution was still decreasing at the end of five hours, but it was not considered advisable to continue the experiments to a steady value because of the danger of contamination of the surface. Similar results were obtained by Adam and Shute⁷ in their study of cetylpyridinium bromide and cetyltrimethylammonium bromide, and it is suggested that the linear decrease may continue for weeks in the case of dilute solutions. An attempt was made to obtain the value

(7) N. K. Adam and H. L. Shute, *Trans. Faraday Soc.*, **34**, 758 (1938).

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

(2) G. C. Nutting, F. A. Long and W. D. Harkins, *THIS JOURNAL*, **62**, 1496 (1940).

(3) H. V. Tartar, V. Sivertz and R. E. Reitmeier, *ibid.*, **62**, 2375 (1940).

(4) A. E. Alexander, *Trans. Faraday Soc.*, **37**, 15 (1941).

(5) A. W. Ralston, E. J. Hoffman, C. W. Hoerr and W. M. Selby, *THIS JOURNAL*, **63**, 1598 (1941).

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

of γ at t_∞ , but the curves were of such a nature that this was unsuccessful. In Fig. 3 are shown the values of π plotted against time.

Discussion

It is evident from an examination of the curves in Fig. 1a that the surface tension of these solutions is almost independent of the temperature in the range 25 to 50° although the surface tension at 40° shows a slightly deeper minimum than the surface tensions at other temperatures. Beyond the minimum, the values at this temperature are in agreement with those at other temperatures well within the limits of experimental error.

An examination of the values in Fig. 1b shows that the film pressure at a given concentration actually 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 hydrochloride in the surface is actually less at higher temperatures. Between concentrations of approximately 2×10^{-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°.

It is seen from Fig. 2 that temperature has very little effect on the rate of attainment of equilibrium in the $5 \times 10^{-3} N$ solution. This may indicate a low activation energy for the adsorption process.

The surface tension-concentration curves for this cationic paraffin-chain salt are similar to those obtained by other investigators in a study of anionic colloidal electrolytes.¹ Thus it appears that the sign of the charge on the group containing the hydrocarbon chain is of little importance in determining the surface properties of

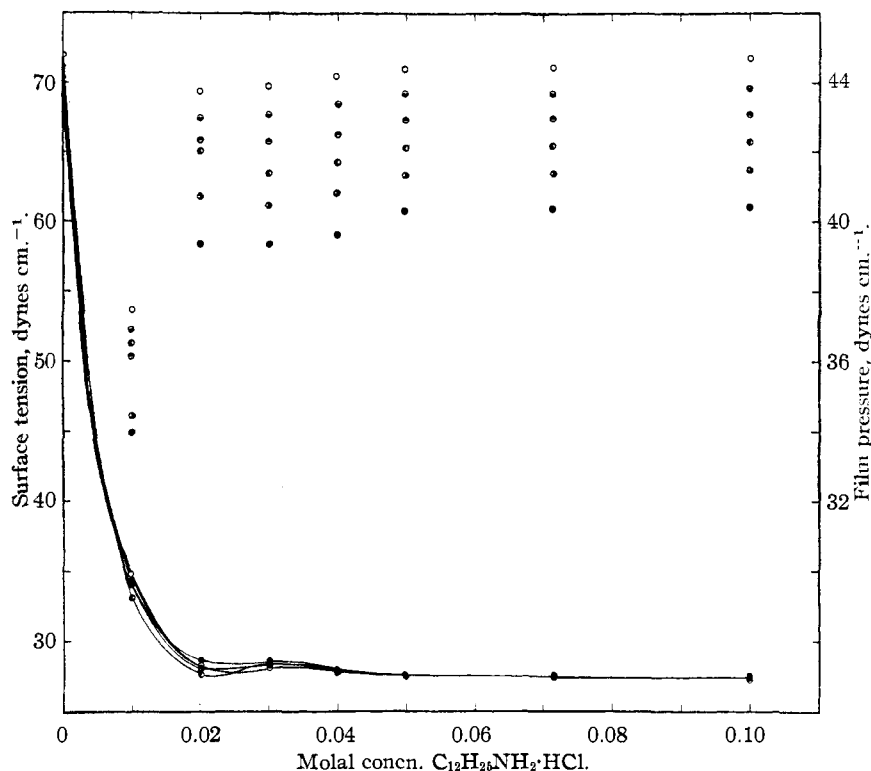


Fig. 1.—(a) Surface tension-concentration curves for aqueous solutions of dodecylamine hydrochloride; (b) film pressure-concentration values for aqueous solutions of dodecylamine hydrochloride: ○, 25°; ◐, 30°; ◑, 35°; ◒, 40°; ◓, 45°; ◔, 50°.

solutions of paraffin-chain salts. It is generally believed that the minimum in the surface tension-concentration curve is at the concentration at which micelles begin to form. This is the same concentration at which there is an abrupt decrease in the equivalent conductance. A comparison of the concentration for minimum surface tension with that for the break in the conductance curve⁸ shows that they are in reasonably good agreement. Time effects were observed only below this concentration as predicted by previous experimenters.

Although the results indicate a low activation energy, it is evident that the process cannot be one of simple diffusion since the duration of the time effect is much too great.²

B. Pressure-Area Relations of Octadecylamine Hydrochloride Monolayers on Various Sub-solutions

Introduction.—Up to the completion of this work, no systematic study of the effect of anions on insoluble films of long-chain amines had appeared in the literature. In 1930, N. K. Adam⁹

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

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

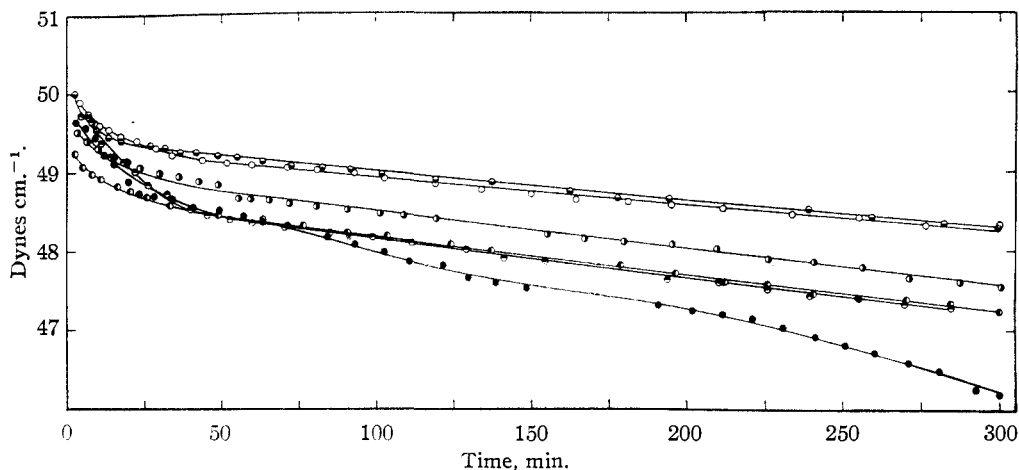


Fig. 2.—Surface tension–time curves for $5 \times 10^{-3} N$ dodecylamine hydrochloride solution: \circ , 25° ; \ominus , 30° ; \bullet , 35° ; \odot , 40° ; \ominus , 45° ; \bullet , 50° .

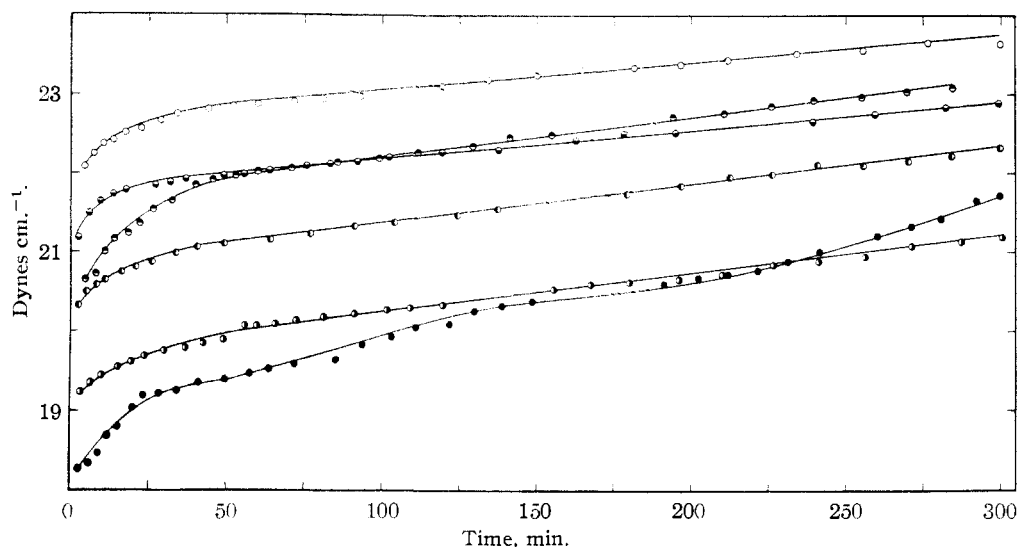


Fig. 3.—Film pressure–time curves for $5 \times 10^{-3} N$ dodecylamine hydrochloride solution: \circ , 25° ; \ominus , 30° ; \bullet , 35° ; \odot , 40° ; \ominus , 45° ; \bullet , 50° .

reported an extensive study of the variation of the character of these films with pH in which the importance of the nature of the anion was noted. The general observations made by him on the films on acid sub-solutions have been confirmed by us, and, in the one experiment in common, namely, that on $10^{-2} N$ sulfuric acid at 20° , good agreement was obtained. However, the large change in the packing of this amine sulfate with temperature found by Adam has not been confirmed by this research.

Experimental

Preparation of Materials: Octadecylamine hydrochloride was prepared by the method previously described.⁵

Water.—The water for the preparation of the sub-solutions was that obtained from the initial distillation de-

scribed in Part A. It was stored in Pyrex flasks which had been cleaned in the manner described above for the apparatus used in the surface tension experiments.

Preparation of Sub-solutions.—Sub-solutions were prepared by dilution of purified samples of the appropriate acids with water to a concentration of approximately $10^{-2} N$.

Apparatus and Procedure.—The film balance was that described in detail by Nutting and Harkins.¹⁰ One degree of the divided circle corresponded to 0.0634 dyne cm^{-1} pressure on the float; the circle was read to 0.2° .

Octadecylamine hydrochloride (*ca.* 14 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 ligroin to 25 ml. This solution was stored in a 50-ml. ground-glass stoppered volumetric flask in a desiccator flask over ligroin to prevent

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

TABLE I				
Compound	h_s , erg cm. ⁻²	s_s , erg cm. ⁻² deg. ⁻¹	Remarks	Ref.
C ₁₄ H ₂₉ COOH	278	0.959	$t = 20^\circ$; $\sigma = 34.3 \text{ \AA}^2$	12
C ₁₈ H ₃₇ COOH	230		$\sigma = 35.4 \text{ \AA}^2$	12
C ₁₆ H ₃₃ COOC ₂ H ₅	ca. 200		$t = 15^\circ$	13
C ₁₅ H ₃₁ COOC ₂ H ₅			$t = 14^\circ$	
C ₁₄ H ₂₉ COOC ₂ H ₅			$t = 15^\circ$	
C ₁₃ H ₂₇ COOC ₂ H ₅			$t = 15^\circ$	
C ₁₇ H ₃₅ CN	154	0.537	$t = 20^\circ$; $\sigma = 32 \text{ \AA}^2$	14
C ₁₈ H ₃₇ NH ₂ ·HCl	320	1.04	$t = 25^\circ$; $\sigma = 35 \text{ \AA}^2$	<i>This paper</i>

evaporation. Solutions were spread from a pipet (0.0722 ml. capacity) of the type described by Harkins and Anderson.¹¹ A period of fifteen minutes after the spreading of the film was permitted before the experiment was started. Because of the possibility of loss of some of the film material by solubility at high film pressures, compressions were made as rapidly as possible. Repeated experiments under varying conditions later indicated that error due to this source must be very small indeed. For example, the position of the isotherms did not change throughout wide variations in the rate of compression. Furthermore, at no time were values for the area per molecule observed less than 20.5 Å.² the limiting value for close packed hydrocarbon chains.

Experimental Results

Pressure-area isotherms for films of octadecylamine hydrochloride on a 10⁻² N hydrochloric acid sub-solution at 19.9, 25.1, and 30.3° are given in Fig. 4. At large areas per molecule the film is vapor expanded in all three cases, but increased pressure produces condensed films. A plot of πσ (π = pressure and σ = area per molecule) against π indicates that below the kink point the film is a very imperfect gas.

The entropy of spreading is defined by the equation¹²

$$s_s = \frac{q_s}{T} = \left(\frac{\partial S}{\partial \sigma}\right)_T = \left(\frac{\partial \pi}{\partial T}\right)_\sigma \quad (1)$$

A plot of π against T for σ = 35 Å.² gives a value of 1.04 erg cm.⁻² deg.⁻¹ for s_s.

The increase of heat content on spreading may be calculated by use of the equation¹²

$$h_s = \left(\frac{\partial H_s}{\partial \sigma}\right)_T = - \left[\frac{\partial(\pi/T)}{\partial(1/T)}\right]_\sigma \quad (2)$$

At σ = 35 Å.², h_s = 320 erg cm.⁻².

Harkins and Boyd¹³ have investigated the ethyl esters of the aliphatic acids containing from fourteen to seventeen carbon atoms inclusive as well as myristic and pentadecylic acids, and Copeland¹⁴ has studied films of stearonitrile. The results of these investigations have been included

(11) W. D. Harkins and T. F. Anderson, *THIS JOURNAL*, **59**, 2189 (1937).
 (12) W. D. Harkins, T. F. Young and G. E. Boyd, *J. Chem. Phys.*, **8**, 954 (1940).
 (13) W. D. Harkins and G. E. Boyd, *J. Phys. Chem.*, **45**, 20 (1941).
 (14) L. E. Copeland, unpublished results.

in Table I with our result for purposes of comparison of the effect of head groups.

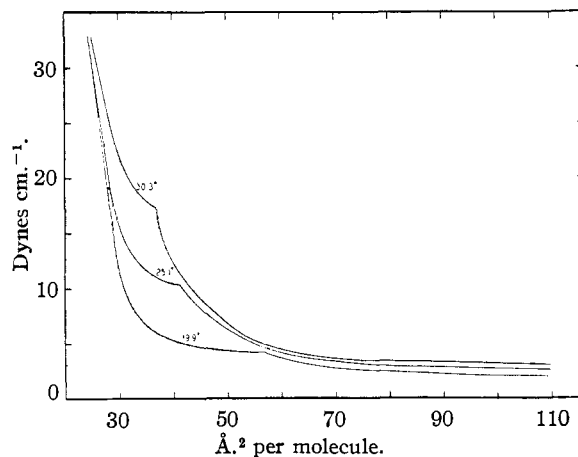


Fig. 4.—Pressure-area isotherms for octadecylamine hydrochloride monolayers on 10⁻² N hydrochloric acid.

Pressure-area isotherms at 25.0° for octadecylamine hydrochloride spread on the following 10⁻² N acids: (1) hydrochloric, (2) hydrobromic, and (3) hydriodic are given in Fig. 5. In the last two cases the films are undoubtedly those of the octadecylamine hydrobromide and octadecylamine hydriodide since a film of octadecylamine spread on hydriodic acid gave the same results as a

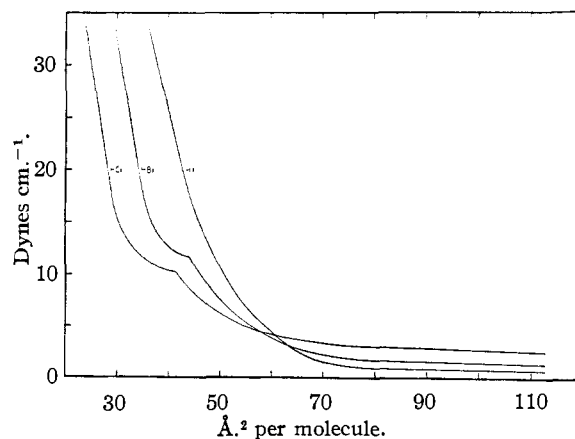


Fig. 5.—Pressure-area isotherms (25°) for octadecylamine hydrochloride monolayers.

film of octadecylamine hydrochloride spread on the same sub-solution. At large areas per molecule, the amine hydrobromide gives an expanded film exerting a lower pressure than the amine hydrochloride film, but the two curves cross ($\sigma = 58 \text{ \AA}^2$ and $\pi = 4.35 \text{ dynes cm.}^{-1}$), and the remaining portion of the amine hydrobromide film exerts a greater pressure than the amine hydrochloride film at corresponding areas. The kink point is raised from $\sigma = 41.3 \text{ \AA}^2$ and $\pi = 10.35 \text{ dynes cm.}^{-1}$ to $\sigma = 44.2 \text{ \AA}^2$ and $\pi = 11.15 \text{ dynes cm.}^{-1}$. At large areas per molecule, the amine hydriodide gives an expanded film exerting a lower pressure than either the amine hydrochloride or the amine hydrobromide film. It crosses both curves (the hydrobromide curve at $\sigma = 62.6 \text{ \AA}^2$ and $\pi = 3.25 \text{ dynes cm.}^{-1}$ and the hydrochloride curve at $\sigma = 60.8 \text{ \AA}^2$ and $\pi = 4.00 \text{ dynes cm.}^{-1}$). The amine hydriodide film remains as an expanded film to the point of collapse.

Pressure-area isotherms at the same temperature for octadecylamine hydrochloride spread on the following $10^{-2} N$ acids: (1) perchloric, (2) nitric, (3) sulfuric, (4) chromic, and (5) phosphoric are given in Fig. 6. The film on the chromic acid sub-solution was completely condensed; the films on nitric and sulfuric acids were expanded at low pressures; and the films on the remaining acids were expanded at all pressures.

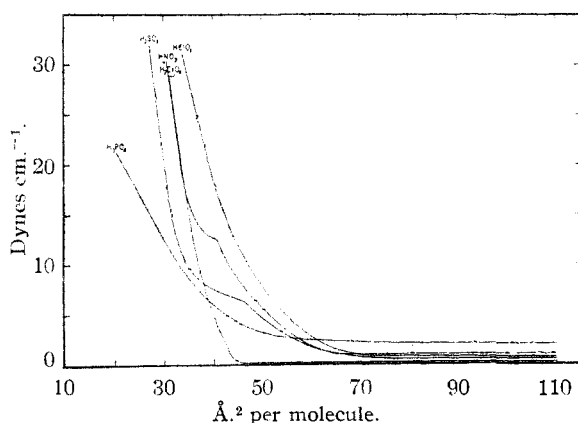


Fig. 6.—Pressure-area isotherms (25°) for octadecylamine oxygen-acid-salt monolayers.

Discussion

A comparison of the curves in Fig. 5 shows the effect of temperature on the pressure-area relations of mono-layers of octadecylamine hydrochloride. They show the normal trend, the film becoming more expanded with increasing temperature.

The effect of changing the head group on the characteristics of octadecylamine hydrohalide films is shown by a comparison of the curves in Fig. 5. The van der Waals forces of attraction for the halide ions is in the following order: $I^- > Br^- > Cl^-$. It appears that these forces may be responsible for the fact that at large areas the amine hydriodide film exerts a lower pressure than the amine hydrobromide film which in turn exerts a lower pressure than the amine hydrochloride film. At smaller areas the size of the anionic head group appears to be the determining factor in the behavior of the films since the area at high pressure increases with increasing size of the head group. All three films collapse at pressures of approximately $30 \text{ dynes cm.}^{-1}$.

It is of interest to point out that the ratio of the molecular areas of the amine salts at $30 \text{ dynes cm.}^{-1}$ of the halogen acids is nearly the same as the ratio of the squares of the ionic radii of the halide ions. This cannot mean that the halide ions are close packed at these areas, however, since the areas in the film are considerably too large. The possibility of appreciable hydration of these ions may not be excluded.

The only evident regularity shown by the oxygen acids is that with increasing valence of the anion the film may be condensed to smaller limiting areas per molecule at high film pressures. The relatively high vapor pressure shown at large molecular areas by the amine phosphate film is not easily explained. A comparison of perchloric and nitric acids is in point since the anions in both cases are of the same charge and cross-sectional area,¹⁵ and, therefore, similar characteristics might be expected. As may be seen from Fig. 6, specific effects seem to be of greater importance than simple stereochemistry. This conclusion appears to hold in the comparison of sulfuric and chromic acids also.

Studies of the effects of organic anions, pH , and of film viscosities are in progress.

The authors wish to thank Professor W. D. Harkins for his participation in many stimulating conversations during the course of this work.

Summary

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

(15) W. L. Bragg, "Atomic Structure of Minerals," Cornell University Press, Ithaca, N. Y., 1937, p. 30.

2. Time effects of long duration were encountered in solutions below the critical concentration for micelle formation.

3. Insoluble monolayers of octadecylamine hydrochloride spread on various sub-solutions have been investigated by means of the film balance.

4. An increase in temperature causes octadecylamine hydrochloride films to become more expanded. The heat of spreading at an area of

35 Å.² per molecule was estimated to be 320 ergs cm.⁻². This value was compared with values for other insoluble films possessing different polar groups.

5. An increase in the size of the anion in the case of the hydrohalide films at small areas gives the effect of increased temperature.

6. The behavior of oxygen acid salts of octadecylamine has been studied.

CHICAGO, ILLINOIS

RECEIVED AUGUST 4, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

Hydrous Cupric Hydroxide and Basic Cupric Sulfates

By HARRY B. WEISER, W. O. MILLIGAN AND E. L. COOK

The hydrous blue gel thrown down by the addition of a base to a cupric salt solution is transformed into black cupric oxide at a rate which depends on the conditions of formation and subsequent treatment. A survey of the literature¹ concerned with the composition and stability of the blue gel discloses certain moot questions which are cleared up, at least in part, by the following phase rule and X-ray diffraction study.

I. The System CuO-H₂O

The blue gelatinous mass obtained by the addition of dilute alkali to a cupric salt solution is hydrous cupric hydroxide which gives an X-ray diffraction pattern distinct^{2,3} from that of black cupric oxide formed by its decomposition. Earlier investigators claimed to have prepared a number of hydrates of cupric oxide varying in composition from CuO·3H₂O to 8CuO·H₂O.¹ Since the samples analyzed were not obtained under equilibrium conditions, the compositions formulated were the accidental result of the conditions of drying. More recently, however, Losana⁴ concluded from dehydration isobars that the decomposition of cupric hydroxide under suitable conditions may yield definite lower hydrates corresponding to 3, 4, 6, and 8 moles of cupric oxide per mole of water. This conclusion was questioned by Champetier and Thuau⁵ who dehydrated cupric hy-

droxide at 105° and, at intervals, removed samples which were examined by X-ray diffraction methods. The diffraction data disclosed the existence of only two crystalline phases, the patterns being for cupric hydroxide or cupric oxide or for a mixture of the two. At 105° the decomposition of cupric hydroxide is fairly rapid, and therefore, unfortunately, the sample was probably never in equilibrium during the dehydration; hence the alleged hydrates claimed by Losana may have been passed over because of too rapid decomposition of the hydroxide. Accordingly, the more comprehensive experiments reported in the following paragraphs were carried out.

Experimental

Preparation of Stable Samples of Cupric Hydroxide.—

Under otherwise constant conditions, the rate of the transformation at room temperature of cupric hydroxide to cupric oxide is higher the smaller the crystals of the hydroxide. Relatively large crystals, sufficiently stable for accurate phase rule studies, may be obtained in several ways.¹ Two samples were prepared: one by a modification of Böttger's⁶ method and a second by the slow decomposition of complex cupric-ammonia hydroxide.

Sample 1.—Following Böttger's general procedure, a green basic salt⁷ was precipitated from boiling *N* cupric sulfate solution by the slow addition of 6 *N* ammonium hydroxide until the blue color of the cupric ammonia complex just began to appear in the supernatant solution. After the green precipitate had been washed several times to remove excess sulfate ions, it was placed in an evaporating dish and triturated with 5% sodium hydroxide solution to convert it into cupric hydroxide. The preparation was washed by the aid of a centrifuge until the wash water gave no test for sulfate ions with barium chloride, and was then

(1) Weiser, "Inorganic Colloid Chemistry," Vol. II, John Wiley and Sons, New York, N. Y., 1935, p. 149.

(2) Posnjak, unpublished results reported at the 76th meeting of the American Chemical Society, Swampscott, Mass., September, 1928.

(3) Neville and Oswald, *J. Phys. Chem.*, **35**, 60 (1931).

(4) Losana, *Gazz. chim. ital.*, **53**, 75 (1923).

(5) Champetier and Thuau, *Compt. rend.*, **194**, 93 (1932); cf. Levi, *Giorn. chim. ind. applicata*, **12**, 97 (1930).

(6) Böttger, *Jahrsberichte*, 198 (1858).

(7) The X-ray diffraction pattern of this green material is identical with the pattern designated as 4CuO·SO₄·3H₂O in diagram 8, Fig. 4.