specific effect one would expect that per unit total surface area the promoted catalyst would be at least 50 to 75% less active than the pure iron catalyst. This seems to be the case. Five grams of catalyst 931 was only about 1/60 as active at −79° as 17.9 g. of pure iron. The total surface area of the 5 g. of 931 is about the same as that of the 17.9 g. of pure iron. At −50° the rate on the 5 g. of catalyst 931 is about 1/15 of that on 17.9 g. of catalyst 973 in spite of the fact that the run on the latter catalyst was made with hydrogen containing some unidentified poison. The inhibitive effect of the promoter over the −50 to −79° range seems, therefore, to be definite. Its exact magnitude cannot be stated with certainty, however, until additional experiments have been carried out.

Throughout the present work it was noted that the total pressure decrease during an experiment corresponded invariably to that expected for the hydrogenation of ethylene to form ethane. There seemed to be little doubt, therefore, that the hydrogenation rather than the polymerization of ethylene was the principal reaction occurring. Nevertheless, in one reaction rate experiment on a 50:50 hydrogen: ethylene mixture the gas re-remaining at the end of the run was freed of 2.6% ethylene which it contained and then passed into a trap at −100°. Complete condensation occurred, indicating that the product was ethane and that no free hydrogen remained. Accordingly, no appreciable amount of ethylene polymerization was occurring in the present experiments.

Summary

The hydrogenation of ethylene in the presence of pure and promoted iron synthetic ammonia catalysts has been studied between −40 and −89°. The reaction on the promoted iron catalyst in this temperature region was considerably slower than on unpromoted iron. The promoter of the synthetic ammonia catalyst appears to inhibit the hydrogenation of ethylene.

Evidence has been presented which indicates that the activated adsorption of hydrogen alone is involved in the reaction, ethylene being physically adsorbed. The lower temperature type of activated hydrogen adsorption plays the dominant part in the reaction.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Surface Electrification Due to the Recession of Aqueous Solutions from Hydrophobic Surfaces

BY IRVING LANGMUIR

Porter and Wyman[1] have shown that calcium stearate multilayers of X-type deposited on a metallic plate give contact potentials of about 70 mv. per layer. Thus with a film of 100 layers there is a potential difference of about 7 v. in the air between a point just above the stearate layer and another point in the air close to the bare metal surface. This potential in the air, which Porter and Wyman have measured, suggests that there is an internal polarization in the film.

If the plate bearing the film is immersed in water, the external field is short circuited by the water because of its relatively high conductivity and thus a current flows through the water until surface charges have been delivered to the film and the underlying metal which are sufficient to compensate for the original polarization.

Since the plate after being withdrawn from the water possesses the same contact potential as before dipping, it must follow that the act of withdrawal restores the original electric condition of the surface.

A contact potential such as that observed by Porter and Wyman may be due to one or more of the three following factors:

1. Internal Dipoles.—If the film is built up of layers of polar molecules all oriented in one direction, there should be a definite number of fixed dipoles per unit volume. Let m be the dipole moment per unit volume. If t is the thickness of the film, and D is the dielectric constant, the effect of the dipoles is to cause an apparent contact potential V equal to

$$V = (4\pi/D) \int m\mathrm{d}t \qquad (1)$$

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[1] E. F. Porter and J. Wyman, Jr., THIS JOURNAL, **59**, 2746 (1937).

Besides the fixed dipoles there may be dipoles which are free to turn in any direction and which contribute to the dielectric constant, as considered in the Debye theory.

2. Surface Charges.—A surface charge of σ elementary charges ($+e$) per unit area on the outside layer of a built-up film, together with the corresponding induced surface charge ($-\sigma e$) at the surface of the underlying metal, gives an apparent contact potential of

$$V = 4\pi\sigma e t/D \qquad (2)$$

3. Internal Surface or Volume Charges.—During the building process, surface charges may be covered by subsequent layers so that internal charges are built into the film. Under the influence of intense fields a redistribution of these charges throughout the volume of the film may occur. It is also possible that if the films are subjected to an intense field sufficient conductivity of the film will occur to carry surface charges into the interior. The potential which results from such internal charges may be calculated by the Poisson equation.

Let us examine the experimental data of Porter and Wyman, including those given in their second paper,[2] to determine the relative importance of these three factors in their contributions to the contact potential.

If we assume that the observed polarization is due to the presence of internal dipoles, there would be no free surface charge with the film in air, but when the plate is immersed in water, there would have to be a surface charge σe sufficient to neutralize the external field. If this field is to reappear when the plate is taken out of the water, it is necessary that this surface charge σe shall be removed from the surface by the act of withdrawing the plate. This could not occur if the plate were hydrophilic, for it would then be covered with a relatively thick film of water, the charge being bound at the interface between the water and the multilayer. If, however, the surface is hydrophobic so that it sheds water and comes out dry, there is a definite line of contact between the water and the film along which the recession of the water from the film takes place. This line of contact can have a width of only a few Ångströms so that, with a surface tension of the order of 40 dynes/cm., the intensity of the force corresponds to a pressure of about 1000 atmospheres.

When the film is under water some of the ions, particularly the polyvalent ones, may be adsorbed by the film. As the contact line passes over the surface of the film, some of these adsorbed ions may remain attached to the film, thus producing a surface charge σe, or the ions may be torn away from the surface by the strong forces and so pass into the water phase. The high dielectric constant of the water would suggest that normally relatively few ions remain on a hydrocarbon surface. If the surface charge is removed in this way the external field due to the internal dipoles reappears when the plate is withdrawn from the water. The recession of the water boundary from the hydrophobic surface is essential for the restoration of the contact potential.

On the basis of the foregoing hypothesis, the differences between the X- and the Y-films should be due to the presence of dipoles in the X-films and their absence in the Y-films. In this case the total potential in any film built of X- and Y-films should according to Eq. (1) be proportional to the number of X-layers and independent of the number of Y-layers.

Porter and Wyman in their second paper show that the total potential of a composite film is brought nearly to zero by the addition of one or two pairs of Y-layers, whereas a very few X-layers raise the potential to nearly as high a value as if the whole film were built of X-layers, giving potentials which are approximately proportional to the total thickness of the film, regardless of the relative numbers of X- and Y-layers. This unexpected result seems to indicate that the major cause of the observed contact potential is a surface electrification produced by withdrawing the film from water.

Let us assume that we have a film which contains no internal dipoles but which acquires a surface charge σe on being withdrawn from water. It is evident then from Eq. (2) that the contact potential will increase in proportion to the number of layers.

The surface charge σe depends only upon the nature of the last layer which is deposited and upon the composition of the water, for example, on the *p*H and presence of certain cations, but not upon the composition of the internal layers.

The observations of Porter and Wyman are thus consistent with the hypothesis that the Y-films are uncharged when they come out of the water, while the X-films carry a positive charge

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[2] E. F. Porter and J. Wyman, Jr., THIS JOURNAL, **60**, 1083 (1938).

sufficient to give an apparent polarization of 70 mv./layer; which, according to Eq. (2), taking $D = 2.56$, corresponds to $\sigma = 4 \times 10^{11} +$ ions per sq. cm., or only 1 ion for every 1200 stearic acid molecules in the surface.

This difference between the X- and Y-films seems to be primarily due to the fact that the X-films are deposited from a solution of *p*H 9.5, while the Y-films are built from a solution of *p*H 7.

During the building of X-films there is the possibility of the development of a surface charge as a kind of frictional electrification, resulting from the slipping of the water surface, with its stearate monolayer, past the film on the plate while this is being withdrawn from the water during the up-trip (no film is deposited during this up-trip). When Y-layers are formed, the up-trip brings the two hydrophilic surfaces of the A- and B-layers together, and the water is expelled by cohesive forces between these surfaces, but there is no slipping of one layer past another. Thus it would seem that conditions do not favor the formation of surface charges on Y-layers.

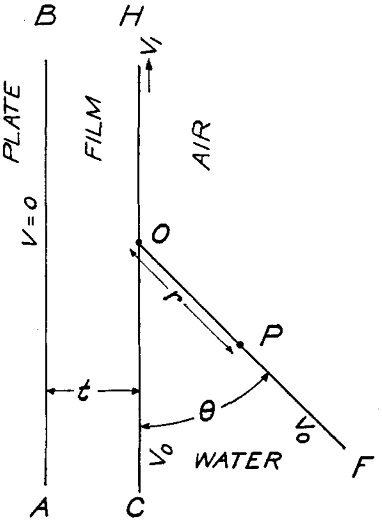

Fig. 1.

Dr. F. J. Norton, of this Laboratory, has repeated many of Porter and Wyman's experiments and has also studied the effect of dipping X- and Y-films into water containing various salts at different *p*H's. These experiments also indicate that the composition of the solution is apparently a far more important factor in determining the value of σ than is the nature of the outside deposited layer.

Dr. Blodgett recently has found that lead stearate X-films can be built at *p*H 5.8. These give no contact potentials that increase with the number of layers. This supports the conclusion that it is the *p*H of the solution rather than the peculiar properties of X-films that gives high potentials. We have found no case in which Y-layers give potentials increasing with the number of layers.

If a film is rendered hydrophilic by dipping into a solution of aluminum chloride or thorium nitrate, it loses all surface charge, regardless of its previous condition. The progressive differences in the contact potential caused by repeated dippings into water solutions are apparently due to partial skeletonization of the film by the removal of stearic acid, thus modifying the surface so that the tendency to pick up ions from the water is changed.

By applying potentials of a few volts between the plate and the metallic tray during the deposition of stearate monolayers, it has been found possible to alter the surface charge σe on X- or Y-films and to obtain either positive or negative values of σe over wide ranges in *p*H.

Dr. Norton also has applied surface charges to stearate films on metal by ionizing the air above the film by means of polonium and by applying various potentials. He is able in this way to charge the films to voltages of about 0.9 v./layer With more intense fields currents can be made to pass through the films. It is planned to investigate the effect of such currents in producing volume charges within the film. We believe that internal charges can be recognized by time-lag effects like those of the residual charges in Leyden jars. Secondary effects associated with redistributions of internal charges are probably responsible for some of the phenomena observed by Porter and Wyman which indicate departure from the simple theory of surface charges which is here proposed as an explanation of the main features of the phenomena.

The surface charge σe left on the X-films after each up-trip must theoretically modify the contact angle Θ and must produce electric fields parallel to the surface which tend to limit the development of the charge.

Let BA in Fig. 1 represent the cross section of the surface of a metallic plate on which there is a deposited film of thickness t whose other surface is CH. Consider that the plate is being raised out of water which gives a contact angle Θ against the film. Thus OC is the film–water interface, OF the water–air interface, and OH the film–air interface on which a positive surface charge σe is left by the receding water.

Let the potential of the metallic plate be zero and V_0 be the potential of the water along OC and OF.

The potential on the surface OH increases from V_0 at O toward a limiting value V_1 at distances from O which are large compared to t. Here

$$V_1 = 4\pi\sigma e t/D \qquad (3)$$

By means of a Schwartz–Christoffel transformation it is possible when $D = 1$ to calculate the potential distribution in terms of an auxiliary complex variable η. The electric field at the surface OF is perpendicular to OF and is of an intensity E given by[3]

$$E = D\,(V_0 - V_1)/t\;\eta^\alpha \qquad (4)$$

where

$$\alpha = (\pi - \Theta)/\pi \qquad (5)$$

Θ being expressed in radians. On the surface OF, η is real and is defined by

$$r = (t/\pi D)\int_0^\eta \eta^\alpha \mathrm{d}\eta/(1 + \eta) \qquad (6)$$

where r is the distance of the point P, on the surface OF, from the contact line represented by O. For values $\eta \ll 1$ the relation between r and η is given approximately by

$$r = (t/D\pi)\eta^2[\ln\,(1 + \eta) - \alpha\eta/(1 + \alpha) + \alpha\eta^2/4(1 + \alpha/2) -] \qquad (7)$$

At large distances, $\eta \gg 1$, we have

$$r = (t/D\pi)\eta^\alpha[(1/\alpha) + \ln\,(1 + 1/\eta) + \alpha/\eta - \alpha/4\eta^2 +] - (t/DR)\,[(1/\alpha) + \alpha\pi^2/6] \qquad (8)$$

The field E exerts a pressure $-E^2/8\pi$ on the water surface OF whose integral from $r = 0$ to $r = \infty$ (per cm. of length of contact line) is

$$F = (1/8\pi)\int_0^\infty E^2\mathrm{d}r = D(V_1 - V_0)^2G/8\pi^2t\alpha(1 - \alpha) \qquad (9)$$

where G is a function of α that varies only between the limits of 1.00 (at $\alpha = 0$ and at $\alpha = 1$) and 0.785 (at $\alpha = 1/2$) and is expressed in terms of gamma functions by

$$G = \Gamma(1 + \alpha)\cdot\Gamma(2 - \alpha) \qquad (10)$$

The "force" F has the dimensions of a surface tension, dynes/cm., and its effect is to decrease the contact angle Θ by an amount

$$\Delta\Theta = F/\gamma \qquad (11)$$

where γ is the surface tension of the water surface DF. The work of adhesion W ordinarily given by

$$\Delta W = \gamma(1 + \cos\Theta) \qquad (12)$$

is increased by an amount

$$W = F\sin\Theta \qquad (13)$$

Very close to the contact line O the field E can be obtained by eliminating η from Eqs. (4) and (7), taking only first order terms

$$E = [D(V_0 - V_1)/t](t/D\pi r)^{\alpha/(1+\alpha)} \qquad (14)$$

Let us apply these equations to an X-film of N layers which give a contact potential of 70 mv./layer. We take $D = 2.56$; $V_0 = 0$; $V_1 = 0.070\,N$ volt cm.$^{-1}$, and $t/N = 24.4 \times 10^{-8}$ cm. as found for barium stearate films in this Laboratory, and obtain

$$E = 7.3 \times 10^5\,(3.03 \times 10^{-8}N/r)^{\alpha/(1+\alpha)}\ \text{v./cm.} \qquad (15)$$

and, if $G = 0.8$

$$F = 0.006\,N/\alpha(1 - \alpha)\ \text{dynes/cm.} \qquad (16)$$

If the contact angle $\Theta = 90°$ (about right for X-films), $\alpha = 0.5$ and thus E varies in inverse proportion to the cube root of r and reaches values of 10^6 v./cm. when $r = 1.2 \times 10^{-8}N$. Thus with 50 layers the field of 10^6 v./cm. would extend to a distance of 60 Å., while at a distance of 6 Å. the field would be 2.15×10^6 v./cm., a not unreasonably large value. If, however, we should build a film of 500 layers, the field at $r = 6$ Å. would be 4.6×10^6 v./cm. There should thus be some limiting thickness of film beyond which the contact potential no longer increases in proportion to N. Porter and Wyman's data seem to show such a limit at about 200 layers.

By Eqs. (16) and (11), taking $\gamma = 40$ dynes/cm. (for a monolayer under oleic acid pressure), the change of contact angle should be $\Theta = 0.035\,N$ degrees. Thus up to $N = 100$ the change in contact angle would be only 3.5° and would be unnoticeable, but with several hundred layers the surface would tend to become hydrophilic and the surface charge could no longer be found.

The author is obligated to Dr. H. Poritsky for an outline of the method used for calculating the potential distribution illustrated in Fig. 1.

Summary

The progressively increasing contact potentials observed by Porter and Wyman during the building up of calcium stearate multilayers of

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[3] The treatment as given is rigorous only when $D = 1$, but should give a reasonably good approximation for $D \neq 1$. The assumption has been made that the effect of the dielectric constant is equivalent to a change in thickness, thus t in the original equation has been replaced by t/D.

type X on alkaline solutions seem to be due to a surface charge on the uppermost monolayer rather than to the presence of dipole molecules within the film. A theory is given for the potential distribution produced by these surface charges and it is shown that with potential gradients of the order of 3 × 10^6 v./cm. over distances of a few Ångström units the contact potentials can increase at a linear rate of 70 mv. per layer only up to films of a thickness of a few hundred layers.

SCHENECTADY, NEW YORK RECEIVED FEBRUARY 11, 1938

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

The Structure of Trisodium Tricyanmelamine Trihydrate

BY J. L. HOARD

Introduction

Tricyanmelamine or cyanuric tricyanamide, $C_3N_3(NCNH)_3$, belongs to an interesting group of closely related and quite stable compounds which are discussed by Franklin[1] under the heading of ammono polycarbonic acids. Tricyanmelamine is soluble in water, yielding a highly conducting, strongly acid solution; both acid and normal salts are readily prepared. The normal sodium salt, $Na_3C_6N_9\cdot 3H_2O$, crystallizes from aqueous solution as brilliant, colorless, hexagonal needles with well-defined faces not at all affected by long exposure to the atmosphere. Water of crystallization, indeed, is not lost below 160°. The sodium salt is formed, moreover, by the spontaneous polymerization in aqueous solution of sodium dicyanimide, NaC_2N_3.

The stability and high symmetry of crystals of trisodium tricyanmelamine trihydrate single it out as an appropriate representative for X-ray study of this interesting class of compounds. The crystal structure of this salt and the information obtained therefrom about the structure of the anion are discussed in this paper.

Determination of the Structure

The crystals used in this investigation were obtained from the late Professor E. C. Franklin of Stanford University.[2] A Laue photograph taken with the X-rays passing through a basal section of one of the hexagonal needles, the incident beam being accurately normal to (00·1), showed the six-fold axis and six planes of symmetry of the point-group D_6^h. The character of the face development observed on the ends of a number of the hexagonal needles was, however, in every case only trigonal. D_3^h is indicated unambiguously as the true point-group since it is the only one which can satisfy simultaneously these symmetry conditions.

Oscillation and rotation photographs about the needle axis were prepared using CuKα and MoKα radiation. Layer line spacings lead to $c_0 = 6.56$ Å., equatorial reflections to $a_0 = 10.23$ Å., these values being accurate to within about 0.1%. It was possible, indeed, to index all reflections appearing upon rotation and oscillation photographs upon the basis of this unit, reflections in the equator being observed for values of $2 \sin \theta$ as high as about 1.96 when CuKα was the radiation employed.

The further observation that no reflection of the type $\{mm\cdot l\}$, l odd, appears leads to the unique selection of $D_{3h}^4 - C\bar{6}2c$ as the correct space-group with a high degree of probability. The structure of $Na_3C_6N_9\cdot 3H_2O$ is then to be based upon the hexagonal unit with $a_0 = 10.23$ Å., $c_0 = 6.56$ Å., containing $2Na_3C_6N_9\cdot 3H_2O$, space-group $D_{3h}^4 - C\bar{6}2c$.

Chemical evidence indicates that the tricyanmelamine ion, $C_3N_3(NCN)_3^{3-}$, is isoelectronic with the cyanuric triazide molecule. D_{3h}^4 affords positions[3] for carbon and nitrogen atoms which permit of the existence of such anions in the unit cell. The two anions may be considered as centered at positions 2(b): 0,0,1/4; 0,0,3/4, with a minimum molecular symmetry (C_3^h) consisting in a three-fold axis with a reflection plane perpendicular to it. Structurally speaking, there are two sets of carbon and three sets of nitrogen atoms, each of these be-

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(1) Franklin, "Nitrogen System of Compounds," Am. Chem. Soc. Monograph, Reinhold Publishing Corp., New York, N. Y., 1935, pp. 101–107.

(2) Crystals of this substance were given also by Professor Franklin to Professor Linus Pauling and Dr. J. H. Sturdivant of the California Institute of Technology, and the early stages of the X-ray investigation, leading to an approximate sketch of the correct structure, were duplicated in its essentials by us. Upon discovery of this duplication, Professor Pauling and Dr. Sturdivant very kindly relinquished their claim to the problem.

(3) R. W. G. Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," Carnegie Institution of Washington, 2d ed., 1931, pp. 159–160.