amino sulfonamide compounds corresponding to diphenoquinone, 2,6-naphthoquinone and the phenanthrene quinones for pharmacological and dipole moment studies. Such studies are now in progress in this Laboratory.

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RECEIVED NOVEMBER 18, 1940

Reactions of Atoms and Free Radicals in Solution. III. The Introduction of a Mercaptan Group into Cyclohexane

BY M. S. KHARASCH AND KENNETH EBERLY[1]

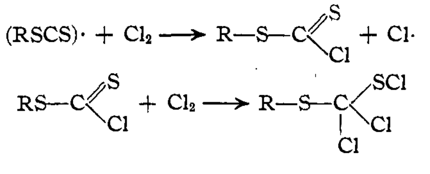
In previous articles from this Laboratory, it has been postulated that substitution reactions of aliphatic hydrocarbons (bromination,[2] chlorination,[3] sulfonation,[4] carboxylation,[5] etc.) proceed through the intermediate formation of atoms or free radicals. It appeared reasonable that under certain conditions useful synthetic reactions might be obtained by employing these. Specifically, it seemed probable that if cyclohexane were mixed with a large quantity of carbon disulfide and chlorine gas introduced slowly in the illuminated mixture, the following sequence of reactions would take place

$$\mathrm{Cl_2} \xrightarrow{h\nu} 2\mathrm{Cl}\cdot \tag{1}$$

$$\mathrm{RH} + \mathrm{Cl}\cdot \longrightarrow \mathrm{R}\cdot + \mathrm{HCl} \tag{2}$$

$$\mathrm{R}\cdot + \mathrm{CS_2} \longrightarrow (\mathrm{RSCS})\cdot \tag{3}$$

$$\mathrm{R}\cdot + \mathrm{Cl_2} \longrightarrow \mathrm{RCl} + \mathrm{Cl}\cdot \tag{4}$$



$$(\mathrm{RSCS})\cdot + \mathrm{Cl_2} \longrightarrow \mathrm{R{-}S{-}C({=}S)Cl} + \mathrm{Cl}\cdot \tag{5}$$

$$\mathrm{RS{-}C({=}S)Cl} + \mathrm{Cl_2} \longrightarrow \mathrm{R{-}S{-}CCl_2(SCl)} \tag{6}$$

These expectations were fully realized. When a mixture of one gram molecular equivalent of carbon disulfide and of cyclohexane (and a few drops of pyridine) was illuminated (1000 watt Mazda), and chlorine passed slowly into the solution, an energetic reaction took place. The temperature of the reaction mixture was controlled by external cooling, and by the rate of introduction of the chlorine. An effort was made to keep this temperature below 40°, and it was found necessary to use about five hours for the introduction of 30 g. of chlorine.

The reaction mixture was then transferred to an all-glass distillation apparatus and the carbon disulfide, cyclohexane, cyclohexyl chloride, and the perchloromethyl mercaptan removed at reduced pressure. At no time was the temperature of the mixture allowed to rise above 80°, since violent decomposition of the condensation product occurs at 90–100°. The last traces of volatile materials were removed by maintaining the mixture for two hours at 80° under a pressure of 4 mm. A clear light yellow non-distillable oil was thus obtained (30 g.).

Because of the impossibility of distilling this material at even low pressures (10^{-4} mm.), the analytical results in various experiments did not agree as well as they probably would have if this material could have been purified. Thus, the chlorine content of various lots of the oil varied from 39 to 43%, and the sulfur content from 24 to 25%. In view of the fact that cyclohexyl dithiochlorocarbonate contains only 18.22% chlorine and 32.94% sulfur, the oil obviously is not that substance. However, if further chlorination of that substance is assumed (as in 6) to cyclohexyl dithiotrichlorocarbonate (Cl, 40.05%; S, 24.14%), then the analytical data are good enough for an oil which cannot be purified by distillation.

To prove that the postulated cyclohexyl dithiotrichlorocarbonate actually contains a cyclohexyl residue attached to sulfur, the oil was heated with alcoholic potassium hydroxide (2.5 times the calculated amount). The oil (30 g.) was added slowly (two hours) to the hot solution and the reaction brought to completion by heating for three hours longer. The alcohol was removed *in vacuo*, and water added to the residue. Upon acidification with hydrochloric acid, a dark, vile smelling oil separated. This oil was extracted with ether, and the ether extract dried over sodium sulfate. Upon distillation of the ether an oil remained. This oil was distilled and the fraction which boiled at 157–162° was collected. This fraction contained sulfur and no chlorine.

Anal. Calcd. for $C_6H_{12}S$: S, 27.60. Found: S, 27.16.

The recorded boiling point of cyclohexyl mercaptan is 158–161°.

The identity of the cyclohexyl mercaptan thus prepared was further confirmed by treating it with mercuric chloride and by the analysis of the cyclohexyl mercaptomercuric chloride.

Anal. Calcd. for $C_6H_{11}SHgCl$: Hg, 57.1. Found: Hg, 56.6.

The series of reactions cited prove conclusively that a mercaptan group can be introduced directly into cyclohexane.

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RECEIVED NOVEMBER 20, 1940

Application of the Gibbs Adsorption Equation to Solutions of Paraffin-Chain Salts

BY F. A. LONG AND G. C. NUTTING

The validity of the application of the Gibbs adsorption equation to aqueous solutions of

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[1] The authors wish to express their appreciation to the du Pont Company for support which made this work possible.

[2] For references, see Kharasch, Fineman and Mayo, THIS JOURNAL, **61**, 2139 (1939).

[3] For references, see Kharasch and Brown, *ibid.*, **61**, 2142 (1939).

[4] Kharasch and Read, *ibid.*, **61**, 3089 (1939).

[5] Kharasch and Brown, *ibid.*, **62**, 454 (1940).

paraffin-chain salts (soaps and soap-like molecules) has frequently been questioned.[1,2,3]

In view of the recent work on such solutions,[4,5,6] it seems worth while to consider explicitly the results of an application of the Gibbs theorem to solutions of such substances.

One of the primary objections to the application of the Gibbs equation has been the frequent appearance of a surface tension–concentration curve of McBain's Type III, in which a minimum in the surface tension appears, usually at a surface tension value of around 35 dynes. The doubtful point has been the paradox of a surface tension much lower than that of water and yet a *negative* surface excess of solute as calculated from the Gibbs equation. The object of this note is to point out that the paradox is more apparent than real.

The Gibbs equation in its usual form

$$\Gamma_2^{(1)} = -\frac{1}{RT}\frac{d\gamma}{d \ln a_2} \qquad (1)$$

allows the calculation of the surface excess of one component (usually taken as the solute) of a two component solution, with reference to the *particular geometrical surface* chosen to make $\Gamma_1^{(1)}$, the surface excess of the other component, equal to zero. Physically, this means that the moles of solute in a given volume which includes one sq. cm. of surface are compared with the moles of solute in a volume of the bulk solution which contains the *same quantity* of solvent.[7] It is clear that the calculation involves a consideration of all parts of the surface region wherein the actual concentrations differ from the bulk values. Also, the approximate formulation of the Gibbs equation in terms of concentrations instead of activities can never give surface excesses differing in sign from the true values since the activity must increase as the concentration increases.

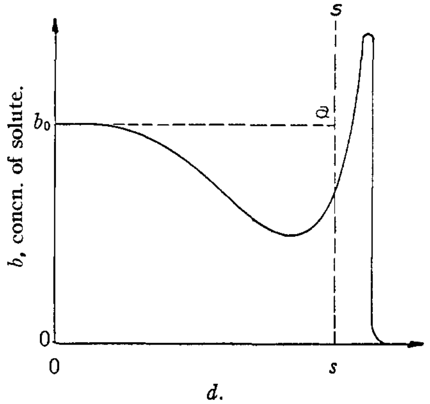

Fig. 1.—A schematic representation of the concentration of solute in a solution of a paraffin-chain salt. The abscissa is distance from an arbitrary point in the bulk of the solution out through the surface region. The maximum in the concentration curve represents a surface layer of ions; the minimum represents the diffuse double layer region.

As an example, let us consider a dilute aqueous solution of an alcohol in the region where the decrease of surface tension with concentration indicates a surface excess. We may imagine the geometrical surface, parallel and near to the interface, so placed as to give a zero surface excess of water. A consideration of the short-range forces entering for water–alcohol and alcohol–alcohol interaction suggests that the concentration of alcohol will maintain its bulk value up to within a few Ångströms of the actual interface. Consequently the surface excess of solute will be localized in a narrow region of the physical interface. In such a case it is probably safe to speak interchangeably of the surface excess and "positive adsorption at the surface" and perhaps even to localize the surface excess in a monomolecular surface layer.[7]

Now a situation which is by no means as simple as this occurs with solutions of paraffin-chain salts, for example, cetylpyridinium bromide in water.[4] At the air–liquid interface of a solution of a paraffin-chain salt the outer surface layer is undoubtedly a layer of paraffin-chain ions with the paraffin chains oriented outwards.[6,8] The presence of this ionic layer will result in a concentration of "gegenions" near to it and a diffuse double layer extending down into the solution. Also, because of the long-range coulombic forces involved, the region in which the concentrations differ from the bulk values will be of considerable extent.

Figure 1 gives a schematic plot of the solute concentration for such a solution. The distance, *d*, is reckoned from a point in the bulk of the solution outwards, normal to the surface. The geometrical surface, *s*, is placed so that the surface

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[1] McBain and Mills, "Reports on Progress in Physics," Vol. 5, 1939, p. 30; McBain and Wood, *Proc. Roy. Soc.* (London), **A174**, 286 (1940).

[2] Powney and Addison, *Trans. Faraday Soc.*, **33**, 1243 (1937).

[3] See also Adam, "Physics and Chemistry of Surfaces," Oxford, 1938, p. 115.

[4] Adam and Shute, *Trans. Faraday Soc.*, **34**, 758 (1938).

[5] McBain, Vinograd and Wilson, This Journal, **62**, 244 (1940).

[6] Nutting, Long and Harkins, *ibid.*, **62**, 1496 (1940).

[7] Guggenheim and Adam, *Proc. Roy. Soc.*, (London), **139A**, 219 (1933).

[8] Doss, *Kolloid-Z.*, **86**, 205 (1939).

excess of water is zero. The Gibbsian surface excess will be proportional to the difference between the area under the concentration curve and the area of the rectangle a-b_0-0-s. For this case it is easy to see that, even though there is a surface *layer* of solute (positive adsorption at the interface), the Gibbsian *surface excess* may be positive, zero or negative depending on the concentrations in the double layer region below the interface. It is also plausible that changes in the bulk concentration will change the concentrations in this region, and thus change the surface excess, even though only slight changes occur in the outer ionic layer. Thus the apparent paradox of a surface deficiency and yet a surface tension less than that of water is readily understandable.

Actually the argument may be reversed. A surface deficiency along with a low surface tension, *i. e.*, a Type III surface tension–concentration curve, suggests a state of affairs such as illustrated in Fig. 1. Also, because only electrostatic forces seem likely to be of sufficiently long range to produce such an effect, a result of this type strongly suggests that much or all of the material actually in the physical surface is present in the form of ions.

Because of the paradox of a low surface tension and a negative surface excess, McBain and Mills[1] have concluded that the Gibbs equation is a limiting law, similar to the ideal gas law. They suggest that additional terms should be included to take account of such factors as molecular orientation, submerged electrical double layer, free electrical charges and perhaps others. It is well known that free electrical charges, introduced by *external means*, do necessitate a different treatment. However, the great generality of the thermodynamic derivation of the Gibbs equation[9] makes it apparent that all these phenomena, if of spontaneous origin, are within the scope of the equation. Thus one may conclude that the Gibbs equation in its usual form is valid for solutions of paraffin-chain salts just as for other two-component solutions.

The recently reported[1] measurements of the Gibbs surface excess for a typical paraffin-chain salt indicate a surface excess in the concentration region where the Gibbs equation predicts a surface deficiency. The significant measurements are those done by the microtome method of McBain. The data, if substantiated, will imply serious added complications for the problem. However, it might be pointed out that because of two factors, one, the great depth of the surface region as compared to almost any other type of solution, and two, the fact that establishment of equilibrium between the surface and the underlying solution is a slow process,[8] it is probable that this type of solution represents about the most difficult possible case for an experimental verification of the adsorption equation.

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RECEIVED MAY 31, 1940

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[9] See, for example, Gibbs, "Collected Works," Vol. I, p. 219 ff.; Guggenheim, "Modern Thermodynamics," p. 160 ff.; Guggenheim, *J. Chem. Phys.*, **4**, 689 (1936).

Reaction between Maleic Anhydride and the Isomers of Piperylene

BY RICHARD F. ROBEY, CHARLES E. MORRELL AND HERBERT K. WIESE

In recent studies on the quantitative aspect of the reaction between maleic anhydride and piperylene (pentadiene-1,3), we have observed what is apparently an important difference in the rates of reaction of the isomers of this diolefin with the anhydride. The observation was made on piperylene from two different sources, namely, gas oil cracking and dehydrochlorination of dichloropentane, when the diolefin, which had been concentrated and subsequently purified, was analyzed using maleic anhydride as reagent. In the analysis the samples were vaporized under reduced pressure, blended with hydrogen gas in known proportions to prevent condensation at room temperature, and submitted to analysis for conjugated dienes in the vapor phase.[1] It was found that although the initial rate of absorption was rapid, the reaction stopped short of the quantitative figure, some 18% in one case and 35% in the other. The high purity of the diolefin is evidenced in each case by an index of refraction (n^{20}D 1.4309) which agrees with the best value in the literature,[2] and by its reaction with two moles of hydrogen per mole, within experimental error, on catalytic hydrogenation.

In lieu of any better explanation, we have ascribed the incomplete absorptions to the presence of both *cis* and *trans* isomers of piperylene which apparently present somewhat different chemical behavior toward maleic anhydride. As

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[1] Tropsch and Mattox, *Ind. Eng. Chem.*, *Anal. Ed.*, **6**, 104 (1934).

[2] Farmer and Warren, *J. Chem. Soc.*, 3221 (1931).