solution of ferric chloride in isopropyl ether. A heavy liquid containing most of the iron separated out. It had a visible absorption spectrum containing all of the maxima found in the spectrum of an ether layer from a 5.6 WF. extraction. Such a two-phase anhydrous system is present in a simple phase rule diagram of the two-ether-phase system. In this diagram the two two-phase regions ($FeCl_3 \cdot nHCl$–isopropyl ether and HCl aq.–isopropyl ether) meet at certain acid concentrations to form a three-phase system.

Houben and Fischer[5] have isolated the compound $FeCl_3 \cdot HCl \cdot 2Et_2O$ from a mixture of ferric chloride, hydrogen chloride, and ethyl ether. However, when the above experiment is performed with either ethyl or β,β'-dichloroethyl ether two phases do not form, while both isopropyl and *n*-butyl ether do form these two phases. In the extraction of iron with either ethyl or β,β'-dichloroethyl ether a two-ether-phase region has never been observed. The authors have also been unable to find the conditions for the extraction of iron whereby *n*-butyl ether forms two ether phases, although in this case it would be expected that such a region should exist.

Summary

From the distribution data of the first paper of this series, the effective polymerization of the ethereal iron has been evaluated. The variation of the distribution constant with the acid concentration and the effect of acid upon the apparent polymerization of the ethereal iron have been measured. Also, the formation of two ether phases and the effect of acid concentration upon the composition of the two phases were investigated.

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[5] J. Houben and W. Fischer, *J. prakt. Chem.*, **123**, 89 (1929).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY No. 1435]

The Distribution of Ferric Iron between Hydrochloric Acid and Isopropyl Ether Solutions. III. Spectral, Isopiestic and Magnetic Susceptibility Studies

BY DAVID E. METZLER AND ROLLIE J. MYERS

This paper presents the results of spectral measurements made for the purpose of determining the various species present in the aqueous and ether layers, and of isopiestic and magnetic susceptibility studies of the iron in the ether layer.

Spectrophotometric Measurements.—A model DU Beckman spectrophotometer was used. The absorption cells were 1-cm. quartz cells, some use also being made of 0.9-cm. quartz spacers. As a blank the identical solvent without iron was used. It was not necessary to purify the "reagent grade" hydrochloric acid, but the isopropyl ether was purified as described in Part I.

The extinction coefficients (ϵ) were calculated by means of the formula

$$I = I_0 10^{-\epsilon c l}$$

where c is the concentration in formula weights/liter and l is the cell path in centimeters. The measurements were made at room temperatures of about 24° with an unthermostated instrument.

Absorption Spectra of the Ether Extracts.—The light absorption of the isopropyl ether layers was studied extensively both for analytical purposes and because of general interest. The ultraviolet absorption was studied with respect to dependence upon both the iron and acid concentrations. The relative values of the absorption at 364, 340, 316 and 287 mμ were found to be constant with initial acid concentrations ranging from 2–9 VF., and at 5 VF. the values of these extinction coefficients were constant in ether layers containing 8×10^{-5} to 10^{-3} fwts./l. of iron. Since this ethereal iron concentration range represents a region over which distribution studies have demonstrated near ideality for the extraction, the ordinate of the spectrum shown in Fig. 1 and the extinction values listed in Table I, Part I, may be called molal extinction.

The absorption spectrum from 420 to 460 mμ was studied very little, but because a small maximum is present the spectrum is shown in Fig. 2. Since the visible spectrum is most conveniently studied in a region where the distribution studies indicate polymerization of the ethereal iron, this spectrum was studied to check any possible effect of such polymerization. As shown in Table I the visible absorption shows no deviation from Beer's law over the concentration range studied. It was also found that for ether layers from extractions with acid concentrations of 5–7.3 VF. the extinction coefficients were constant within experimental error. The visible spectrum is shown in Fig. 3.

The visible spectrum given by Nachtrieb and Conway[1] qualitatively compares favorably with ours. The average values of the extinction coefficients given by them, however, are higher than ours by 10–30%. It is apparent from their data that some of their light density values for the dilute solutions are very high. We have recalculated new average extinction coefficient values from Nachtrieb and Conway's data, rejecting all

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[1] N. H. Nachtrieb and J. G. Conway, THIS JOURNAL, **70**, 3547 (1948).

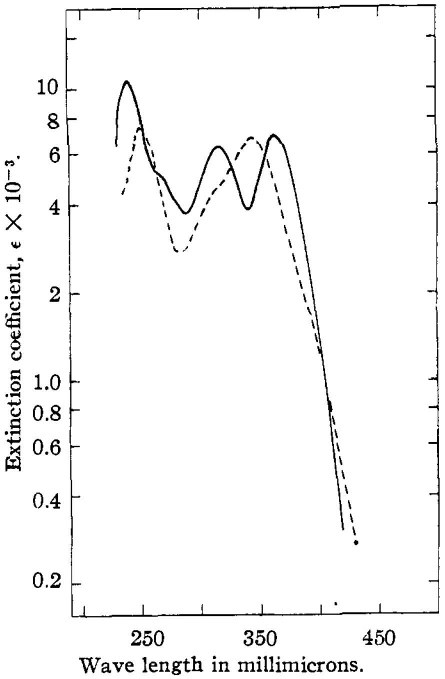

Fig. 1.—The ultraviolet spectrum of the extracted complex and that of ferric chloride in isopropyl ether: —— the extracted complex. The ether layer was from 5 VF. acid and was 6×10^{-5} VF. in iron; $\epsilon_{241} = 10.55 \times 10^3$. Other values are given in Table I of Part I. - - - Anhydrous ferric chloride: the ether was 1.4×10^{-4} VF. in $FeCl_3$.

measurements made with light density values less than 0.030. Thus using their data we get:

Wave length, mμ	532	618	685	725
ε, liter mole^{-1} cm.$^{-1}$	1.31	0.424	0.624	0.459
Av. dev.	0.03	0.011	0.016	0.015

It can be seen that these values are very similar to ours given in Table I.

TABLE I

ETHEREAL IRON VISIBLE EXTINCTION COEFFICIENTS

Measurements were made on four ether layers from 5 VF. acid with iron concentrations from 0.3 to 0.6 VF.

Wave length, mμ	ε, liter mole^{-1} cm.$^{-1}$	Av. dev., %
531	1.314	0.4
615	0.410	0.3
640	0.328	1.0
682	0.619	0.3 (2 detn.)

It should be noted, however, that the absorption spectrum in the ethereal iron concentration range where the iron changes from monomeric to predominantly polymeric species was not studied, because of a lack of the proper cells. It is in such a region that one might expect the greatest effect of polymerization upon the absorption spectrum.

Absorption Spectra of Anhydrous Ferric Chloride in Ether.—The ultraviolet spectrum of anhydrous ferric chloride in isopropyl ether was measured in order to compare it with the spectrum of the ethereal iron layer. This spectrum is also shown in Fig. 1. Care was employed to insure anhydrous conditions. No evidence of hydrolysis was observed during the experiment. However, the solutions turned cloudy the next day. The positions of the minimum and the maxima check with those obtained from a previous experiment.

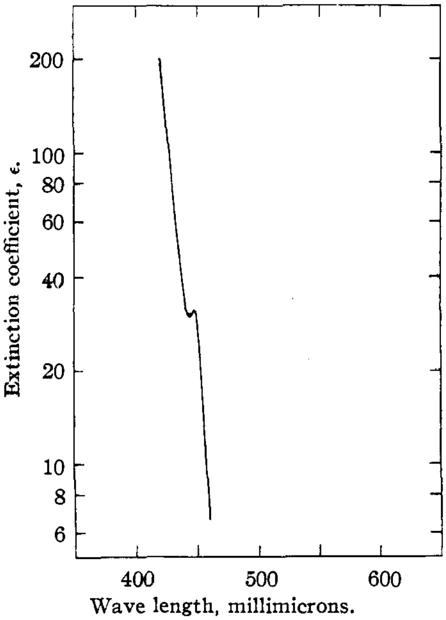

Fig. 2.—Ethereal iron spectrum: the ether layer was from 5 VF. acid and was 8.5×10^{-3} VF. in iron.

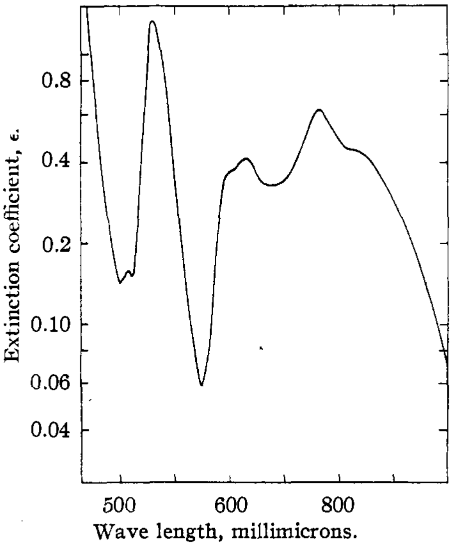

Fig. 3.—Ethereal iron spectrum: a composite of four spectra from 5 VF. acid with iron concentrations from 0.3 to 0.6 VF.

Absorption Spectra of Ferric Iron in Hydrochloric Acid.—It is also interesting to compare the ethereal iron spectrum with that of ferric iron in aqueous hydrochloric acid. The variation of the spectrum with acid concentration is shown in Fig. 4. The similarity between the absorption spectrum of a ferric chloride, hydrogen chloride, and ethyl ether mixture (or an ethereal iron layer) and that of ferric iron in concentrated hydrochloric acid has been noted by others.[2,3] However, the quantitative comparison shown here is very striking. This suggests that the predominant species of ferric iron in 12 VF. hydrochloric acid may be $FeCl_4^-$. It is assumed that $HFeCl_4$ is a strong acid in hydrochloric solutions, for unpublished experiments on the extraction from a mixture of HCl and NaCl at a constant ionic strength of 5 VF. have given no evidence of its being a weak acid.

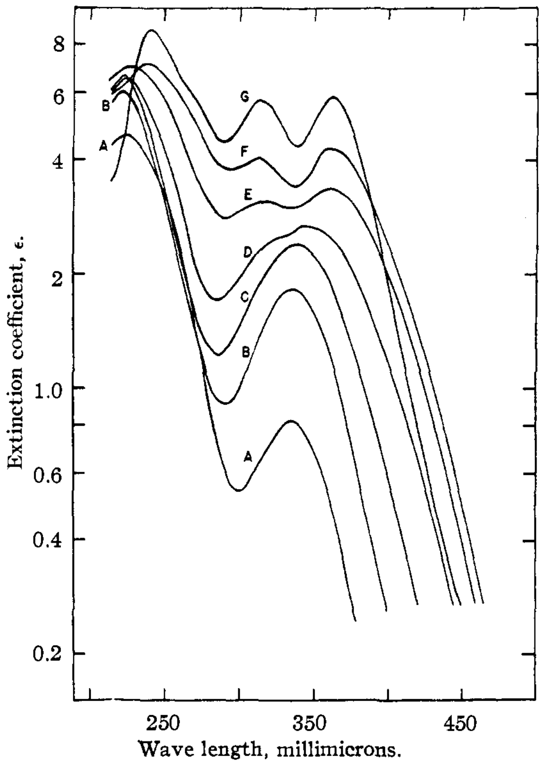

Fig. 4.—Spectra of 10^{-4} VF. ferric chloride in hydrochloric acid of VF. values: A, 0.097; B, 0.97; C, 2.9; D, 4.9; E, 6.8; F, 8.8; G, 11.7.

The similarity between the absorption spectra of the ethereal and strong aqueous acid solutions is not as great between 400 and 550 mμ as in the ultraviolet. Apparently this is due to the masking of this spectrum by the edge of the strong ultraviolet absorption region of the ionic species predominantly present at the lower acidities. This hypothesis is suggested by the fact that the solutions of lower acid concentration have a much stronger absorption in this region of the spectrum than those of the highest acid concentration. However, careful inspection of the curves of Kiss, *et al.*,[4] for 12 *M* acid shows that there are definite inflections at 450 and 530 mμ, and in aqueous solutions saturated with hydrogen chloride at about one atmosphere pressure we have recorded a small maximum for the latter wave length. From 550 to 800 mμ the spectra again show striking similarities.

An interpretation of the ionic constitution of solutions of ferric chloride in aqueous hydrochloric acid on the basis of these spectra alone is difficult, but some suggestions concerning the constitution can be made. From the work of Rabinowitch and Stockmayer[5] the following approximate percentages of ionic species can be stated to be present at the acid concentrations shown

HCl	Fe^{+++}	$FeCl^{++}$	$FeCl_2^+$	$FeCl_3$
0.1 VF.	67	29	4	3×10^{-2}
1.0 VF.	9	39	50	2

In Fig. 4 the crossing over of the 0.97 and 2.9 VF. curves by the 0.097 VF. curve between 250 and 270 mμ is apparently due to the ferric ion in the latter solution, for Fe^{+++} has an absorption maximum at 238 mμ.[3,4] From the similarity between the 0.097 and 0.97 VF. curves, and from the above data, it appears that $FeCl^{++}$ and $FeCl_2^+$ might have similar spectra with absorption maxima around 225 and 335 mμ.[6]

A careful inspection of Fig. 4 shows that the curves of intermediate acid concentration cannot be resolved into a combination of the two extremes, but that an intermediate iron species must exist with strong absorption in the regions between 250 and 300 mμ and between 350 and 400 mμ. This is particularly evident in the 6.8 and 8.8 VF. curves, in which we cannot otherwise explain the shallowness of the 290 mμ minimum and the height of the maximum at 364 mμ as compared with that at 316 mμ. If the 11.7 VF. curve is assumed to be due mainly to $FeCl_4^-$ it is evident that this intermediate species is $FeCl_3$. This hypothesis is compatible with the calculation of Rabinowitch and Stockmayer[5] that the extinction coefficient of $FeCl_3$ is 20 times that of $FeCl^{++}$ or $FeCl_2^+$ at 400 mμ.

The variation of the extinction coefficient with acid concentration at 225 mμ should be noted. The extinction coefficient exhibits two maxima at acid concentrations of around 3 and 7 VF. This situation could result if $FeCl^{++}$ and $FeCl_3$ have stronger absorption in this region than does $FeCl_2^+$. On the basis of this interpretation it should be mentioned that the spectrum of aque-

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(2) W. J. Russel and W. J. Orsman, *Chem. News*, **59**, 93 (1889); see Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green, London, 1935, Vol. 14, p. 56.

(3) S. Kato and R. Ishii, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **36**, 82 (1939).

(4) A. Kiss, J. Abraham and I. Hegedus, *Z. anorg. allgem. Chem.*, **244**, 98 (1940).

(5) E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

(6) In a review article Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942), gives in a figure the absorption spectrum of $FeCl^{++}$ down to 300 mμ. It contains a single maximum at 320 mμ.

ous $FeCl_3$ could not be the same as that of anhydrous $FeCl_3$ in the ether which is shown in Fig. 1.

Others[4,5] have assumed that the complex ion $FeCl_6^{---}$ would appear in the concentrated acid; our interpretation, however, rests upon the assumption that the highest complex formed in quantity is $FeCl_4^-$. This assumption is suggested both by the similarity of the absorption spectra already pointed out and by the fact reported by Axelrod and Swift[7] that with β,β'-dichloroethyl ether the distribution ratio is still increasing with acid concentration at 11.5 VF. acid and the formula of the extracted complex ($HFeCl_4$) apparently does not change with the acid concentration.

It should be mentioned that Rabinowitch and Stockmayer,[5] in drawing a conclusion regarding the decrease in light absorption at 400 mμ with increasing acid concentration, assumed that $FeCl_3$ or Fe_2Cl_6, rather than $HFeCl_4$ or a polymer, is extracted by ethyl ether, and that the decrease in extraction above 6 VF. acid by ethyl ether is due to the decrease in the aqueous $FeCl_3$ concentration. We attribute this decrease in extraction to the high solubility of ethyl ether in hydrochloric acid at concentrations above 6 VF., and as pointed out above this decrease in extraction is not observed when β,β'-dichloroethyl ether is used.

The present work indicates that a further elucidation of the composition of aqueous hydrochloric acid–ferric chloride solutions may be easier than was previously realized. It should perhaps be pointed out that the data presented in Part II on the variation of the distribution constant with acid concentration cannot be directly used to calculate equilibria in pure hydrochloric acid because of the effect that the dissolved ether has upon these equilibria. However, by the use of a more insoluble ether, such as β,β'-dichloroethyl ether, calculations relating to the $FeCl_4$–$FeCl_3$ equilibrium might be made.

Isopiestic Studies.—In an attempt to confirm the polymerization number values obtained by the distribution experiments, on the assumption of ideality in the acid layer, another method of determining these values was tried. Because of the complexity of the ether layer and the desirability of a method applicable at 25°, an isopiestic molecular weight method was selected. At first a macroscopic equilibration method was attempted. In this case an acid layer, two iron ether layers, and a reference ether layer were allowed to approach equilibrium in a desiccator. In these experiments equilibrium was never reached, but a considerable discrepancy was shown between the formality and the molality of the iron in the ether at the concentration range studied (0.3 VF. iron, $n > 5$).

The Barger[8] micro method was also tried. In this case alternate drops of an iron ether layer and a reference ether layer, from a distribution of the same acidity containing p-bromobiphenyl, were introduced into a capillary tube. Then the change in the size of the drops was noted by means of a microscope. Because only a null or inflection concentration is obtained the method is a tedious one.

Since the ether contains 0.1 to 0.2 mole/l. of water, establishment of accurate polymerization numbers for the range of concentration shown in Fig. 2, Part II, is difficult. Despite this the isopiestic and distribution polymerization numbers shown in Table II compare favorably. Since the two methods are in agreement, the procedure used in Part II, defining the activity of the aqueous iron as a linear function of its formality, appears to be a valid one.

TABLE II

A COMPARISON OF ISOPIESTIC AND DISTRIBUTION POLYMERIZATION NUMBERS

Ethereal iron concentration, fwts./l. × 10^3	Polymerization number Isopiestic Upper value	Polymerization number Isopiestic Lower value	Distribution[a]
48.9	3.17	3.07	2.95
40.6	2.86	2.77	2.60
28.6	2.14	2.05	2.19
25.0	2.12	(2.01)	2.07
20.2	1.74	..	1.90
10.1	1.30	..	1.45

[a] These values were obtained by interpolation of those given in Fig. 2 of Part II of this series of papers.

Susceptibility Measurements.—The Gouy method was employed. The sample tube contained air in the lower compartment, and the apparatus was thermostated at 25.0°. The apparatus was calibrated by the use of 30% nickel chloride solution and the data of Nettleton and Sugden.[9] Diamagnetic corrections were made for air, the solvent and ions; the formula of the iron compound in the ether layer was assumed to be $Fe^{+++}.HCl{\cdot}3Cl^-{\cdot}5H_2O$ and no correction was made for the diamagnetism of the iron core.

The magnetic moment of ferric iron in hydrochloric acid has been studied by Werbel, Dibeler and Vosburgh.[10] They found that the magnetic moment has the normal value of 5.92 Bohr magnetons in hydrochloric acid at 1 to 4.8 M acid. It is of interest in connection with the apparent poly-

TABLE III

ETHEREAL IRON MAGNETIC MOMENT

Solvent blank = −15.5 mg. in air; 29.95% $NiCl_2$ soln. = 341.0 mg. in air

Iron concentration, fwts./l.	ΔW in air, mg.	μ, Bohr magnetons	Diamagnetic corrections Species	Diamagnetic corrections $-\chi \times 10^6$
0.181_0	55.4	5.96	Cl^-	25
$.372_0$	130.7	5.94	HCl	22
$.574_8$	210.8	5.96	H_2O	13

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(7) J. Axelrod and E. H. Swift, THIS JOURNAL, **62**, 33 (1940).

(8) G. Barger, *J. Chem. Soc.*, **85**, 286 (1904).

(9) Nettleton and Sugden, *Proc., Roy. Soc.*, **A173**, 313 (1939).

(10) B. Werbel, V. H. Dibeler and W. C. Vosburgh, THIS JOURNAL, **65**, 2329 (1943).

merization of the ethereal iron to establish its magnetic moment. This was done by means of the formula $\mu_{\text{eff}} = 2.84\sqrt{\chi_m T}$, and the data are presented in Table III. The distributions examined were 5.60 WF. in aqueous hydrochloric acid.

Acknowledgment.—The authors of this paper thank Ernest H. Swift for his continuous advice and counsel during the experimental work, and for his helpfulness during the preparation of these papers for publication.

Summary

The visible and ultraviolet absorption spectrum of the isopropyl ether layers has been examined. The ultraviolet spectrum of anhydrous ferric chloride in isopropyl ether has also been measured. For the purpose of comparison the ultraviolet spectra of hydrochloric acid solutions of ferric iron were measured, and a great similarity was found between the spectrum of a concentrated hydrochloric acid solution and that of the iron complex in isopropyl ether. Some suggestions regarding the constitution of hydrochloric acid solutions of ferric chloride are made.

The isopiestic measurements indicate the polymerization of the extracted iron, while the magnetic susceptibility study gives a value of 5.95 Bohr magnetons for the magnetic moment of the ethereal iron.

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Effect of Electrolytes Upon the Solubilization of Hydrocarbons and Polar Compounds

BY H. B. KLEVENS[1]

The presence of at least two loci of solubilization has been established by the difference in changes in long X-ray spacings upon the addition of hydrocarbons and of polar compounds.[2,3,4] The existence of these two loci has also been indicated by comparison of solubilization data.[5] In the solubilization of non-polar compounds, the rate of increase in solubilization increases with soap concentration; for polar compounds, this rate shows no change or decreases. These results indicate that the solubilized hydrocarbon occupies a volume in the central hydrocarbon portion of the micelle resulting in a swollen micelle and that the polar compounds, such as long-chain alcohols take a position which is essentially similar to the soap molecules which make up the micelle.

Further evidence for the presence of these two loci and their apparent independence of each other has recently been obtained.[6] This is based on the fact that there is an enhancement of solubilizing power of a soap for a hydrocarbon when polar compounds in the form of long chain alcohols and amines are used as additives and further that the presence of added hydrocarbon increases the solubilization of a long chain alcohol by a soap. The effect of these additives has essentially been to result in the formation of an alcohol–soap micelle with a greatly enhanced solubilization power.

The addition of the long chain alcohols and amines probably results in a change in the curvature of the micelle surface due to a penetration of the alkyl chain of these additives into the palisade of soap hydrocarbon tails as well as to an increase in micellar size. This concept can be readily understood if one accepts a sphere or an oblate spheroid as the shape of the initial micelle. This penetration results in a considerable expansion of the volume available for hydrocarbon solubilization as is evidenced by a marked increase in amount of *n*-heptane solubilized by these alcohol–soap micelles.[6] In those cases where long chain alcohols are the additives, there is no expansion along the minor axis of the oblate spheroid micelle (distance = 2 × length of the soap molecule) as can be seen from the fact that there is no increase in X-ray spacing.[3,4] The increase in volume can probably be considered to be due to an increase in the major axis of this spheroid micelle.

Other additives, which result in such changes in curvature of the micelle surface and in corresponding changes in volume available for solubilization, should show similar solubilization changes. The addition of electrolytes will result in an effective decrease in the energy of repulsion of the like charged soap heads, will thus result in a decrease in curvature of the surface, and will increase the equilibrium size of the micelle. Debye has shown that there was a linear increase in molecular weight of the dodecylamine hydrochloride micelle with equivalents of added chloride ion concentration.[7] Thus, for solubilization of hydrocarbons, those which enter the micelle center and show increases in long X-ray spacings, it is to be expected that there will be an enhancement of solubility upon the addition of electrolytes. Further, since there is this decrease in energy of repulsion upon addition of electrolytes, it would follow that there would be a corresponding decrease in the effective volume available for solubilization in the soap palisade layers. Thus one would expect a marked

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[1] Agricultural Biochemistry, University of Minnesota, Minneapolis, Minn.

[2] H. Kiessig and W. Philippoff, *Naturwissen.*, **27**, 593 (1939).

[3] J. W. McBain and O. R. Hoffman, *J. Phys. Colloid Chem.*, **53**, 39 (1949).

[4] W. D. Harkins and R. Mittelmann, *J. Colloid Sci.*, **4**, 367 (1949).

[5] H. B. Klevens, *J. Am. Oil Chem. Soc.*, **26**, 456 (1949).

[6] H. B. Klevens, *J. Chem. Phys.*, **17**, 1004 (1949); THIS JOURNAL, **72**, 3581 (1950).

[7] P. Debye, *Ann. N. Y. Acad. Sci.*, **51**, 575 (1949).