Since the analogous sum was $N^3/6$ for the free linear pearl necklace, it appears that *the ring formation has reduced the influence on the friction to $\frac{1}{2}$ of the original amount.*

For a linear pearl necklace with fixed angle α between two successive links $\sum_\nu \langle(\mu\nu)\rangle_{\text{Av}}$ was equal to $\mathrm{ctg}^2 \frac{1}{2}\alpha$, and the sum needed only to be taken over a small number of neighboring links (unless α would be too close to zero). It is clear that in the case of rings, the formula (44) must then be replaced by

$$\langle(\mu\nu)\rangle_{\text{Av }\mu\neq\nu} \cong -\frac{1}{N}\,\mathrm{ctg}^2\,\tfrac{1}{2}\alpha,$$

and that the sum (45) must also be multiplied by a factor $\mathrm{ctg}^2\,\frac{1}{2}\alpha$. Thus, here again, as was to be expected, it still holds good that ring closing reduces the effect ,to $\frac{1}{2}$ of the original figure.

There will now be no further difficulty in the problem of arbitrarily ramified molecules containing one or more separate rings. As soon, however, as the different rings are no longer separate, i.e., if they have one or more chain segments in common, the $\langle(\mu\nu)\rangle_{\text{Av}}$'s can no longer be determined in this simple manner.

Editor's Note:

This article is a translation by J. J. Hermans and H. A. Kramers of an original appearing in Physica in January, 1944. Because of wartime restrictions imposed by the Germans, the original appeared in Dutch. The innovation of publishing a translation was thought to be justified by the inaccessibility of the original to many readers because of the language barrier. The editors and publishers of Physica gave their kind permission for the publication of this translation.

Conductometric Investigation of Electrolytic Solutions in Hydrocarbons

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Conductometric investigations were made of electrolytic solutions in xylene and of a hydrocarbon oil both of which have conductivities of from 10^{-12} to 10^{-11} mho/cm at room temperature. The electrolytes introduced were composed of an organic basic and an organic acidic material, the former being an amine. A three-component system (amine, aliphatic acid, and a phenol) was generally required in order to obtain high conductivities at relatively low concentrations of electrolytes. It is shown that the effect of the phenol is only partly caused by the increase of dielectric constant; the chief process is probably a specific one. On the theory that the mechanism consists in the formation of an addition-compound that subsequently dissociates into ions, the experimental data were subjected to an analysis. It appears that generally five or more single molecules combine to form a compound and that the concentration of the compound is a small percentage of the total solute present. The results have a bearing on the problem of deterioration of insulating oils. The high conductivities of the latter, even in the presence of certain colloidal constituents, are ultimately caused by electrolytic ions of the type investigated.

1. INTRODUCTION

IN certain previous publications[1-3] the author has introduced e.m.f. measurements in the study of insulating liquids for the purpose of obtaining additional information on the nature of electrolytic ions in such systems. Up to that time, the measurement of the electrical conductivity was essentially the only tool used for this particular purpose and it seemed that the addition of the e.m.f. method, which is most useful in the study of aqueous and alcoholic solutions, would be of value in this field, too. Results obtained in this series of researches to date seem to justify this enterprise.

The author used the glass electrode for the measurement of hydrogen ion concentrations in hydrocarbon solvents and hydrocarbon oils. E.m.f. data obtained from oils to which a strong acid (organic sulfonic acid) was added could be interpreted quantitatively on the basis of a reversible electrode action of the glass. When,

[1] Andrew Gemant, J. Chem. Phys. **10**, 723 (1942).
[2] Andrew Gemant, J. Chem. Phys. **12**, 79 (1944).
[3] Andrew Gemant, J. Chem. Phys. **13**, 146 (1945).

however, the technique was used for oils that were oxidized in the laboratory, or deteriorated in service, the hydrogen ion concentration appeared much too low to account for the measured electrical conductivity. The conclusion was drawn, therefore, that the cation in such oils was not the hydrogen ion. It should be pointed out that this conclusion was based on direct proof obtained from specific e.m.f. data. This result is in keeping with those obtained by J. D. Piper and co-workers[4]; these authors showed that solutions of purified acids in paraffin oil do not produce the high conductivity present in oxidized oils.

Since the cations in oxidized or deteriorated oils, which exhibit increased conductivity, are not hydrogen ions, the further conclusion was drawn that they must in all probability be organic in nature, just as are the anions. What their exact chemical nature is could probably be found from e.m.f. measurements, if appropriate electrodes were available. In attempting to do further work in this direction, the next step in the research seemed to be the establishment and conductometric investigation of solutions in hydrocarbon oils of electrolytes of which both ions are organic. Obviously, organic amines are best suited for such a purpose, although there are other compounds (certain triphenylcarbinol derivatives, for instance) that under certain circumstances, particularly in combination with halogens, show cation-like behavior. The conclusion that the cations in hydrocarbon solvents are amines is supported in the literature. Fuoss and Kraus[5] investigated the conductivities of tetraisoamylammonium nitrate in mixtures of dioxane and water. J. B. Dickey[6] has obtained a series of patents on treating yarns with certain compounds (diethylcyclohexylamine salts of phosphinated ketones and the like) in order that static electricity be avoided during subsequent weaving. Since the yarns during weaving are in oil, it is likely that the organic salts are dissolved in the oil and form semi-conducting solutions. J. D. Piper and collaborators[4] also have ex-

amined, among a great variety of added materials, the effect of salts of organic amines upon the electrical conductivity of paraffin oil; they obtained high conductivities at 80°C.

2. SOLUTIONS IN XYLENE

Although the majority of data in this paper refer to a hydrocarbon oil, several sets of measurements were carried out with xylene and benzene as solvents. As will be shown in the section dealing with hydrocarbon oil, appreciable conductivities at relatively low concentrations of the electrolytes are obtainable only in a three-component system, consisting of an amine, an aliphatic acid, and a phenolic compound. In solvents such as xylene or benzene, however, probably because of their higher dielectric constant, two-component systems (amine and aliphatic acid or amine and phenolic) are sufficient to cause reasonably high conductivities, although even in these solvents the three compounds together are far more effective. In this section solutions in xylene of α-naphthylamine and phenol are dealt with in detail. All chemicals used in this research were high grade commercial products, and were used without additional purification.

The tests consisted in preparing a series of solutions of various normalities with regard to the solutes added, and measuring the conductivities at room temperature in a cell designed by J. C. Balsbaugh.[7] A variable-frequency power factor bridge was used, and the range of frequencies extended from 50 to 20,000 c.p.s. As explained later in this paper in the part dealing with solutions in oil, no variation of the conductivity with frequency was observed during the many checks at several frequencies. In addition to the conductivity, the dielectric constant, too, was determined for each solution of the series.

The obtained conductivities were corrected for the conductivities observed when either of the two components was added separately. This was necessary because the ion formation from electrolytes consisting of organic cations *and* anions was the only point of interest in this connection. Thus, the conductivities caused by either component alone were deducted from the total. If the

[4] J. D. Piper, A. G. Fleiger, C. C. Smith, and N. A. Kerstein, Ind. Eng. Chem. **32**, 1510 (1940); **34**, 1505 (1942).
[5] R. M. Fuoss and C. Kraus, J. Am. Chem. Soc. **55**, 2387 (1933).
[6] J. B. Dickey, U. S. Pat. 2,256,112; 2,286,791, and 2,286,794, 1941 and 1942.

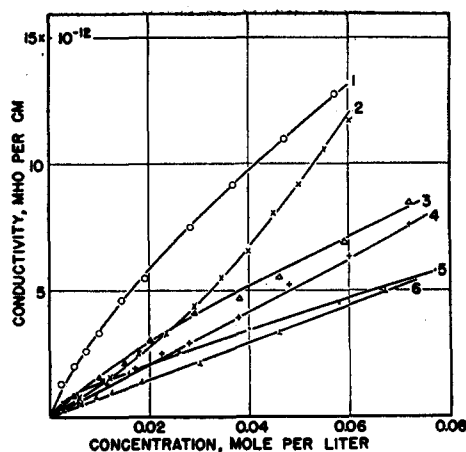[7] J. C. Balsbaugh and A. G. Assaf, Ind. Eng. Chem. **13**, 515 (1941).

FIG. 1. Conductivity at room temperature *vs.* concentration of solutions in xylene. The conductivities in this as in all other figures are corrected for initial conductivities of the starting solutions, as explained in the text.

Curve 1 = Concentration of α-naphthylamine: varying; that of phenol: 0.23 normal.
Curve 2 = Concentration of α-naphthylamine: 0.23 normal; that of phenol: varying.
Curve 3 = Concentration of α-naphthylamine: varying; that of phenol: 0.16 normal.
Curve 4 = Concentration of α-naphthylamine: 0.16 normal; that of phenol: varying.
Curve 5 = Concentration of α-naphthylamine: varying; that of phenol: 0.08 normal.
Curve 6 = Concentration of α-naphthylamine: 0.08 normal; that of phenol: varying.

hypothesis that ion formation from such types of electrolytes plays an important role in liquid dielectrics is correct, then the corrections applied should be relatively small parts of the total. This expectation was very strikingly fulfilled in the case of oil as solvent, as will be shown later. For xylene the deducted amounts were larger, ranging from about 20 to 35 percent of the total.

In each series the concentration of one component was kept constant while that of the other was increased by steps. In three sets the concentration of α-naphthylamine was kept at, respectively, 0.08, 0.16, and 0.23 normal; in three other sets the concentration of phenol was kept at the same percentages. The results obtained from these six series is shown in Fig. 1 in which the conductivity in mho/cm is plotted against the normality of the component that was varied by steps. The conductivities are all corrected as described above; they are of the order of 10^{-12} to 10^{-11} mho/cm. It was not deemed necessary to present the uncorrected conductivities, as observed, for all series of measurements presented in this paper; as an illustration, however, the
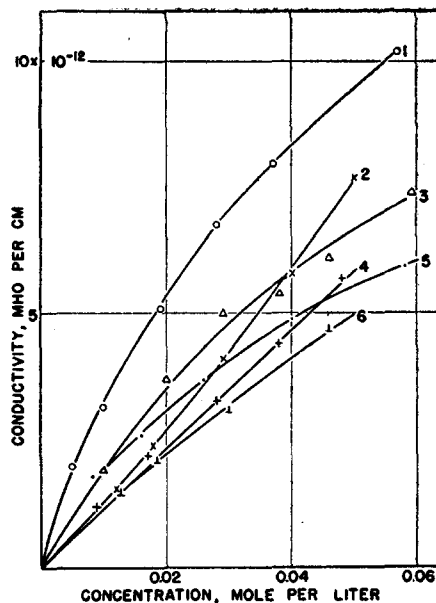

FIG. 2. Conductivity *vs.* concentration of solutions in xylene; conductivity data reduced to a dielectric constant of 2.45.

Curves 1 to 6: the same as in Fig. 1.

uncorrected data will be given for three particular series of solutions dealt with in Section 3a.

One of the reasons for the increase in conductivity with increasing concentration is the increase of the dielectric constant. In order to find out in what manner the conductivity depends on the concentration of dissociable material, the effect of the varying dielectric constant must be eliminated. Although the variation of the latter was rather small in this series (from 2.39 to 2.48), such a procedure was considered necessary. It was carried out in the following manner.

One of the six series (with $0.08n$ α-naphthylamine) was repeated with 3.5 percent by volume chloroform added to the solutions. It was assumed that the essential role of the chloroform was to raise the dielectric constant without acting specifically upon the various solutes. By this means the dielectric constant was increased throughout by an increment close to 0.06. The conductivities at corresponding concentrations of phenol were found to differ by a factor close to 1.60. In the narrow range of dielectric constants involved it is safe to take a simple exponential variation between the conductivity and the dielectric constant. In other sections of this paper

a different procedure was employed, in which no use of the special assumption of an exponential variation was made. In order to eliminate the role of the dielectric constant, all conductivities were reduced to an arbitrarily selected value of dielectric constant. The value 2.45, lying in the middle of the range, was selected. The conductivity σ at a dielectric constant D is then reduced to $\sigma_{2.45}$, its value at a dielectric constant 2.45, by the relation:

$$\sigma_{2.45} = \sigma 1.60^{(2.45-D)/0.06}. \tag{1}$$

The corrected conductivity data are presented in Fig. 2; the curves, as can be seen, are somewhat different from those in Fig. 1. The variation of σ shown in Fig. 2 is caused solely by the increase in concentration of the two solutes.

A possible mechanism of ion generation as observed in these systems is the formation of an addition compound with subsequent ionic dissociation (this subject is further discussed at the end of this paper). While it is not maintained that the experimental data furnish compelling proof for this explanation, it is thought to be at least a useful guiding hypothesis for the interpretation of the data. It is possible that a continuation of these studies will indicate the desirability of a different approach to the problem; one of the various other possibilities is, for instance, the theory of multiple ion formation, as suggested by Fuoss and Kraus.[5]

Let us then denote the basic constituent by B, the acidic one by A, and assume that n molecules of B and m of A form a compound B_nA_m:

$$nB + mA \rightleftarrows B_nA_m.$$
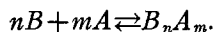
If concentrations in mole/liter are denoted by c with respective indices, we have

$$K_a c_B{}^n c_A{}^m = c_{B\,A_m}, \tag{2}$$

TABLE I. Conductivities of solutions in hydrocarbon oil.

| | Concentration in mole/liter | | Conductivity in mho/cm |
Tributylamine	Oleic acid	o-Cresol	
0.05	0.05	—	1.7×10^{-14}
0.05	—	0.05	2.9
—	0.05	0.05	2.1
0.05	0.05	0.05	90
0.205	—	0.20	36
0.205	0.038	0.20	1700

where K_a = association constant. If B^+ denotes a positive and A^- a negative ion, formed by dissociation of the addition compound (this is the simplest, although by no means the only possible kind of dissociation), the reaction is

$$B_nA_m \rightleftarrows B^+ + A^-$$
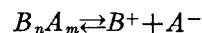
and, with K_d = dissociation constant:

$$K_d c_{B_nA_m} = c_{B+} c_{A-}. \tag{3}$$

Since

$$c_{B+} = c_{A-} = c_i, \tag{4}$$

where c_i = ionic concentration:

$$K_a K_d c_B{}^n c_A{}^m = c_i{}^2. \tag{5}$$

Since the conductivity σ is given by

$$\sigma = 10^{-3} \Lambda_0 c_i, \tag{6}$$

with Λ_0 = equivalent conductivity, Eq. (5) yields

$$\sigma = k c_B{}^{n/2} c_A{}^{m/2}, \tag{7}$$

with

$$k = 10^{-3} \Lambda_0 (K_a K_d)^{\frac{1}{2}}. \tag{8}$$

In applying Eq. (7) and (8) to the present case, an inspection of Fig. 2 reveals that curves 1, 3, and 5 (variable amine content) follow approximately a square root function, while curves 2, 4,
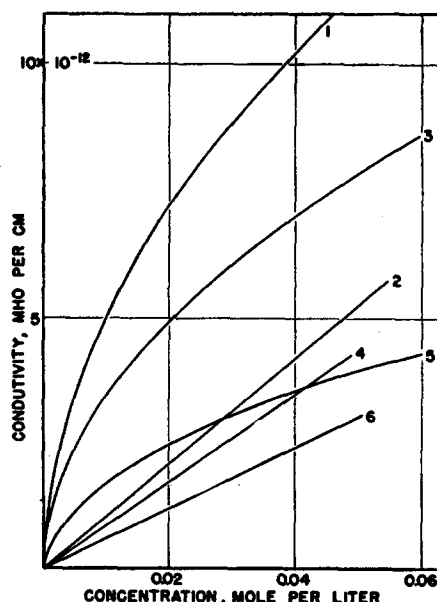

FIG. 3. Conductivity *vs.* concentration of solutions in xylene; calculated from Eq. (7).

Curves 1 to 6: the same as in Figs. 1 and 2.

TABLE II. Dielectric constants and conductivities (uncorrected) for three series of solutions in hydrocarbon oil.

Starting solution: 0.05n oleic acid 0.05n o-cresol			Starting solution: 0.05n tributylamine 0.05n o-cresol			Starting solution: 0.05n tributylamine 0.05n oleic acid		
Normality of tributylamine	Dielectric constant	Conductivity in 10^{-14} mho/cm	Normality of oleic acid	Dielectric constant	Conductivity in 10^{-14} mho/cm	Normality of o-cresol	Dielectric constant	Conductivity in 10^{-14} mho/cm
0.0000	2.210	2.1	0.0000	2.232	2.9	0.0000	2.234	1.75
0.0096	2.245	14	0.0092	2.266	22.5	0.011	2.253	7.1
0.019	2.281	39	0.018	2.289	37	0.022	2.275	17
0.028	2.301	58	0.027	2.303	51	0.032	2.290	32.5
0.036	2.310	71	0.035	2.312	62	0.042	2.310	60
0.044	2.317	80	0.047	2.323	77	0.053	2.325	93
0.052	2.319	91	0.058	2.331	89	0.062	2.341	135
0.060	2.324	100	0.069	2.337	101	0.072	2.355	187
0.067	2.326	106						

and 6 (variable phenol content) are approximately linear. It appears, then, that the main addition compound consists of one molecule of amine ($n=1$) and two molecules of phenol ($m=2$). The obvious disagreement of some of the curves (clearly of curve 2) with this simple behavior indicates that probably several addition compounds are formed, but that the one just mentioned prevails.

The conductivities at concentrations corresponding to the set of curves in Fig. 2 were calculated from Eq. (7) with $n=1$ and $m=2$. The value of k was adjusted so as to obtain an order of magnitude of 10^{-11} for σ at $c=0.06$. The value used was 2.2×10^{-10}. The plot of these calculated data is shown in Fig. 3 which is reasonably similar to Fig. 2.

In further verification of the mechanism here depicted, the measurements of Lucasse[8] may be quoted. The melting points of mixtures of p-toluidine and acetic acid have a maximum of 49°C at 66 percent of acetic acid, corresponding to a compound: 1 amine, 2 acid molecules—exactly the same ratio as the conductivity curves in Fig. 2 indicate. Thus Eq. (7) reproduces the measured data with one arbitrary constant k in a satisfactory manner.

The value of this constant, as required to satisfy the experimental data, may be used for an estimate of K_a, the association constant. In Eq. (8) the order of magnitude of Λ_0 is 60 (mobility of organic ions in a solvent of viscosity of 1 centipoise is around 30) and that of K_d is

[8] W. W. Lucasse, R. P. Koob, and J. G. Miller, J. Phys. Chem. 48, 85 (1944).

10^{-18}; this order of magnitude was obtained[2] for a number of strong electrolytes (acids) in xylene and dioxane. With these figures a value of 10 is obtained for K_a from Eq. (8). This order of magnitude is significant: It shows that the compound formation is not complete (which is the case if K_a is much larger than 1), nor is the amount of compound formed only a very small fraction of the components (which is the case if K_a is much smaller than 1). From Eq. (2) the concentration of the compound can be computed, using $K_a=10$; if, for instance, both components are present in a normality of 0.05, the concentration of the compound is 0.001 which is about 2 percent of the amine.

3. SOLUTIONS IN HYDROCARBON OIL

The hydrocarbon oil used was a typical transformer oil of a viscosity of 0.14 poise at 25°C, a dielectric constant 2.18, and an electrical conductivity 1×10^{-14} mho/cm at 25°C. Three different systems of solutes were investigated which will be treated separately in the following.

(a). Tributylamine—Oleic Acid— o-Cresol Solutions

In testing hydrocarbon oils, it was observed that addition of an acidic and a basic component did not as a rule produce a noticeably increased conductivity at room temperature. The author was first inclined to believe that, concerning hydrocarbon oils, his conclusions with regard to the importance of organic cations were incorrect. Neither aliphatic acids, nor phenolic compounds —both weak acids in aqueous solutions—pro-

duced an effect, when added separately to solutions of the amine. When, however, acids of both types were added simultaneously to an oil containing an amine, the effect became pronounced. Table I shows that none of the three possible combinations in pairs of the three materials added produced a conductivity noticeably higher than that of the oil alone, while the three materials together had a rather pronounced effect. The last two lines show that even if the amine and cresol were present in excessively high concentrations, producing a conductivity of medium level, addition of relatively small amounts of acid increased the conductivity about fifty times. The correction to be applied to values of σ, in order to obtain the conductivity resulting from the combination alone, is only 2 to 3 percent.

Three series of measurements were carried out, each starting with a combination of two of the three solutes in concentrations of 0.05 mole/liter each. To these solutions the third solute was added in increasing concentrations. The dielectric constants and the total conductivities, as measured, for these three series are shown in Table II.

The dielectric constant D of the starting solutions was about 2.23, increasing with increasing concentration to about 2.34. This increase, while rather small, is significant because of the generally low level of D. The process of reducing the σ-values to one selected value of D was rather important. It was done by repeating all three series with an oil containing 10 percent by volume of chloroform. By this means the above quoted
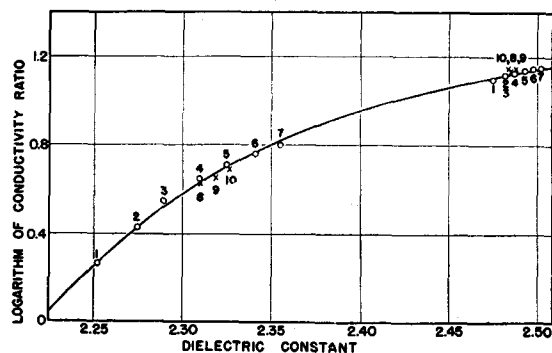
range of dielectric constants was raised to a level of about 2.40 to 2.50. By examining corresponding pairs of data (with and without $CHCl_3$), having conductivities σ and σ' and dielectric constants D and D', various values of σ/σ' were correlated with values of $(D-D')$. Or, since a
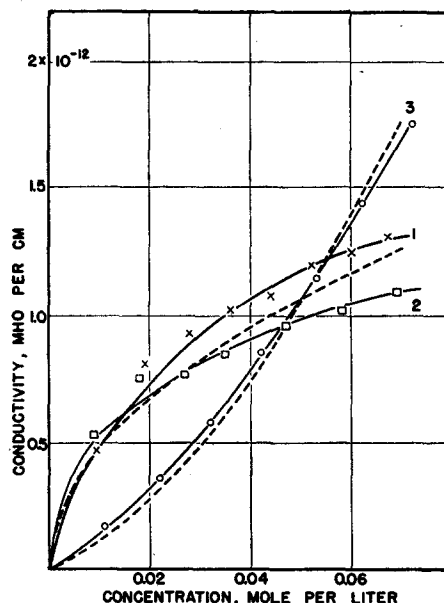

FIG. 5. Conductivity *vs.* concentration of solutions in hydrocarbon oil.

Curve 1: Tributylamine varying; oleic acid 0.05n; o-cresol 0.05n.
Curve 2: Tributylamine 0.05n; oleic acid varying; o-cresol 0.05n.
Curve 3: Tributylamine 0.05n; oleic acid 0.05n; o-cresol varying.
(Conductivity data reduced to a dielectric constant of 2.35.)
X □ O and solid lines: experimental data.
Dotted lines: calculated from Eq. (10).

FIG. 4. Logarithm of conductivity ratio of tributylamine—oleic acid—o-cresol solutions in hydrocarbon oil *vs.* difference in dielectric constants.

Corresponding figures on curve refer to identical solutions except 10 percent by volume of chloroform added to increase the dielectric constant. X refers to curve 1 of Fig. 5. O refers to curve 3 of Fig. 5.
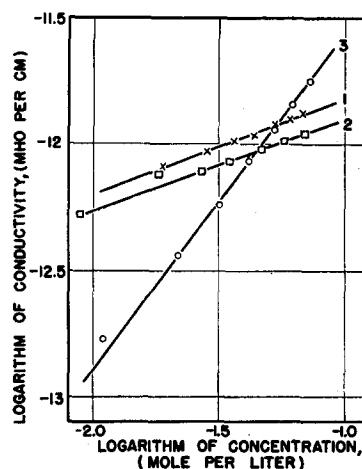

FIG. 6. The same as the solid lines of Fig. 5, plotted on a bilogarithmic scale.

Slope of curve 1 =0.38.
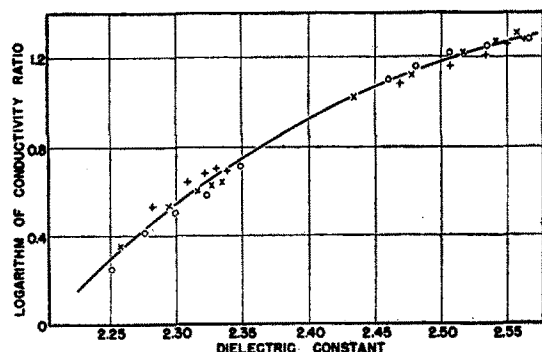Slope of curve 2 =0.38.
Slope of curve 3 =1.35.

FIG. 7. Logarithm of conductivity ratio of tributylamine-myristic acid—α-naphthol solutions in oil $vs.$ difference in dielectric constants.

X refers to curve 1 of Fig. 8.
+ refers to curve 2 of Fig. 8.
O refers to curve 3 of Fig. 8.

plot of log (σ/σ') $vs.$ D was attempted, values of $(\log \sigma - \log \sigma')$ were correlated with values of $(D - D')$.

These correlated data were then plotted in the manner shown in Fig. 4: differences in ordinates were plotted against differences in abscissas, pairs of data being shown by identical figures on the curve. As can be seen, the absolute value of the conductivity does not enter into the plot, and the curve is assumed to hold independently of the latter. With the aid of this curve all data were reduced to $D = 2.35$, an average value for the range covered. Curve 1 of Fig. 5 refers to varying amine concentration, curves 2 and 3 to varying acid and o-cresol concentrations, respectively. The conductivities increase to about 2×10^{-12} mho/cm, an order of magnitude often found in deteriorated oils. The values are lower than for corresponding concentrations in xylene partly because of the higher viscosity of the solvent.

The same guiding hypothesis that was used in the previous case might be used here, too. Apart from the n molecules of base B, and m molecules of acid A, l molecules of a phenolic compound P will combine into a compound $B_nA_mP_l$:

$$nB + mA + lP \rightleftarrows B_nA_mP_l$$
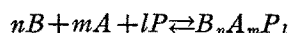
that subsequently supplies a positive and a negative ion. Instead of Eq. (5) we then have:

$$K_aK_dc_B{}^nc_A{}^mc_P{}^l = c_i{}^2, \tag{9}$$

and instead of Eq. (7):

$$\sigma = kc_B{}^{n/2}c_A{}^{m/2}c_P{}^{l/2}. \tag{10}$$

Inspecting Fig. 5, curves 1 and 2 are found to follow approximately a square root function, while curve 3 is a $1\frac{1}{2}$ power function. The same curves plotted bilogarithmically in Fig. 6 reveal straight lines with slopes of 0.38, 0.38, and 1.35, respectively. The dotted lines in Fig. 5 were calculated from Eq. (10) according to these powers and made to cross at $c = 0.05$ as they should if Eq. (10) were strictly correct. Since curves 1 and 2 do not coincide, Eq. (10) can be only approximately valid.

With $n = 1$, $m = 1$, and $l = 3$, it appears that one molecule of amine, one molecule of acid, and three molecules of phenol combine into one: thus, a fairly large molecule results. The possible structure of such an addition compound will be discussed in the last section (discussion) of this paper.

The constant k corresponding to the calculated dotted lines in Fig. 5 has a value of 1.9×10^{-9}. This permits K_a to be estimated from Eq. (8). In the oil of viscosity 0.14 poise, it can be estimated[3] that Λ_0 is around 4 and K_d is of the order of magnitude of 2×10^{-16}. This gives $K_a = 1 \times 10^3$. Hence, with all three components present in a concentration of 0.05 mole/liter each, the concentration of the compound is 4×10^{-4}, about 1 percent of the amine present.

(b). Tributylamine—Myristic Acid—α-Naphthol Solutions

As mentioned in Section 2, the chemicals used in this research were not subjected to laboratory purification. This implies that a repetition of these tests with purified materials would yield numerically somewhat different results. In particular, the objection could be raised against the data presented under (a) that oleic acid and o-cresol always contain admixtures and that the effect was, at least in part, caused by them. The low conductivity found in any pair of the three

TABLE III. Conductivities of solutions in a hydrocarbon oil.

Concentration in mole/liter			Conductivity in mho/cm
Tributylamine	Myristic acid	α-Naphthol	
0.05	0.05	—	1.4×10^{-14}
0.05	—	0.05	7.9
—	0.05	0.05	5.5
0.05	0.05	0.05	400

materials, however, can be brought against such objection.

To clarify this point further, a combination was chosen in which oleic acid was replaced by myristic acid and o-cresol by α-naphthol, both crystalline materials. The program for this part of the work was the same as that for the previous part. Three sets of solutions were investigated; each set contained two of the materials each 0.05 normal and the third material in increasing amounts. The "zero values" are shown in Table III. The conductivity of the solution containing all three components is 4×10^{-12}, more than four times that of the previous combination. This finding is reassuring in that impurities have probably only a secondary role in the effect observed.

The effect of the dielectric constant was evaluated in the same manner as before; the result of this "plot of differences" is shown in Fig. 7. Both this plot and Fig. 4 show that the effect of the dielectric constant increases with decreasing value of the latter, in keeping with the theory of Bjerrum.[9]
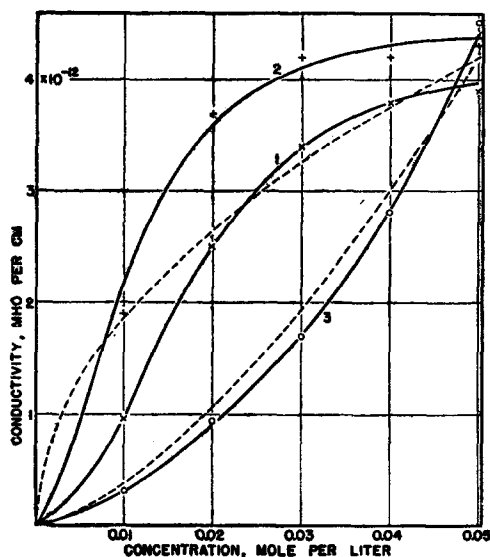
The conductivities, reduced to $D = 2.35$, are shown in Fig. 8. As the dotted curves ($\frac{1}{2}$ and $1\frac{1}{2}$ power) show, the former is not in agreement with the experimental data below 0.01 normality. It appears that the type of the reaction changes with increasing concentration of the components. The experimental data are, however, not considered sufficiently complete to permit further interpretation of this upward trend of the curves at the origin. Using the location of the dotted lines, an evaluation analogous to the previous one gives $k = 7.5 \times 10^{-9}$; $K_a = 2 \times 10^4$, and the concentration of the compound for all three components present in 0.05 molar concentration is 6×10^{-3}, i.e., twelve percent of the amine present. The large conductivity effect obtainable with this combination is caused, according to the mechanism assumed, by an increased tendency for addition compound formation. The compound molecule containing three molecules of α-naphthol must have appreciable size.

(c). Triethanolamine—Oleic Acid Solutions

In addition to the series discussed, some tests were carried out with an amine containing

FIG. 8. Conductivity vs. concentration of solutions in hydrocarbon oil.

Curve 1: Tributylamine varying; myristic acid: 0.05n; α-naphthol: 0.05n.
Curve 2: Tributylamine 0.05n; myristic acid: varying; α-naphthol: 0.05n.
Curve 3: Tributylamine 0.05n; myristic acid: 0.05n; α-naphthol: varying.
(Conductivity data reduced to a dielectric constant of 2.35.)
X + O and solid lines: experimental data.
Dotted lines: calculated from Eq. (10).

[9] D. A. MacInnes, The Principles of Electrochemistry (Reinhold Publishing Corporation, New York, 1939), p. 372.
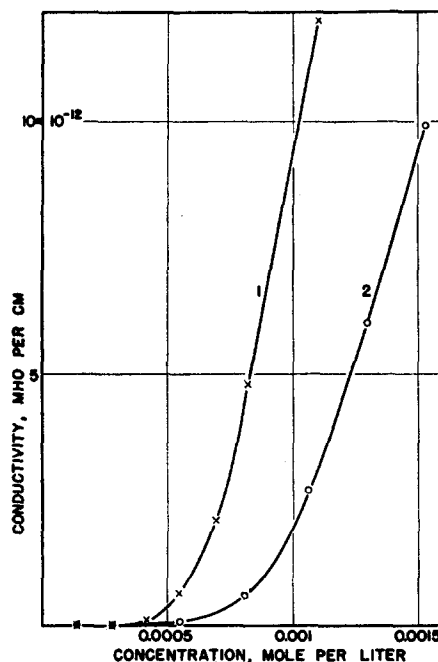

FIG. 9. Conductivity vs. concentration of solutions in hydrocarbon oil.

Curve 1: Triethanolamine: varying; oleic acid: 0.06n
Curve 2: Triethanolamine: varying; oleic acid: 0.03n.

hydroxyl groups: triethanolamine. Because of the low solubility of this compound only low concentrations were investigated, giving clear solutions —at least to the naked eye. The concentration limit at which inhomogeneity appeared was rather sharp, and measurements were carried out only well below that limit.

The dielectric constant was remarkably constant in these measurements (from 2.20 to 2.22), so that no correction in this respect was necessary. The results from two series are presented in Fig. 9. Curve 1 refers to an oleic acid content of 0.06 normal; curve 2, to one 0.03 normal. The concentrations of the amine are shown on the abscissa; the range covered was below 0.0015 normal. Solutions up to an amine concentration of about 0.01 normal were clear.

Because of the low solubility of this amine (in fact, it is insoluble in oil alone and dissolves only in the presence of the acid) the existence of a second phase, contributing by a Maxwell-Wagner effect to the high conductivity, might be suspected. In this case σ should be a function of frequency, and in particular, if measured with d.c. voltages, distinctly less. While a check of σ using several frequencies was occasionally carried out in all the series reported, a few data relating to this particular combination are given in Table IV. Even the second of the listed solutions, having the high conductivity of 10^{-10} at room temperature, shows no variation in the range between a frequency of 20,000 and d.c. voltages; this solution, by the way, remains clear to the naked eye even after prolonged standing. Accordingly, a Maxwell-Wagner effect on interphases can be ruled out.

The data obtained in this combination are not deemed sufficiently complete for the drawing of

TABLE IV. Conductivities at various frequencies of solutions in hydrocarbon oil.

| Concentration in mole/liter | | Frequency, | Conductivity in |
Triethanolamine	Oleic acid	c.p.s.	mho/cm
0.00082	0.06	10,000	4.8×10^{-12}
0.00082	0.06	1,000	4.6
0.00082	0.06	100	4.4
0.00082	0.06	50	4.6
0.0068	0.06	20,000	96×10^{-12}
0.0068	0.06	10,000	96
0.0068	0.06	1,000	96
0.0068	0.06	d.c.	100

quantitative conclusions. In attempting to apply the mechanism suggested (compound formation with subsequent dissociation), the steepness of the curves suggests that a relatively large number of molecules are involved in the compound formation. An estimate of about eight molecules of amine and four molecules of acid is in keeping with the trend of the curves; the relatively large size of the compound is in agreement with the observed low solubility of the amine.

4. DISCUSSION OF THE RESULTS

While, for the sake of a systematic presentation, part of the discussion, particularly a quantitative interpretation of the data, has been included in the corresponding sections dealing with experimental results, two subjects deserve special consideration. One of these is the mechanism of conductivity in the three-compound systems in oil. The other subject is the bearing of the presented results on the problem of deterioration of insulating oils.

(a). Mechanism of Conductivity in the Three-Component Systems in Oil

If the conductivity is produced in a two-component, base-acid system, there can be little doubt that the mechanism is compound formation with subsequent ionic dissociation. Consequently the equations presented in Section 2 of this paper are probably safely founded. The extension of this mechanism to the three component base-acid-phenolic system, however, is not quite as obvious. One might first think of another possibility, namely, that the phenol simply plays the role of an addition to the solvent, increasing the dielectric constant of the latter. Hence, its action would be merely electrostatic. This possibility cannot be strictly disproved, but tests carried out with chloroform to show the effect of the dielectric constant upon the conductivity rule against it. Table V gives a few figures that are instructive in this respect. Solutions containing the phenolic component have a σ over 10^{-12}; those without the phenolic have, in spite of a considerable amount of CHCl$_3$, a σ below 10^{-12}. The first solution has a σ larger than the second, although its dielectric constant is lower than that of the second; the same is true if

TABLE V. Conductivities of solutions in hydrocarbon oil.

Tributyl-amine	Concentration, mole/liter					Dielectric constant	Conductivity mho/cm
	Oleic acid	Myristic acid	o-cresol	α-naphthol	Chloroform		
0.05	0.05	—	0.072	—	—	2.35	1.9×10^{-12}
0.05	0.05	—	—	—	1.25	2.46	0.47
0.05	0.05	—	0.072	—	1.25	2.50	4.7
0.05	—	0.05	—	0.05	—	2.35	4.4
0.05	—	0.05	—	—	1.25	2.46	0.45
0.05	—	0.05	—	0.05	1.25	2.56	17

the fourth and fifth solutions are compared. It can be concluded that, although the purely electrostatic effect of the components is not negligible, the phenols have an effect on σ markedly greater than the electrostatic one.

Assuming, therefore, a compound formation between the three components, a question arises regarding the chemical structure of the compound. The amount of information contained in this paper is clearly not sufficient to answer this question in a definite manner. However, some indication as to the correct answer can be found in using the concept of resonance.[10]

The unshared pair of electrons of the amino nitrogen attracts a proton; this is the reason for the formation of an addition compound between an amine and an acid. The same holds for an addition between an amine and a phenol or a naphthol. If, now, an addition between an acid and a phenol should take place that leaves both hydroxyls free (hence, *not* an ester formation), then such a compound would be considerably stabilized through resonance in the presence of an amine, even if such a compound would be unstable in the absence of an amine. As an illustration of such resonating structures, formulas I and II are given; the position of the electron pair of the nitrogen is different in the two cases. If more than one molecule of the phenol or naphthol is attached to the acid, the stability of the compound is further increased. The experimental data presented indicate this to be the case. The addition of the phenol to the acid is probably due to secondary valencies; this structure obviously needs further elucidation. It should be pointed out that there are theoretical considerations that might be raised against the

likelihood of such resonating structures.

I   II
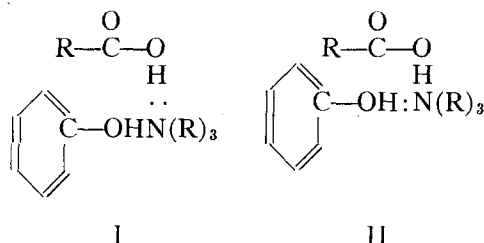
Once a compound of the type suggested is formed—and, if it is formed, its concentration should be reasonably large, as shown in the previous sections—its dissociation to a small extent into ions is understandable. Even if the aliphatic acid itself in the oil is extremely weak, the presence of the phenol groups considerably strengthens its acidity.[10] The reason for this effect is, partly at least, the $-CO^+$ dipole-moment of the phenol. More than one phenol group in the compound would further enhance this effect. The result of the dissociation is then the positive $HN^+(R)_3$ ion with the rest of the compound as the negative ion.

(b). Bearing of the Results Presented on the Problem of Deterioration of Oils

In investigating ionic solutions in oils, the question arises, to what extent are the ionic components responsible for the high conductivities of deteriorated oils. It is certain that such oils quite often reveal the presence of colloidal materials that appear to be related to their high conductivity. This standpoint is particularly emphasized by J. D. Piper and his co-workers.[11]

In the following it is shown that, even if colloidal particles add to the conductivity of oils,

[10] G. W. Wheland, *The Theory of Resonance* (John Wiley and Sons, Inc., New York, 1944), p. 167 *et seq.*

[11] Joseph Sticher and J. D. Piper, Ind. Eng. Chem. **33**, 1567 (1941).

the ultimate carriers of the electricity are in all probability molecularly dispersed ions. Three cases are now considered.

(1) If the inhomogeneity takes the form of a microscopic second phase dispersed in the oil, a Maxwell-Wagner effect might contribute to the conductivity. This, as the theory of the effect reveals, is ultimately caused by the bulk conductivity of the two phases, hence, by electrolytic ions.

(2) If the inhomogeneity is a colloidally dispersed second phase, a so-called lyophobic colloid, the particles might, owing to their charge, exhibit cataphoresis, thus contributing to the total conductivity.[12] Judging from aqueous solutions, the charges upon such particles are caused by preferential adsorption of one kind of the electrolytic ions present in the bulk of the liquid.

(3) If the inhomogeneity is a lyophilic colloid, in the majority of cases a so-called macromolecular solution, then an electrolytic dissociation of such macromolecules contributes to the conductivity. Examples are proteins, soaps, and the particles in Oden's sulphur sol. In these cases the concepts of the collodial particle and of the macromolecular electrolytic ion merge into one.

It is not maintained that the solutions investigated are identical with deteriorated oils. The

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[12] Andrew Gemant, J. Phys. Chem. **43**, 743 (1939).

exact nature of the ionic components can certainly vary within considerable limits.

Concerning the presence of acids and aromatic alcohols, these are probably formed during the oxidation of the oil. Concerning the basic component, the average total nitrogen content of oils appears to be about 0.03 percent, i.e., 0.02 molar. Assuming this nitrogen to be largely basic in character, this concentration is exactly in the range that was found to produce conductivities of the order of magnitude 10^{-12} to 10^{-11} mho/cm (the same as in deteriorated oils). In particular, if traces of hydroxyamines are formed during oxidation, the effectiveness of the nitrogen is considerably increased, as has been shown. It is generally agreed that the nitrogen in oils is present in the form of cyclic compounds, and it is of interest to note in this connection that substitution of the cyclic piperidine for tributylamine produced conductivities comparable to those presented in Section 3. Nevertheless, the presence of other types of organic cations, such as oxonium ions and triarylcarbinols, has also to be considered, although they are much weaker bases than the amines.

A more accurate answer as to the chemical nature of organic ions present in oxidized oils could be given, if specifically acting electrodes for e.m.f. measurements could be developed. The author is at present engaged in a research to find out whether this is possible.