Studies on the Interaction of Paraffin Chain Alcohols and Association Colloids

IV. The Effect of Decanol-1 on the Viscosities of Some Association Colloid Solutions

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The effect of decanol on the viscosities of solutions of sodium oleate, sodium lauryl sulphate and sodium myristyl sulphate has been studied. When the oleate concentration is low, below about 0.2 M, the viscosity increases slowly with the amount of decanol added and the viscosity curve reveals no noticeable irregularities at the turbidity point where a new phase composed of decanol, oleate and water begins to separate. At higher oleate concentrations three ranges can be distinguished in which the effect of decanol on the viscosity differs depending on the amount of decanol added. As long as all the decanol is solubilized in the micelles, the viscosity increases. When the new phase appears, the viscosity decreases at first as decanol is added, then passes through a minimum and begins to increase again when more decanol is added. Some observations on the effect of p-xylene on the viscosity of a sodium oleate solution have also been made. The factors which determine the observed variation of the viscosity are discussed. In homogeneous systems at low oleate concentrations the increase in the viscosity caused by decanol (or xylene) can be fairly well explained on the assumption of an increase in the micelle volume; at higher oleate concentrations (above *ca.* 0.2 M) large changes in the form and the structure of the micelles must be assumed. The decrease in the viscosity in the heterogeneous systems depends on the decrease in the concentration of the mixed micelles in the aqueous solution caused by the separation of the new phase. When the amount of this new phase becomes so large that it influences strongly the flow of the solution, the viscosity begins to increase rapidly.

The viscosities of solutions of association colloids with and without added inorganic salts have been thoroughly investigated, but the effect of solubilized substances on the viscosities of association colloid solutions has not been systematically studied.

The effect of lower paraffin chain alcohols was investigated by Bose and coworkers [1-5] (methanol to hexanol, different soaps, sodium chloride) and by Rossi and Ragno [6] (ethanol, sodium oleate). The measurements were carried out on clear homogeneous solutions; the alcohol contents used were very high, between 10 and 50 % of the volumes of the soap solutions. The alcohols caused an increase in the viscosity; in some cases Bose observed that the viscosity decreased when greater amounts of alcohol were added. The effect of higher alcohols seems to have been studied only by Klevens [7] (octanol, potassium myristate, potassium chloride), de Jong and van Alphen [8] (methanol to octanol, sodium oleate, potassium chloride) and Ekwall, Passinen and Danielsson [9] (decanol, sodium oleate). The qualitative observations of Klevens show that in myristate solutions containing potassium chloride the viscosity increases with the amount of octanol, passes through a maximum and then begins to decrease; the maximum appears at an octanol content less than that required to effect turbidity. Also Ekwall and coworkers observed a viscosity maximum but this maximum occurs at the point where the system becomes heterogeneous; their solutions contained no added inorganic electrolyte.

The effect of polar-nonpolar compounds other than alkanols has also been studied. Thus, Angelescu and coworkers [10-13] studied the effect of different cresols on the viscosities of some soap solutions. They found that the viscosity increases slowly with the amount of cresol added when the soap concentration is low. At higher soap concentrations, the viscosity increases rapidly to a maximum, then decreases to a minimum and subsequently begins to increase slowly as the amount of cresol is increased further. All the systems studied were homogeneous. The effect of cresols on the viscosities of solutions of soap mixtures was also studied [13]; the viscosity curves were similar in form to those for solutions of the single soaps. Angelescu and coworkers studied also the joint effect of fatty acid and cresol [14] and of electrolytes and cresol [15] and the effect of some other substances [16,17] (phenol, hydroquinone, resorcinol, nitrophenol, aminophenol, naphthol). In most cases curves similar to those obtained with cresol were obtained, but in some cases no maximum was observed. Philippoff [18] studied the effect of m-cresol on the viscosity of a 0.45 M sodium oleate solution and found that the viscosity increases with the amount of cresol added, then passes a maximum and begins to decrease. He also established that the addition of cresol effects a pronounced structural viscosity. Ekwall and Henriksson [19] found that the addition of terpineol first effects a pronounced increase in the viscosity of a 0.3 M sodium oleate solution, and as more terpineol is added, the system becomes heterogeneous and the viscosity of the system decreases rapidly, goes through a minimum, passes a second less pronounced maximum and finally remains approximately constant. McBain and McHan [20] showed that a 0.10 M potassium laurate solution saturated with dimethyl phthalate has a slightly greater viscosity than the pure laurate solution.

Some observations on the effect of solubilized nonpolar compounds have also been made. Hahne [21] and Kiessig and Philippoff [22] studied the effect of benzene on a sodium oleate solution (0.3 M) and found that the viscosity first increases rapidly to a maximum when benzene is added, decreases then to a minimum and finally increases slowly. The maximum in the viscosity curve appears at a benzene content much below the solubility value. When the system becomes saturated with benzene, addition of more benzene does not effect any further change of viscosity. No structural viscosity was established in the pure oleate solution, in the solution of maximum viscosity, or in the system saturated with benzene [22]. Stainsby and Alexander [23] found that the addition of chlorobenzene produces marked changes in the viscosities of hexadecyl pyridinium chloride solutions.

It thus seems to be typical of the effect of solubilization on the viscosity that the viscosity attains a maximum when a certain amount of solubilizate has been added. In most cases this maximum occurred in homogeneous systems [7,10-18,21,22] but in two cases it appeared at the point where the system became heterogeneous [9,19]. The results are complicated by the fact that the systems studied have in most cases contained varying amounts of inorganic electrolytes in addition to association colloid, the solubilized substance and water.

The purpose of the present work was to study the effect of a relatively long paraffin chain alcohol, decanol-1, on the viscosity of association colloid solutions without any other additives and to correlate these data with our previous studies of the solubility of decanol and the effect of decanol on the electrical conductance of these same solutions (Part I [24], Part II [25] and Part III [26] of this series). Some experiments have also been made with the purpose of comparing the effect of solubilization of a hydrocarbon on the viscosity with that of decanol.

MATERIALS AND METHODS

The compounds used were those employed in our previous studies [24-26]. The solutions were prepared in the manner described in Part I[24]. They were shaken at 40° C for periods from three to six days.

The viscosities were measured with an Ostwald viscosimeter. The temperature was held constant at 40° C $\pm$ 0.05° C. The viscosity of each solution was measured three times, and the average values were recorded. The viscosities are relative viscosities, η_{rel} (water = 1). The relative viscosity values are accurate to $\pm$ 0.5 to 1 %. When the value of $\eta_{rel} = (d_s/d_w)/(t_s/t_w)$, where d_s and d_w are the densities of the solution and water, and t_s and t_w the times of flow of the solution and water, respectively, was calculated, the density ratio d_s/d_w was taken to be unity.

The concentration of the association colloid is given in moles per 1 000 g of solution (denoted by M).

EXPERIMENTAL RESULTS

Sodium oleate solutions containing decanol. The effect of decanol on the viscosities of sodium oleate solutions has been studied at oleate concentrations between 0.05 and 0.3 M (Fig. 1). When the oleate concentration is low, below approximately 0.15 M, the viscosity increases slowly as the amount of decanol is increased. In these dilutions no marked change is observed in the course of the viscosity curve at the point where the addition of decanol effects the separation of a new phase. When the oleate concentration is 0.189 M, the rise of the viscosity curve is slightly arrested in this region. When the oleate concentration is above 0.2 M, the viscosity rises rapidly as long as the decanol added is solubilized in the micelles. When the amount of decanol is so great that the system becomes heterogeneous, the viscosity begins to decrease with increasing amount of decanol added, then passes a minimum and finally increases again rapidly. When more decanol is added the system becomes gel-like.

Thus, at oleate concentrations above 0.2 M, three different regions can be distinguished in which the effect of decanol on the viscosity of the oleate solutions differs. There is first a region where an addition of decanol increases the viscosity, then a region where the viscosity decreases and finally a region where the viscosity increases again as more decanol is added. The boundary between the first and second region coincides with the point where the system becomes heterogeneous owing to the separation of a new phase composed of decanol, oleate and water (turbidity point) and above which the electrical conductance of the solution undergoes an abrupt decrease [25]. The minimum in the viscosity curve appears at a decanol content of approximately 0.3—0.4 mole of decanol per mole of oleate and in the vicinity of the turbidity maximum in the same system [25]; the experimental data are, however, too meagre to permit a
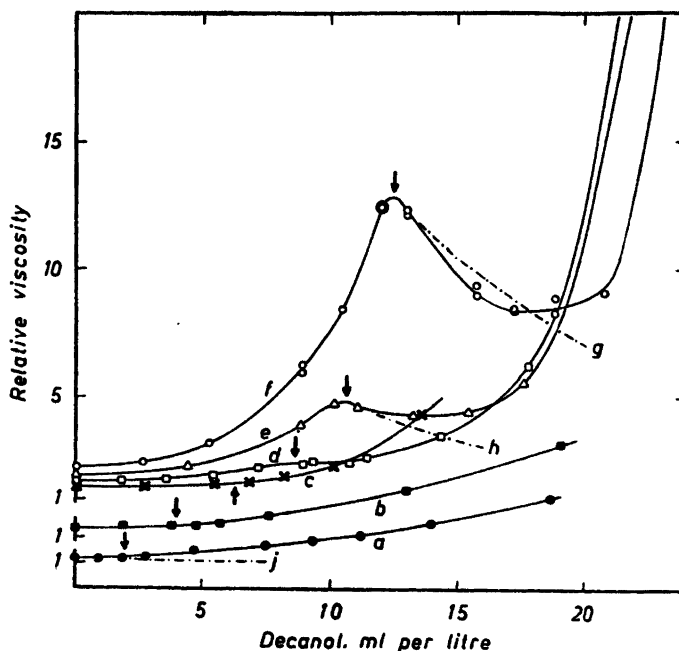
Fig. 1. Relative viscosities of sodium oleate solutions containing decanol. 40° C. The arrows indicate the points where the systems become heterogeneous.

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a) 0.0493 M sodium oleate
b) 0.0972 M    »        »
c) 0.143  M    »        »
d) 0.189  M    »        »
e) 0.232  M    »        »
f) 0.275  M    »        »
g—j) Calculated curves (see text, p. 224)
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decision whether viscosity minimum and turbidity maximum always coincide. In every case the viscosity minimum appears at a much lower decanol content than that at which the electrical conductance becomes constant (see Part II[25]); e. g. in a 0.232 M oleate solution the viscosity minimum occurs when 14 ml of decanol have been added per litre of solution, whereas the conductance becomes constant when approximately 30 ml of decanol have been added per litre.

The curves in Fig. 2 show how the effect of decanol on the viscosity varies with the concentration of oleate. Curve a gives the viscosities of the pure oleate solutions and is of the type generally found for the concentration dependence of the viscosity in solutions of association colloids. It increases slowly and linearly to a concentration of about 0.2 M and then begins to increase more rapidly. Curve b gives the viscosities of the oleate solutions containing decanol at the turbidity point, and curve c the viscosities of solutions containing 0.10 mole of decanol per mole of oleate. The difference between the
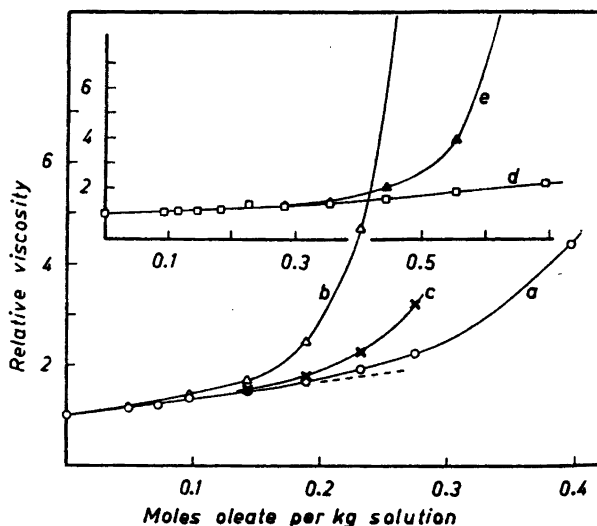
Fig. 2. a) Relative viscosities of pure sodium oleate solutions. 40° C.
  b) Relative viscosities of sodium oleate solutions containing decanol at the turbidity points. 40° C.
  c) Relative viscosities of sodium oleate solutions containing 0.10 mole of decanol per mole of oleate. 40° C.
  d) Relative viscosities of pure sodium lauryl sulphate solutions. 40° C.
  e) Relative viscosities of sodium lauryl sulphate solutions containing 0.116 mole of decanol per mole of lauryl sulphate. 40° C.

viscosity values of curves b and a, the increase in viscosity at the turbidity point, is very small up to an oleate concentration of about 0.15 M, but above this limit the difference increases rapidly with the oleate concentration. In respect of the oleate concentration there are thus two regions, the first up to a concentration of about 0.15 M and the second above this limit where the effect of decanol on the viscosity differs greatly.

Sodium oleate solutions containing p-xylene. The viscosities of a series of 0.200 M oleate solutions containing various amounts of p-xylene were also measured (Fig. 3, curve a). The viscosity rises slowly and nearly linearly with increasing additions of xylene up to a point close to the solubility limit of xylene where it becomes approximately constant. The increase of viscosity caused by xylene is much smaller than that caused by the same volume of decanol (Fig. 3, curve b).

The specific volumes of sodium oleate solutions containing decanol. In order to determine whether the density ratio d_s/d_w can be taken as unity in the calculation of the relative viscosities, the densities of oleate solutions containing decanol were measured. Fig. 4, curve a, shows that the specific volume of a 0.300 M solution increases linearly with the amount of decanol added until the new phase is formed; at the latter point the curve changes its slope and continues again as a straight line. The density ratio is seen to be very near unity even for the highest decanol contents. Curve b shows the variation of the
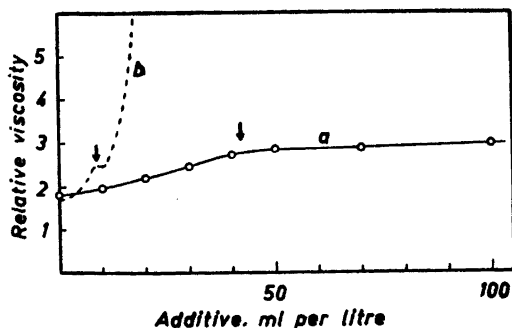
Fig. 3. a) *Relative viscosities of 0.200* M *sodium oleate solutions containing p-xylene.*
40° C.
    b) *Relative viscosities of 0.189* M *sodium oleate solutions containing decanol.*
40° C.
    The arrows indicate the points where the systems become heterogeneous.

partial molar volume of decanol with the amount of decanol added. The dotted horizontal line in the figure gives the molar volume of pure decanol, 193.7 ml per mole. In the mixed micelles of oleate and decanol the partial molar volume of decanol is 190.9 ml per mole and in the turbid solutions 196.9 ml per mole. The decanol is thus slightly more densely packed in the mixed micelles than in the pure state, and its partial volume in the two-phase system is greater than that of pure decanol.

Sodium myristyl and sodium lauryl sulphate solutions containing decanol. The effect of decanol on the viscosity of sodium myristyl sulphate solutions has
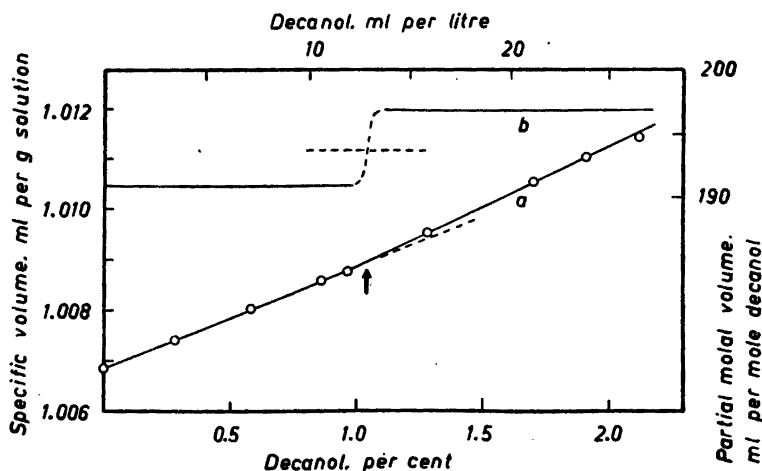

Fig. 4. a) *The specific volumes of 0.275* M *sodium oleate solutions containing decanol.*
40° C.
    b) *The partial molal volume of decanol in the same solutions.* 40° C.
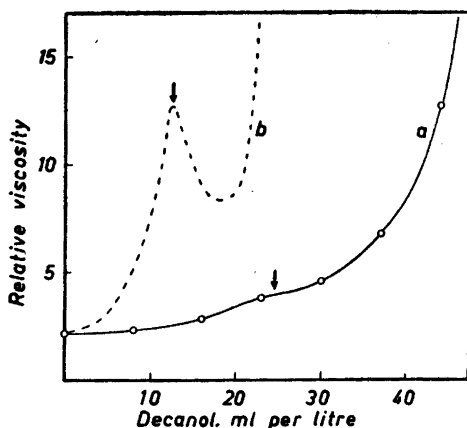   *The arrow indicates the point where the system becomes heterogeneous.*

Fig. 5. *a) Relative viscosities of 0.300 M sodium myristyl sulphate solutions containing*
decanol.   40° C.
b) Relative viscosities of 0.275 M sodium oleate solutions containing decanol. 40° C.
The arrows indicate the points where the systems become hetrogeneous.

been studied only at one colloid concentration, 0.300 M (Fig. 5, curve a). The
viscosity increases slowly at first, then more rapidly with the amount of deca-
nol added. In spite of the relatively high concentration of myristyl sulphate,
no maximum and minimum values analogous to those observed in equally
concentrated decanol-oleate systems were observed. Weak signs of a break
point can, however, be noted at the point where the new phase composed of
decanol, myristyl sulphate and water begins to separate. The viscosity curve
for a decanol-oleate system with approximately the same colloid concentration
has been drawn in Fig. 5 (curve b) for the sake of comparison; the viscosity of
the oleate solution increases appreciably more rapidly than that of a myristyl
sulphate solution on adding decanol.

The curves d and e in Fig. 2 show the variation of the viscosities of pure
sodium lauryl sulphate solutions and of solutions containing 0.116 mole of
decanol per mole of lauryl sulphate. These systems are homogeneous. The
curves are similar in form to the corresponding curves for the decanol-oleate
system (Fig. 2, curves a and c).

DISCUSSION

As we have seen above, the viscosities of pure and decanol-containing
oleate solutions increase linearly with the oleate concentration up to the
approximately 0.2 M concentration. Decanol effects a definitely greater in-
crease in viscosity above the latter limit than below it. We have previously
observed [24] that in the higher concentration range the solubility of decanol
begins to increase faster than at lower concentrations. The effect of this in-
crease of solubility on the viscosity is, however, very small. We have also found

that the effect of decanol on the conductance is altered at this same concentration (Part III[26], Table 1). Furthermore, the solubility of hydrocarbons undergoes a change [27, 28], the conductance of pure oleate solutions passes through a minimum [29, 30] and the so-called I band appears in the X-ray diffraction pattern [31] at the same colloid concentration. There is thus strong evidence that the properties of oleate solutions, both in the absence and presence of foreign substances, undergo pronounced variation at about this concentration $(0.1-0.2\ M)$. There seems to be sufficient reason to speak about a concentration limit in this concentration range; for the lack of a better name, this limit is called the 2nd critical concentration [28, 32, 33].

We shall first consider the homogeneous systems in which the added substance is solubilized, $i.\ e.$ completely incorporated in the micelles. The increase in viscosity that is observed when decanol (or p-xylene) is added to the system may be caused by four factors, 1. the micelle volume increases, 2. changes occur in the electroviscous effect, 3. the micelles become deformed and 4. the degree of aggregation and number of micelles are altered. Actually, of course, these different factors co-operate and depend on each other. Our purpose is, however, to study how great is the effect of each of the factors on the viscosity and to investigate whether any one of them can alone explain the observed increase in viscosity.

The volumes of the micelles increase because the solubilized compound enters the micelles. We have attempted to estimate how much this increase in volume can alter the viscosity. The proportion of the total volume of the solution taken up by the micelles, the volume fraction, can be calculated for a certain concentration from the partial molal volume of the oleate using the data of Ekwall and Smeds [28]. If it is assumed that the incorporated compound effects no other change in the structure of the solution than an increase in the micellar volume, the variation of the specific viscosity with the amount of compound added may be represented by the equation $\eta_{sp} = K\ \Phi$, where Φ is the combined volume fraction of the micelles and the added compound. The value of the constant K is calculated from the known values of the specific viscosity and volume fraction in pure oleate solutions. The viscosity values calculated for solutions containing solubilized p-xylene (0.200 M sodium oleate, Fig. 3) are found to be only slightly lower than the experimental values. For 0.3 M oleate solutions containing benzene, however, the calculated values are much smaller than the values reported by Kiessig and Philippoff [22] for the range where the viscosity passes through a maximum with increasing benzene content. Also the calculated viscosity values for solutions containing decanol are close to the observed values at low oleate concentrations, but are much too small at higher oleate concentrations. In the concentrated oleate solutions other factors than the increase in the volume of the micelles must thus be responsible for the observed great viscosity changes. This is the case also if the hydration of the alcohol molecules is taken into consideration.

The incorporation of decanol brings about a change in the structure and properties of the micelle surface; among other things the charge density on the micelle surface is altered. This may be expected to effect changes in the electroviscous effect but these changes can be assumed to be insignificant in these systems in view of their high electric conductance.

The interaction between the hydroxyl groups of the solubilized alcohol and the ionized carboxyl groups is known to lead to a denser packing in the palisade layers of the micelles [34, 35]. That the solubilized decanol actually is more densely packed than in the bulk is shown by our density measurements (see above). This must obviously influence the form of the micelle. By the light-scattering method it has been found that micelles become more anisodiametric when higher paraffin chain alcohols are solubilized in them [36]. Already a very slight change in the ratio of the axes of the micelle causes a marked increase in viscosity. From Simha's formula for rod-like particles [37] we have computed the degree of deformation that alone can lead to the observed increase in viscosity. From the known viscosities and volume fractions we have computed values of the axis ratio for pure soap solutions and for soap solutions containing solubilized substance. In this way comparatively high axis ratios are obtained for pure oleate solutions (about 10 in the 0.2 M concentration range) due to the fact that the viscosity of these solutions is not only caused by the deformation of the micelles and that Simha's formula is strictly valid only at low colloid concentrations. At oleate concentrations below *ca.* 0.2 M, a 10—20 % increase in the axis ratio at the turbidity point is sufficient to explain the increase in viscosity caused by decanol (or p-xylene). To explain the strong influence of added decanol on the viscosity of concentrated oleate solutions (above *ca.* 0.2 M), it is, however, necessary to assume much higher values for the axis ratio (*e. g.* in the 0.275 M oleate solution, the axis ratio should increase from about 11 in the pure solution to about 42 in the decanol-containing solution at the turbidity point). This implies that the mixed micelles formed by decanol and oleate at high oleate concentrations are long rod-shaped particles. It seems doubtful, however, whether the relatively small amounts of decanol in question are actually able to effect such great changes in the form of the micelle. We are therefore of the opinion that in the oleate solutions exceeding 0.2 M the deformation of the micelles cannot alone explain the observed increase in viscosity.

It has been previously assumed that an aggregation of micelles to larger and more or less anisodiametric lamellar micelles, called large micelles, occurs at higher association colloid concentrations [38, 18]. These aggregates have been assumed to be responsible for the appearance of the so-called I band in the X-ray diffraction pattern and for the pronounced structural viscosity [39] of these solutions. Since apparatus for the measurement of structural viscosity was not available, we cannot present any evidence for the occurrence of micelle aggregation in oleate solutions containing decanol. It may be noted, however, that the decrease in the charge density, and the resulting increase in the hydrophobic properties of the surfaces of the micelles, decreases the stability of the micelles in the solution and hence facilitates an aggregation of the decanol-containing micelles. Even if micelle aggregates were not present in a pure 0.275 M oleate solution, it is possible that such aggregates might be formed when decanol is solubilized. If lamellar micelles or aggregates of cylindrical micelles are formed, water layers must be located between the hydrophilic layers and this must lead to a marked increase in micellar volume.

As a summary of the discussion of the factors which may cause the observed increases in the viscosity in the homogeneous solutions, the following can

be said. At low oleate concentrations an increase in the volumes of the micelles due to the incorporated decanol (or xylene) can explain nearly the whole observed increase. At higher oleate concentrations (above *ca.* 0.2 *M*) the deformation and aggregation of the micellés are apparently the most important factors.

We shall now proceed to discuss the factors which determine the courses of the viscosity curves in the region above the turbidity point.

When xylene in excess of the amount solubilized is added to an oleate solution, the excess is emulsified in the solution. Conductance measurements (Part III [26]) have shown that the emulsified xylene binds practically no oleate and hence the oleate concentration of the solution is not altered. In accordance with this the viscosity remains practically constant.

As already mentioned, the viscosities of oleate solutions above 0.2 *M* decrease when the new phase containing decanol, oleate and water separates on adding decanol. The new phase is composed of microscopic anisotropic particles of marked stability. Its formation reduces the decanol and oleate contents of the aqueous phase and the number of mixed micelles in this phase therefore decreases. We have estimated the magnitude of the decrease in viscosity which results from the decrease in the concentration in the aqueous phase. We have here assumed that the only changes effected by decanol are that the concentration of the mixed micelles in the aqueous phase decreases and particles of a new phase appear. When only a slight excess of decanol has been added above the turbidity point, the number of these particles is so small that they do not alter the viscosity. With the aid of conductance data (Part II [25]), the concentration of mixed micelles in the aqueous phase can be determined above the turbidity point for different amounts of added decanol.

The calculation will be illustrated by an example. The relative viscosity of a 0.275 *M* oleate solution at the turbidity point is 12.7. A concentration of 0.275 mole of mixed micelles per litre thus gives a specific viscosity equal to 11.7 and hence $\eta_{sp}/c = 11.7 / 0.275 = 42.5$. In the solution containing 0.275 mole of oleate and 15 ml of decanol per litre, the mixed micelle concentration is according to the conductance data 0.221 *M*. If the specific viscosity varied linearly with the mixed micelle concentration, the specific viscosity of the solution should be $42.5 \times 0.221 = 9.40$ and the relative viscosity 10.4. The agreement with the experimental value 9.8 is satisfactory.

The calculated viscosities for concentrated oleate solutions containing varying amounts of decanol are plotted in Fig. 1 (curves *g* and *h*). The agreement with the experimental values is good as long as the excess of decanol (above the turbidity point) is small. For greater excesses, the viscosities are much higher than the calculated values owing to the effect of the particles of the separated phase present in the solution.

At low oleate concentrations below *ca.* 0.15 *M*, no marked variation is observed in the viscosity when the solutions become heterogeneous. The calculated curve *j* in Fig. 1 for the 0.0493 *M* oleate solution shows that the decrease in viscosity is more than compensated for by the increase in viscosity caused by the particles of the new phase, and hence the viscosity curve exhibits no break point when the solution becomes turbid. This is because the specific viscosity due to the micelles that are removed from the solution

is so slight that although their concentration in the water phase diminishes greatly on adding decanol, the viscosity does not undergo any appreciable change. Therefore the particles of the separated phase exert their effect on the viscosity immediately and the viscosity increases gradually and uniformly. The same applies in the case of the 0.300 M sodium myristyl sulphate solution, the viscosity curve for which does not either exhibit any pronounced irregularity when the turbidity appears.

The viscosities of concentrated oleate solutions, after passing a minimum, finally begin to increase rapidly with increasing decanol content. The abrupt increase in viscosity begins when the amount of the new phase becomes so large that it begins to influence greatly the flow of the solution.

It is thus possible to connect the changes in viscosity with other phenomena that occur when decanol and p-xylene are solubilized by association colloid solutions, $i.\ e.$ to the formation of mixed micelles and the appearance of a new phase. It has also been possible to point out those factors that influence the viscosity. The viscosity phenomena confirm our earlier conclusions that the properties of oleate solutions undergo appreciable changes in the $0.10-0.20\ M$ concentration region. Decanol promotes the structural changes which occur in this range also in pure oleate solutions.

As pointed out in the introduction, the solubilization of polar-nonpolar compounds generally results in a more or less marked increase in viscosity. The above conclusions apply to all these cases and are in accordance with the views of other investigators. The factors that cause the viscosity to pass through a maximum in homogeneous systems, as reported by various workers, will not be discussed here. In the systems we have studied no such maxima have been reached, the increase in viscosity being terminated by the appearance of a new phase which leads to a decrease in viscosity due to the decrease in the concentration of micellar substance.

When this publication was already written, we noted an abstract of a study of Markina, Posspelova and Rebinder [40] very similar to ours. As far as it is possible to judge from the abstract, their experimental results and conclusions are in accordance with those presented here.

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