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Studies on the Interaction of Paraffin Chain Alcohols and Association Colloids

VIII. The Solubility of Decanol-1 in Soap Solutions below the C.M.C.

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The solubility of decanol in dilute sodium caprate, laurate and myristate solutions at 40°C up to somewhat above the C.M.C.'s of the pure soaps has been determined with the greatest possible accuracy (maximum error ± 0.005 ml per litre). In all three cases a definite and rapid increase of the solubility begins at a concentration about 30 % lower than the C.M.C. of the pure soap. At this point a rapidly increasing formation of alcohol-soap-micelles begins; the C.M.C. of the decanol-containing soap solution is located at this concentration. The shift of the C.M.C. is caused by the facilitated association of the soap ions due to a decrease in the repulsion of their ionic groups owing to the incorporation of decanol. Below the C.M.C. the decanol solubility changes in a characteristic manner; already immediately above the L.A.C. the solubility increases slightly, passes a maximum and decreases again to a minimum value immediately below the C.M.C. These changes in solubility depend on the formation of small soap ion-decanol aggregates of relatively low solubility. The decanol-soap-water phase separating from all solutions above the L.A.C. has other properties and obviously another composition in the concentration range between the L.A.C. and C.M.C. than above the latter concentration limit. The investigation thus shows that below the C.M.C. there is in the solutions of all soaps a fairly wide concentration range where a limited association of alcohol and soap ions occurs. The degree of this association develops slowly until the critical concentration is reached.

A study has been made of the solubility of decanol in dilute sodium caprate, laurate and myristate solutions in the concentration range below the C.M.C. The solubility determinations made use of the fact that the system becomes turbid when a new phase appears. Since the solubility of decanol is very low below the C.M.C. and the turbidities in some cases were rather weak, the greatest care had to be exercised in the performance of the measurements.

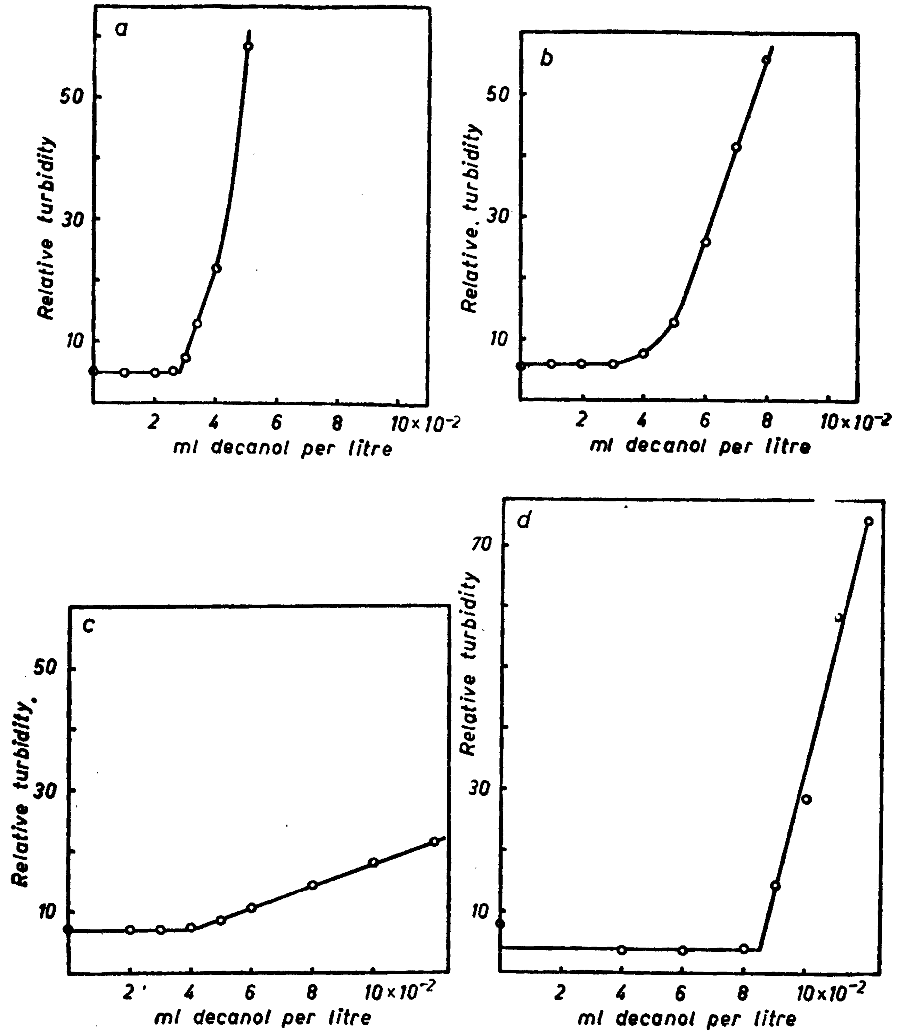

Fig. 1. Typical turbidity curves for soap solutions containing various amounts of decanol.

a. 0.0020 M sodium caprate solution
b. 0.028 M » » »
c. 0.052 M » » »
d. 0.090 M » » »

MATERIALS AND METHODS

The fatty acids were purified by repeated crystallization from ethanol. The melting points of the acids were: capric acid 31—31.5°C, lauric acid 42—43°C, myristic acid 56—57°C. Soaps were prepared from the acids in the usual manner by neutralization in abs. ethanol with sodium ethylate. The decanol was purified by repeated freezing;

the melting point of the final product was -6°C. The specific conductance of the twice distilled water used in the preparation of the solutions was less than 1×10^{-6} ohm^{-1} cm^{-1}.

In most of the experiments, 100-ml cylindrical glass-stoppered Pyrex flasks (30 mm in diameter) were used both as storage vessels and as cuvettes in the turbidity measurements. Several series of solutions were prepared in each of which the soap concentration was constant but the amount of added decanol varied. The flasks were shaken 24 hours in a thermostat at 40° until all decanol had dissolved or the solutions had become saturated and the excess of decanol or separated interaction product was dispersed throughout the solutions. It was found advisable to allow the solutions to stand four hours before measuring the turbidities. The turbidities were measured at 40°C with a Zeiss nephelometer combined with a Pulfrich photometer.

All the flasks were thoroughly cleaned and then rinsed several times with distilled water, after which they were dried and stored so that they did not collect dust.

In order to avoid turbidities caused by separated hydrolytic products, 0.1 mole of sodium hydroxide was added per mole of soap to the solutions.

The decanol was added to the solutions with an Agla micrometer syringe in which the scale is divided into 0.0002 -ml divisions.

EXPERIMENTAL RESULTS

a) The variation of the turbidity with the excess of decanol

Decanol added to a soap solution in excess of the amount dissolved causes the appearance of a turbidity. The turbidity increases with the amount of decanol added but our experiments showed that the increase in turbidity effected per unit volume of decanol added varied greatly with the soap concentration. This is illustrated by the nephelometer curves relating to sodium caprate solutions reproduced in Figs. 1 a, 1 b, 1 c, 1 d.

As seen from the curves, the nephelometric value remains constant when small amounts of decanol are added, but rises when larger amounts are added. The slope of the rising part of the curve is very different in the four cases. The turbidity curve for the 0.002 M caprate solution rises rapidly as soon as decanol is added in excess (Fig. 1a). For the 0.028 M solution the increase is slow at first, but later the curve rises steeply (Fig. 1b). The turbidity curve for the 0.052 M solution rises very slowly above the breakpoint with a constant slope (Fig. 1 c). A linear increase is also seen in the curve for the 0.090 M solution, but the slope is large (Fig. 1d).

It is of interest to note that this variation of the slope of the rising part of the curve is common to all the soaps studied. This is seen in Figs. 2, 3 and 4. The abscissae of these figures give the soap concentrations and the ordinates the slopes of the turbidity curves (above the breakpoint), *i. e.* the increase in turbidity due to a unit volume of decanol in excess per litre of solution. In those cases where the slope is different for small (a) and large (b) excesses of decanol (as in Fig. 1 b), both curves are given. Figs. 2, 3 and 4 are based on all the experimental data obtained in this study. In all cases the slope of the turbidity curve is large in dilute soap solutions, but decreases to a low value as the soap concentration increases; it then remains constant over a certain concentration range and begins to increase again at higher soap concentrations. This shows that the degree of dispersion of the separating substance and/or the refractive index and the nature of the substance causing the turbidity varies in the different concentration ranges.

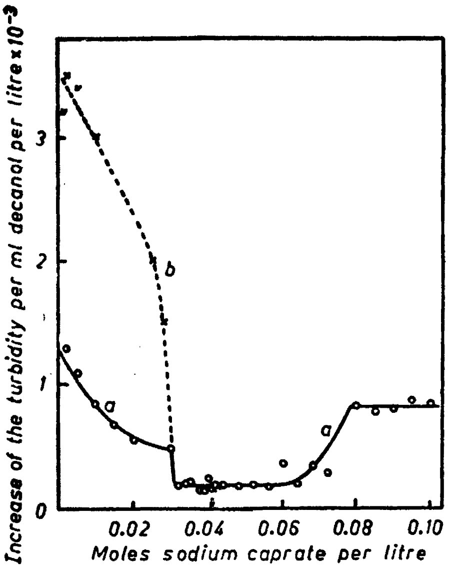

Fig. 2. The dependence of the soap concentration on the increase in turbidity due to a unit volume of decanol per litre of sodium caprate solution. a. Small excesses of decanol above the turbidity point. b. Large excesses of decanol above the turbidity point.

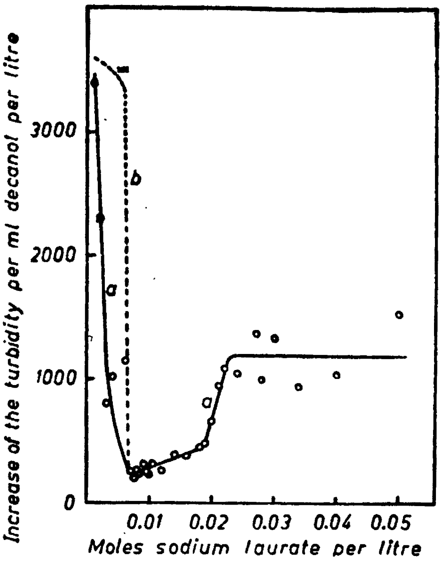

Fig. 3. The dependence of the soap concentration on the increase in turbidity due to a unit volume of decanol per litre of sodium laurate solution. a. Small excesses of decanol above the turbidity point. b. Large excesses of decanol above the turbidity point.

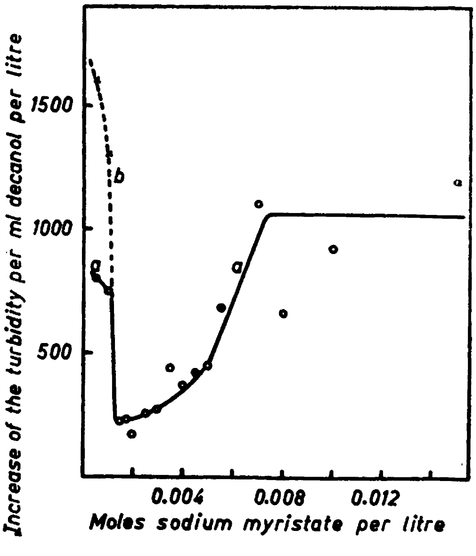

Fig. 4. The dependence of the soap concentration on the increase in turbidity due to a unit volume of decanol per litre of sodium myristate solution. a. Small excesses of decanol above the turbidity point. b. Large excesses of decanol above the turbidity point.

The intermediate concentration ranges, where the turbidity curves rise slowly, *i. e.* the separating substance causes only a slight turbidity, are for the various soaps: sodium caprate, from 0.030 M to 0.064 M; sodium laurate, from 0.007 to 0.019 M; sodium myristate, from 0.0015 to 0.005 M. The lower limits are very close to the limiting concentrations L.A.C., of the soaps, (0.02—0.03 M for sodium caprate, 0.005—0.006 M for sodium laurate and 0.0013—0.0015 M for sodium myristate), where, according to our previous studies, the interaction between decanol and soap begins [1-8]. Whereas the excess of decanol separates below the L.A.C. as emulsified free decanol, the separating substance above this limit is a fine-disperse semitransparent mesomorphic phase composed of decanol, soap and water. Already the turbidity-soap concentration curves reproduced in our earlier papers showed that this latter substance (separating above the L.A.C.) produces a relatively weak turbidity [1,2,5-7]. In those cases where we now found the turbidity-decanol content curves to rise slowly immediately above the turbidity point (as in Fig. 1 b) but later to exhibit a large slope, a mesomorphic phase separates at first, but when decanol is added in greater excess, free alcohol separates and is emulsified. Conductance measurements support this interpretation.

b) The solubility of decanol in the soap solutions

The solubility of decanol is given by the point where the horizontal and rising parts of the nephelometric curves intersect. We have attempted to determine in various ways the accuracy with which this point of intersection can be determined. Only in a few unfavourable cases, in which the slope of the curve was low and the nephelometric values scattered more than normally, the method of least squares gave standard deviations up to ± 0.005 ml of decanol per litre of solution. In most cases the standard deviation was less than this value.

The solubility values are shown in Tables 1, 2 and 3.

Table 1. The solubility of decanol in sodium caprate solutions at 40°C.

Sodium caprate mole/litre	Decanol ml/litre	Sodium caprate mole/litre	Decanol ml/litre
Aqua	0.028		
0.001	0.028	0.042	0.046
0.002	0.028	0.044	0.049
0.005	0.028	0.048	0.040
0.010	0.028	0.052	0.040
0.015	0.028	0.056	0.038
0.200	0.027	0.060	0.037
0.025	0.029	0.064	0.042
0.030	0.033	0.068	0.100
0.032	0.030	0.072	0.104
0.034	0.030	0.080	0.260
0.035	0.032	0.085	0.535
0.039	0.036	0.090	0.855
0.040	0.037	0.095	1.285
0.041	0.037	0.100	1.700

Table 2. The solubility of decanol in sodium laurate solutions at 40°C.

Sodium laurate mole/litre	Decanol ml/litre	Sodium laurate mole/litre	Decanol ml/litre
Aqua	0.028		
0.0020	0.028	0.0160	0.022
0.0030	0.028	0.0180	0.024
0.0040	0.028	0.0190	0.031
0.0050	0.031	0.0200	0.064
0.0060	0.032	0.0210	0.114
0.0070	0.028	0.0220	0.162
0.0076	0.039	0.0240	0.250
0.0080	0.043	0.0270	0.480
0.0084	0.045	0.0280	0.510
0.0090	0.045	0.0300	0.720
0.0095	0.038	0.0340	1.000
0.0105	0.039	0.0400	1.450
0.0120	0.035	0.0500	2.235
0.0140	0.028		

Table 3. The solubility of decanol in sodium myristate solutions at 40°C.

Sodium myristate mole/litre	Decanol ml/litre	Sodium myristate mole/litre	Decanol ml/litre
Aqua	0.028		
0.00050	0.027	0.00400	0.012
0.00100	0.032	0.00450	0.009
0.00150	0.042	0.00500	0.018
0.00175	0.032	0.00550	0.038
0.00200	0.038	0.00600	0.064
0.00250	0.030	0.00700	0.133
0.00300	0.025	0.00800	0.198
0.00350	0.016	0.0100	0.316
		0.0150	0.630

Fig. 5a shows the variation of the solubility of decanol with the soap concentration in sodium caprate solutions. From 0.065 M caprate upwards, the solubility increases rapidly and especially above the 0.08 M concentration, the solubility curve rises steeply. In pure caprate solutions the critical concentration is 0.097 M at 20° C. The solubility of decanol thus begins to increase rapidly already at a lower concentration, 0.065—0.080 M, of sodium caprate.

A very slight increase in solubility can, however, be detected at even lower concentrations; this is shown by the enlarged lower part of the curve in Fig. 5b. We observed the first signs of an increased solubility already at caprate concentrations between 0.025 M and 0.030 M. The solubility of decanol rises from 0.028 ml of decanol per litre, the solubility in pure water and in very dilute caprate solutions, to a value of 0.049 ml per litre in the 0.044 M caprate

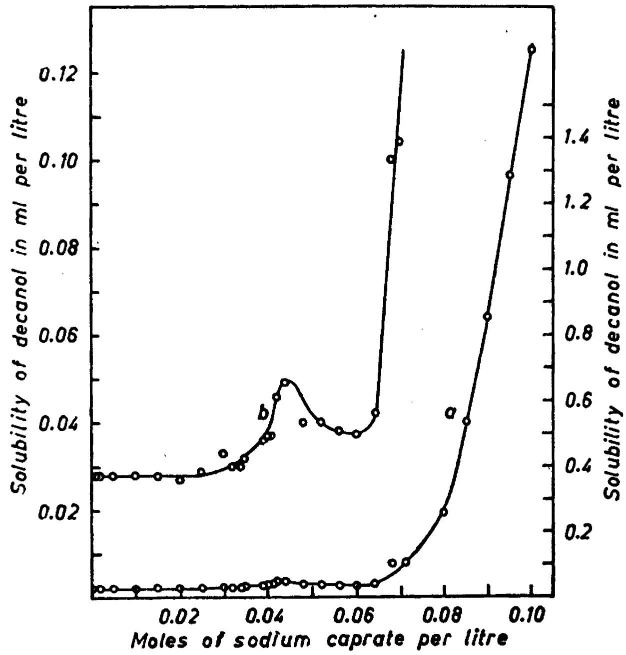

Fig. 5. The solubility of decanol in sodium caprate solutions at 40°C. a. The increase of the solubility around the C.M.C. (scale on the right). b. The solubility between the L.A.C. and the C.M.C. on an enlarged scale (scale on the left).

solutions, an increase of 75 %. At higher caprate concentrations, the solubility decreases again to a minimum in the 0.060 M caprate solution, after which the above-mentioned rapid increase begins.

The first increase in decanol solubility coincides with the limiting concentration, 0.025—0.030 M, of sodium caprate. The range in which the increase and decrease occur, 0.025—0.065 M sodium caprate, is practically the same as the range (0.03—0.064 M caprate) where the effect of the separated substance on the turbidity is especially weak. These two phenomena are thus seen to be closely connected.

Fig. 6a illustrates the variation of the solubility of decanol with the sodium laurate concentration. The solubility begins to increase when the laurate concentration exceeds 0.019—0.020 M. The critical concentration of sodium laurate is 0.028 M (20° C). Decanol thus begins to dissolve in laurate solutions at a laurate concentration somewhat below the C.M.C. of pure sodium laurate.

Also in the laurate solutions a slight increase in solubility is noted even at lower concentrations (Fig. 6b). The first signs of an increase are noted at the laurate concentrations of 0.005—0.007 M. The solubility increases to a value in the 0.008—0.009 M solution which is about 64 % higher than in water. It then undergoes a decrease to a minimum at the 0.016—0.018 M concentration, after which the rapid increase begins.

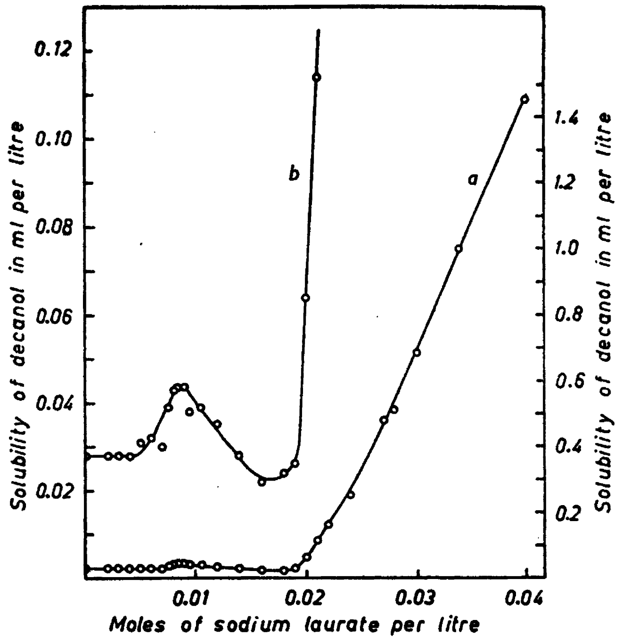

Fig. 6. The solubility of decanol in sodium laurate solutions at 40°C. a. The increase of the solubility around the C.M.C. (scale on the right). b. The solubility between the L.A.C. and the C.M.C. on an enlarged scale (scale on the left).

The first solubility increase begins at the limiting concentration of sodium laurate, 0.005—0.006 M. The solubility variations occur in the same concentration range (0.006—0.019 M laurate) where the separating substance effects only a weak turbidity.

The variation of the decanol solubility in sodium myristate solutions is shown in Fig. 7. The solubility begins to increase when the sodium myristate concentration exceeds 0.0045—0.0050 M and more rapidly when the soap concentration increases above 0.006 M. The critical concentration of sodium myristate is 0.007 M at 40° C. Thus decanol begins to dissolve at a myristate concentration definitely below the C.M.C. of pure sodium myristate. Also in the myristate solutions we have noted solubility changes at still lower concentrations (Fig. 7b). The solubility begins to increase already at the 0.001 M myristate concentration; it is about 50 % higher than the solubility in water in the 0.0015 M myristate solution, but then decreases until it is only one-third of the solubility in water in the 0.0045 M sodium myristate solution. Above this point a rapid increase in the solubility begins.

Also in sodium myristate solutions, the first increase in solubility occurs in the vicinity of the limiting concentration, which is 0.0013 M. The variations in the solubility are observed in the same concentration range (0.0015 M—0.0050 M myristate) where the separating substance effects only a weak turbidity.

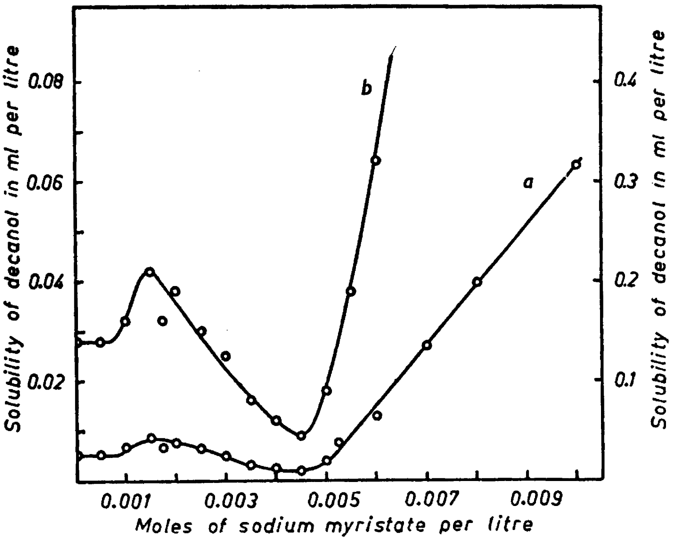

Fig. 7. The solubility of decanol in sodium myristate solutions at 40°C. a. The increase of the solubility around the C.M.C. (scale on the right). b. The solubility between the L.A.C. and the C.M.C. on an enlarged scale (scale on the left).

c) The effect of added sodium hydroxide on the solubility of decanol

In all the above experiments, the solutions contained 0.1 mole of sodium hydroxide per mole of soap to suppress hydrolysis. We have not undertaken any systematical study of the effect of sodium hydroxide or that of the products of hydrolysis on the solubility of decanol, but certain observations throw some light on this question.

The solubility of decanol was measured in 0.008 M sodium myristate solutions containing various amounts of sodium hydroxide up to 0.14 mole per mole of soap. From Fig. 8 it is seen that the solubility is very low in the absence of alkali hydroxide, increases at first rapidly with the amount of sodium hydroxide added but attains a constant limiting value when the concentration of sodium hydroxide increases to about 0.1 mole per mole of soap. A similar increase in the decanol solubility in a 0.006 M myristate solution was also observed when 0.05 and 0.1 mole of sodium hydroxide was added per mole of soap.

The addition of 0.1 mole of sodium hydroxide per mole of soap to a 0.04 M sodium laurate solution increased the solubility of decanol only from 1.30 to 1.44 ml per litre. No increase was noted in the case of a 0.014 M laurate solution when the sodium hydroxide content was increased from 0.05 to 0.15 mole per mole of soap.

The solubility of decanol in a 0.064 M sodium caprate solution did not increase when the sodium hydroxide concentration was increased from 0.1 to 0.15 mole per mole of soap.

In the concentration range immediately above and below the C.M.C. of pure soaps, where we have observed the solubility of decanol to increase rapidly, the sodium hydroxide increases the decanol solubility; 0.1 mole of sodium hydroxide per mole of soap seems, however, to be sufficient to effect maximum solubility of decanol in most cases (in myristate solutions a slightly larger amount may be necessary). In the region above the L.A.C. where the first increase in decanol solubility occurs, sodium hydroxide does not seem to influence the solubility, but the small number of observations does not permit any definite conclusions.

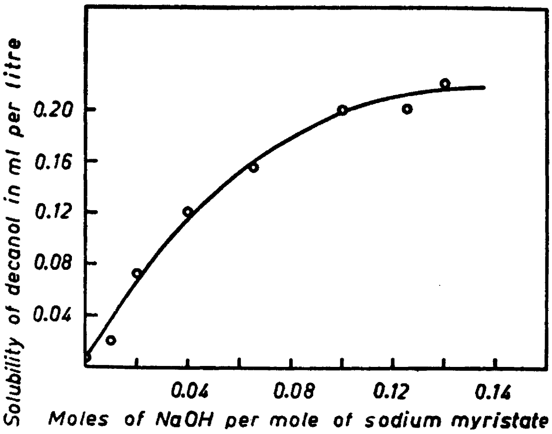

Fig. 8. The influence of added sodium hydroxide on the solubility of decanol in a 0.008 M sodium myristate solution at 40°C.

The addition of sodium hydroxide to a colloid solution generally influences the micelle formation in such a way that the C.M.C. shifts to a somewhat lower value. The effect of sodium hydroxide on the decanol solubility may be partly due to this shift. We think, however, that the results may be considered to indicate that the hydrolysis products (fatty acid, acid soap) present in solutions containing no added alkali decrease the capacity of the soap to dissolve decanol, at least in solutions in which micelle formation has not progressed very far.

d) Solubility of *p*-xylene in soap solutions containing decanol

It is known that soap solutions begin to solubilize hydrocarbons when the critical concentration is exceeded and that the solubilization of hydrocarbons is increased in the presence of long-chain alcohols. We have conducted a few experiments to determine the effect of decanol on the solubilization of *p*-xylene in sodium laurate solutions below the C.M.C. The results are given in Table 4.

The solubility of *p*-xylene in pure water is 0.20 ml per litre at 40°C. The solubility is the same also in dilute soap solutions below the C.M.C. The data in Table 4 show that the solubility is no larger in 0.003 and 0.009 M laurate solutions when these contain

Table 4. The solubilization of p-*xylene in sodium laurate solutions containing different amounts of decanol. The solutions contained 1 mole of sodium hydroxide to 10 moles of soap. 40°C.*

Sodium laurate mole/litre	Decanol ml/litre	*p*-xylene ml/litre
0.003	0.028	0.21
0.009	0.046	0.20
0.018	0.026	0.33
0.023	0.19	0.56

decanol, but a slightly higher solubility is noted in the 0.018 M solution and a definitely higher solubility in the 0.023 M solution.

These results show that solubilization of the hydrocarbon begins at about the same concentration where the solubility of decanol begins to increase rapidly. This seems to indicate that the decanol-laurate mixed micelles are of the usual spheroidal (or double-layer) type. Micelles of this type do not seem to be formed at lower soap concentrations although decanol is present.

DISCUSSION

In the case of all three soaps studied, the first signs of an increase in the decanol solubility appear in the region of the limiting concentration of the soap [1-5]. As the soap concentration is increased, the increase in solubility slows down and the solubility begins to decrease until slightly before the C.M.C. of the pure soap is reached, the solubility again begins to increase [5]. The changes in solubility below the abrupt rise are admittedly rather small, but yet considerably greater than the error of the experimental method. The changes must hence be considered significant.

The regions where these changes in solubility are observed are given in Table 5.

The second increase in the decanol solubility begins at soap concentrations that are about 30 % lower than the C. M. C.'s in pure soap solutions. Above this point the increase in solubility is very rapid. It is obvious that this increase is due to the formation of mixed micelles containing soap and decanol and that their formation progresses rapidly from the solubility minimum upwards. The minimum points thus give the C. M. C. values for soap solutions containing decanol. This is supported by the observation that the 0.018 and 0.023 M laurate solutions begin to solubilize *p*-xylene only after decanol has been added to them. These mixed micelle C. M. C. values lie only a little below the approximate values we have previously obtained for decanol-containing soap solutions by the turbidity method [6]. Our data thus give the lowest soap concentrations to which the C. M. C. can be decreased by decanol at 40° C. These values are appreciably lower than the values recently obtained by Shinoda for decanol-containing soap solutions at 10° and 18° C with the pinacyanol method [9].

Table 5. Variation of the solubility of decanol in soap solutions containing 0.1 mole of NaOH per mole of soap. 40°C.

Soap	L.A.C. M	Soap concentration (mole/l) at which the first increase in decanol solubility begins	the second increase in decanol solubility begins	C.M.C. in pure soap solution M
Sodium caprate	0.022–0.028	0.025–0.030	0.065–0.070	0.097
Sodium laurate	0.004–0.007	0.005–0.007	0.019–0.020	0.027
Sodium myristate	0.011–0.0014	0.001–	0.0045–0.0050	0.0065

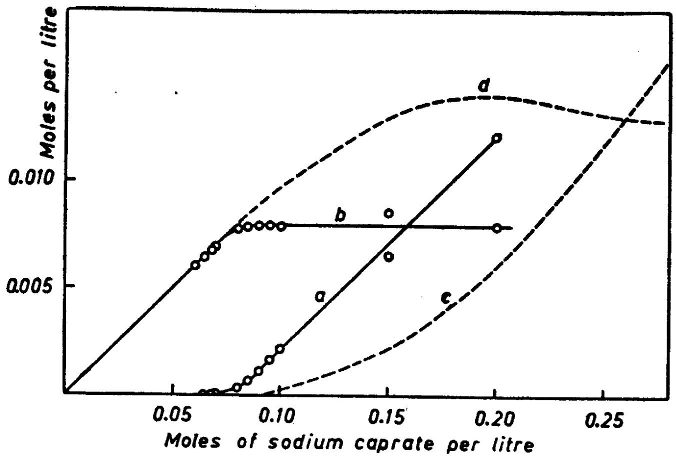

Fig. 9. Micelle formation in sodium caprate solutions. The concentrations of micellar soap (a) and molecular soap (b) in caprate solutions containing decanol, calculated from the solubility of decanol. The concentrations of micellar soap (c) and molecular soap (d) in caprate solutions containing p-*xylene, calculated from the solubility of* p-*xylene.*

On the basis of the solubility values it is possible to estimate the amount of soap bound in the mixed micelles above the critical concentration. Already from concentrations only slightly higher than the C. M. C., the solubility curves begin to rise linearly; this means that the maximum ratio of decanol to soap in the mixed micelles remains constant above this point. The ratio is found to

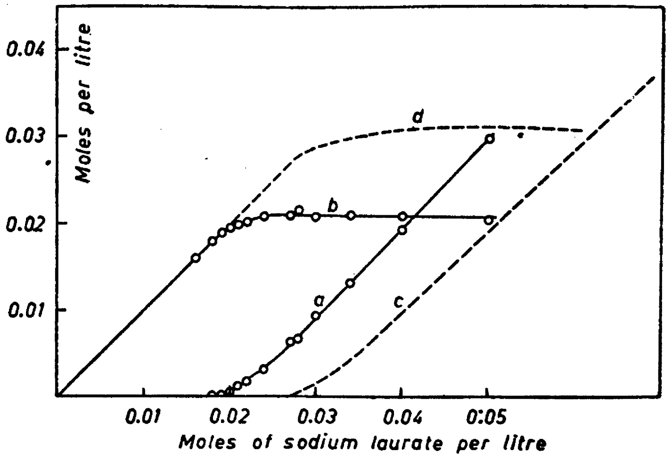

Fig. 10. Micelle formation in sodium laurate solutions. The concentrations of micellar soap (a) and molecular soap (b) in laurate solutions containing decanol calculated from the solubility of decanol. The concentrations of micellar soap (c) and molecular soap (d) in laurate solutions containing p-*xylene, calculated from the solubility of* p-*xylene.*

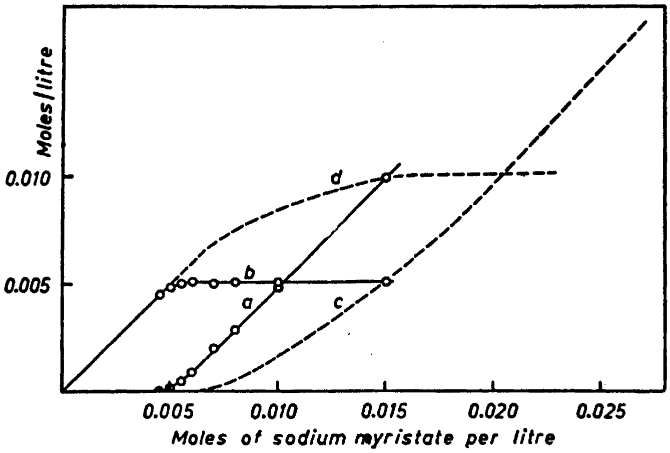

Fig. 11. Micelle formation in sodium myristate solutions. The concentrations of micellar soap (a) and molecular soap (b) in myristate solutions containing decanol calculated from the solubility of decanol. The concentrations of micellar soap (c) and molecular soap (d) in myristate solutions containing p-*xylene calculated from the solubility of* p-*xylene.*

be 0.41 mole of decanol per mole of sodium caprate, 0.39 mole of decanol per mole of sodium laurate, and 0.33 mole of decanol per mole of sodium myristate, at 40° C. If it is assumed that the mixed micelles have the same composition down to the point of minimum decanol solubility, the values given in Figs. 9, 10 and 11 (curves a) can be calculated for the amounts of soap bound in the mixed micelles. Also the amounts of molecular soap calculated from the difference between total and micellar soap are given in the figures (curves b). The curves show that after a relatively narrow transition region, in which the proportion of micellar soap increases rapidly, there is a concentration range where all the added soap is bound in the mixed micelles and hence the concentration of free soap remains constant. This range begins already before the C. M. C. of the pure soap is reached.

For comparison also the amounts of soap present in the micellar state and in the molecular state in decanol-free soap-solutions, calculated in a corresponding manner from the data for the *p*-xylene solubilization, are given in Figs. 9, 10 and 11 (the dotted curves c and d)[11]. In these latter cases the formation of micelles begins at the C. M. C.'s of the pure soaps and proceeds at first much more slowly than in the presence of the alcohol. Though all these values are only approximate, they show clearly the effect of the polar-nonpolar substance on the micelle formation. As we have seen above, the concentration of decanol at the solubility minimum (C. M. C.) is in all cases very low compared with that of the soap (only about 0.5—1.5 % of the latter). Our calculation thus indicates that the effect of decanol is not caused by an increase in the amount of micelle-forming hydrocarbon chains in solutions, but by an increased association of the soap ions due to a decrease in the repulsion of their ionic groups [7]. In other cases, however, when the solubility of the polar substance is greater, the former factor may play a part in lowering the C. M. C.

The first slight increase in the decanol solubility above the L. A. C. must also be caused by the formation of soluble decanol-soap aggregates. These aggregates are formed only sparingly, however. Therefore the previously (Parts V and VI) described rapid fall at the L. A. C. in the turbidity-soap concentration curves of solutions containing alcohol in excess [6,7] is due only to a minor extent to the increase in the solubility of the alcohol but for the most part to a weak turbidity of the alcohol-soap-water phase formed above the mentioned concentration limit.

It is very interesting to note that the decanol-soap-water phase separating immediately above the L.A.C. effects a much weaker turbidity per unit volume of decanol added than the corresponding phase separating above the C.M.C. This fact conforms with our microscopic observations of the different appearance of the separated phase below and above the latter concentration in sodium laurate solutions (Part VII); these observations suggested that the water content of the former product is greater than that of the latter [8]. On the other hand, we have found (Parts II and III) that the decanol content per mole of soap in the separated phase increases with decreasing concentration of the soap solution in which it is formed [10]. From all these results we conclude that both the properties and the composition of the decanol-soap-water phase formed between L.A.C. and C.M.C. differs from that formed above the latter concentration limit; in the former case the molar ratio of decanol to soap and the water content is larger and the refractive index is nearer that of the aqueous soap solution.

Our investigations thus show that in the concentration range between L.A.C. and C.M.C. the solubility of decanol is different from that in other ranges and the separating phase deviates in properties and composition from those separating in other ranges. As to the composition and properties of the soluble soap ion-alcohol aggregates existing in this range, calculations show that these aggregates are small and composed of only very few soap ions and alcohol molecules. The hydrophilic properties and thus the solubility of such small aggregates must decrease rapidly with increasing molar ratio of decanol to soap. The range of composition of these aggregates is therefore rather limited. If one assumes that two kinds of small aggregates with different decanol-soap ratios, and thus different solubilities, are formed, the course of the observed solubility curve between L.A.C. and C.M.C. with its solubility maximum and decrease to and below the value for pure water can be readily understood. We will return to this question in a later paper of this series.

Now we only wish to emphasize that the solubility measurements presented in this paper show clearly that the limiting concentration should not be confused with the critical concentration [6,7]. Below the latter there is a fairly wide concentration range in solutions of all soaps where a limited association of alcohol and soap ions occurs. The degree of this association increases slowly until the critical concentration is reached.

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