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Studies on the Interaction of Paraffin-Chain Alcohols and Association Colloids

VI. The Sodium Caprate Concentration where Interaction with Long-Chain Alcohols Begins and its Dependence on the Chain Length of the Alcohol

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Turbidity measurements show that interaction of sodium caprate with hexanol-1, octanol-1, decanol-1, and dodecanol-1 begins at approximately the same concentration of the soap, at the L. A. C., and hence irrespective of the chain-length of the alcohol. Also with tetradecanol-1, hexadecanol-1 and octadecanol-1, at temperatures above their melting points, interaction begins at only slightly higher soap concentrations. The temperature dependence of the interaction concentration is the same for all alcohols. The first step in the interaction is the formation of soluble alcohol-soap aggregates. The part different intermolecular interactions play in determining the L. A. C. is discussed and it is shown that the most decisive factor in determining the position of the L. A. C. is the chain length of the soap.

In the preceding paper of this series [1], it was shown on the basis of extensive experimental data that the soap concentration where interaction between decanol-1 and different fatty acid soaps begins shifts to lower values with increasing chain length of the soap molecule. The interaction concentration was observed to increase slightly with temperature. It was further established that the lowest concentration limit for interaction between soap and decanol is approximately the same as the concentration where the soap begins to react with its parent fatty acid (the limiting concentration, L. A. C.). We have used the same nephelometric technique to determine how the concentration where the soap begins to interact with different long-chain alcohols varies with the chain length of the alcohol and how this concentration depends on the temperature.

EXPERIMENTAL

The soap employed in the experiments was sodium caprate. The interaction with the following alcohols was studied: hexanol-1 (B. D. H. London), octanol-1, decanol-1, dodecanol-1, tetradecanol-1, hexadecanol-1, and octadecanol-1 (Eastman Kodak Company, Rochester). The samples were distilled or recrystallized.

The solutions of soap and alcohols were prepared and their turbidities measured as described in the previous paper[1].

The measurements were conducted at temperatures between 20° and 60° C, but in each case only above the melting point of the alcohol in question. In most cases the amounts of alcohol added were also varied.

The following series were investigated;

Sodium caprate + 0.65 ml of hexanol per litre at 20°, 30°, 40°, 50° and 60° C and with 0.61 ml of hexanol per litre at 20° C.

Sodium caprate + 24.6 and 36 moles of octanol per 100 moles of soap at 20°, 30°, 40°, 50° and 60° C.

Sodium caprate + 2, 3, 4 and 6 moles of decanol per 100 moles of soap at 20°, 30°, 40°, 50° and 60° C.

Sodium caprate + 1.5, 2.5 and 6.1 moles dodecanol per 100 moles of soap at 20°, 30°, 40°, 50° and 60° C.

Sodium caprate + 1.2, 1.9 and 2.8 moles tetradecanol per 100 moles of soap at 40°, 50° and 60° C.

Sodium caprate + 0.65 and 0.95 moles hexadecanol per 100 moles of soap at 60° C.

Sodium caprate + 0.4 moles octadecanol per 100 moles of soap at 60° C.

THE RESULTS OF THE MEASUREMENTS

The measurements gave turbidity curves that are similar in form to those previously found for decanol in which two turbidity ranges are separated by a

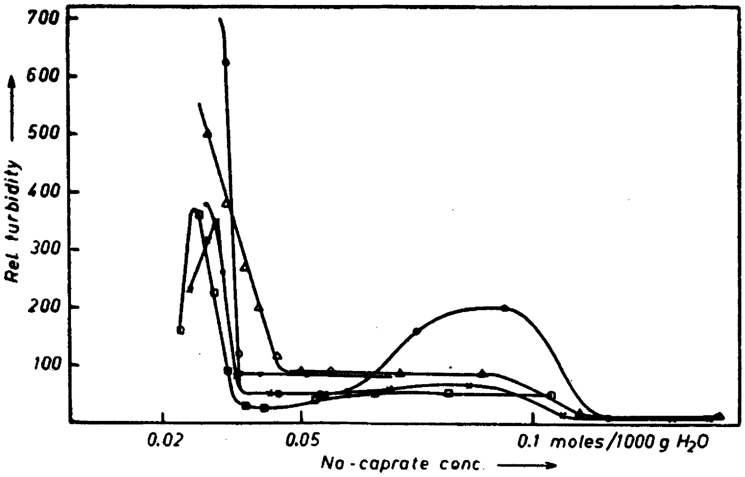

Fig. 1. The turbidity of sodium caprate solutions containing different long-chain alcohols. 50° C.

Curve 1 ●—●, *0.65 ml of hexanol-1 per litre of soap solution.*
Curve 2 ○—○, *24.8 moles of octanol-1 per hundred moles of soap.*
Curve 3 ×—×, *4 moles of decanol-1 per hundred moles of soap.*
Curve 4 □—□, *6.1 moles of dodecanol-1 per hundred moles of soap.*
Curve 5 △—△, *1.9 moles of tetradecanol-1 per hundred moles of soap.*

Table 1. The sodium caprate concentrations where interaction begins with different alcohols. Concentrations in moles per 1 000 g of water.

Alcohol	°C	Maximum of turbidity range I	Upper limit of turbidity range I
Hexanol-1	20	0.024–0.027	0.028–0.029
	30		0.030–0.031
	40		0.032–0.033
	50		0.035–0.037
	60		0.037–0.039
Octanol-1	20	0.023–0.026	0.028–0.029
	30	0.024–0.027	0.030–0.031
	40		0.031–0.033
	50		0.034–0.037
	60		0.036–0.039
Decanol-1	20	0.020–0.022	0.025–0.029
	30	0.023–0.025	0.027–0.030
	40	0.025–0.027	0.030–0.032
	50	0.028–0.031	0.035–0.037
	60	–0.035	0.039–0.041
Dodecanol-1	40	–0.023	0.029–0.031
	50	–0.028	0.036–0.037
	60	–0.035	0.040–0.041
Tetradecanol-1	40	–0.035	0.042–0.044
	50	–0.035	0.044–0.046
	60	–0.038	0.049–0.051
Hexadecanol-1	60	–0.038	0.049–0.052
Octadecanol-1	60	–0.039	0.057–0.059

region of almost clear solutions. The turbidity in the first range (I) is due to emulsified alcohol, in the second range (II) to a birefringent liquid substance composed of alcohol, soap and water. The last-mentioned substance results from the interaction between alcohol and soap that begins in the concentration range between the point of maximum turbidity of the first turbidity range and the upper limit of this range. The purpose of the study was to determine the sodium caprate concentrations at which interaction begins, and hence the complete nephelometric curves were not recorded in all cases. Only one curve recorded at 50° C for each of the alcohols, hexanol, octanol, decanol, dodecanol, and tetradecanol (with different additions of these alcohols) is reproduced in Fig. 1. The results of all the experiments are collected in Table 1.

The caprate concentration at which the turbidity due to emulsified alcohol disappears completely is clearly defined. As previously, we shall use this concentration to define the conditions where interaction begins (last column in Table 1) although the interaction actually begins at a somewhat lower con-

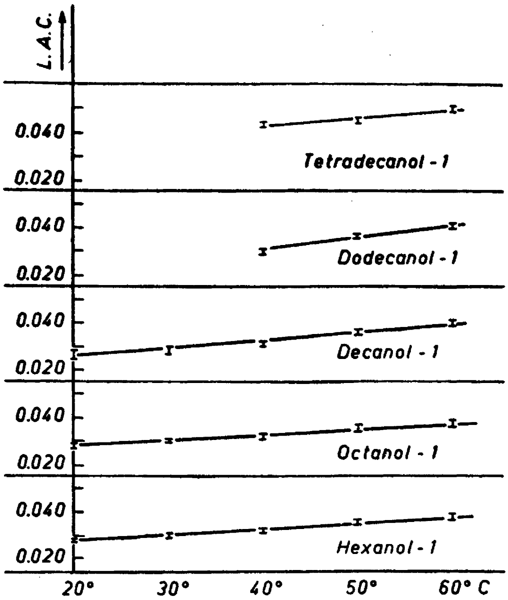

Fig. 2. The temperature dependence of the limiting concentration, L. A. C., of sodium caprate.

centration, *i. e.* at the turbidity maximum. Fig. 2 shows how the concentration mentioned varies with temperature; the curves are seen to be practically linear for all of the alcohols studied.

From the data in Table 1 it is seen that the interaction between the caprate and the four lower alcohols begins at almost the same caprate concentration. This is illustrated by the curves in Fig. 3. With tetradecanol, hexadecanol and octadecanol, the upper limits of the first turbidity range occur at somewhat higher caprate concentrations than with the lower alcohols. In the case of the two highest alcohols, measurements were conducted at only 60° C; only two different additions of hexadecanol and only one of octadecanol were employed (the temperature 60° lies close to the melting point of octadecanol).

DISCUSSION

It is seen that the lower limit for interaction between the soap and the various alcohols, at least for those with 6 to 12 carbon atoms, occurs at approximately the same soap concentration irrespective of the chain length of the alcohol (in the case of the higher alcohols, this soap concentration deviates only slightly from that found for the lower alcohols). As mentioned above, this limit coincides with the lowest concentration at which interaction occurs between the soap and its parent fatty acid. For the fatty acid and all the alcohols the interaction concentration is observed to shift with increasing temperature in a similar manner. We may therefore conclude that this limit is

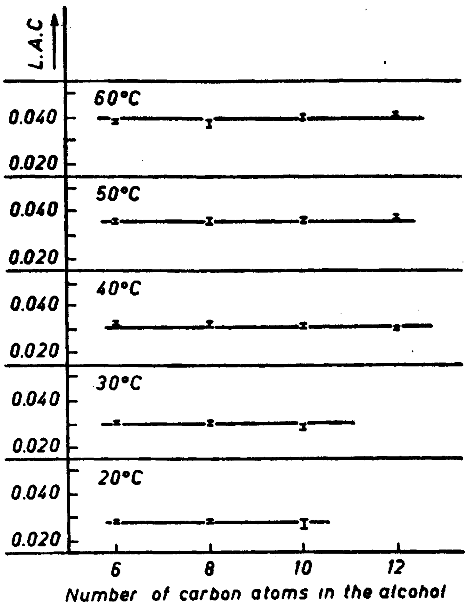

Fig. 3. The dependence of the limiting concentration, L. A. C., of sodium caprate on the chain-length of the alcohol.

fairly well defined and that it thus seems appropriate to refer to it by a special term, the limiting association concentration (L. A. C.) of the soap.

At the maximum of the first turbidity range, the soap solutions contain more alcohol than dissolves in water and in dilute soap solutions. Although the alcohol content increases with the soap concentration, the turbidity disappears completely, *i. e.* the alcohol dissolves in cases where the mole ratio of alcohol to soap is not too high. This shows that the solubility of alcohol increases when the limiting concentration is exceeded. This conclusion has been verified by measurements of the solubility of decanol [2,3]. The increase of the solubility must be due to the formation of complexes between the alcohol molecules and soap ions. The first phenomenon occurring at the limiting concentration is thus the formation of soluble alcohol-soap aggregates and not the formation of a new precipitate. That this is the case also in the interaction between fatty acid and soap has been shown previously [4,5]. The alcohol-soap aggregates (and fatty acid-soap aggregates) formed at the limiting concentration must, however, be rather hydrophobic, for the increase in the solubility is fairly small and the new liquid phase composed of soap, water and alcohol (or of soap, water and fatty acid; in some cases crystalline acid soap is formed) begins to separate when more alcohol (or fatty acid) is added.

When the mole ratio of alcohol to soap exceeds a certain value, the turbidity does not disappear completely but decreases considerably. The new precipitate that is formed effects a much weaker turbidity than emulsified alcohol [3]. In these cases both factors, the increase in the solubility of the alcohol and the decrease of the opacity of the reaction product together effect the rapid fall in the turbidity curve at the L. A. C.

The association or complex formation above the limiting concentration complies with the law of mass action. The first steps of the interaction may be described by general equations such as (1) and (2);

$$\mathrm{xR'Ac^-} + \mathrm{yR''OH} = \mathrm{(R''OH)y\ (R'Ac^-)x} \tag{1}$$

$$\frac{[\mathrm{(R''OH)y\ (R'Ac^-)x}]}{[\mathrm{R'Ac^-}]^{\mathrm{x}} \cdot [\mathrm{R''OH}]^{\mathrm{y}}} = K \tag{2}$$

In a later paper of this series, when more experimental observations have been published, we will return to a quantitative treatment of the interaction between alcohols and soap. Now we only wish to make some comments.

The same forces that effect the association in pure soap solutions must take an active part also in the formation of the soluble aggregates between soap and polar-nonpolar compounds such as alcohols and fatty acids. In addition, there occurs ion-dipole interaction and probably also formation of hydrogen bonds between the carboxylate groups of the soap ions and the hydroxyl groups of the alcohols or the carboxyl groups of the fatty acids.

An interesting question is the part these different intermolecular interactions play in determining the concentration level where the L. A. C. occurs. Surely the interaction between the ionized carboxyl groups and the alcohol groups determines in some degree the phenomena that are characteristic of the interaction between soaps and alcohols. An interesting fact is, however, that for a certain soap the L. A. C. occurs at almost the same concentration level also when the polar-nonpolar compound is not an alcohol but a fatty acid. This shows that in any case the ion-dipole interaction and the formation of hydrogen bonds do not alone determine the position of the L. A. C. The van der Waals forces between the hydrocarbon chains seem to play a decisive role.

Another interesting fact is that while the L. A. C. is displaced to lower soap concentrations when the chain length of the soap ions increases, the position remains nearly unchanged with increasing chain length of the alcohol (from 6 to 12 carbon atoms). It may be that the lower solubility of the alcohols in water with increasing chain length contributes to this behaviour. The fact remains, however, that according to all our observations made hitherto the most decisive factor in determining the position of L. A. C. is the chain length of the soap ion. This could be interpreted as an indication that the intermolecular forces between the soap ions themselves are decisive for the phenomena that occur at the concentration we have termed the limiting association concentration and that the association tendency between the soap ions is a predominating factor. In the same direction points also the fact that there exists a formally similar relation between the number of carbon atoms in the soap ions and the position of L. A. C. as in the case of the C. M. C. [8,9]; this relation applies up to at least 60° C.

If this last interpretation were correct, it would mean that the phenomena occurring at the L. A. C. are not primarily caused by the alcohol or fatty acid, but must be ascribed to the fact that the association tendency of the soap anions attains a threshold value at this concentration. The role of the alcohol and fatty acid would then be to promote the association, for instance by decreasing the repulsion between the ionic groups and thus to function like an indicator, which makes the tendency to associate observable.

Whether the phenomena at the limiting concentration only give evidence of the association between soap ions and the molecules of the polar-nonpolar substance or indicate that the tendency to associate has attained a certain level also in the pure soap solution, they must be characterized as deviations from the typical behaviour of normal 1-1 electrolytes, and as far as we know, the first deviations from this behaviour that occur with increasing soap concentration. It seems, however, that the location of the limiting concentration cannot be defined by giving an absolute value for the concentration and it must suffice to report a concentration range within which the first signs of association become evident. Depending on the experimental method employed, the first signs may be observed at somewhat different points in this range. Of importance is, however, that it is possible to detect association phenomena in soap solutions far below the C. M. C's of the pure soaps and also far below the concentrations where the micelle formation occurs in soap solutions containing alcohol or fatty acid.

Our present experimental material relates primarily to fatty acid soap solutions. We have, however, previously found [6,7] that similar phenomena occur also in solutions of alkali metal alkyl sulphates and of alkyltrimethyl ammonium and cetylpyridinium salts; also in these solutions the limiting concentrations (sodium myristyl sulphate 0.0003 M, hexadecyl trimethyl ammonium bromide 0.0004 M) are far below the critical concentrations of the colloids. We believe that a limiting concentration can be determined for all association colloids of the paraffin-chain type.

REFERENCES

1. Ekwall, P., Söderberg, O. and Danielsson, I. *Acta Chem. Scand.* **10** (1956) 227.
2. Ekwall, P., Passinen, K. and Danielsson, I. *Finska Kemistsamfundets Medd.* **63** (1954) 1.
3. Ekwall, P. and Vittasmäki, T. *Unpublished experiments.*
4. Ekwall, P. *Kolloid-Z.* **94** (1941) 42.
5. Ekwall, P. *Kolloid-Z.* **97** (1941) 71.
6. Ekwall, P. *Svensk Kem. Tidskr.* **63** (1951) 277.
7. Ekwall, P. and Danielsson, I. *Acta Chem. Scand.* **5** (1951) 973.
8. Ekwall, P. *Kolloid.-Z.* **8** (1937) 77.
9. Stauff, J. *Z. physik. Chem.* **183** (1938) 55.

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