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

V. The Soap Concentration where Interaction with Decanol-1 Begins and its Dependence on the Chain Length of the Soap

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Turbidity measurements show that interaction of decanol-1 and fatty acid soaps begins at a clearly defined soap concentration. This concentration is the same as that where the soap begins to interact with its parent fatty acid (the limiting concentration, L. A. C.). The value of the L. A. C. decreases with increasing chain-length of the soap; there is a nearly linear correlation between the logarithm of the L. A. C. and the number of carbon atoms in the hydrocarbon chain of the soap. The value of the L. A. C. increases somewhat with temperature. The L. A. C. lies considerably lower than the C. M. C. of the pure soap and below the concentration where micelle formation begins to increase rapidly in soap solutions that contain added alcohol.

We have previously established [1-5] two separate turbidity maxima in dilute association colloid solutions containing small amounts of decanol-1. The curves showing the variation of the turbidity with the association colloid concentration are similar in form to the schematic curve drawn in Fig. 1.

In the turbidity range I observed at low colloid concentrations, the turbidity is due to emulsified decanol. The turbidity in range II at higher colloid concentrations is caused by a birefringent liquid composed of decanol, association colloid and water which is dispersed in very small droplets. The upper limit of the turbidity range I is sharply defined. It lies considerably below the critical concentration for micelle formation in pure association colloid solutions and it defines the conditions at which interaction between decanol and association colloid begins.

In this and in three following papers of the present series, a considerable body of experimental data relating to the first stages of the above-mentioned interaction will be presented and some of the factors on which this interaction

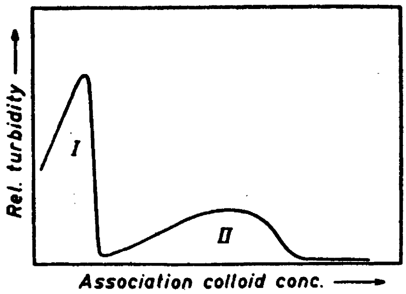

Fig. 1. The turbidity of association colloid solutions containing added decanol. Schematic curve.

depends will be discussed. In the first place, we wish to illustrate how the concentration where interaction between decanol and fatty acid soaps begins depends on the chain length of the soap and on the temperature.

EXPERIMENTAL

The soaps investigated were potassium caprylate, caprate, laurate, myristate, palmitate and stearate, and sodium caprylate, caprate, laurate, and myristate. The soaps were prepared in the usual manner from purest fatty acids and potassium or sodium ethylate.

Dilution series were prepared from each soap in which the molar ratio of decanol-1 (Eastman Kodak Co, Rochester, redistilled) to colloid was constant. Aliquots of the solutions were sealed in glass ampoules and mixed by shaking in a thermostat. The specific conductance of the water employed as solvent was less than 10^{-6} rec. ohm. To suppress the hydrolysis of the soaps, a known quantity of alkali was added to each of the solutions. Care was taken to prevent carbon dioxide from the air from entering the solutions.

In a number of cases it was found more advantageous to add a constant weight of decanol to each of the solutions instead of keeping the molar ratio constant. The decanol was added from an Agla micrometer syringe.

The turbidites were measured directly in the ampoules without opening them. Since the measurements were to be conducted at several temperatures, the shaking of the ampoules was begun and the turbidity first measured at the lowest temperature and then the ampoules were transferred to the next higher temperature and shaken two hours before the turbidity was again measured.

The turbidities were measured with a Zeiss nephelometer fitted to a Pulfrich photometer.

The following series were investigated:

Potassium caprylate + 2, 5, 7.5 and 10 moles of decanol per 100 moles of soap at 20, 30, 40, 50 and 60° C.
Potassium caprate + 1, 2, 3 and 8 moles of decanol per 100 moles of soap at 20, 30, 40, 50 and 60° C.
Potassium laurate + 1, 2, 5, 10 and 15 moles of decanol per 100 moles of soap at 20, 30, 40, 50 and 60° C.
Potassium myristate + 13, 20, 25, 30 and 35 moles of decanol per 100 moles of soap at 20, 30, 40, 50 and 60° C.
Potassium palmitate + 10, 20, 30, 40, 50 and 60 moles of decanol per 100 moles of soap at 50, 55, 60 and 65° C.
Potassium stearate + 0.33 ml of decanol per litre at 47, 59, 72.5, 84 and 97° 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 laurate + 3.2, 5.25, 7.35, 10.5, 15.7 and 21 moles of decanol per 100 moles of soap at 40° C.

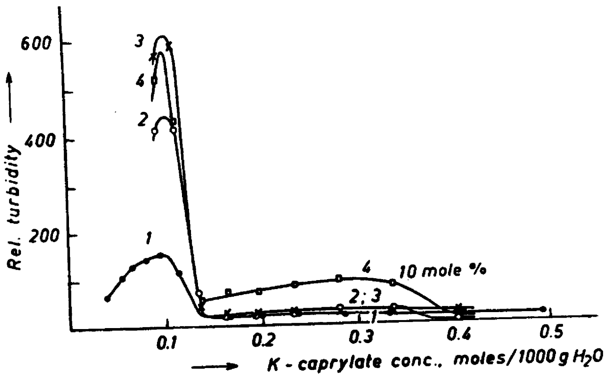

Fig. 2. *The turbidities of potassium caprylate solutions containing decanol-1, 20° C. Curve 1* ●—●, *2 moles; Curve 2* ○—○, *5 moles; Curve 3* ×—×, *7.5 moles; Curve 4* □—□, *10 moles decanol per hundred moles caprylate.*

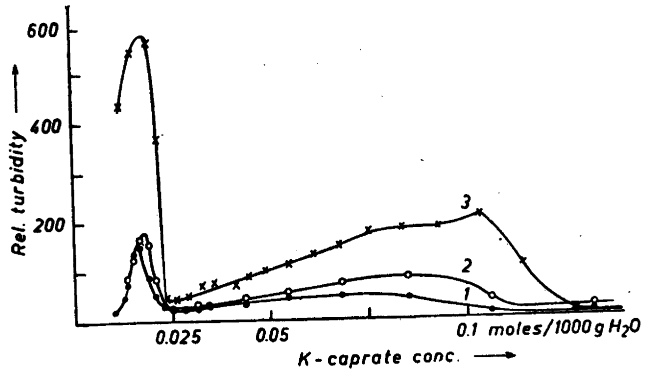

Fig. 3. *The turbidities of potassium caprate solutions containing decanol-1. 20° C. Curve 1* ●—●, *2 moles; Curve 2* ○—○, *3 moles; Curve 3* ×—×, *8 moles decanol per hundred moles caprate.*

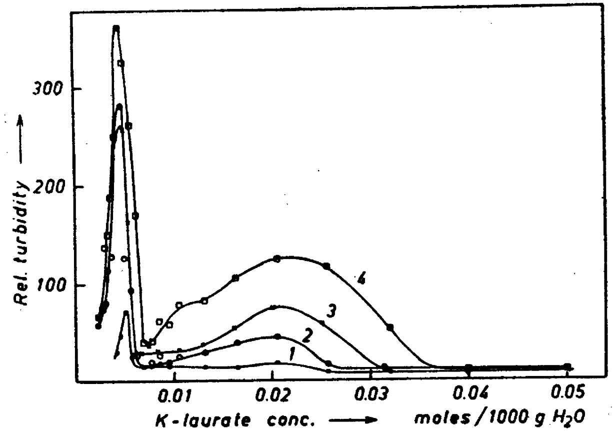

Fig. 4. *The turbidities of potassium laurate solutions containing decanol-1. 40° C. Curve 1* ●—●, *2 moles; Curve 2* ○—○, *5.1 moles; Curve 3* ×—×, *10 moles; Curve 4* □—□, *15 moles decanol per hundred moles laurate.*

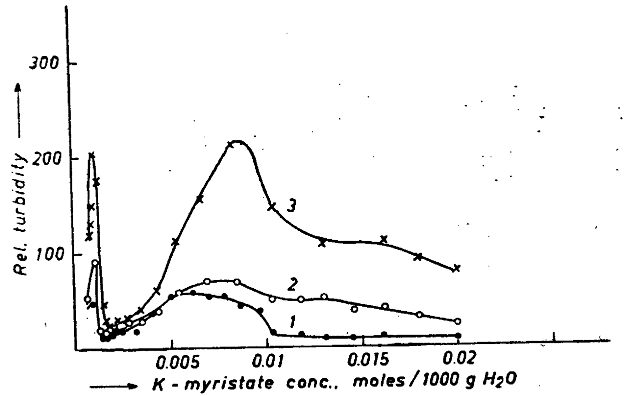

Fig. 5. *The turbidities of potassium myristate solutions containing decanol-1. 40° C. Curve 1* ●—●, *20 moles; Curve 2* ○—○, *25 moles; Curve 3* ×—×, *30 moles decanol per hundred moles myristate.*

THE RESULTS OF THE MEASUREMENTS

The experimental data have been used to draw curves which plot the relative turbidity as a function of the soap concentration. Figs. 2—6 show typical turbidity curves for several potassium soaps; each curve represents a series of measurements at constant temperature on solutions with different soap concentrations but with a constant mole ratio of added decanol to soap.

It is evident in all the curves that a marked turbidity occurs in relatively high dilutions (turbidity range I) and that this turbidity disappears completely or practically completely when the soap concentration attains a certain level. This concentration level is quite independent of the amount of added decanol as long as this remains within moderate limits. It is obvious that the ability of the soap to bind decanol undergoes a pronounced change at this concentration. Microscopic examination and other studies (*e. g.* conductance measurements) show that below this soap concentration decanol is present in the free form in an emulsified state, while above this concentration decanol interacts with the soap [2,3,9,10]. The decanol-soap complex that is formed in the latter case appears to have a limited solubility in water, and when somewhat larger amounts of decanol are added, a new extremely finely dispersed precipitate is formed which produces a turbidity (turbidity range II) differing from that due to free emulsified decanol observed at low colloid concentrations. The amount of decanol necessary to effect this turbidity varies with the soap. In caprylate solution the turbidity is almost undetectable when 7.5 moles of decanol are added per hundred moles of soap, whereas in the case of caprate and laurate solutions a similar addition produces a quite marked turbidity. This second turbidity range extends to higher soap concentrations when the amount of decanol added is increased until finally, when the amount of the latter is high enough, the turbidity no longer disappears with increasing soap concentration.

As mentioned above the turbidity phenomena were studied at several temperatures. All curves in each of the Figs. 7—11 refer to a constant decanol content (expressed in moles per hundred of soap); they were, however, measured at different temperatures. In range I the intensity of the turbidity increases somewhat with increasing temperature in many cases, but in range II the intensity decreases. The upper limit of the first turbidity range shifts to higher soap concentrations, while the upper limit of the second turbidity range shifts to lower soap concentrations with increasing temperature.

We have observed quite similar turbidity phenomena also in solutions of sodium soaps containing added decanol [1,2].

DISCUSSION

The reaction that causes the free decanol to disappear from the solution occurs in a narrow concentration range. This range lies between the maximum of the first turbidity range and the somewhat higher concentration where this turbidity disappears. We have used data from all series to determine the limits of this concentration range for the different soaps at different temperatures (Table 1). When doing this, we have taken into consideration that the range

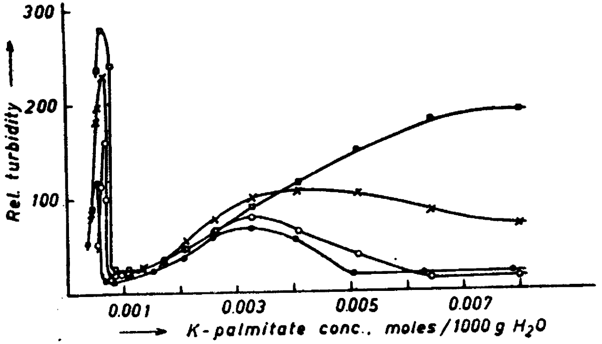

Fig. 6. The turbidities of potassium palmitate solutions containing decanol-1. 60° C. Curve 1 ●—●, 10 moles; Curve 2 ○—○, 30 moles; Curve 3 ×—×, 40 moles; Curve 4 □—□, 50 moles decanol per hundred moles palmitate.

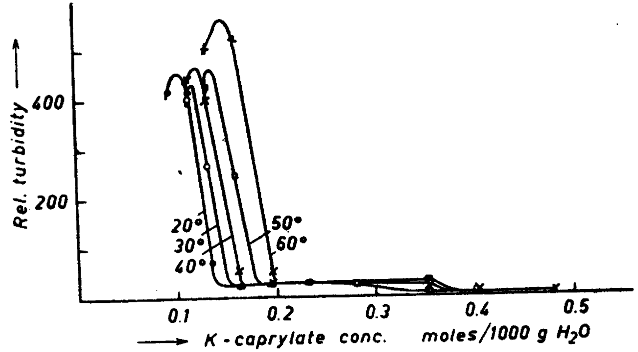

Fig. 7. The turbidities of potassium caprylate solutions containing 5 moles of decanol-1 per hundred moles of soap at different temperatures.

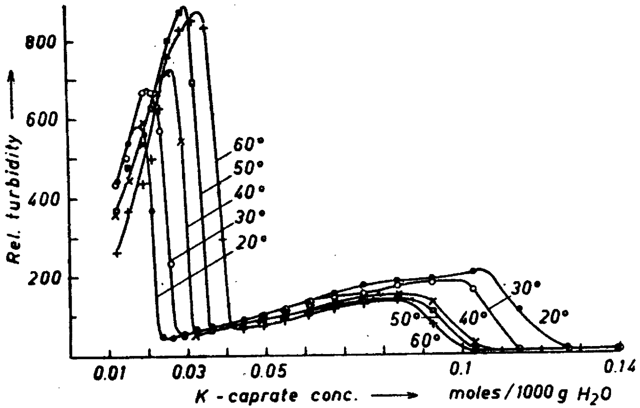

Fig. 8. The turbidities of potassium caprate solutions containing 8 moles of decanol-1 per hundred moles of soap at different temperatures.

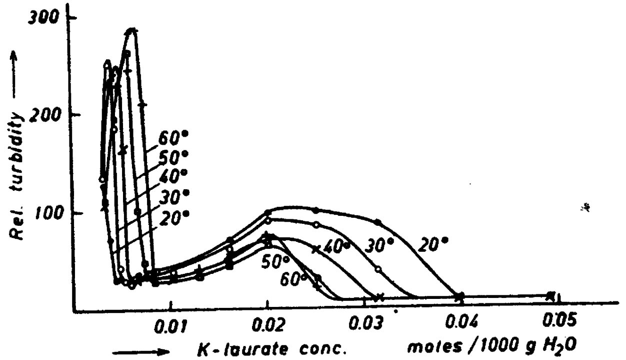

Fig. 9. The turbidities of potassium laurate solutions containing 10 moles of decanol-1 per hundred moles of soap at different temperatures.

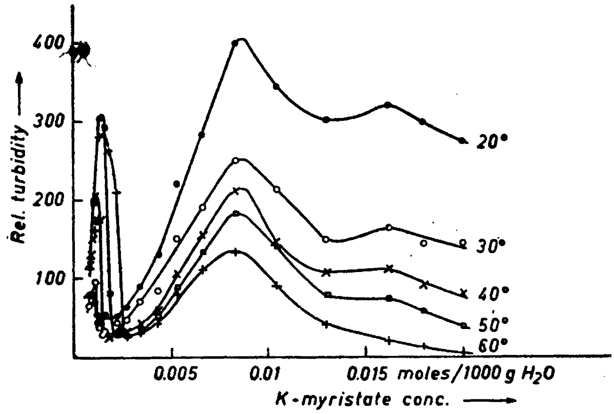

Fig. 10. The turbidities of potassium myristate solutions containing 30 moles of decanol-1 per hundred moles of soap at different temperatures.

certainly becomes more clearly defined when the amount of added decanol increases, but that at high decanol contents a tendency of the range to shift to higher concentrations is observed in some cases. It was in most cases easier to determine the upper limits of the turbidity range than the turbidity maximum. Because of this we shall in the following in general use the concentration at the upper limit to define the conditions where the interaction between soap and decanol begins, although we are fully aware that the interaction actually begins at a somewhat lower concentration.

The interaction begins at about the same soap concentrations in the solutions of the sodium and potassium salts of a fatty acid.

The variation of the upper limit of turbidity range I with increasing temperature is shown in Fig. 12. In most cases the dependence on temperature is practically linear.

From the data in Table 1 it is seen that the soap concentration at which the interaction begins decreases as the length of the hydrocarbon chain of the soap increases. In Fig. 13 the logarithm of the soap concentration at which inter-

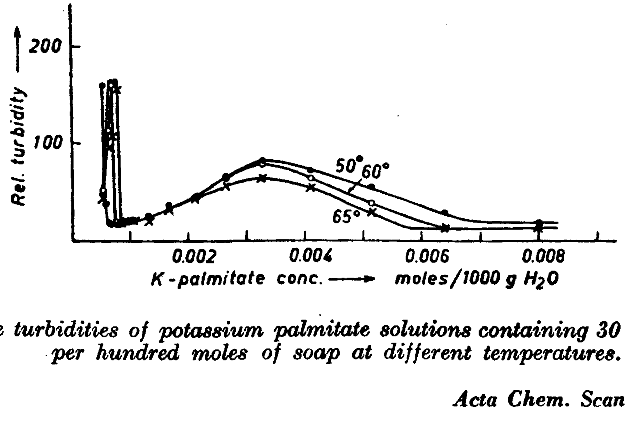

Fig. 11. The turbidities of potassium palmitate solutions containing 30 moles of decanol-1 per hundred moles of soap at different temperatures.

Table 1. The soap concentrations where the interaction between decanol and soap begins. Concentrations in moles per 1 000 g of water.

Soap	°C	Maximum of turbidity range I	Upper limit of turbidity range I
Potassium caprylate	20	0.10—0.11	0.13—0.14
	30	0.11—0.12	0.14—0.15
	40	0.12—0.13	0.15—0.16
	50	0.13—0.15	0.16—0.18
	60	0.15—0.16	0.18—0.19
Potassium caprate	20	0.016—0.019	0.021—0.023
	30	0.020—0.021	0.024—0.027
	40	0.022—0.024	0.026—0.028
	50	0.025—0.029	0.029—0.035
	60	0.028—0.032	0.034—0.037
Potassium laurate	20	0.003—0.004	0.004—0.005
	30	0.003—0.004	0.005—0.006
	40	0.004—0.005	0.006—0.007
	50	0.005—0.006	0.007—0.008
	60	0.006—0.007	0.008—0.009
Potassium myristate	20	~0.0009	~0.0012
	30	~0.0011	0.0012—0.0013
	40	0.0011—0.0012	0.0013—0.0014
	50	0.0012—0.0014	~0.0016
	60	0.0019—0.0020	0.0021—0.0023
Potassium palmitate	50	0.0004—0.0005	0.0005—0.0006
	55	0.0005—0.0006	0.0006—0.0007
	60	0.0006—0.0007	0.0007—0.0008
	65	0.0006—0.0008	0.0008—0.0009
Potassium stearate	47		~0.000080
	59		~0.000085
	72		~0.000090
	84		~0.000096
	97		~0.000102
Sodium caprylate	40	0.12—0.13	0.15—0.16
Sodium caprate	40	0.025—0.027	0.030—0.032
Sodium laurate	40	0.0045—0.0055	0.006—0.007

action with decanol begins is plotted against the number of carbon atoms in the hydrocarbon chain of the soap molecule. These curves are not quite linear; the curvatures are, however, so slight that the interaction concentration can be approximately calculated from the following logarithmic equations, where n indicates the number of carbon atoms in the paraffin chain of the fatty acid.

20° C.: $\log C = -0.364\, n + 1.66$
30° C.: $\log C = -0.345\, n + 1.53$
40° C.: $\log C = -0.334\, n + 1.48$
50° C.: $\log C = -0.326\, n + 1.45$
64° C.: $\log C = -0.310\, n + 1.40$

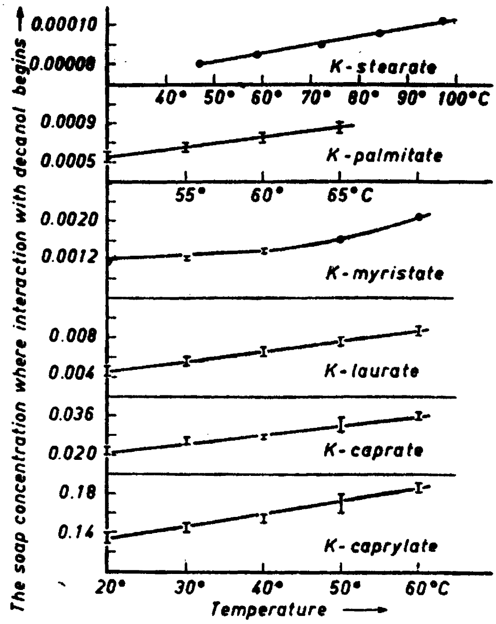

Fig. 12. The temperature dependence of the upper limit of the turbidity range I.

We have noted earlier[1-5] that the concentration at which interaction between decanol and soap begins lies very close to the lowest concentration at which hydrolysis in the soap solution leads to the formation of acid soap or at which the soap forms acid soap when fatty acid is added to the solution. In

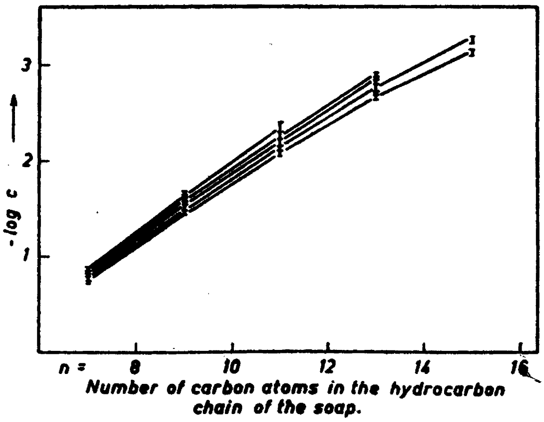

Fig. 13. The dependence of the upper limit of the turbidity range I on the chain length of the soap.

Table 2. Comparison of the soap concentrations where soaps begin to interact with fatty acid and with decanol (the upper limits of the turbidity range I).

Interaction with fatty acid			Interaction with decanol		
Soap	°C	Molarity	Soap	°C	Molarity
Sodium caprate	20	0.020–0.025	Potassium caprate	20	0.021–0.023
				20–60	0.021–0.037
Sodium laurate	20	0.005–0.0068	Potassium laurate	20	0.004–0.005
	20–58	0.005–0.008		20–60	0.004–0.009
			Sodium laurate	40	0.006–0.007
Sodium myristate	20	0.0010–0.0014	Potassium myristate	20	0.0012
	20–60	0.001–0.002		20–60	0.001–0.0023
Sodium palmitate	20	0.00025–0.0004	Potassium palmitate		
	45–65	0.00025–0.0007		50–65	0.0005–0.0009
Sodium stearate	65–80	(0.0002–0.0005)	Potassium stearate	50–77	0.00008–0.0001

Table 2 the concentrations at which acid soap is formed are compared with the concentrations at which soap and decanol begin to interact. From these data it is seen that in the case of caprate, laurate and myristate solutions the concentration ranges where interaction begins with fatty acid and with decanol are almost identical. Also for palmitate solutions the two concentration ranges are nearly the same. In the case of the interaction between stearate and stearic acid, only earlier observations on strongly hydrolysed stearate solutions are available and for this and other reasons the upper limit of the first turbidity range is probably too high.

It is thus established that interaction between soap and decanol begins at approximately the same soap concentration as the interaction between a soap and its fatty acid. The concentration in question is that which has been previously termed the limiting concentration or the limiting association concentration (L. A. C.)[6,7,1,2].

Also the location of the critical concentration in decanol-containing soap solutions becomes evident in some cases in the turbidity curves although not always very clearly. The C. M. C. is as usually defined as the concentration where the aggregation to micelles begins to increase rapidly. When the amounts of decanol added are small, the C. M. C. appears at the upper limit of the turbidity range II or at the maximum of the turbidity curve in this range, *i. e.* at that soap concentration where the precipitate of the second turbidity range has just disappeared or begins to disappear because of the formation of soluble decanol-containing mixed micelles. At higher decanol contents however, the turbidity maxima, tend to shift to higher concentrations and above a certain decanol content characteristic for each soap the turbidity does not disappear at all. Because of this and the fact that soap is precipitated from the solution it is difficult to determine exactly where micelle formation begins from the turbidity curve.

The values in the last column of Table 3 are from experiments with small amounts of added decanol, and are the lowest values of the C. M. C. in decanol-

Table 3. The critical concentrations in pure and decanol-containing soap solutions.

	Pure soap solutions		Soap solutions containing decanol	
Soap	°C	C. M. C.	°C	C. M. C.
Caprylate	25	0.40	60	0.24 −0.28
Caprate	20	0.097	60	0.055−0.085
Laurate	20	0.028	60	0.020−0.025
Myristate	30	0.007	60	0.005−0.007
Palmitate	50−60	0.0032	60	0.003

containing soap solutions that we have observed in the turbidity measurements. (They agree rather well with the results of solubility measurements which will be presented in later parts of this series.) These C. M. C. values are somewhat lower than the C. M. C.'s in pure soap solutions, but appreciably higher than the limiting concentrations.

The limiting concentration may be confused with the critical concentration and the appearance of the former may be considered an indication of a displacement of the C. M. C. to very low concentrations due to presence of the added alcohol. This is not correct, however. The phenomena at the critical concentrations and those at the limiting concentrations have been known for more than 25 years and numerous experimental measurements (measurements of surface tension, hydrolysis, and conductance, microscopical observations, determination of the solubility of fatty acids and later also of alcohols, conductometric and potentiometric titrations, *etc.*) have shown that they appear simultaneously in numerous colloid systems, but at different colloid concentrations.

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