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Effect of Lower Fatty Acids on the Solubilization of Butanol-1 in Aqueous Solutions of Sodium Salts of Fatty Acids. I

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Inhaltsübersicht

Es wird über Arbeiten berichtet, die das Studium der Löslichkeitsbeeinflussung von Fettsäuren auf Butanol-1 in Gegenwart von fettsauren Salzen beinhalten. Viskositätsmessungen an den Systemen sollen einen Hinweis auf die Flüssigkeitsstruktur geben.

Summary

It has been concluded that the tendency of formation of Hydrophilic Oleomicelles decreases with the increase in the concentration of free acids in the solution where as the tendency to form Lipophilic Hydromicelles is not at all effected by the presence of free acids. The shorter is the chain length of the acid, more effective it is, in decreasing the extent of solubilization of Butanol-1. The effectiveness of the acids in decreasing the solubilization of Butanol-1 is in the order:

Propionic acid > Butyric acid > Caproic acid > Caprylic acid.

It may also be pointed out that Laurate is a better Solubilizer for the solubilization of Butanol-1 than Caprate and Caprylate systems in presence of same amount of free acids. The capacity of the soap solutions to solubilize Butanol-1 decreases with the increase in the amount of free acid in the solutions.

From the viscosity results it has been confirmed that two types of micelles are formed.

Introduction

In a previous communication[1]), the effect of oleic acid and sodium hydroxide on the solubilization of butanol-1 and 3-methyl butanol-1 in aqueous solution of sodium oleate has been studied. In the present communication the effect of free propionic, butyric, caproic and caprylic acids on the solubilization of butanol-1 in aqueous solution of sodium salts of caprylic, capric and lauric acids have been studied with a view to finding out if these acids have any influence on the nature of the micelles present at different concentrations of butanol-1.

The effect of free fatty acids on the viscosity of these systems has also been studied.

[1]) A. N. Bose and K. N. Mehrotra, Jour. Colloid Sc. **11**, 250–53 (1956).

Materials used

Merck reagent grade Butanol-1 was used after purification (B. P. 117° C). The acids were purified by keeping over anhydrous sodium sulphate for a week and then twice distilled and the fractions distilling at following boiling points were collected for experimental purposes.

n-propionic acid (B. D. H. Analar)	140—141° C,
n-butyric acid (B. D. H.)	162.5—163.5° C,
n-caproic acid (B. D. H.)	204—205° C,
n-caprylic acid (B. D. H.)	236—237° C.

n-capric acid (B. D. H.) and lauric acid (B. D. H.) were used without further purification. Sodium hydroxide was prepared from sodium (Analar B. D. H.) in conductivity water.

Experimental

Calculated amount of fatty acid (corresponding to 0.2 N) was weighed in a standard flask and this was titrated with sodium hydroxide solution and made up to the mark by adding requiste amount of Butanol-1, free acid and conductivity water. In this way a number of solutions of 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80% and 90% Butanol-1 containing same amount of soap (0.2 N) but different amounts of free acid have been prepared. Attempts have been made to find out the exact solubility of free acids within 1% in Aqueous solutions of soaps in presence of different concentrations of Butanol-1.

The Viscosity of the solutions which are stable at or below 35° C has been determined by means of OSTAWALDS Viscometer at 35° ± 0.5° C. The densities have been measured by means of Pyknometer. The results obtained are given in tables I, II, III.

Results and Discussion

From the results given in table I, it is observed that in presence of free Propionic acid it has been possible to prepare the solutions of 80% and 90% Butanol-1 concentrations in case of all the soaps. It has not been possible to prepare the solutions of 5% to 70% Butanol-1 in presence of even 1% of the Propionic acid where as the solutions of these concentrations of Butanol-1 have been prepared in neutral soaps. This shows that the extent of solubilization of Butanol-1 decreases as the amount of free acid increases.

In the presence of 1% Butyric acid, the solution of 10% Butanol-1 has also been prepared in all the soaps in addition to the solutions of 80% and 90% Butanol-1 concentrations prepared in presence of 1% Propionic acid. In the solutions of 5% and 70% Butanol-1 the presence

of 1% Butyric acid, separates the layers at room temperature and the clear solutions were only possible at a temperature higher than 35° C in Sodium Caprylate system. In the case of Sodium Caprate, the solution of 5% Butanol-1 was highly viscous at room temperature and the solution of 20% Butanol-1 clears up above 47° C. In the case of Sodium Laurate it has been possible to prepare the solutions of 20% Butanol-1 in presence of 1% free Butyric acid in addition to the solutions prepared in Caprate system.

The results show that the tendency of the Micelle formation in presence of free Butyric acid is low as compared to that in neutral soaps and this tendency in presence of Propionic acid is less than in presence of same amount of Butyric acid. It may also be pointed out that Laurate is a better solubilizer than Caprate and Caprylate due to its longer chain length.

In the presence of 1% and 2% Caproic acid, it has been possible to prepare the solutions of all concentrations of Butanol-1 in all the soaps. In Caprylate the presence of 2% free Caproic acid, separates the layers below 48° C in 5% Butanol-1 solution. In case of Caprate system the solution containing even 1% of Caproic acid was not clear at room temperature but remains clear at 35° C. In Laurate system the solution of 5% Butanol-1 in presence of 1% Caproic acid remains clear at a temperature higher than 35° C.

In presence of 3% Caproic acid, it has been possible to prepare the solutions for 50% to 90% Butanol-1 in case of all the soaps. In Caprylate system the presence of 3% Caproic acid separates the layers in 40% Butanol-1 solution below 46° C. In case of Caprate this solution remains highly milky at room temperature and in case of Laurate this solution remains clear at 35° C.

In presence of 4% Caproic acid it has not been possible to prepare the solutions for 5% to 40% Butanol-1 concentrations in case of all the three soaps. In case of Caprylate system, the solution of 50% Butanol-1 separates out into layers in presence of 4% Caproic acid below 46° C whereas in case of Caprate and Laurate the solutions remain clear below 35° C.

It has been possible to prepare the solutions of 60% to 90% Butanol-1 in presence of any amount of free Caproic acid.

The results show that even in presence of Caproic acid, Laurate is a better solulizer than Caprate and Caprylate and the extent of solubilization of Butanol-1 decreases as the amount of free Caproic acid increases. This decrease is more rapid in presence of Propionic and Butyric acids than in presence of Caproic acid.

It has been possible to prepare the solutions of all concentrations of Butanol-1 in presence of 1% and 2% Caprylic acid in case of all the soaps. The solution of 5% Butanol-1 in presence of 2% Caprylic acid remains clear above 50° C in case of Laurate whereas in case of Caprate this solution remains clear even at room temperature. In the case of Caprate system the solution of 5% Butanol-1 in presence of 3% Caprylic acid remains clear above 50° C but the solution in presence of 4% Caprylic acid does not remain clear even at high temperature.

In presence of Caprylic acid upto 5%, it has been possible to prepare the solutions for 10% to 80% Butanol-1 in case of Caprate and Laurate systems. The solution of 10% Butanol-1 in presence of 6% Caprylic acid remains highly viscous at room temperature but remains clear at 35° C in case of Caprate and Laurate system. In presence of 7% Caprylic acid the solution clears up above 42° C in case of Laurate system and above 39° C in case of Caprate system.

It has been possible to prepare the solutions of 20%, 30% and 40% Butanol-1 concentrations in presence of Caprylic acid upto 11%, 13% and 19% respectively in Laurate system whereas in case of Caprate system these values are 10%, 11% and 17% respectively.

It has been possible to prepare the solutions for 50% to 80% Butanol-1 concentrations in presence of any amount of free Caprylic acid.

Results show that Laurate is a better solubilizer than Caprate and Caprylate. It has also been pointed out that the free acid lowers the solubilization of Butanol-1 below 50% Butanol-1 concentrations but above 50% Butanol-1 concentrations the extent of solubilization is not at all effected by the presence of free acid. According to the classification of SCHULMAN and RILEY[2]) the tendency of formation of Lipophilic Hydromicelles are not effected by the presence of free acid whereas the tendency of formation of Hydrophilic Oleomicelles decreases with the increase of amount of free acid. This is due to the fact that above 50% Butanol-1 concentration the free acid remains in solution and is not incorporated in the micelles but below 50% Butanol-1 concentration the free acid tries to get into micelles and so tries to replace the alcohol from the palisade layers of the micelles as a result of which separation of alcohol from the solution takes place. The effectiveness of replacing the alcohol is in the order:

Propionic acid > Butyric acid > Caproic acid > Caprylic acid.

Viscosity

Propionic acid systems. From the results given in table I it has been observed that the viscosity of 80% Butanol-1 solutions is higher

[2]) J. H. SCHULMAN and D. P. RILEY, Jour. Colloid Sc. **3**, 383 (1948).

than that of 90% Butanol-1 solutions. This is due to the fact the size of the micelles in 80% Butanol-1 solution is bigger than those of 90% solutions and hence the viscosity is higher in the former.

Table I

Viscosity of the systems: water-sodium salts of the fatty acids-Butanol-1 and Propionic acid

Viscosity in milli poise Temperature 35° C

Con. of Butanol-1 in volume %	Con. of free acid in volume %	Sodium salts of the acids		
		Caprylate	Caprate	Laurate
5%	1%			16.88
80%	1%	25.10	25.63	26.99
	4%	24.38	24.73	25.23
	8%	23.45	23.69	23.72
	10%	23.02	23.38	23.52
90%	1%	23.81	24.06	24.45

It may also be pointed out that the viscosity of 80% and 90% Butanol-1 solutions decreases as the concentration of free propionic acid in solutions increases. This is due to the fact that in presence of 80% and 90% Butanol-1, free acid is not incorporated in the micelles but is present as free molecules and therefore the addition of free acid does not increases the size of the micelles.

The comparision of the results of different soaps show that the viscosity of the solutions increases as the length of the acid chain in the soap increases due to which the size of the micelles increases.

Butyric acid in different soaps. From the results given in table II, it is observed that the viscosity of the solution in presence of 10% and 20% Butanol-1 increases as the concentration of free Butyric acid increases whereas in presence of 80% and 90% Butanol-1 the viscosity decreases as the concentration of free Butyric acid increases. This difference in behaviour is due to the fact that in presence of 10% and 20% Butanol-1, as free acid is also incorporated in the micelles, the size of the micelles is bigger and hence the addition of free acid results in the increase of viscosity. In presence of 80% and 90% Butanol-1, the free acid is present as free molecules in the solutions and so does not result in the increase in viscosity. In the case of Butyric acid too, the viscosity of the solutions increases as the length of the acid chain in the soap increases. It may also be pointed out that the viscosity of the solutions in presence of Butyric acid is higher than the viscosity of the

Table II

Viscosity of the systems: water-sodium salts of the fatty acids-Butanol-1 and Butyric acid

Viscosity in milli poise Temperature 35° C

Con. of Butanol-1 in volume %	Con. of free acid in volume %	Sodium salts of the acids		
		Caprylate	Caprate	Laurate
10%	1%	12.58	15.12	18.05
20%	1%			21.74
80%	1%	25.17	25.78	25.96
	4%	24.96	25.10	25.25
	8%	24.56	24.61	24.84
	12%	23.79	24.20	24.61
90%	1%	23.86	24.13	24.77

solutions containing same volume of Propionic acid. This may also be due to the larger chain of Butyric acid as compared to Propionic acid.

Caproic acid in different soaps. From the results given in table III, it is observed that the viscosity of the solutions in case of Caprate and Laurate systems increases with the increase in the concentration of free Caproic acid in presence of Butanol-1 upto 60% but decreases in presence of 70% to 90% Butanol-1 concentrations. In the case of Caprylate system the viscosity increases with the increase in free acid concentration even in 70% Butanol-1 solutions and shows a decrease only in 80% and 90% Butanol-1 solutions.

In the case of Caproic acid also, the viscosity increases as the length of the acid chain in the soap increases. It may also be pointed out that the viscosity of the solutions containing same amount of Butanol-1 and free acid is higher in the case of Caproic acid than in case of Butyric acid. This is due the larger chain length of the Caproic acid as compared to Butyric acid.

From the results it can also be concluded that the viscosity at first increases as the Butanol-1 concentration increases upto 50% and then decreases with the increase in the Butanol-1 concentration. This is due to the change in the nature of the micelles from Hydrophilic Oleomicelles to Lipophilic Hydromicelles.

All the results are in accordance with the results given in the previous communications [1]) and [3]).

[3]) A. N. Bose and K. N. Mehrotra, Z. physik. Chem. (In Press.)

Table III

Viscosity of the systems: water-sodium salts of the fatty acids-Butanol-1 and Caproic acid

Viscosity in milli poise Temperature 35° C

Con. of Butanol-1 in volume %	Con. of free acid in volume %	Sodium salts of the acids		
		Caprylate	Caprate	Laurate
5%	1%	10.70	12.08	
10%	1%	12.62	14.50	16.61
	2%	13.50	15.63	18.78
20%	1%	18.05	19.21	20.65
	2%	18.81	20.12	21.66
30%	1%	22.60	23.83	24.87
	2%	23.51	24.99	26.01
40%	1%	25.94	27.00	27.80
	2%	27.35	28.46	29.24
	3%			31.95
50%	1%	26.81	28.62	29.47
	2%	27.68	29.49	30.33
	3%	30.58	30.97	31.37
	4%		32.10	33.13
60%	1%	27.90	28.47	29.09
	2%	28.20	28.78	29.37
	3%	28.51	29.07	29.63
	8%	29.17	29.62	30.03
	16%	29.23	29.69	30.14
70%	1%	26.79	27.52	27.90
	3%	27.03	27.50	27.87
	8%	27.12	27.48	27.83
	16%	27.27	27.28	27.72
80%	1%	25.22	26.06	26.55
	4%	25.15	25.82	26.28
	8%	25.07	25.57	26.10
90%	1%	23.91	24.42	24.77

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