

The Surface Tension and the Critical Micelle Concentration in Aqueous Solution of β -D-Alkyl Glucosides and their Mixtures

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There have not been many research works on the pure non-ionic agents¹⁻³. Future progress in this field should be assured by the study of pure non-ionic agents. Some colloid chemical properties of a series of pure octyl polyol ethers in aqueous solution have been studied to determine the effect of differences in the hydrophilic group³. In the present paper, we have measured the surface tension vs. concentration of octyl, decyl and dodecyl glucosides in order to know the effect of paraffin chain length on the physico-chemical properties of alkyl glucosides. The CMC was determined from the inflexion of the surface tension vs. concentration curve. The surface tension of

mixtures of alkyl glucosides solutions and the effect of added salts on the surface tension of octyl glucoside were also measured.

Experimental

The procedures and purifications of alkyl glucosides were similar⁴ as in the case of octyl glucoside⁵. The melting points and specific rotations of β -D-octyl, decyl and dodecyl glucosides were m. p. 63.8~65°C, $[\alpha]_D^{25} = -33.8^\circ$ (H₂O); m. p. 135°C, $[\alpha]_D^{25} = -27.8^\circ$ (H₂O); m. p. 143.5°C, $[\alpha]_D^{25} = -24.7^\circ$ (H₂O), respectively.

The materials were further purified by foam fractionation. The concentration of the solution foam fractionated was chosen slightly below the CMC, because the foam stability and the efficiency of the elimination of highly surface active impurities were optimum in this concentration⁵. Surface

1) C. R. Bury and J. Browning, *Trans. Faraday Soc.*, **49**, 209 (1953).

2) T. Nakagawa et al., *J. Chem. Soc. Japan, Pure Chem. Soc. (Nippon Kagaku Zasshi)*, **77**, 1563 (1956); **79**, 345, 348 (1958).

3) K. Shinoda, T. Yamanaka and K. Kinoshita, *J. Phys. Chem.*, **63**, 648 (1959).

4) R. Hori, Ph. D. Dissertation, Kyoto University (1959) (in Japanese).

5) K. Shinoda and K. Mashio, *J. Phys. Chem.*, **64**, 54 (1960).

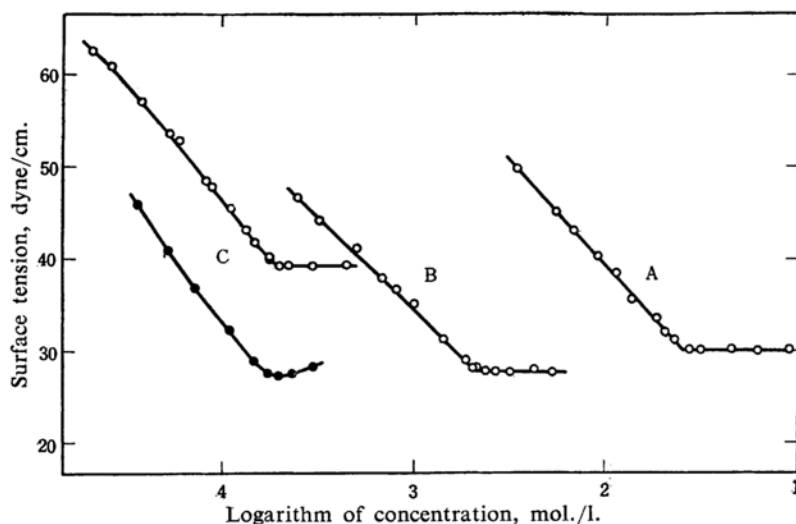


Fig. 1. The surface tension vs. log. concentration curves of β -D-alkyl glucosides at 25°C: A, octyl glucoside; B, decyl glucoside; C, dodecyl glucoside; ●, before foam fractionation.

tension was measured by the drop weight method, with a tip 0.576 cm. in diameter in an air thermostat at $25 \pm 0.2^\circ\text{C}$. The correction of Harkins et al.⁶⁾ was applied. There was appreciable change, 2~4 dyne/cm. of surface tension, with time durations of 4~20 min. and 10~60 min. for decyl and dodecyl glucosides, respectively.

Results

The surface tension vs. concentration relations are shown in Fig. 1 and summarized in Tables I, II and III. There was great change in surface tension between foam fractionated unfraction-

TABLE I. THE SURFACE TENSION IN AQUEOUS SOLUTION OF β -D-OCTYL GLUCOSIDE AT 25°C

Concentration, mol./l. $\times 10^2$	Time per drop in min.	Number of measurements	Surface tension dyne/cm.	Mean variation dyne/cm.
0.343	20	4	49.8	0.2
0.549	15	4	45.0	0.6
0.686	10	4	43.1	0.35
0.915	10	4	40.3	0.4
1.14	10	4	38.4	0.2
1.37	10	4	35.6	0.3
1.83	5	8	33.6	0.9
2.05	5	4	32.1	0.05
2.29	5	2	31.2	0.05
2.75	5	4	30.2	0.3
3.07	5	3	30.3	0.2
4.61	5	4	30.4	0.1
6.15	5	3	29.9	0.6
9.23	5	2	30.1	0.0

TABLE II. THE SURFACE TENSION IN AQUEOUS SOLUTION OF β -D-DECYL GLUCOSIDE AT 25°C

Concentration, mol./l. $\times 10^3$	Time per drop in min.	Number of measurements	Surface tension dyne/cm.	Mean variation dyne/cm.
0.255	20	2	46.7	0.1
0.325	15	3	44.2	0.1
0.513	15	4	41.2	0.3
0.683	10	4	37.8	0.1
0.816	10	2	36.7	0.0
1.025	10	4	35.0	0.3
1.46	10	2	31.2	0.2
1.91	5	3	29.0	0.0
2.06	5	3	28.1	0.1
2.14	5	2	28.3	0.0
2.41	5	4	27.8	0.1
2.67	5	2	27.7	0.1
3.22	5	3	27.7	0.1
4.28	5	3	28.0	0.3
5.35	5	4	27.7	0.5

ated solution of dodecyl glucoside. However, there was no appreciable change in solutions of octyl and decyl glucosides.

The inflexion in the surface tension vs. logarithm of concentration curve was distinct and there was no minimum in foam fractionated solution. The surface tension of mixtures of alkyl glucosides has been measured. The results are summarized in Fig. 2. The surface tension vs. concentration curve showed the minimum in the mixture of octyl-decyl glucosides. The effect of added sodium chloride, calcium chloride and sodium sulfate on the surface tensions of aqueous solution of octyl glucoside has also been measured. The results are shown in Fig. 3.

6) W. D. Harkins and F. E. Brown, *J. Am. Chem. Soc.*, **41**, 519 (1919).

TABLE III. THE SURFACE TENSION IN AQUEOUS SOLUTION OF β -D-DODECYL GLUCOSIDE AT 25°C

Concentration, mol./l. $\times 10^4$	Time per drop in min.	Number of measurements	Surface tension dyne/cm.	Mean variation dyne/cm.
0.213	60	3	62.5	0.1
0.270	60	3	60.8	0.3
0.385	60	3	57.0	1.0
0.540	50	3	53.6	1.1
0.609	40	3	52.8	0.1
0.835	30	3	48.5	0.1
0.900	20	3	47.9	0.2
1.13	20	4	45.4	0.4
1.35	15	4	43.1	0.3
1.51	15	4	41.8	0.4
1.81	10	4	40.2	0.2
1.82	10	4	39.8	0.9
2.00	10	4	39.3	0.25
2.26	10	4	39.3	0.1
3.01	10	4	39.4	0.15
3.77	10	4	39.4	0.4

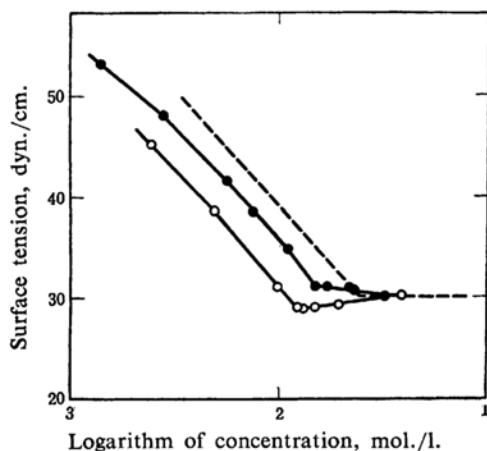


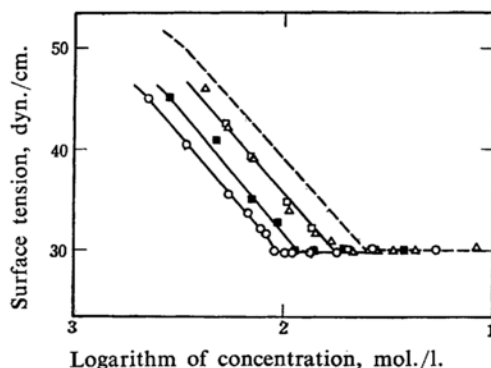
Fig. 2. The surface tension vs. log. concentration of mixtures of alkyl glucosides at 25°C: O, decyl and octyl glucosides in mole ratio of 0.089 to 0.911; ●, dodecyl and octyl glucosides in mole ratio of 0.0084 to 0.9916; dotted curve shows pure octyl glucoside.

Discussion

The CMC was obtained from the inflexions in the curves. As the surface tension remains constant, the activity of solute is constant over the flat portion of the surface tension vs. concentration curve. Because, in Gibbs adsorption isotherm,

$$\left(\frac{\partial \gamma}{\partial \ln c_2}\right)_T \left(\frac{\partial \ln c_2}{\partial \ln a_2}\right)_T = -RT\Gamma_2 \quad (1)$$

if $(\partial \gamma / \partial \ln c_2)_T = 0$ and $\Gamma_2 > 0$, then $(\partial \ln a_2 / \partial \ln c_2)_T = 0$ and therefore $a_2 = \text{const.}$ with concentration.

Fig. 3. The effect of added salts on the surface tension of β -D-octyl glucoside at 25°C: Δ , 0.93 N CaCl_2 ; \square , 0.47 N NaCl ; \blacksquare , 0.93 N NaCl ; \circ , 0.93 N Na_2SO_4 .

The fact that the activity vs. concentration remains constant suggests that something similar to a phase separation is occurring in the solution. Namely, the micelle formation begins above the concentration of inflexion and the concentration of single species stays constant.

Table IV gives the CMC, surface excess and residual area per molecule calculated from the data in Tables I, II and III under the assumption that $(\partial \ln a_2 / \partial \ln c_2)_T = 1$ below the concentration of inflexion point.

TABLE IV. THE CMC, SURFACE EXCESS AND RESIDUAL AREA OF β -D-ALKYL GLUCOSIDES AT 25°C

Substance	CMC mol./l.	Surface excess 10^{-10} mol./cm ²	Residual area Å ²
Octyl glucoside	0.025	3.9	42
Decyl glucoside	0.0022	3.5	47
Dodecyl glucoside	0.00019	4.6	36

The CMC of ionic agents was given as a function of hydrocarbon chain length and the concentration of gegenions⁷⁻¹⁰,

$$\log \text{CMC} = -\frac{m\omega}{kT} + K_6 \ln C_i + \text{const.} \quad (2)$$

where ω is the cohesive energy change per methylene group passing from the bulk of the solution to the micelle, m the number of carbon atoms in hydrocarbon chain, K_6 the experimental constant, C_i the concentration of uni-valent gegenions.

As there is no electrical work accompanying

7) A. B. D. Cassie and R. C. Palmer, *Trans. Faraday Soc.*, **37**, 156 (1941).

8) H. Lange, *Kolloid-Z.*, **117**, 48 (1950).

9) M. E. Hobbs, *J. Phys. & Colloid Chem.*, **55**, 675 (1951).

10) K. Shinoda, *This Bulletin*, **26**, 101 (1953).

the formation of micelles of non-ionic agents, the electrical term in Eq. 2 disappears. The change in CMC as a function of the paraffin chain length may be expressed as,

$$\log \text{CMC} = -\frac{m\omega}{kT} + \text{const.} \quad (3)$$

Actually the CMC of octyl, decyl and dodecyl glucosides decreased to 1/3.4 per one additional methylene group. This relation is similar to that of ionic agents under the condition of a definite concentration of gegenions¹¹⁾ as will be expected from Eq. 2. In a case where no salt is added, the decrease in CMC of ionic agent is much smaller. Lange has found similar results for octyl, decyl and dodecyl polyoxyethylene ether¹²⁾.

The CMC's of mixtures of ionic agents have been studied and interpreted rather well^{13,14)}. As there is no electrical energy involved in micellization of non-ionic agent, the theoretical treatment is far simpler and the CMC is given as a function of the mole composition of the mixture.

$$\sum \text{CMC}_{m_i} \cdot x_i = \text{CMC}_{\text{mix}} \quad (4)$$

$$\sum \text{CMC}_{m_i} \frac{x_i' \exp(m_i \omega / kT)}{\sum x_i' \exp(m_i \omega / kT)} = \text{CMC}_{\text{mix}} \quad (5)$$

Where x_i is the mole fraction of the i th component in the micelle and x_i' the mole fraction of the i th component in the bulk of the solution. The comparison between the calculated and observed CMC values is shown in Table V.

TABLE V

Substance	Mole fraction of the latter compound	CMC mol./l.	Calcd. CMC mol./l.
Octyl/Decyl glucoside	0.089	0.0125	0.013
Octyl/Dodecyl glucoside	0.0084	0.015	0.012

It seems very interesting to us that the surface tension vs. concentration curve showed the minimum in the mixture of decyl and octyl glucoside, but the mixture of dodecyl octyl glucoside did not show the recognizable minimum as shown in Fig. 2. The existence of the minimum in the former and non-existence in the latter can be explained as being based on the change in composition at the surface. In the mixture of decyl and octyl glucosides, the more surface-active molecule, decyl glucoside, has lower surface tension over the flat portion, as shown in Fig. 1. The

mole fraction of decyl glucoside is relatively large at the surface at the minimum, i.e., at the beginning of micelle formation, whereas the fraction of decyl glucoside decreases above the CMC, due to the increase of the micellar species, and the surface tension approaches that of pure octyl glucoside solution. This discussion may hold for the mixture of homologous compounds of non-ionic agents.

The addition of salts to solutions of non-ionic agents has a relatively small effect compared with ionic agents. Moreover, the slope of surface tension vs. logarithm of concentration curve does not change appreciably in contrast with ionic agents¹⁵⁾. The effect is not electrical and probably rather indirect. Sodium chloride showed a greater effect than calcium chloride depressing the cloud point¹⁶⁾ and increasing relative viscosity and turbidity¹⁷⁾ of non-ionic agents. The same trend was observed in depressing the CMC. Sodium sulfate of the same concentration shows an even greater effect than sodium chloride. The CMC obtained from the inflexions of surface tension vs. concentration curves are summarized in Table VI.

TABLE VI. THE EFFECT OF ADDED SALTS ON THE CMC DETERMINED BY SURFACE TENSION MEASUREMENTS AT 25°C

Substance	Medium	CMC mol./l.
Octyl glucoside	H ₂ O	0.025
"	0.93 N CaCl ₂	0.017
"	0.47 N NaCl	0.017
"	0.93 N NaCl	0.012
"	0.93 N Na ₂ SO ₄	0.009

The salts of the same ionic strengths do not exhibit the same effect. The volume of salts added, including hydration water, may change the effective concentration of agents and the change in solvent property may decrease the hydration and the CMC decreases.

Summary

The surface tension in aqueous solutions of β -D-alkyl glucoside and their mixtures at 25°C has been measured. The CMC was determined from the inflexions of the curves; octyl glucoside, 0.025 mol./l., decyl glucoside 0.0022 mol./l., dodecyl glucoside, 0.00019 mol./l. The effect of hydrocarbon chain length was explained theoretically. The CMC of mixtures has been also explained by the extension of the theory of ionic agents. The effect of added sodium chloride, calcium chloride and sodium sulfate

11) K. Shinoda, *J. Phys. Chem.*, **59**, 432 (1955).12) H. Lange, *Kolloid-Z.*, **163**, 9 (1959).13) H. Lange, *ibid.*, **131**, 96 (1953).14) K. Shinoda, *J. Phys. Chem.*, **58**, 1136 (1954).15) H. Lange, *Kolloid-Z.*, **153**, 155 (1957).16) W. N. Macleay, *J. Colloid Sci.*, **11**, 272 (1956).17) T. M. Doscher, G. E. Myers and D. C. Atkins, Jr., *ibid.*, **6**, 223 (1951).

on the surface tension in aqueous solution of octyl glucoside has been measured. The effect of added salts on the CMC was determined from the inflexions of the surface tension vs. logarithm of concentration curves.

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