Surface Chemical Properties in Aqueous Solutions of Glucosyl Alkylbenzenes

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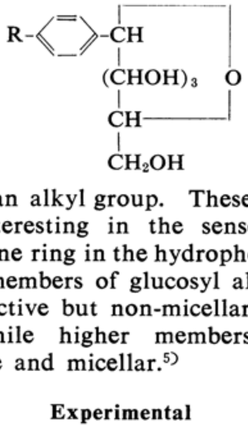
For aqueous solutions of fatty acids and alcohols the surface chemical relationships between surface tension and concentration are now well understood.[1-3] However, investigations to extend the concept of the adsorption of solutes at an air/water interface, derived from the above relationships, to surface active non-ionic compounds have scarcely been made, probably because of the difficulties in obtaining pure materials. Thus, in the case of polyoxyethylated non-ionic compounds there is a considerable difficulty either in the synthesis of sharply defined compounds or in the purification of commercial materials.[4]

In the present experiment the author has investigated the surface tension vs. concentration relationship of aqueous solutions of a series of glucosyl alkylbenzenes obtained in a pure state, from which the free energy of adsorption and the attraction between hydrophobic portions in the surface layer were discussed. Glucosyl alkylbenzenes have the structure



where R is an alkyl group. These compounds are also interesting in the sense that they have a benzene ring in the hydrophobic portion. The lower members of glucosyl alkylbenzenes are surface-active but non-micellar in aqueous solution, while higher members are both surface-active and micellar.[5]

Experimental

Materials.—Glucosyl alkylbenzenes were synthesized[6] and purified by Hutchinson et al.[5] The synthesis and purification will be reported in a separate publication. The glucosyl alkylbenzenes studied in this work include *p*-(β-D-glucosyl)methylbenzene, *p*-(β-D-glucosyl)ethylbenzene, *p*-(β-D-glucosyl)propylbenzene and *p*-(β-D-glucosyl)butylbenzene.

Surface Tension.—Surface tension measurements on aqueous solutions of these compounds were carried out by the drop-volume method, to which the corrections of Harkins et al.[7] were applied. The drops were formed slowly on a tip 0.408 cm. in diameter, attached to a micrometer syringe, in a thermostat at 25°C. Using drop forming times of five minutes or longer no evidence of aging was found.

Results and Discussion

Results[5] for the surface tension of aqueous solutions of glucosyl alkylbenzenes at 25°C are shown in Fig. 1* in which the surface tension, γ, is plotted against the logarithm of the concentration, c.

Gibbs' adsorption isotherm for the adsorption of a soluble substance at an interface is written in the following form, if the solution is sufficiently dilute to replace the activity with the concentration.

$$\Gamma = -(c/\boldsymbol{R}T)(\mathrm{d}\gamma/\mathrm{d}c) \qquad (1)$$

where Γ is the surface excess of the solute, T is the absolute temperature, and $\boldsymbol{R}$ is the gas constant. On the other hand, the adsorption isotherm developed by Langmuir is written in the form

$$q = k_1 k_2 c/(1 + k_2 c) \qquad (2)$$

where q is the amount of the solute adsorbed per unit area of the surface, and k_1 and k_2 are constants. Here, let us assume that one can put $\Gamma = q$ when the solute molecules are adsorbed in the surface layer.

Combining Eqs. 1 and 2 we obtain

$$\gamma = \gamma_0 - \boldsymbol{R}Tk_1 \ln(1 + k_2 c) \qquad (3)$$

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[1] I. Langmuir, *J. Am. Chem. Soc.*, **39**, 1883 (1917).

[2] A. E. Alexander and P. Johnson, "Colloid Science," Oxford University Press, Oxford (1950), p. 513.

[3] K. L. Wolf, "Physik und Chemie der Grenzflächen," Springer-Verlag, Berlin (1959), p. 148.

[4] T. Nakagawa and K. Shinoda, "Colloidal Surfactants," Academic Press, New York (1963), p. 163.

[5] E. Hutchinson, V. E. Sheaffer and F. Tokiwa, *J. Phys. Chem.*, **68**, 2818 (1964)

[6] C. D. Hurd and W. A. Bonner, *J. Am. Chem. Soc.*, **67**, 1972 (1945).

[7] W. D. Harkins and F. D. Brown, ibid., **41**, 519 (1919).

* Micellization is generally reflected in a fairly abrupt change in the slope of the surface tension vs. logarithm of concentration curve. By this criterion micelle formation is absent in the case of glucosyl methylbenzene and glucosyl ethylbenzene. No evidence for micelle formation with these two compounds was provided by other measurements[5] as well.

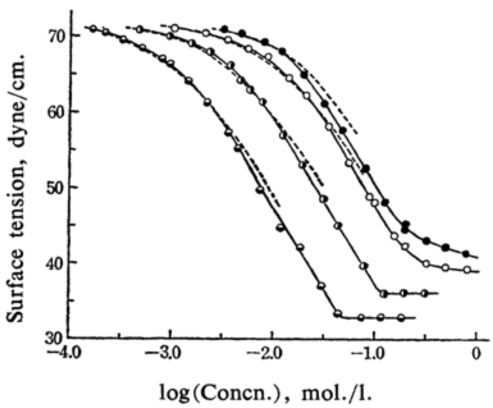

Fig. 1. Surface tension vs. log concentration curves of aqueous solutions of glucosyl alkylbenzenes at 25°C : ●, glucosyl methylbenzene ; ○, glucosyl ethylbenzene ; ◑, glucosyl propylbenzene ; ◒, glucosyl butylbenzene. (Broken lines indicate theoretical curves by Eq. 3, which are in accord with observed curves in the region of relatively low concentrations.)

where γ_0 is the surface tension of pure water. Equation 3 is consistent with Szyszkowski's empirical equation generally accepted for a series of fatty acids.[1)] For concentrated solutions where k_2c is large compared to unity, Eq. 3 reduces to

$$-\mathrm{d}\gamma/\mathrm{d}\ln c = \boldsymbol{R}Tk_1 \tag{4}$$

Thus the value of k_1 was estimated from the slope in the region of the γ-log c curve where k_2c is large compared to unity. The reciprocal of this value gives us the area covered by each molecule, when the surface is saturated. On the other hand, for very dilute solutions where k_2c becomes small compared to unity $-\mathrm{d}\gamma/\mathrm{d}c$ becomes constant and

$$-\mathrm{d}\gamma/\mathrm{d}c = \boldsymbol{R}Tk_1k_2 \tag{5}$$

Thus the value of k_2 was also estimated from the initial slope of the γ-c curve and k_1 according to Eq. 5. The values of k_1 and k_2 for each glucosyl alkylbenzene are listed in Table I; k_1 is nearly independent of the alkyl chain-length. In Fig. 1 the curves thus obtained from Eq. 3 are compared with the observed curves.

TABLE I. VALUES k_1 AND k_2, AND FREE ENERGY OF ADSORPTION FOR GLUCOSYL ALKYLBENZENES

Compound	k_1 $\times 10^{10}$	k_2 $\times 10^{-2}$	$-\Delta G^\circ$ kcal./mol.
Glucosyl methylbenzene	3.65	0.52	3.53
Glucosyl ethylbenzene	3.61	1.00	3.91
Glucosyl propylbenzene	3.66	2.98	4.56
Glucosyl butylbenzene	3.77	9.80	5.26

The standard free energy of adsorption, ΔG°, can be calculated from the equilibrium between surface and solution. Provided that both regions are sufficiently dilute for concentration to replace activity then[2)]

$$\Delta G^\circ = -\boldsymbol{R}T\ln(c_s/c) \tag{6}$$

where c_s is the concentration in the surface region. The amount of solute Γ adsorbed in the surface layer per square centimeter may be roughly taken to be

$$\Gamma = \tau(c_s - c)/1000 \tag{7}$$

where τ is the thickness of the surface layer in which adsorption takes place. Combining Gibbs' equation 1 with Eq. 5 we obtain

$$\Gamma = k_1k_2c \tag{8}$$

Eliminating Γ from Eqs. 7 and 8 and combining with Eq. 6 gives for dilute solutions

$$\Delta G^\circ = -\boldsymbol{R}T\ln\{1 + (1000k_1k_2/\tau)\} \tag{9}$$

Assuming a reasonable value for τ (5A), the values of ΔG° given in Table I were calculated from Eq. 9.

If $\Delta G^\circ{}_n$ and $\Delta G^\circ{}_{n-1}$ are the free energies of adsorption for members with n and $n-1$ carbon atoms in the alkyl chain, then

$$\Delta G^\circ{}_n - \Delta G^\circ{}_{n-1} = -\boldsymbol{R}T\ln\left\{\frac{1 + (1000k_{1,n}k_{2,n}/\tau)}{1 + (1000k_{1,n-1}k_{2,n-1}/\tau)}\right\} \tag{10}$$

Here $k_{1,n}$ is nearly equal to $k_{1,n-1}$ and $(1000\,k_1k_2/\tau)$ is large compared to unity, therefore Eq. 10 reduces to

$$\Delta G^\circ{}_n - \Delta G^\circ{}_{n-1} = -\boldsymbol{R}T\ln(k_{2,n}/k_{2,n-1}) \tag{11}$$

The free energy, $-\Delta G^\circ$, increases by 650—700 cal. for each additional CH_2 group, except for the increase in $-\Delta G^\circ$ in going from glucosyl methylbenzene to glucosyl ethylbenzene. (In the above exceptional case the increase in $-\Delta G^\circ$ is 380 cal. Probably, this could be attributed to the effect of the benzene ring on the hydrophobicity of the methyl group attached to the ring.)

The results shown above are comparable with the results obtained by Langmuir for compounds having a straight alkyl chain as a hydrophobic portion, such as fatty acids and alcohols,[1)] and also indicate that Traube's rule can be applied to the non-ionic surface active compounds having a benzene ring in their hydrophobic portion.

The surface pressure-area (Π-A) relation for the adsorbed monolayer can be found by the use of Gibbs' equation and identifying the surface excess with an adsorbed monolayer. The result shown in Fig. 2 is plotted in the form $\Pi A/\boldsymbol{k}T$ against Π, where $\boldsymbol{k}$ is the Boltzmann constant. At low pressures the ideal

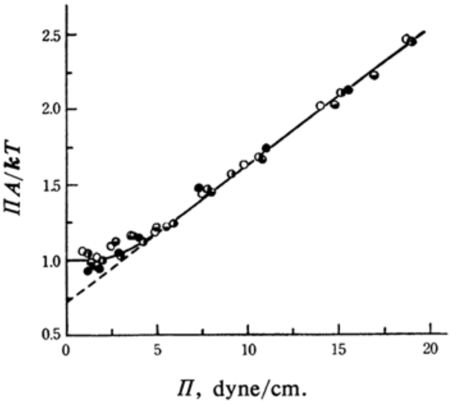

Fig. 2. $\Pi A/kT$-Π curves for glucosyl alkylbenzenes: ●, glucosyl methylbenzene; ○, glucosyl ethylbenzene; ◑, glucosyl propylbenzene; ◒, glucosyl butylbenzene.

two-dimensional gas equation $\Pi A = kT$ is approached; at higher pressures an equation of the Amagat type

$$\Pi(A-A_O)=xkT \qquad (12)$$

is followed.

As expected, A_O, termed the "co-area," is independent of alkyl chain-length ($A_O=37.4$ Å^2). It is generally accepted that the deviation of x from unity is a measure of attractive force between hydrophobic portions.[2)] Therefore, it was expected, as in the case of a series of fatty acids,[2)] that the value of x decreases as the alkyl chain-length increases. However, contrary to expectation, the value of x seems to be nearly independent of the chain-length, as is seen in Fig. 2 ($x=0.72$). The following explanation may be possible for this. The attraction between the hydrophobic portions, which is responsible for the deviation of x from unity, occurs predominantly between the benzene rings in the hydrophobic portion. This will reduce the effect of the alkyl chain attached to the benzene ring on the attraction, in other words, the attraction between the alkyl chains will be overwhelmed by the attraction between the benzene rings. Thus, the chain-length is not reflected in the change in x. The benzene ring seems to play an important role in the attraction between the hydrophobic portions.

Summary

The surface tension in aqueous solutions of glucosyl alkylbenzenes having various alkyl chain-lengths has been measured. The surface tension vs. concentration relation of these compounds obeys Szyszkowski's equation in a relatively wide range of concentrations. For these compounds the free energy, ΔG°, of adsorption was calculated; ΔG° changes by 650—700 cal./mol. for each CH_2 added to the alkyl chain, except in the case of going from glucosyl methylbenzene to glucosyl ethylbenzene. The adsorbed monolayer obeys an equation of state of the form $\Pi(A-A_O)=xkT$ at relatively high pressures, where A_O is independent of alkyl chain-length in the present experiment. Contrary to expectation, the value of x, which is governed by the attractive force between hydrophobic portions, is not influenced by the alkyl chainlengths; the benzene ring in the hydrophobic portion seems to play an important role in this attraction between the hydrophobic portions.

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