Traube's Rule for Soluble Monolayers of Homologous Strong Electrolytes

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(Received May 8, 1965)

On the surface tension of dilute aqueous solutions of a homologous series of aliphatic alcohols or carboxylic acids, Traube$^{1)}$ showed that the concentrations required for an equal lowering of the surface tension diminished by a constant factor for each additional methylene group in the hydrocarbon chain. This relation, commonly called Traube's rule, is conveniently expressed as;

$$C_n/C_{n+1}=K \tag{1}$$

where C_n and C_{n+1} are, respectively, the concentrations for successive members of the series with n and $n+1$ methylene groups at the equal lowering of surface tension, and K, termed "Traube's factor" in this paper, is a constant. Many experimental data for the homologous series of nonelectrolytes, such as aliphatic alcohols, or of weak electrolytes, such as aliphatic carboxylic acids, indicate that K is about 3.

On the other hand, Traube's factor for a homologous series of strong electrolytes seems to be about 2. The object of this paper is to interpret the significance of Traube's factor for soluble monolayers of homologous strong electrolytes, especially for perfluoro acids.

Traube's Factor for Nonelectrolytes and Weak Electrolytes.—Langmuir,$^{2)}$ Tamamushi,$^{3)}$ Ward$^{4)}$ and Davies$^{5)}$ interpreted Traube's rule in terms of the free energy of the adsorption of each additional methylene group.

The chemical potentials of a solute, μ, in the surface film and in the water may be written, respectively, as;

$$\left.\begin{aligned}\mu_s&=\mu_s^\circ+\boldsymbol{R}T\ln C_s\\ \mu_b&=\mu_b^\circ+\boldsymbol{R}T\ln C_b\end{aligned}\right\} \tag{2}$$

where $\boldsymbol{R}$ is the gas constant; T, the absolute temperature, and C, the concentration; the superscript $\circ$ is used to identify the standard state, while the subscripts s and b refer to the surface and the bulk phases respectively. The activity coefficients are omitted in this paper. When surface and bulk are in equilibrium, $\mu_s=\mu_b$; therefore,

$$C_s=C_b\exp\frac{\mu_b^\circ-\mu_s^\circ}{\boldsymbol{R}T}=C_b\exp\frac{-\Delta F^\circ}{\boldsymbol{R}T} \tag{3}$$

where ΔF° $(=\mu_s^\circ-\mu_b^\circ)$ is the standard free energy of the adsorption of the solute molecule from the bulk to be the surface, which is written as;

$$\Delta F^\circ=W_0+nW \tag{4}$$

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1) I. Traube, *Ann. Chem. Liebigs*, **265**, 27 (1891).

2) I. Langmuir, *J. Am. Chem. Soc.*, **38**, 1948 (1917).

3) B. Tamamushi, This Bulletin, **9**, 363 (1934).

4) A. F. H. Ward, *Trans. Faraday Soc.*, **42**, 399 (1946).

5) J. T. Davies and E. K. Rideal, "Interfacial Phenomena," Academic Press, New York and London (1961), p. 154.

where W is the free energy of the adsorption of an additional methylene group from the bulk to the surface and W_0 is the free energy contribution of a polar group. Then, from the great resemblance of the surface tension versus the logarithm of concentration curve for each homologous compound, it may be assumed that the surface concentration, C_s, is approximately equal at the equal lowering of surface tension for each compound. From the two equations corresponding to Eq. 3 for successive members of the series with n and $n+1$ methylene groups, one obtains;

$$\frac{C_n}{C_{n+1}} = \exp\left(\frac{\Delta F_n^\circ - \Delta F_{n+1}^\circ}{\boldsymbol{R}T}\right) \qquad (5)$$

From Eqs. 1, 4 and 5, we obtain;

$$K = \exp\left(-W/\boldsymbol{R}T\right) \qquad (6)$$

At the air-water interface, the interchain cohesion increases with the adsorption and the standard free energy of the adsorption of long-chain molecules is dependent on the surface concentration, as has been discussed by Tamamushi⁶⁾ in his early work and by Davies⁷⁾ in recent years. If, however, we set $W = -650$ cal./mol. at 25°C, as an approximate value, in Eq. 6, Traube's factor becomes 3.0.

Traube's Factor for Strong Electrolytes.—For soluble ionized monolayers, one must take into consideration the electrical repulsive potential of the surface, which tends to make the adsorbed long-chain ions repel each other; the standard free energy of the adsorption per mole, ΔF°, is expressed as;

$$\Delta F^\circ = nW + \boldsymbol{N}Ze\psi \qquad (7)$$

where $\boldsymbol{N}$ is the Avogadro number; Z, the valency of the long-chain ion; e, the proton charge, and ψ, the electrical potential of the surface. According to Gouy's theory, ψ may be given as;

$$\psi = \frac{2\boldsymbol{k}T}{Ze}\sinh^{-1}\left(\sigma\sqrt{\frac{500\pi}{CD\boldsymbol{R}T}}\right) \qquad (8)$$

where $\boldsymbol{k}$ is the Boltzmann constant; σ, the surface charge density; C, the molar concentration, and D, the dielectric constant of the solvent. Further, at a high potential, Eq. 8 may be simplified to;

$$\psi = \frac{\boldsymbol{k}T}{Ze}\ln\frac{2000\sigma^2\pi}{CD\boldsymbol{R}T} \qquad (9)$$

The combination of Eqs. 7 and 9 gives;

$$\Delta F^\circ = nW + \boldsymbol{R}T\ln\frac{2000\sigma^2\pi}{CD\boldsymbol{R}T} \qquad (10)$$

From the two equations corresponding to Eq. 10 for successive members of the series with n and $n+1$ methylene groups, and by assuming that the surface charge density, σ, is approximately equal at equal lowerings of the surface tension for homologous compounds, as has been mentioned above, we obtain;

$$\Delta F_n^\circ - \Delta F_{n+1}^\circ = -W + \boldsymbol{R}T\ln C_{n+1}/C_n \qquad (11)$$

By the substitution of Eq. 11 into Eq. 5, we find that;

$$C_n/C_{n+1} = K = \exp\left(-W/2\boldsymbol{R}T\right) \qquad (12)$$

Table I summarizes the values of Traub's factor calculated from the published data of Kling and Lange⁸⁾ on the heptane-water interfacial tensions for sodium alkyl sulfates at 50°C. From this table Traube's factor is found to be about 2. With $W = -810$ cal./mol. as the free energy of the adsorption for each methylene group at the oil-water interface, Eq. 12 gives $K = 1.9$. It may, therefore, be concluded that Eq. 12 can be used to obtain a very good approximation of Traube's factor for soluble monolayers of homologous strong electrolytes.

TABLE I. CALCULATION OF THE TRAUBE'S FACTOR FOR SODIUM ALKYL (C_8-C_{16}) SULFATES AT THE HEPTANE-WATER INTERFACE AT 50°C USING DATA OF KLING AND LANGE⁸⁾

Substance	Concn. required to give interfacial tension of 30 dyne/cm., M	K^2
C_8	0.021	$(1.8)^2$
C_{10}	0.0063	$(2.0)^2$
C_{12}	0.0016	$(2.0)^2$
C_{14}	0.00042	$(2.0)^2$
C_{16}	0.00011	

Traube's Factor for Perfluoro Acids.—Aranow and Witten⁹⁾ proposed a theory of Traube's rule on the assumption that on the surface each methylene group has 3 equal energy potential minima with respect to the torsion whose effect contributes $\boldsymbol{R}\ln 3$ to the entropy, and that if the enthalpy increment per methylene group is zero, the increment in the free energy per methylene group is given by $\boldsymbol{R}T\ln 3$. Further, they pointed out, as an example of the applicability of their theory, that Traube's factor for homologous series with perfluorochains is found to be about 3, and that this can be explained by similarily assuming that each CF_2 group has 3 positions of potential minima about carbon-carbon bonds, regardless of the different strengths of the interactions between water-CF_2 and water-CH_2.

According to our view, however, Traube's

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6) B. Tamamushi, *Kolloid-Z.*, **71**, 150 (1935).

7) J. T. Davies, *J. Colloid Sci.*, **11**, 377 (1956).

8) W. Kling and H. Lange, "Proceedings of IInd International Congress on Surface Activity," Vol. 1, Butterworths, London (1957), p. 295.

9) R. H. Aranow and L. Witten, *J. Chem. Phys.*, **28**, 405 (1958), **35**, 1504 (1961).

rule for homologous perfluoro acids can be interpreted using Eq. 12, because perfluoro acids are of the strong electrolyte type. Phillips[10] obtained the free energy of the transfer of the CF_2 group from the water phase to the oil phase as about -1300 cal./mol. By the substitution of this value into Eq. 13, Traube's factor K becomes 3.3 Therefore, it is a fortuitous fact that Traube's rule with the same constant holds for molecules with fluorocarbon chains as well as for hydrocarbon chains.

Recently, Kauzmann,[11] and Némethy and Scheraga[12] evaluated the thermodynamic parameters pertaining to the transfer of such nonpolar molecules as hydrocarbons from the water phase to the oil phase, termed the " hydrophobic bond " or " hydrophobic interaction "; they concluded that the entropy increment caused by the change of the " iceberg " around the nonpolar molecules to the original water is the most important part of the process. The entropy effect may be a main contribution to the free energy of the adsorption of nonpolar molecules from the water phase to the surface phase; however, this effect would not originate from the potential minima of the internal rotation about carbon-carbon bonds, but probably from the hydrophobic interaction. More recently, Spaull and Nearn[13] have discussed the thermodynamic parameters of the adsorption of fatty alcohols at the air-water interface along the same lines.

Summary

By using the free energy of the adsorption of the CH_2 or the CF_2 group from water to the surface, W, and the surface potential of Gouy's theory, Traube's factor, K, that is, the ratio of the respective concentrations, C_n and C_{n+1}, required to effect the equal lowering of surface or interfacial tension for successive homologous strong electrolytes with n and $n+1$ CH_2 or CF_2 groups, has been derived as;

$$K=C_n/C_{n+1}=\exp(-W/2\boldsymbol{R}T)$$

where $\boldsymbol{R}$ is the gas constant and T, the absolute temperature. This equation has been shown to be applicable also in obtaining a very good approximation for homologous sodium alkyl sulfates or perfluoro acids.

The author wishes to express his sincere gratitude to Professor Bun-ichi Tamamushi, of Tokyo Woman's Christian College, for his many helpful discussions throughout this work.

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[10] J. N. Phillips, *Trans. Faraday Soc.*, **51**, 561 (1955).

[11] W. Kauzmann, *Advances in Protein Chem.*, **14**, 1 (1959).

[12] G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382, 3401 (1962); *J. Phys. Chem.*, **66**, 1773 (1962).

[13] A. J. B. Spaull and M. R. Nearn, ibid., **68**, 2043 (1964).