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Time-Dependence of Surface Tension of Solutions

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The slow rate of change of surface tension observed by Addison with aqueous solutions of fatty alcohols cannot be explained by diffusion alone. It is assumed that the adsorption of non-electrolyte solutes in the surface film is opposed by a constant potential energy barrier, and, on this basis, a relation between spreading pressure and surface age is developed. With the resulting equation, the experimental data of Addison are employed to evaluate the energy term. Nearly constant values for the assumed barrier are obtained, the actual calculated values, in calories per mole at 20°C, being about 1900 for isoamyl alcohol, 1300 for *n*-hexyl alcohol, and 700 for *n*-heptyl alcohol. A second relation between spreading pressure and surface age is derived on the assumption that the energy barrier is a linear function of spreading pressure. The use of Addison's data for isoamyl alcohol in this relation indicates that the spreading pressure-dependent portion of the barrier is small and of the same order of magnitude as the energy required to compress the surface film sufficiently to admit the entering solute molecule.

THE curious slow attainment of surface tension equilibrium of solutions has often been observed.^{1,2} In solutions of organic electrolytes this variation of surface tension with time is much slower than with solutions of non-electrolytes. Addison,³⁻⁵ employing the vibrating jet technique, has measured the surface tension of fatty alcohol solutions as a function of time, and has found that the final steady value is reached in times of less than one second.

Repeated attempts^{2,6-8} to describe this phenomenon in terms of rate of diffusion of solute molecules to the surface have been unsuccessful. Ross⁷ was forced to the untenable conclusion that a polymolecular layer was formed on the surface of alcohol solutions, while Addison⁵ concluded that the "migration velocity" of the solute molecules *increased* with increasing molecular weight. It appears that even with the non-electrolytes the rate of change of surface tension is much less than can be accounted for by diffusion alone. Doss² made the reasonable suggestion that an energy barrier may account for

the phenomenon of slow adsorption in high molecular weight electrolyte solutions and attempted, in the case of these solutions, to describe the barrier qualitatively in terms of electrical effects at the surface.

With solutions of non-electrolytes, electrical double layer effects would presumably be absent. The results of Addison, particularly with isoamyl alcohol, thus present an opportunity to explore the nature of the adsorption barrier in a relatively simple system.

In the somewhat similar problem relating to the evaporation of water through compressed monolayers, Langmuir and Schaefer⁹ were able to describe the very low evaporation rates observed by the concept of an energy barrier of the form:

$$\lambda = (A + BF)kT, \quad (1)$$

where A and B are constants, and F is the surface film pressure. By analogy, it might be expected that a similar form of barrier would appear in the formation of a surface film from solutions. In this instance, however, since the solute molecules need not go entirely through the surface film, it would seem reasonable to expect the coefficient B in Eq. (1) to be smaller than in the process studied by Langmuir and Schaefer. If B is small, it would be difficult, in the absence of extremely accurate experimental

¹ N. K. Adam and H. L. Shute, *Trans. Faraday Soc.* **31**, 205 (1935); *ibid.* **34**, 758 (1938).

² K. S. G. Doss, *Kolloid Zeits.* **84**, 138 (1938); *ibid.* **86**, 205 (1939).

³ C. C. Addison, *J. Chem. Soc.*, 535 (1943).

⁴ C. C. Addison, *J. Chem. Soc.*, 252 (1944).

⁵ C. C. Addison, *J. Chem. Soc.*, 98 (1945).

⁶ W. N. Bond and H. O. Puls, *Phil. Mag.* [7] **24**, 864 (1937).

⁷ S. Ross, *J. Am. Chem. Soc.* **67**, 990 (1945).

⁸ A. F. H. Ward and L. Tordai, *J. Chem. Phys.* **14**, 453 (1946).

⁹ I. Langmuir and V. J. Schaefer, *J. Frank. Inst.* **235**, No. 2, 119 (1943).

TABLE I. Values of constants of Eq. (7) for various alcohols at 20°C.

Alcohol	J (cm ² × 10 ¹⁸)	L	D (cm ² sec. ⁻¹ × 10 ⁸)
Isoamyl	16.7	0.827	7.9
<i>n</i> -Hexyl	19.7	0.710	7.1
<i>n</i> -Heptyl	18.4	0.600	6.4

data, to differentiate between a constant energy barrier and one varying with film pressure.

Depending upon the equation of state describing the surface film and the form of the assumed barrier function, a number of different relations between spreading force and time are obtained. We shall herein derive two such relations, employing an equation of state applicable to films of soluble alcohols and two simple potential functions of the Langmuir type. The extent to which either of these relations can be fitted to the experimental results will serve to indicate the *possible* correctness of assumptions involved.

CASE I

A constant energy barrier and a surface film obeying the two-dimensional Amagat equation are assumed.

Solutions of many soluble substances, including the fatty acids and alcohols, form surface films obeying the equation¹⁰

$$F = N(FJ + LkT), \quad (2)$$

TABLE II. Energy barrier to adsorption of alcohols in surface film (at 20°C).

Conc. of solution (Wt. %)	$F\frac{1}{2}$ (dynes cm ⁻¹)	$t\frac{1}{2}$ (sec. × 10 ³)	$\exp(\lambda/kT)$	λ (cal. mole ⁻¹)
<i>Isoamyl alcohol</i>				
0.122	4.3	12.4	27.6	1930
0.203	6.1	8.0	28.2	1940
0.325	9.3	5.7	28.4	1950
0.406	10.4	5.3	31.6	2010
<i>n-Hexyl alcohol</i>				
0.050	5.4	24	10.4	1360
0.100	9.0	9.5	8.9	1270
0.150	11.4	6.0	9.3	1300
0.200	13.2	4.9	10.3	1350
<i>n-Heptyl alcohol</i>				
0.020	6.1	36	3.30	690
0.040	10.0	17	3.31	700
0.060	12.6	10	3.38	710

¹⁰ N. K. Adam, *The Physics and Chemistry of Surfaces* (Oxford University Press, London, 1941), p. 118.

where N is the number of molecules of solute per cm² of surface and J and L are constants.

Ward and Tordai⁸ have shown that diffusion theory leads to the following expression for the rate of arrival of diffusing solute molecules at one cm² of surface of a solution,

$$\partial M / \partial t = Dn_0 / (\pi Dt)^{\frac{1}{2}}, \quad (3)$$

where n_0 is the bulk concentration of solute and D is the diffusion constant.

We have assumed, however, that the actual adsorption of molecules in the surface film is opposed by a constant barrier of height λ . Therefore, the rate of adsorption of solute is given by

$$\partial N / \partial t = \partial M / \partial t \exp(-\lambda/kT). \quad (4)$$

Hence,

$$N = 2n_0(Dt/\pi)^{\frac{1}{2}} \exp(-\lambda/kT). \quad (5)$$

Combining Eq. (5) and Eq. (2), we obtain the desired relation between spreading pressure and time:

$$F/FJ + LkT = 2n_0(Dt/\pi)^{\frac{1}{2}} \exp(-\lambda/kT), \quad (6)$$

which may be written in the form,

$$\exp(\lambda/kT) = 2n_0(FJ + LkT)(Dt/\pi)^{\frac{1}{2}}/F. \quad (7)$$

Equation (3) was originally obtained by neglecting any backward diffusion of solute molecules from the surface, and accordingly can only be correct at times short of equilibrium. In order to test Eq. (7), therefore, we shall consider the times required for the surface pressure to go only half of its way to equilibrium. The work of Addison^{4,5} on the rate of change of surface tension of solutions of isoamyl alcohol, *n*-hexyl alcohol, and *n*-heptyl alcohol furnishes enough experimental data to permit calculation of the approximate values of the energy barriers by Eq. (7).

The required values of J and L may be obtained from the data given by Addison on the equilibrium surface tension and the rate of change of surface tension with concentration for solutions of the above mentioned alcohols. The diffusion constants (at 20°C) were taken from the curve of Ward and Tordai.⁸ Table I gives the numerical values of the various constants of Eq. (7) so obtained, at 20°C.

Table II gives the spreading force-time data for the three alcohols as interpolated from

Addison's experimental results, and the values of the energy barriers as calculated from these data and those of Table I by insertion in Eq. (7). In Table II, $F_{\frac{1}{2}}$ denotes the spreading force of the surface film when the surface tension has proceeded one-half of its way toward equilibrium, and $t_{\frac{1}{2}}$ is the time required for the spreading force to reach this value. $F_{\frac{1}{2}}$ and $t_{\frac{1}{2}}$ are used for F and t in Eq. (7) for the reason previously cited.

It is evident that with each alcohol the calculated energy barrier values are essentially constant within the range of accuracy of the spreading force measurements. However, there is a consistent suggestion in the trend of calculated values that the barrier may increase slightly with increasing film pressure, or, in other words, that B of Eq. (1) should have a small positive value rather than the value of zero assumed in this case. It is also found that the height of the barrier decreases markedly with increase in molecular weight of the alcohol, a result which may be related to the fact that the lateral adhesion of the molecules in a surface film increases rapidly with increasing hydrocarbon chain length.

CASE II

An energy barrier of the Langmuir type, and a surface film obeying the two-dimensional Amagat equation are assumed.

Expressed formally, these assumptions are that

$$\lambda = (A + BF)kT^*$$

and

$$F = N(FJ + LkT)^{**}$$

Therefore,

$$dN/dt = LkT/(FJ + LkT)^2 (dF/dt).$$

Substituting these values and Eq. (3) in Eq. (4), we obtain

$$\exp(BF)dF/(FJ + LkT)^2 = n_0(D/\pi t)^{\frac{1}{2}} \exp(-A)/LkT dt. \quad (9)$$

Integration of Eq. (9) leads to the desired relation between spreading pressure and time,

* See Eq. (1).

** See Eq. (2).

namely

$$\begin{aligned} \exp(A) - LkT \exp(A + BF)/FJ + LkT \\ + BLkT/J \{ Ei[B(FJ + LkT)/J] \\ - Ei[BLkT/J] \} \exp(A - BLkT/J) \\ = 2n_0J(Dt/\pi)^{\frac{1}{2}} \quad (10) \end{aligned}$$

where Ei is the exponential integral function.¹¹

When the coefficient B has the value of zero, the conditions are those of Case I, and Eq. (10) reduces to Eq. (7).

For accurate evaluation of the constants A and B , the use of Eq. (10) is somewhat cumbersome, and, in addition, requires more precise experimental data on the relation between spreading pressure and time than are now available for non-electrolyte solutions. However, in the case of isoamyl alcohol, the appropriate constants from Table I and the experimental data from Table II have been employed in Eq. (10) to obtain approximate values of A and B . These are found to be 3.2 and 0.040, respectively. Therefore, for the adsorption of isoamyl alcohol in the surface of its aqueous solution at 20°C, the apparent energy barrier is given by

$$\lambda = (3.2 + 0.040F)kT$$

or, in calories per mole at 20°C,

$$\lambda_{\text{cal./mole}} = 1860 + 23F. \quad (11)$$

This result conforms with the indicated slow increase of the energy barrier value with increasing spreading pressure observed in Case I.

DISCUSSION OF RESULTS

The results of calculations presented in Table II and under Case II show that the concept of a potential energy barrier, of reasonable magnitude, hindering the adsorption of solute molecules in the surface is sufficient to describe the slow attainment of surface tension equilibrium in solutions of some organic non-electrolytes. For more accurate determinations of the energy barriers and their dependence on spreading pressure, more precise experimental data on the relation between surface tension and time would

¹¹ Numerical values of the exponential integral function are given by E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, New York, 1943), p. 6 *et. seq.*; and by A. N. Lowan, *Tables of Sine, Cosine, and Exponential Integrals* (Works Progress Administration, New York, 1940), Vols. I and II.

be desirable. Also, experiments on this relation at different temperatures would be helpful in evaluating the barrier.

In considering the possible origin of a potential barrier to adsorption of a solute molecule, there immediately appears the work required to compress the surface film sufficiently to make space for the molecule entering the film from solution. This energy requirement would be roughly equal to Fa , where a is the effective area occupied by the entering solute molecule. Such a potential barrier would, of course, be directly proportional to the spreading pressure and would increase with increasing molecular weight of solute. We have found, for the fatty alcohols discussed above, only a very slight dependence of λ on F and a smaller value of λ for the higher alcohols. The value of Fa will also be far too small, in general, to account for the λ values calculated. Taking isoamyl alcohol as an ex-

ample, and using a molecular cross-sectional area calculated from its density at 20°C, we find Fa to have a value of about 57*F* cal. per mole. This is of the same order of magnitude as the spreading pressure-dependent portion of the potential barrier calculated for isoamyl alcohol and given in Eq. (11). It thus appears that, at most, the work of compressing the surface film can only account for the small portion of λ which is dependent on spreading pressure.

Although in carrying out the present calculations, F_1 and t_1 values have been employed in Eq. (7) and Eq. (10), it should be pointed out that the use of other corresponding F and t values up to the point where F is at least 80 percent of its equilibrium value yields essentially the same values of λ . Therefore, it appears that back diffusion from the surface probably leads to no important errors in the calculations, within the range of F values used.

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Search for Near Ultraviolet Bands in Borazole*

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Borazole, $B_3N_3H_6$, shows no absorption bands in the region 2000A–4600A, at pressures of about 2 atmospheres in a 4-cm cell. Since bands analogous to those of benzene are expected on theoretical grounds, it is concluded that the analogues of the benzene 2600A and 1830A bands are the borazole 1995A and 1720A bands, with the analogues of the benzene 2080A bands perhaps being hidden in between.

AN attempt has been made to find bands in triborine-triamine or borazole, $B_3N_3H_6$, corresponding to the 2600A bands in benzene—that is, having the same general appearance as the latter bands and lying, like these, in the quartz ultraviolet. Pressures of about 2 atmospheres, higher than any previously used in this experiment, were obtained but with a 4-cm path no bands were found in the region 2000A–4600A.

This experiment was suggested by Dr. E. H. Hutten. He attempted earlier to detect these

bands in this laboratory, but only enough borazole was available at that time to obtain vapor pressures of about 20 cm in a 4-cm cell. His work was the result of the belief that the ring structure and electronic structure of borazole are very similar to those of benzene (see Bibliography in reference 1).

In support of this belief was later work from this laboratory on borazole solutions¹ in which bands at 1995A and a peak at 1720A seemed to be similar to the benzene bands at 2080A and

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¹ J. R. Platt, H. B. Klevens, and G. W. Schaeffer, *J. Chem. Phys.* 15, 598 (1947).