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Abstract

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ON THE ADSORPTION OF FATTY ACIDS AT THE INTERFACE OF A SOLUTION WITH AIR AND MERCURY

(Presented by Academician A. N. Frumkin, 12 XII 1963)

Studying the surface tension of dilute solutions of fatty acids, Traube ([1]) established that the ability of a dissolved substance to lower the surface tension of water increases by a factor of 3.0-3.5 when the chain is lengthened by one CH_2 group. According to Langmuir ([2]), this is equivalent to an increase in the work of adsorption by the same amount with lengthening of the chain by each CH_2 group. In connection with the study of the influence of various functional groups on the work of adsorption at solution-air and solution-mercury interfaces, it was of interest to test the applicability of Traube' s rule to adsorption in homologous series of aliphatic compounds at the solution-mercury interface, as had been done in studies for the case of the free surface of a solution ([1–6]).

In the present work, results are given of a comparison of the adsorption activity of acids at the solution-air and solution-mercury interfaces. The adsorption of fatty acids on mercury was studied by measuring electrocapillary (e.c.) curves with a Gouy electrometer. The e.c. curves were recorded in a thermostated cell at $20^\circ \pm 1$. A normal calomel electrode served as the reference electrode. All substances used were first purified by double distillation; their characteristic physical constants are presented in Table 1, with values from ([7]) given in parentheses.

Table 1

Acids	$n_D^{20^\circ}$	$d_4^{20^\circ}$
Acetic	1.3718 (1.3720)	1.047 (1.049)
Propionic	1.3874 (1.37736)	0.991 (0.992)
Butyric	1.3994 (1.3991)	0.958 (0.9587)
Valeric	1.4090 (1.4086)	0.940 (0.942)
Caproic	1.4145 (1.4144)	0.925 (0.922)

In Fig. 1 the e.c. curves for 0.35 M solutions of acetic, propionic, and butyric acids are compared. As is evident from the figure, the e.c. curves obtained by us have the form already described earlier ([8,9]). All the fatty acids studied lower the surface tension predominantly in the region of the electrocapillary maximum. In the region of large negative and large positive surface charges they are desorbed, and the curves of the solutions studied coincide with the background curves. With increasing length of the hydrocarbon chain, the surface activity of the acids increases. This regularity is also evident from the curves of the dependence of acid adsorption on potential (Fig. 2) and from the isotherms of surface-tension lowering (Fig. 3). The adsorption values were calculated from the Gibbs adsorption equation, assuming that the activity coefficient is equal to unity. As is evident from Fig. 2, in the region of large negative potentials the adsorption of acids decreases the more rapidly, the longer the hydrocarbon chain.

From the isotherms of surface-tension lowering at various potentials, the coefficient of Traube' s rule was determined, i.e., the quantity showing by how many times the acid concentration changes upon lengthening of the chain by one CH_2 group when the same lowering of surface tension is attained. Table 2 gives the values of the concentrations

Table 2

Acid	$\Delta\sigma =$ 1 conc., mol/L	$\Delta\sigma =$ 1 $\mathcal{K}$	$\Delta\sigma =$ 3 conc., mol/L	$\Delta\sigma =$ 3 $\mathcal{K}$	$\Delta\sigma =$ 5 conc., mol/L	$\Delta\sigma =$ 5 $\mathcal{K}$	$\Delta\sigma =$ 20 conc., mol/L	$\Delta\sigma =$ 20 $\mathcal{K}$
Acetic	0.079	3.9	0.264	4.4	0.514	4.4	–	–
Propionic	0.02	3.3	0.06	3.6	0.118	3.7	0.742	4.5
Butyric	0.006	3.7	0.0166	3.3	0.032	4.2	0.166	4.2
Valeric	0.0016	3.2	0.005	3.7	0.0075	3.7	0.039	4.8
Caproic	0.0005		0.0014		0.002		0.008	

(in mol/L) of the acids studied at which a decrease in surface tension $\Delta\sigma$ equal to 1, 3, 5, and 20 dyn/cm is observed at the potential of the electrocapillary maximum, as well as the values of the coefficient in Traube' s rule. From these data it is evident that the surface activity increases with increasing chain length in a ratio that rises with increasing $\Delta\sigma$ and for $\Delta\sigma$ 3 is on average equal to ~3.6.

Fig. 1. Electrocapillary curves of solutions: **1** –1N Na_2SO_4 + 0.05 NH_2SO_4 (background), **2** –background + 0.35 M acetic acid, **3** –background + 0.35 M propionic acid, **4** –background + 0.35 M butyric acid

Fig. 2. Curves of the dependence of fatty-acid adsorption on potential for 0.1 M solutions: **1** –valeric acid, **2** –butyric acid, **3** –propionic acid

Fig. 1. Electrocapillary curves of solutions: 1 –1 N Na_2SO_4 + 0.05 N H_2SO_4 (background), 2 –background + 0.35 M acetic acid, 3 –background + 0.35 M propionic acid, 4 –background + 0.35 M butyric acid

Figure 1: Fig. 1. Electrocapillary curves of solutions: 1 –1 N Na_2SO_4 + 0.05 N H_2SO_4 (background), 2 –background + 0.35 M acetic acid, 3 –background + 0.35 M propionic acid, 4 –background + 0.35 M butyric acid

Fig. 2. Curves of the dependence of fatty-acid adsorption on potential for 0.1 M solutions: 1 –valeric acid, 2 –butyric acid, 3 –propionic acid

Figure 2: Fig. 2. Curves of the dependence of fatty-acid adsorption on potential for 0.1 M solutions: 1 –valeric acid, 2 –butyric acid, 3 –propionic acid

In view of the fact that the literature data on the adsorption of fatty acids at the free surface of a solution ([1,3–6]) refer to pure aqueous solutions without the addition of salts, which was done in our work when measuring electrocapillary curves, in order to compare the surface activity of the substances studied at the solution boundaries with air and with mercury, we measured the surface tension by the maximum bubble pressure method using solutions of the same composition.

As is evident from Fig. 3, where the isotherms of the decrease in surface tension at both of the interfaces studied are compared, in agreement with previously obtained data ([10]), the activity of fatty acids at the free surface of a solution is somewhat greater than at the boundary between the solution and mercury. With increasing length of the hydrocarbon chain, the difference between the adsorption activities at the two interfaces decreases and, for caproic acid, almost disappears.

Table 3

Acid	$\Delta\sigma$ = 1 conc., mol/L	$\Delta\sigma$ = 1 $\mathcal{K}$	$\Delta\sigma$ = 3 conc., mol/L	$\Delta\sigma$ = 3 $\mathcal{K}$	$\Delta\sigma$ = 5 conc., mol/L	$\Delta\sigma$ = 5 $\mathcal{K}$	$\Delta\sigma$ = 20 conc., mol/L	$\Delta\sigma$ = 20 $\mathcal{K}$
Acetic	0,066	3,3	0,166	3,2	0,275	3,6	–	–
Propionic	0,02	3,3	0,052	3,4	0,076	3,8	0,457	3,9
Butyric	0,006	3,5	0,015	3,7	0,020	3,6	0,118	4,1
Valeric	0,0017	3,4	0,004	3,6	0,0056	3,7	0,029	4,1
Caproic	0,0005		0,001		0,0016		0,007	

Table 3 gives the values of the concentrations of fatty acids (in mol/L) at which a lowering of the surface tension $\Delta\sigma$ at the solution-air interface equal to 1, 3, 5, and 20 dyn/cm is attained, and the corresponding values of the Traube coefficient.

Fig. 3. Isotherms of surface-tension lowering. Curves: 1—acetic, 2—propionic, 3—butyric, 4—valeric, 5—caproic acids on the uncharged surface of mercury; 1′, 2′, 3′, 4′, and 5′—for the same acids (respectively) on the free surface of the solution

Figure 3: Fig. 3. Isotherms of surface-tension lowering. Curves: 1—acetic, 2 —propionic, 3—butyric, 4—valeric, 5—caproic acids on the uncharged surface of mercury; 1′, 2′, 3′, 4′, and 5′—for the same acids (respectively) on the free surface of the solution

Fig. 4. Curves of the dependence of the Traube coefficient $\mathcal{K}'$ on $\Delta\sigma$; 1—for the solution-mercury boundary, 2—for the solution-air boundary

Figure 4: Fig. 4. Curves of the dependence of the Traube coefficient $\mathcal{K}'$ on $\Delta\sigma$; 1—for the solution-mercury boundary, 2—for the solution-air boundary

From these data it is seen that, in the adsorption of fatty acids on the free surface of the solution, the average Traube coefficient at small $\Delta\sigma$ ($\leqslant 3$)

Fig. 3. Isotherms of surface-tension lowering. Curves: **1**—acetic, **2**—propionic, **3**—butyric, **4**—valeric, **5**—caproic acids on the uncharged surface of mercury; **1′**, **2′**, **3′**, **4′**, and **5′**—for the same acids (respectively) on the free surface of the solution.

is equal to 3.4 and, as in the case of the solution-mercury interface, increases with increasing $\Delta\sigma$. Comparison of the curves for the dependence of the Traube coefficient $\mathcal{K}$ on $\Delta\sigma$ for the two interfaces studied (Fig. 4) shows that, in the case of the free surface of the solution, $\mathcal{K}$ changes somewhat more slowly with increasing $\Delta\sigma$ than for the solution-mercury interface, but the character of the dependence is the same in both cases. The increase in the Traube coefficient with increasing $\Delta\sigma$ is explained by the fact that, at high coverages, attractive interaction between hydrocarbon chains becomes apparent; this increases the work of adsorption and grows with increasing chain length.

The increment of the adsorption work ΔW upon lengthening the chain by a CH_2 group, calculated from the equation $\Delta W = RT \ln \mathcal{K}$ from the values of the Traube coefficient obtained for small $\Delta\sigma$ (up to 3 dyn/cm), is equal to 740 cal/mole for the solution boundary with uncharged mercury, instead of 710 cal/mole for the free surface of the solution. The validity of Traube' s rule in the adsorption of fatty acids at the boundary of a solution with mercury confirms the idea of the identical structure of the surface adsorption layers at the boundary of the solution with air and with mercury. This is also evidenced by the values of the maximum adsorption and the area per molecule given below. The values of the maximum adsorption were obtained graphically from the $\Gamma = f(C)$ curves.

Fig. 4. Curves of the dependence of the Traube coefficient $\mathcal{K}'$ on $\Delta\sigma$; 1—for the solution-mercury boundary, 2—for the solution-air boundary.

	$\Gamma_\infty \cdot 10^{10}$, mole/cm^2	$S_\infty \cdot 10^{16}$, cm^2
Solution–mercury	5.7	29.0
Solution–air	5.6	29.5

The closeness of the surface activities and of the values of the Traube coefficient in the case of adsorption of fatty acids at the interface of the solution with air and mercury shows that their adsorbability at the boundary with mercury is determined mainly by the expulsion of the hydrocarbon chains from the bulk of the solution to the surface, and that the replacement of water molecules by CH_2 groups at the boundary with mercury has no substantial effect on the adsorption work, increasing it only slightly.

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