

ADSORPTION OF FATTY ACIDS AT SOLUTION / AIR AND SOLUTION/MERCURY INTERFACES

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From an investigation of the surface tension of dilute solutions of fatty acids, Traube [1] established that the capacity of a dissolved substance to reduce the surface tension of water increases 3.0-3.5 times for a lengthening of the chain by one CH_2 group. According to Langmuir [2], this is equivalent to an increase in the energy of adsorption by the same value with lengthening of the chain by one CH_2 group. In connection with the investigation of the effect of different functional groups on the energy of adsorption at interfaces of a solution with air and mercury, it seemed of interest to check the applicability of Traube's law to adsorption in homologous series of aliphatic compounds at a solution/mercury interface as for the case of a free surface of a solution [1-6].

This paper gives the results of a comparison of the adsorption activity of acids at solution air and solution/mercury interfaces. The adsorption of fatty acids on mercury was investigated by measuring the electrocapillary (e.c.) curves by a Gouy electrometer. The e.c. curves were determined in a thermostatically controlled cell at $20^\circ \pm 1$. A normal calomel electrode served as the comparison electrode. All substances were first purified by double distillation; their physical constants are given in Table 1, the values taken from [7] being given in parentheses.

Figure 1 gives a comparison of the e.c. curves for 0.35 M solutions of acetic, propionic and caproic acids. It may be seen that our e.c. curves have the same appearance as in [8, 9]. All the investigated fatty acids reduce the surface tension primarily in the region of the electrocapillary maximum. At high negative and positive charges of the surface they are desorbed and the curves of the solutions coincide with those of the background. With increasing length of the hydrocarbon chain the surface activity of the acids increases. This trend is also evident from plots of fatty acid adsorption versus potential (Fig. 2) and from isotherms of the reduction in surface tension (Fig. 3). The adsorption values were calculated from Gibbs' adsorption equation, assuming that the activity coefficient is equal to unity. As may be seen from Fig. 2, at high negative potentials acid adsorption decreases more rapidly the longer the hydrocarbon chain.

From the isotherms of the reduction in surface tension at different potentials, we determined the coefficient of Traube's law, i.e., the number showing how much the acid concentration changes with an increase in chain length by one CH_2 group (for the same reduction in surface tension). Table 2 gives the concentrations (in mole/liter) of the investigated acids at which a surface tension reduction $\Delta\sigma$ of 1, 3, 5 and 20 dyne/cm is observed at the potential of the electrocapillary maximum; it also gives the values of the Traube law coefficient. From these data, it is clear that the surface activity increases with increasing chain length in a ratio increasing with a rise in $\Delta\sigma$, being ~ 3.6 (av.) for $\Delta\sigma \leq 3$.

TABLE 1

Acids	n_D^{20}	d_4^{20}
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)

Information on fatty acid adsorption on the free surface of a solution [1, 3-6] relates to pure aqueous solutions without addition of salts, which was a feature of our work; therefore, to compare the surface activity of the investigated substances at the solution air and solution mercury we interfaces measured the surface tension by the method of maximum pressure in bubbles, using solutions of the same composition.

It may be seen from the comparison of the isotherms of the surface tension reduction on both the investigated boundaries

TABLE 2

Acids	$\Delta\sigma = 1$		$\Delta\sigma = 3$		$\Delta\sigma = 5$		$\Delta\sigma = 20$	
	concn., mole/l	$\mathcal{K}$	concn., mole/l	$\mathcal{K}$	concn., mole/l	$\mathcal{K}$	concn., mole/l	$\mathcal{K}$
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	

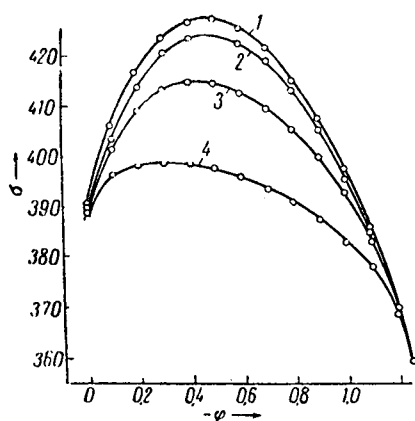


Fig. 1. Electrocapillary curves of solutions: 1) 1 N Na_2SO_4 + 0.05 N H_2SO_4 (background); 2) background + 0.35 M acetic acid; 3) background + 0.35 M propionic acid; 4) background + 0.35 M butyric acid.

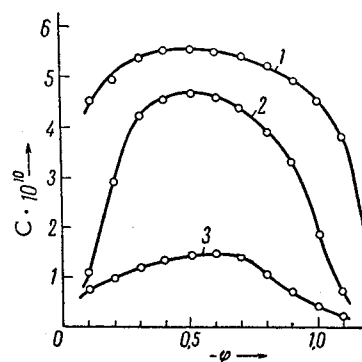


Fig. 2. Adsorption of fatty acids versus potential for 0.1 M solutions: 1) valeric acid; 2) butyric acid; 3) propionic acid.

(Fig. 3) that, in accordance with [10], fatty acid activity on the free surface of a solution is somewhat greater than at a solution mercury interface. With increasing hydrocarbon chain length the difference between the adsorption activity on both, interfaces decreases, and in the case of caproic acid virtually disappears.

Table 3 gives the fatty acid concentrations (mole/liter) at which a surface tension reduction, $\Delta\sigma$, of 1, 3, 5 and 20 dyn/cm is obtained at the solution air interface, and the corresponding values of Traube's coefficient.

From these data, it may be seen that in the case of fatty acid adsorption on the free surface of a solution the average Traube coefficient at low $\Delta\sigma$ (≤ 3) is 3.4 and, as in the case of the solution mercury interface, increases with increasing $\Delta\sigma$. A comparison of plots of the Traube coefficient $\mathcal{K}$ versus $\Delta\sigma$ for both boundary media (Fig. 4) shows that in the case of a free solution $\mathcal{K}$ changes somewhat more slowly with increasing $\Delta\sigma$ than for a mercury interface, but the character of the relationship is the same in both cases. The increase in $\mathcal{K}$ with increasing $\Delta\sigma$ is due to the fact that at high degrees of occupation an attraction reaction occurs between the hydrocarbon chains, increasing the energy of adsorption and becoming more marked with increasing chain length.

The increase in the energy of adsorption ΔW with a chain increase by one CH_2 group, calculated from the equation $\Delta W = RT \ln \mathcal{K}$ from the Traube coefficient values obtained for low $\Delta\sigma$ (up to 3 dyn/cm), is 740 cal/mole for a solution/uncharged mercury interface as against 710 cal/mole for the free surface of a solution. The applicability of Traube's law to fatty acid adsorption at a solution/mercury interface confirms the theory that surface adsorption layers at a solution/air and a solution/mercury interface have the same structure. This is indicated by the values of the maximum adsorption and energy given below. The maximum adsorption values were obtained graphically from

TABLE 3

Acid	$\Delta\sigma = 1$		$\Delta\sigma = 3$		$\Delta\sigma = 5$		$\Delta\sigma = 20$	
	concn., mole/l	$\mathcal{K}$	concn., mole/l	$\mathcal{K}$	concn., mole/l	$\mathcal{K}$	concn., mole/l	$\mathcal{K}$
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	

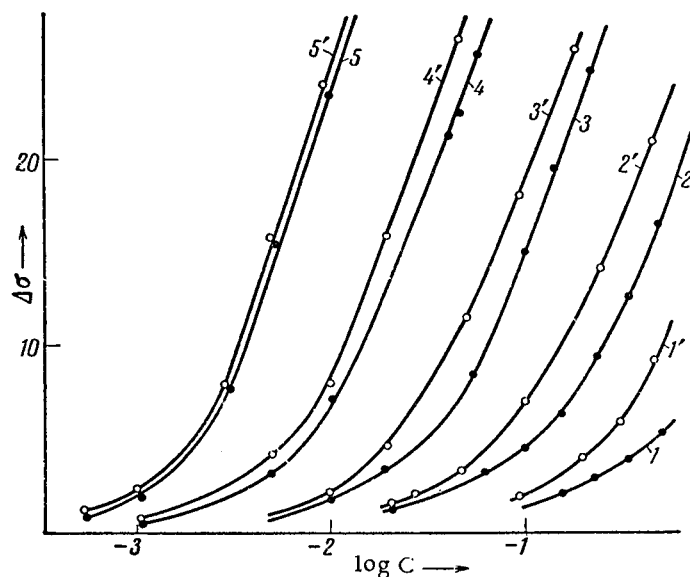


Fig. 3. Isotherms of the reduction in surface tension. Curves: 1) acetic; 2) propionic; 3) butyric; 4) valeric; 5) caproic acids on an uncharged mercury surface; 1', 2', 3', 4' and 5' for the same acids (respectively) on the free surface of a solution.

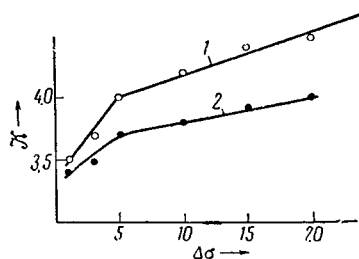


Fig. 4. Traube coefficient $\mathcal{K}'$ versus $\Delta\sigma$; 1) for solution/mercury interface; 2) for solution/air interface.

the $G = f(C)$ curves.

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

The similarity of the surface activities and Traube coefficients in the case of fatty acid adsorption at a solution/air and solution/mercury interface shows that their adsorbability at the latter is due mainly to ejection of hydrocarbon chains from within the solution to the surface, and that replacement of water molecules by CH_2 groups at the solution/mercury interface does not have a marked effect on the energy of adsorption, but merely increases it slightly.

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