If any other of the accepted values for 25° is taken as standard in place of the classical value of Kohlrausch's selected by me, the agreement between my method and the others which have been used will be found to be better than was stated in my earlier publication. This is so obvious on inspection of my table[1] that it seems unnecessary to quote figures.

To Professor Thiel's conclusion with reference to the partial solubilities of silver bromide and sulfocyanate, may be added the conclusion that in these cases solid solution is not a factor of sufficient influence to affect the solubility equilibria noticeably, as proved by the experiments under discussion. The question is also suggested, though its discussion would be out of place in this reply, as to what is really meant by "solid solution" when applied to amorphous bodies such as the salts used by Thiel and myself.

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ABSORPTION AND THE SURFACE TENSIONS OF AQUEOUS SOLUTION OF HOMOLOGOUS FATTY ACIDS AND ALCOHOLS.

BY MARKS NEIDLE.

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Duclaux[2] was the first to present the following relationship between the concentrations of aqueous solutions of homologous fatty alcohols and acids and their surface tensions; the ratio of the concentrations of any two homologous acids or alcohols which have the same surface tension is a constant, independent of the value of the surface tension. In symbols this may be expressed by the following equation, which will be referred to as the Duclaux equation:

$$c = bf(\gamma), \tag{1}$$

where c is the concentration, $f(\gamma)$ a fixed function of the surface tension for all members of a series, and b a constant depending upon the particular member of the series. The experimental basis for this rule comprised the surface tensions of methyl, ethyl, isopropyl, isoamyl and caprylic alcohols, and formic, acetic and butyric acids, determined by a very crude drop method. The values of the concentration ratios reproduced in Table I show as good agreement as could be expected from such rough data. The concentrations c are expressed in percentages by volume, and the temperature of observations is 15°.

Using the Morgan drop-weight method, Morgan and Neidle[3] found the surface tensions of aqueous solutions of methyl, ethyl and amyl alcohols,

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[1] *Loc. cit.*, 74.

[2] *Ann. chim. phys.*, [5] 13, 76 (1878).

[3] THIS JOURNAL, 35, 1856 (1913).

TABLE I.

Rel. surf. tens. (Water = 1.)	$\frac{\text{C(Me.OH)}}{\text{C(Am.OH)}}$.	$\frac{\text{C(Et.OH)}}{\text{C(Am.OH)}}$.	$\frac{\text{C(Prop.OH)}}{\text{C(Am.OH)}}$.	$\frac{\text{C(But.OH)}}{\text{C(Am.OH)}}$.	$\frac{\text{C(Cap.OH)}}{\text{C(Am.OH)}}$.	$\frac{\text{C(Formic acid)}}{\text{C(Acetic acid)}}$.	$\frac{\text{C(But. acid)}}{\text{C(Acetic acid)}}$.
0.90	33	16	...	2.7	...	2.9	0.10
0.85	34	17	...	2.8	...	3.1	0.10
0.80	34	18	9.1	2.8	0.057	3.0	0.11
0.75	33	18	...	...	...	3.0	0.12
0.70	33	18	...	2.8	0.061	2.9	0.10
0.65	31	17	...	2.6	...	3.0	0.10
0.60	..	18	9.3	2.6	0.063	...	0.10
0.55	..	18	...	2.6	...	...	....
0.50	..	16	...	2.6	0.064	...	....
0.45	..	16	...	2.6	...	...	....
0.40	..	16	9.3	2.6	...	...	....

and of formic and acetic acids. With the results obtained, the Duclaux equation was tested and found to hold very well for dilute solutions as is seen from Table II. The concentrations are expressed in grams per 100 cc., and the temperature of observations is 30°.

TABLE II.

Surf. tens. Dynes/cm.	$\frac{\text{C(Me.OH)}}{\text{C(Et.OH)}}$.	$\frac{\text{C(Et.OH)}}{\text{C(Am.OH)}}$.	Surf. tens. Dynes/cm.	$\frac{\text{C(Formic acid)}}{\text{C(Acetic acid)}}$.
46	1.95	18.3	51	3.18
48	1.98	18.3	55	3.13
50	2.01	18.9	56	3.08
52	2.04	18.9	57	3.05
54	2.08	18.9	59	3.05
56	2.10	18.9	61	3.06
58	2.11	19.0	63	3.04
60	2.11	19.0	64	3.05
62	2.13	18.9	65	3.05
64	2.10	18.9	..	....

The concentration ratios for methyl and ethyl alcohols at concentrations which give surface tensions less than 54 dynes/cm. (Et.OH 4.53, Me.OH 9.50 g./100 cc.) agree within less than 1%. The agreement in the pair ethyl and amyl alcohols is even closer and extends to more concentrated solutions, which is also true for the pair, formic and acetic acids. Since the concentrations having the same surface tensions were found by graphic interpolation, and it is difficult to read low values with a high degree of precision, the ratios between 65 and 71.03 dynes/cm., the surface tension of pure water, were not investigated; but it is evident from the graphs that these would show even greater constancy than those at lower surface tensions. The Duclaux equation is thus established for the three alcohols and two acids considered above, and it is very probable that it will also be substantiated for the others investigated by Duclaux, when their surface tensions are determined by the Morgan drop-weight method or any other reliable method.

Having found the surface tensions of aqueous solutions of one member of the series for a number of concentrations, the Duclaux equation may be applied to calculate those of aqueous solutions of another homolog within certain limits of concentration. For this purpose we need only determine the surface tension at any one concentration within the same limits. It will be necessary, however, before making this application to new homologs, to extend the experimental basis in order to see how far down the series the relationship holds. Such work is contemplated in this laboratory.

A relationship will now be deduced, connecting adsorption and surface tensions of aqueous solutions of homologous fatty acids and alcohols, which may be considered the physico-chemical interpretation of the Duclaux equation. The adsorption or excess concentration of the solute in the surface of a solution, expressed in mols per square centimeter, is given by the Gibbs adsorption equation

$$\Gamma = -\frac{C}{i\mathrm{RT}}\frac{d\gamma}{dc}, \tag{2}$$

where c, the concentration of the solution, may evidently be expressed in grams or mols per 100 cc. or liter, and i is the van't Hoff factor.

From Equation 1 we have

$$\frac{dc}{d\gamma} = bf'(\gamma) \quad \text{and} \quad c\frac{d\gamma}{dc} = \frac{f(\gamma)}{f'(\gamma)}.$$

Substituting in (2), we find

$$\Gamma = -\frac{f(\gamma)}{i\mathrm{RT}f'(\gamma)}. \tag{3}$$

But for homologs $f(\gamma)$ and $f'(\gamma)$ are the same, therefore the adsorption of their solutions having the same surface tension and the same temperature is inversely proportional to their van't Hoff factors, *i. e.*,

$$(\Gamma_1/\Gamma_2)_{\gamma,\mathrm{T}} = i_2/i_1.$$

In the case of non-electrolytes, this relation becomes simpler, since $i_1 = i_2 = 1$, and consequently

$$(\Gamma_1)_{\gamma,\mathrm{T}} = (\Gamma_2)_{\gamma,\mathrm{T}}.$$

Hence *in dilute aqueous solutions of the fatty acids the adsorption at a given temperature and surface tension is inversely proportional to the van't Hoff factor, but it is the same for homologous fatty alcohols.*

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