

INTERFACIAL TENSION OF ALIPHATIC ALCOHOLS AND AROMATIC LIQUIDS WITH SURFACE ACTIVE AGENTS. PART I

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Measurements of the interfacial tension of some alcohols and aromatic liquids have been carried out against soap solutions. The tension at the oil droplet interface with increasing soap concentration is initially found to fall rapidly for dilute solutions, and thereafter reach a limiting value, when further increase in soap concentration has practically no effect, except in cases of *n*-hexyl and *sec.*-octyl alcohols which show a maximum in dilute soap solutions, followed by a rapid lowering.

Lowering of interfacial tension of organic liquids brought about by soaps and such substances is generally necessary for their emulsification. Soap solution has a low surface tension which together with the adsorbed interfacial film, contributes to its emulsifying property (Donnan, *Kolloid Z.*, 1910, 208; Bancroft, *J. Phys. Chem.*, 1915, 19, 275; Harkins, *J. Amer. Chem. Soc.*, 1917, 39, 541; Wilson, *J. Chem. Soc.*, 1934, 1360; McBain, "Colloid Science", 1950)

The effect of hydrolysis of soaps has been investigated by various workers (Harkins and Clark, *J. Amer. Chem. Soc.*, 1925, 47, 1854; Powney, *Trans. Faraday Soc.*, 1935, 31, 1510). Traces of free alkali first raise the surface tension to a maximum and then with further increase in alkali concentration, it decreases slowly and almost linearly. Addition of alkali suppresses hydrolysis, and the adsorbed layer consists of neutral soap which gives the maximum tension, while acid soap lowers the tension, as it is more strongly adsorbed than a neutral soap.

Surface tension curves have been classified according to three types (McBain *et al.*, *Kolloid Z.*, 1937, 78, 1). In type I, surface tension of the solvent is increasingly lowered with increasing concentration of the solute. This is the commonest case. In type II, surface tension is increased, though not to a great extent, with increasing concentration of the solute. In type III, there is a very great lowering of surface tension in a very dilute solution, the surface tension thereafter remaining approximately constant, or even, passing through a minimum, followed by a shallow maximum, but still at a value far below that of the solvent. In contrast to surface tension, the interfacial tension between two liquids is often reduced to nearly zero by the addition of a surface active agent. Sometimes, however, the behaviour may be similar to that of the three types mentioned.

EXPERIMENTAL

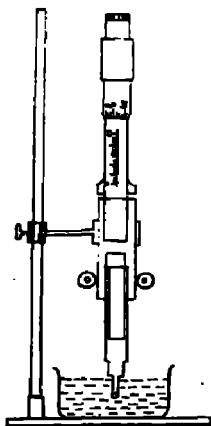
The liquids selected were as follows: *n*-butyl, *isobutyl*, *isoamyl*, *n*-hexyl and *sec.*-octyl alcohols and benzyl alcohol, methyl and ethyl benzoates, benzyl benzoate and hexane. Many of the liquids were from reliable manufacturers, such as Schering-Kahlbaum and E. Merck. They were, however, treated with sodium carbonate, washed with distilled water, dried and distilled under reduced pressure and the middle fractions were used for the purpose. The specific gravities of the liquids were determined using a calibrated 25 c.c. bottle and values obtained at 30° were used in the calculation of their interfacial tension. The substances used to lower the surface tension were sodium oleate, potassium oleate, with excess of acid and alkali, and saponin. They were prepared and purified by the usual methods.

The drop-volume method using a microsyringe (Burroughs and Wellcome) was adopted throughout to determine the interfacial tension of liquids against water and soap solutions. The syringe was scrupulously cleaned by means of alcohol, soap and distilled water and then dried before each measurement. It was then filled with the liquids and kept vertically with the tip at the definite depth in the aqueous medium in the container. By the careful working

of the screw cap, the drops with maximum possible size were slowly allowed to be formed covering the entire tip. All measurements were taken under identical conditions at a temperature $30^\circ (\pm 1.0)$. The measurements were thrice repeated and the mean value was corrected by Harkin's factor (*J. Amer. Chem. Soc.* 1919, **41**, 499).

The arrangements of the apparatus is shown in Fig 1.

FIG. 1



The motion of the piston in the barrel (capacity, 1 c.c.) of the syringe is governed by the micrometer screw head. Each division on the barrel corresponds to a volume of 0.04 c.c. and each sub-division on it is further calibrated by means of the micrometer screw to read 0.0004 c.c. The syringe with the liquids was clamped vertically with its tip pointing downwards for liquids heavier than water (Fig. 1), and the tip pointing upwards for those lighter than water. In the latter case, the barrel was fitted in the container holding aqueous medium by means of a tightly fitting rubber bung. In the case of liquids partly miscible with water, if the syringe be filled with such a liquid, the liquid often forms a continuous stream, instead of drops. If, however, the solubility of water in liquid is considerably less than that of liquid in water and water is filled in the syringe, water may give drops, and thus the tension of water against the liquid can be measured.

The variation in the interfacial tension of liquids with change in the soap concentrations ranging from $0.234 \times 10^{-3} M$ to $14.79 \times 10^{-3} M$ has been studied and the results are shown in Table I and Figs. 2 and 3.

TABLE I

Sodium oleate.	Interfacial tension depression (dyne/cm.)				
	<i>n</i> -BuOH.	<i>iso</i> BuOH.	<i>iso</i> Amyl alcohol.	<i>n</i> -Hexyl alcohol.	<i>sec.</i> -Octyl alcohol.
0.000 $M \times 10^3$	3.021	2.406	5.231	8.239	10.60
0.246	—	—	4.998	8.851	11.50
0.493	2.767	2.338	4.863	9.105	13.77
0.738	—	—	—	8.614	—
0.986	2.537	2.103	4.634	8.239	14.99
1.479	2.410	2.008	4.413	7.769	17.73
1.968	2.354	1.832	4.195	7.278	16.21
2.460	2.105	1.766	3.788	—	15.26
2.950	—	—	3.659	—	13.91
3.940	—	—	—	5.658	—
4.930	1.935	1.646	3.348	—	11.76
9.860	—	—	3.073	—	10.60
14.790	—	—	2.877	4.461	6.76

The interfacial tension in the aliphatic alcohol series is found to increase in the following order: *iso*-BuOH < *n*-BuOH < *iso*amyl alcohol < *n*-hexyl alcohol < *sec.*-octyl alcohol (Table I, Fig. 2). It is found to be increasing with the increase in the length of the aliphatic chain for all concentrations of sodium oleate. Further, it appears that the magnitude of the lowering of the interfacial tension by soap solution depends on the magnitude of the tension of the liquid against pure water, and it is found to be in the following increasing order: *isobutyl* < *n*-butyl < *iso*amyl < *n*-hexyl < *sec.*-octyl alcohol.

With potassium oleate—neutral, 10% free acid and 10% free alkali, the measurements of the interfacial tension were carried out in the case of *iso*- and *n*-butyl alcohols. It was, however, observed that the acidity or alkalinity did not appreciably affect the results and the fundamental behaviour was the same as against sodium oleate.

FIG. 2.

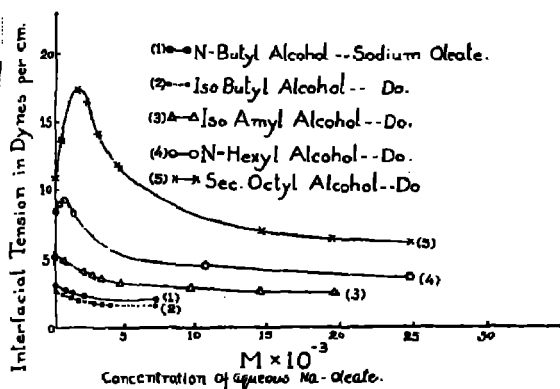
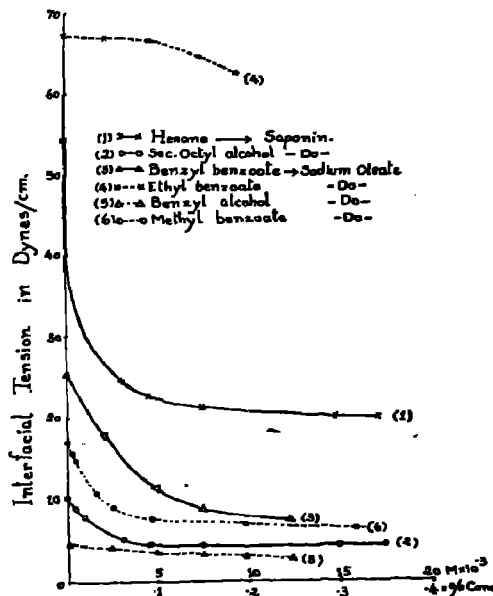


FIG. 3.



In the case of *n*-hexyl and *sec.*-octyl alcohols, it was surprising to note that at lower concentrations of soap solutions, *i.e.*, up to $2 \times 10^{-3} M$, the interfacial tension initially increased with the increasing soap concentration and then decreased as usual with further increase in soap concentration. With saponin (Fig. 3), however, at any concentration, this rather unusual behaviour, as observed with soap solution, was not evident. Addison (*J. Chem. Soc.*, 1945, 98; 1944, 477) has shown that there is an almost linear relation between chain length and the surface tension of the aqueous saturated solution of normal alcohols; but *sec.*-octyl alcohol and *tert.*-hexyl alcohol depict an irregular behaviour. It has been therefore suggested that when the structure of alcohol is altered, other factors in addition to solubility factor, might be operative. The interfacial tension curves of hexyl and *sec.*-octyl alcohols do not come under any of three types, already mentioned, as there is an initial rise of interfacial tension in very dilute solutions of soap, followed by a great lowering and thereafter the interfacial tension slowly decreasing and ultimately remaining approximately constant with increasing soap concentration.

In case of aromatic liquids (Fig. 3) it is apparent that groups $-\text{CH}_2\text{OH}$, $-\text{COOCH}_3$ and even $-\text{COOCH}_2\text{C}_6\text{H}_5$ reduce the tension against water when compared to that of unsubstituted nucleus (benzene, 34.6 dynes/cm.), while the group $-\text{COOC}_2\text{H}_5$ considerably enhances it (67.7 dynes/cm.). This surprisingly high interfacial tension of ethyl benzoate may be attributed to the peculiar effect of the ethyl group, which this group often exerts. Further, the magnitude of the surface tension lowering by sodium oleate also appears to depend on the magnitude of the tension of that liquid against water *i.e.*, greater the tension against water, greater is the lowering, but ethyl benzoate is also in this case an exception which shows much less lowering of tension against soap solution in view of its high tension against water.

In case of fatty acids, Szyszkowski's equation (*Z. physikal. Chem.*, 1908, 64, 385) expresses

the relation between the lowering of the tension and concentration of the solute. For very dilute solutions of any solute, the depression of surface tension, caused by the solute, is proportional to its concentration. As the concentration of the solute, however, increases, the lowering of the tension is no longer proportional to the concentration, but increases more slowly than does the concentration. The portions of the curves of liquids depicting interfacial tension lowering in Figs. 2 and 3, however, indicate that the lowering increases much more rapidly than the soap concentration for dilute solutions, but as the concentration of the soap increases, the interfacial tension lowering generally increases less and less slowly and ultimately reaches a nearly zero value, when further increase in the soap concentration has practically no effect. Thus the interfacial tension at the oil droplet interface with soap solution is generally found to decrease to a greater extent initially with the increase in the soap concentration and then reaches a limiting value. This may be accounted for on the basis of the unimolecular theory of adsorption; when the entire surface area of the droplet is covered with the unimolecular layer of surface active agent, the adsorption becomes independent of the concentration of the active agent, and no further decrease in the interfacial tension takes place. With hexane, these measurements using sodium oleate and saponin (Fig. 3) also indicate that there is at first a considerable reduction in the tension and then a limiting value is reached.

The unusual behaviour of hexyl and octyl alcohols is explained in an earlier communication along with that of esters (Desai and Kazi, *Curr. Sci.*, 1952, 21, 218).

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