# 154. *Mutually Surface-active Liquids. Mixtures of Sulphuric Acid with Nitrobenzene and with Ether.*

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WHEN the surface tensions of a series of mixtures of two liquids are plotted against percentage composition, the curve obtained usually shows neither a maximum nor a minimum surface tension. In a small proportion of the cases examined, mixtures have been found with surface tensions higher, or lower, than that of either pure component. The following examples are on record, but the list is not exhaustive.

[The figures in parentheses give the surface tensions (dynes/cm.) of the component liquids and of the maximum or minimum mixtures.]

*Maximum surface tensions.* Methyl alcohol (21·058) and acetone (21·578) : 33% methyl alcohol (21·775) (at 30°) (Morgan and Scarlett, *J. Amer. Chem. Soc.*, 1917, **39**, 2276). Ethyl alcohol (19·589) and acetone (19·781) : 50% ethyl alcohol (19·831) (at 45°) (Morgan and Scarlett, *loc. cit.*, who observed no maximum at 20° or at 0°). Sulphuric acid (53·66, 98·7% acid) and water (72·82) : 47·58% acid (76·70) (at 18°) (Röntgen and Schneider, *Wied. Ann.*, 1886, **29**, 209; Whatmough, *Z. physikal. Chem.*, 1902, **39**, 129, records a maximum at 45% sulphuric acid). *p*-Cresol (0·437*) and acetone (0·315*) : 21% acetone (0·450*). *m*-Cresol and acetone : slight maximum at 21% acetone. *o*-Cresol and acetone : no maximum (Weissenberger and others, I.C.T., VII, p. 70; from *Monatsh.*, 1925, **45**, 449; **46**, 1, 47).

*Minimum surface tensions.* Carbon disulphide (32·24) and ethylene dichloride (32·66) : 50% carbon disulphide (30·63) (at 18°) (Whatmough, *loc. cit.*, p. 169). Acetic acid (28·08) and ethyl iodide (28·83) : 40% ethyl iodide (26·69) (at 18°) (*ibid.*, p. 170). Acetic acid (28·08) and carbon tetrachloride (27·05) : 50% acetic acid (26·26) (at 18°) (*ibid.*). Acetic acid (28·00) and benzene (28·94) : 50% benzene (27·68) (at 18°) (*ibid.*, p. 171). Acetic acid (25·71) and benzene (26·62) : 62·9% acetic acid (24·96) (at 30°) (Morgan and Scarlett, *loc. cit.*). Acetic acid (27·17) and benzene (28·55) : 65·2% acetic acid (26·71) (at 15°) (*idem*). Acetic acid (28·00) and chloroform (27·40) : 40% chloroform (26·62) (at 18°) (Whatmough, *loc. cit.*, p. 172). Carbon tetrachloride (27·00) and chloroform (27·33) : 45% chloroform (26·92) (at 18°) (*idem*). Ethyl acetate (24·22) and amyl alcohol (24·29) : 68% amyl alcohol (24·13) (at 18°) (*idem*). Benzene (28·94) and ethyl iodide (28·83) : 50% ethyl iodide (28·61) (at 18°) (*idem*). Benzene (25·36) and toluene (25·29) : 25% benzene (25·21) (at 40°) (Morgan and Griggs, *J. Amer. Chem. Soc.*, 1917, **39**, 2265; they did not observe a minimum at 10·8°, nor did Whatmough at 18·0°).

It is noticeable, although perhaps merely a coincidence, that in all the cases of minimum surface tension, the surface tensions of the components are nearly identical, the greatest difference being 1·38 dyne/cm. (acetic acid and benzene at 15°).

In the course of other work, it was desired to determine the surface tensions of dilute solutions of (*a*) nitrobenzene and (*b*) ether in sulphuric acid (100%). It was decided to

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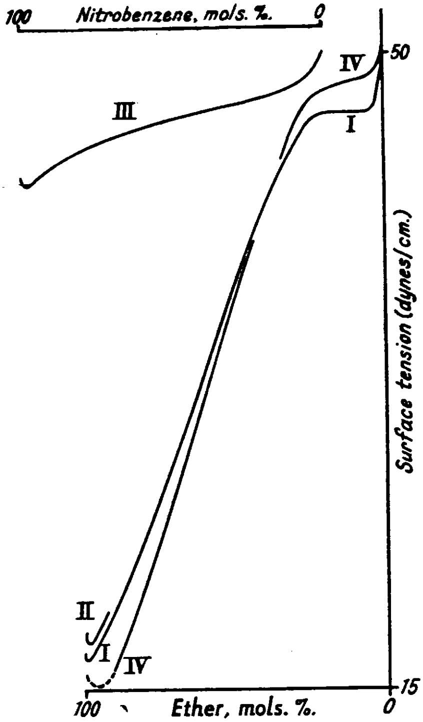
* Surface tension relative to that of water.

extend the series of measurements over the whole range of these mixtures, and it was found that both curves showed minimum points. These cases differ from the above in that the surface tension of sulphuric acid differs widely from those of the other components, being about 7 dynes/cm. higher than that of nitrobenzene, and about three times that of ether.

The surface tensions of mixtures of ether and sulphuric acid were determined by Pound (J., 1911, **99**, 709), who observed no minimum at 30°; however, he made no measurements between 0 and 10·94% sulphuric acid, and a comparison between the curve drawn from his results and that now obtained makes it almost certain that a minimum (as indicated by the broken line) would have been detected at 30° also if the appropriate measurements had been made.

The fall in surface tension at each end of each curve makes it clear that sulphuric acid, in small concentration, in spite of its high surface tension, is positively adsorbed at the surface of ether or nitrobenzene, and that these two substances are adsorbed, in similar circumstances, at the surface of sulphuric acid.



## EXPERIMENTAL.

*Materials.*—The sulphuric acid was purified by repeated crystallisation, and adjusted to 100% by small additions of pyrosulphuric acid similarly recrystallised. The 100% acid (concentration checked by m. p. and by titration) was kept in a desiccator in a very dry constant-temperature room. It was found, by repeated checking, that the rate of acquisition of water was exceedingly small.

The ether and nitrobenzene were purified by repeated distillation of specimens which were already practically pure.

*Method.*—Measurements were made by the drop-weight method, the stalagmometer previously employed by Hickson and Bailey (*Sci. Proc. Roy. Dublin Soc.*, 1932, **20**, 274) being used in conjunction with the device recently described by the author (*Nature*, 1936, **137**, 323) for controlling the rate of fall of the drop. The values of $f(r/l)$ in the equation $\gamma = Wg/2\pi r \, . \, f(r/l)$ were taken from the paper by Harkins and Brown (*J. Amer. Chem. Soc.*, 1919, **41**, 499).

Most of the readings were taken in a constant-temperature room at 17°. To minimise error due to evaporation in the case of ether-rich mixtures, the weight of the first five drops was neglected, and the later drops fell in an atmosphere already saturated with ether vapour. As, however, some inaccuracy is likely to be introduced at a temperature so near the b. p. of ether, a further set of measurements of ether-rich mixtures was made at 9·5° (Table I). These left no doubt about the genuineness of the fall in surface tension when a little sulphuric acid is added to ether.

TABLE I.

*Sulphuric acid and ether at* 9·5°.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Ether, mols. % ... | 94·13 | 97·69 | 98·43 | 98·77 | 99·24 | 99·38 | 99·49 | 100·0 | 100·0 |
| $\gamma$ (dynes/cm.) ...... | 18·90 | 17·82 | 17·84 | 17·48 | 17·58 | 17·88 | 17·96 | 18·12 | 18·16 |

The number of readings taken was considerable, particular attention being paid to the extreme ends of the curves. In the figure, curves I and II represent sulphuric acid–ether mixtures at 17° and 9·5° respectively, and curve III sulphuric acid–nitrobenzene mixtures at 17°. Curve IV is drawn from Pound's results (*loc. cit.*) with the necessary alterations from percentages by weight to molecular percentages.

From these curves, the values in Table II are read off as the most probable surface tensions.

### Table II.

*Mixtures of sulphuric acid with ether or nitrobenzene.*

| $H_2SO_4$, mols. %. | Ether at 17°. | Nitro-benzene at 17°. | $H_2SO_4$, mols. %. | Ether at 17°. | Nitro-benzene at 17°. | $H_2SO_4$, mols. %. | Ether at 17°. | Nitro-benzene at 17°. | Ether at 9·5°. |
|---|---|---|---|---|---|---|---|---|---|
| 100 | 50·33 | 50·33 | 90 | 46·83 | 48·25 | 5 | 17·97 | 43·10 | 18·63 |
| 99·5 | 49·40 | 50·05 | 80 | 46·80 | 47·76 | 4 | 17·60 | 42·80 | 18·31 |
| 99·0 | 48·75 | 49·83 | 75 | 46·30 | 47·52 | 3 | 17·30 | 42·73 | 17·99 |
| 98·5 | 48·24 | 49·66 | 60 | 41·60 | 46·87 | 2 | 17·06 | 42·85 | 17·67 |
| 98·0 | 47·83 | 49·54 | 40 | 32·50 | 46·05 | 1·5 | 16·90 | 42·98 | 17·53 |
| 97·0 | 47·22 | 49·25 | 20 | 23·30 | 44·80 | 1·0 | 16·80 | 43·11 | 17·51 |
| 96·0 | 46·93 | 49·00 | 10 | 19·55 | 43·98 | 0·5 | 16·80 | 43·27 | 17·78 |
| 95·0 | 46·86 | 48·80 | 7 | 18·50 | 43·64 | 0 | 17·06 | 43·47 | 18·13 |

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[*Received, March* 21*st*, 1936.]