ON THE EFFECTS OF GASES UPON THE SURFACE TENSIONS OF SOME LIQUIDS.(1)

By Bun-ichi TAMAMUSHI.

Received June 29, 1926. Published August 28, 1926.

Introduction. Surface tension, being a property of the boundary surface of phases, should be effected by the nature of phases on both sides of the surface. According to the classical works of Quincke,(2) Kundt,(3) and Guye and Renard,(4) it is evident that air has a certain effect, though not so considerable, upon the surface tension of pure water. In later years Ferguson(5) studied the effects of air and carbon dioxide on the surface tensions of some organic liquids. The present paper contains the results of measurements made on the following pairs of gases and liquids. Gas : air, carbon dioxide, nitrous oxide, hydrogen sulphide. Liquid : water, ethyl alcohol, ethyl ether, carbon bisulphide, carbon tetrachloride.

Experimentals. The apparatus of Ramsay and Shields(6) is somewhat modified in the present research as is shown in Fig. 1, particularly for the purpose of easily saturating solvent with gas. This is done by the side tube B, which is connected to a generator of gas and also to a manometer. The top of the wide tube A is provided with a good stop cock and the whole U tube is protected, to its neck, by a water jacket of temperature constant within the fluctuation of less than ±0.1°.

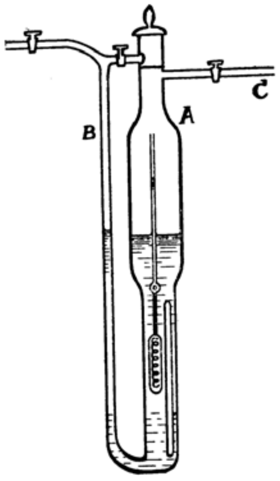

Fig. 1.

Two capillary tubes were very carefully selected and examined and their radii have been found to be 0.0142 cm. and 0.0166 cm. respectively. The rise of liquid in the capillary tube was measured by a cathetometer of Société Genevoise with an accuracy to 0.005 cm., and corrections due to the curvature of meniscus were calculated by means of Lord Rayleigh's(7) formulae.

---

(1) Read before the Chemical Society of Japan, October 1924.
(2) *Pogg. Ann.*, **160** (1877), 573.
(3) *Wied. Ann.*, **12** (1881), 538.
(4) *J. chim. phys.*, **5** (1907), 81.
(5) *Phil. Mag.*, (6), **28** (1914), 403.
(6) *J. Chem. Soc.*, **63** (1893), 1089.
(7) *Proc. Roy. Soc.*, [A] **92** (1915), 184.

In the course of measurement the capillary rise of a pure solvent is at first read under its own vapour pressure (the apparatus being previously evacuated through another side tube C) and then letting the gas pass into the solvent under a certain pressure less than one atmosphere and when the equilibrium is attained the height of the capillary column is again measured, due care being taken of the constancy of temperature in the jacket during all these processes.

The surface tension is calculated by the following formula:

$$\sigma = \frac{1}{2} g\, r\, (h+h')\, (D-d)$$

where g: gravity constant, r: radius of capillary tube, h: capillary rise read by cathetometer, h': correction term, D: density of liquid determined by pyknometer in each case, d: density of gas phase, which was taken from Landolt-Börnstein's Tables and the related small corrections have been calculated by the law of ideal solution. The depression of surface tension is expressed in percentage as $100\frac{\Delta\sigma}{\sigma}$, $\Delta\sigma$ being the difference of surface tensions between solvent and solution, σ being the surface tension of pure solvent. The experimental results are shown in the following tables, in which p denotes the pure solvent and s solution.

TABLE 1. Air.

Solvent	Temp.	$100\frac{\Delta\sigma}{\sigma}$
Water	20	0.22
Ethyl alcohol	19	0.46
Benzene	18	0.32
Ethyl ether	20	0.40

TABLE 2. Carbon dioxide.

Solvent	Temp.		$h+h'$	$D-d$	σ	$100\frac{\Delta\sigma}{\sigma}$
Water	18.0	p	8.694	0.9986	70.95	0.83
		s	8.631	0.9974	70.36	
CCl_4	25.0	p	1.9633	1.5822	25.27	0.96
		s	1.9453	1.5815	25.03	
CS_2	24.8	p	2.960	1.2620	30.39	0.95
		s	2.935	1.2607	30.10	
$(C_2H_5)_2O$	25.3	p	2.759	0.7067	15.82	0.97
		s	2.721	0.7078	15.67	
C_2H_5OH	25.3	p	3.317	0.7860	21.21	0.99
		s	3.287	0.7854	21.00	
C_6H_6	25.1	p	3.803	0.8714	26.96	0.96
		s	3.771	0.8705	26.70	

TABLE 3. Nitrous oxide.

Solvent	Temp.		$h+h'$	$D-d$	σ	$100\frac{\Delta\sigma}{\sigma}$
Water	25.2	p	8.685	0.9968	70.43	0.75
		s	8.635	0.9951	69.90	
C_2H_5OH	25.1	p	3.319	0.7870	21.25	0.97
		s	3.292	0.7858	21.04	
$(C_2H_5)_2O$	25.0	p	2.774	0.7067	15.95	0.82
		s	2.750	0.7071	15.82	
CCl_4	24.8	p	1.962	1.5822	25.26	0.96
		s	1.943	1.5823	25.01	

TABLE 4. Hydrogen sulphide.

Solvent	Temp.		$h+h'$	$D-d$	σ	$100\frac{\Delta\sigma}{\sigma}$
Water	15.2	p	8.740	0.9990	71.36	1.19
		s	8.640	0.9985	70.51	
C_2H_5OH	16.1	p	3.388	0.7948	22.15	1.26
		s	3.340	0.7960	21.87	
C_6H_6	15.3	p	3.954	0.8829	28.67	1.22
		s	3.900	0.8843	28.32	

TABLE 5.

Solvent	Gas	Concentration C	$C^{\frac{1}{3}}$	$100\frac{\Delta\sigma}{\sigma}$
Water	Air	0.00236	0.133	0.22
	N_2O	0.104	0.470	0.75
	CO_2	0.145	0.525	0.83
	H_2S	0.334	0.694	1.19
C_2H_5OH	Air	0.0232	0.285	0.46
	N_2O	0.647	0.865	0.97
	CO_2	0.693	0.885	0.99
	H_2S	1.870	1.232	1.26
C_6H_6	Air	0.0205	0.274	0.32
	CO_2	0.571	0.830	0.96
	H_2S	1.084	1.027	1.22

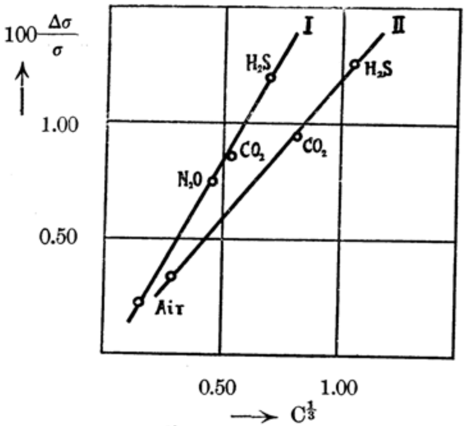

Fig. 2. I: Water.
II: Benzene.

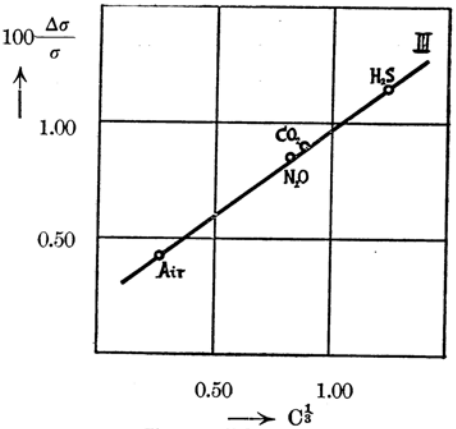

Fig. 3. III: Alcohol.

Discussions. The depressive effects of air upon these liquids are in the mean not greater than five percent; values of the same order were obtained also by the other authors already mentioned.

If we compare the values of $\frac{\Delta\sigma}{\sigma}$ with each other for a given gas and different liquids, it is remarkable that they are almost constant in each series, that is, the greater the surface tension the greater the effect of depression. It must be mentioned that similar facts were observed by Ferguson in his experiments above refered. The rule of this kind is certainly not insignificant, however its theoretical explanation may not be simple as the complex nature of adsorption and of other related phenomena must be taken in consideration.

Table 5 shows the relation between the values of $\frac{\Delta\sigma}{\sigma}$ and the concentrations of different gases dissolved in the same solvent. The values of solubilities are quoted from Seidell's Tables except one, i.e. the solubility of hydrogen sulphide in bengene, which has been determined by the author, the details of the method being here omitted. As it is shown in this table or in Fig. 2 and 3, the relation between the cube root of concentration and $\frac{\Delta\sigma}{\sigma}$ is nearly linear in each case, that is, for a system of same liquid and different gases we have an empirical relation as follows:

$$\frac{\Delta\sigma}{\sigma}=kC^{\frac{1}{3}}+a$$

where k and a are certain constants. In other words, as a is in general very small, $\frac{\Delta\sigma}{\sigma}$ is almost proportional to the linear distances of molecules of the adsorbate. It may be also remarked that this formula has in its form a certain analogy with the adsorption isotherm of Freundlich.

The author wishes to express his sincere thanks to Prof. M. Katayama for his kind guidance during this work.

The Institute of Physical and Chemical Research,
Hongo, Tokyo.