On the Porperties of Water Surface in Contact with Various Vapors*

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The Experimental Procedure and the Results.—The surface tension of water in various vapors was measured by the drop-volume method. The experimental equipment is shown in Fig. 1. The thick capillary polished flat at one end, where the water drop hangs, was joined to a burette filled of distilled water by a thick rubber tube for vacuum use, and to the middle of the tube a screw cock was attached in order to control the rate of dropping. The capillary end is held air-tight in the thick glass globe by a large coutchouc cork through which a glass tube is reserved for sending the air saturated with the vapor to be investigated into the glass globe, and the pressure in the globe may easily be regulated by a pump.

After sending the air saturated with the vapor into the glass globe for about 5 min., the dropping of water is started at the constant rate. From the observations of fifty drops we

* "International Critical Table" IV, 436; Landolt-Börnstein, "Phys-chem. Tabellen" Bd. I, 208, 243 (1923); Erg. Bd. I, 149, 154 (1927); 154, 168 (1931).

obtain the mean volume of an water drop, v cc., and the average life of one drop, τ.

The behaviors at 20° are shown in Fig. 2-a and -b. As it is seen there, the surface tension of water is affected markedly by the sort of vapor in contact, which are arranged in increasing order, that is : in air < benzyl chloride < carbon bisulfide < *n*-hexane, carbon tetrachlóride < benzene < ethylene dichloride < chloroform < isoamyl alcohol < ethyl acetate < isoamyl acetate < ethyl ether.

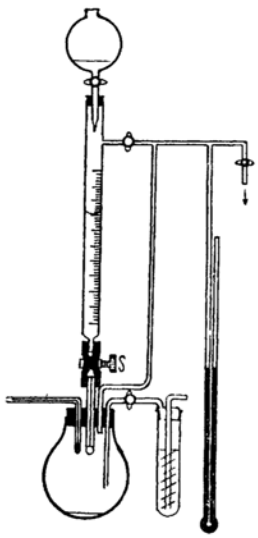

Fig. 1.

The "Ageing" of the Water Surface and its Mechanism.—As is seen in Fig. 2, the water surface developed afresh has its maximum value of surface tension which diminishes to the equilibrium value with time, about 6 seconds in general. Therefore, the aging period of the water surface must be about 6 seconds, which is extremely short as compared with that of solution which demands more than 30 min. or even several hours. In other words, the time demanded to attain the adsorption equilibrium of vapor on the water surface is extremely short as compared with that of the solute in solution. This may be ascribed to the fact that the movement of the molecules in gas phase is by far free as compared with that in solution.

The Vapor-Water Interfacial Tension and the Relation to "Antonoff's Rule".—The surface tension of water (W)-drop in vapor

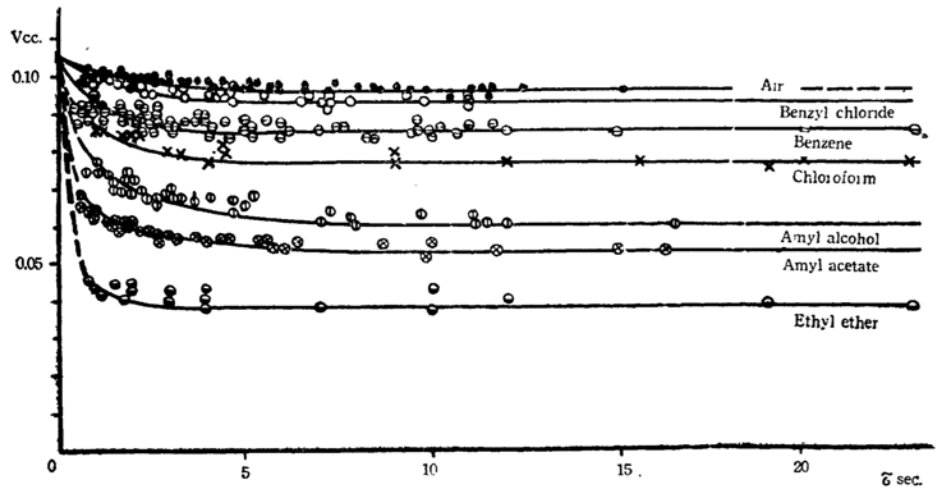

Fig. 2 a.—v_{W-G}, Drop volume of water in vapor.

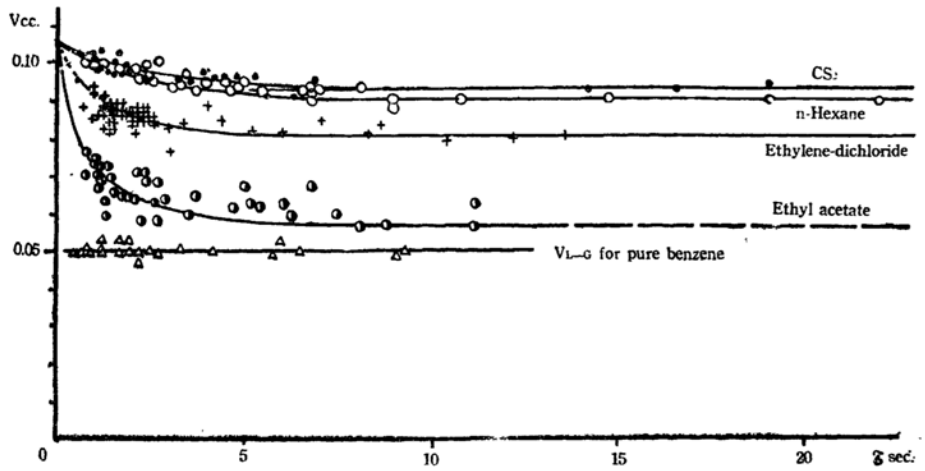

Fig. 2 b.—v_{W-G}, Drop volume of water in vapor.

(G), γ_{W-G}, is calculated by the formula

$$\gamma_{W-G}=\frac{v\cdot\rho\cdot g}{2\pi ar} \quad (1)$$

(taking the contact angle of water for zero) where v is the volume of a water-drop, ρ the density of water, g the acceleration of gravity, r the outer radius of capillary used and a is a correcting constant to be determined by experiment. In our experiment, $r=0.338$ cm., $a=0.610$. The results are shown in Table 1 where v_s (column 2) is the observed volume of one drop in the constant region after its ageing period, about 6 sec., γ_{Z-G} is the surface tension of the "pure" organic liquid in contact with air (with its vapor G), and $\gamma_{W'-L'}$ is the interfacial tension at the interface of water-liquid saturated with each other.

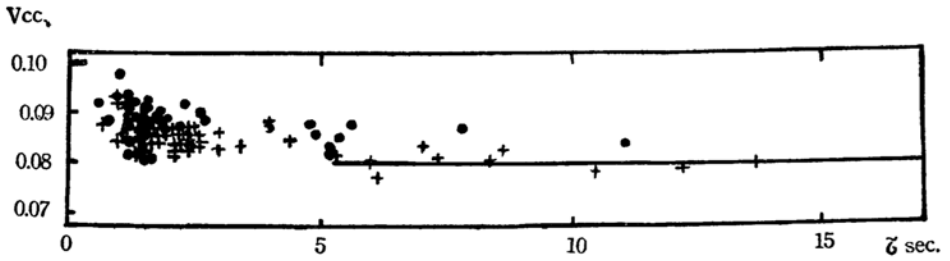

Fig. 3.—The effect of pressure on v_{W-G} (G=ethylene dichloride): + under ordinary pressure, ● under 10~15 cm.Hg.

Table 1 (20°C.)

Name of G or L.	v_s, cc.	γ_{W-G} dyne /cm.	γ_{L-G} dyne /cm.	$\gamma_{W'-L'}$ dyne /cm.	$\gamma_{W'-L'}+\gamma_{L-G}$ dyne /cm.
Air	0.096	72.6	——	——	——
Benzyl chloride	0.093	70.5	39.9*	30.5	70.4
Carbon bisulfide	0.092	69.5	33.58	49.3	82.88
n-Hexane	0.090	68.0	17.34	50.96	68.30
Carbon tetrachloride	0.090	68.0	25.68	43.6	69.28
Benzene	0.085	64.2	28.88	34.96	63.84
Ethylene dichloride	0.080	60.5	31.1	29.2**	(60.3)
Chloroform	0.076	57.5	26.0	31.8	57.8
iso-Amylalcohol	0.060	45.5	23.8	5.0	28.8
Ethyl acetate	0.056	42.5	23.6	6.7	30.3
iso-Amyl acetate	0.053	40.0	24.08	10.8	34.88
Ethyl ether	0.038	28.5	17.10	10.7	27.8

* Observed by capillary height method.

** This value was estimated ftom $\gamma_{W'-L'}=37.2$ dyne/cm. for ethylene dibromide at 20°. In many cases, the value of $\gamma_{W'-L'}$ for aliphatic halogenide decreases by about 8 dynes on replacing the bromine atom by chlorine.

Comparing the columns 3 and 6, we shall see the excellent agreements between them except carbon bisulfide, alcohols, acetic esters. These agreements can not be considered accidental. Thus we may take the following rule

$$\gamma_{W-G}=\gamma_{W'-L'}+\gamma_{L-G}. \quad (2)$$

Using similar expression, the "Antonoff's rule" is expressed in

$$\gamma_{W'-A}=\gamma_{W'-L'}+\gamma_{L'-A}, \quad (3)$$

where W′ and L′ denote the phase W and L saturated with each other, and A the air in contact with W′ or L′. Since the three phases W′, L′ and A are in equilibrium, and since just the surface layer of water-drop in contact with the vapor of L is assumed to be saturated with L, so that we may put $\gamma_{W-G}=\gamma_{W'-A}$. And since the surface tension of organic liquids are not affected exceedingly by whether they are wet or dry,[1] the law (2) may be reduced to the "Antonoff's rule" itself.

As regards the lower membered acetic esters and alcohols, the relation may be expressed as follows:

$$\gamma_{W-G}>\gamma_{W'-L'}+\gamma_{L-G}. \quad (4)$$

On the other hand, the relation for carbon bisulfide is

$$\gamma_{W-G}<\gamma_{W'-L'}+\gamma_{L-G}. \quad (5)$$

The Effects of Pressure.—On decreasing the vapor pressure, the increase in the surface tension of warer, γ_{W-G}, so that in v, might be expected owing to diminishing the attraction of moleules of vapor outside on the surface molecules of water. The observations were made about ethylene dichloride under reduced pressure of the system down to 10 cm.Hg, which corresponds to 0.8 cm.Hg in partial pressure. The increase of v by 0.004 cc. was found with difficulty even at $\tau<6$ sec., but the prolongation of the ageing period up to 10 seconds, which was 6 sec. under ordinary pressure, so that the effect of pressure on v, if any, must appear under sufficient low pressure.

Summary

The surface tension of water in various vapors were measured by the drop-volume method. As a result of the experiment, it was found that the "Antonoff's rule" holds good with some exceptions. In any vapors, a remarkable, but short ageing of water surface was found, which was 6 seconds in general, and which is prolonged by reduced pressure.

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(1) W.D. Harkins, "The 6th Colloid Symposium Monograph," 17 (1928).