

MEASUREMENT OF THE SURFACE TENSION OF ALCOHOL-WATER SOLUTIONS BY THE "TWO-JUMP" METHOD

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Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, Vol. 9, No. 2, pp. 145-148, 1968

Measuring the surface tension of aggressive nontransparent liquids at high saturated vapor pressure and high temperature is a very complicated process.

This paper describes a method appropriate in such circumstances, the so-called "two-jump" method. This method has been tested on alcohol-water mixtures whose surface tension had previously been determined only up to 50° C. Accordingly, the results are also of independent interest. The method is based on the capillary rise in communicating tubes of different diameter. The principle is illustrated in Fig. 1.

Two capillaries with radii r_1 and r_2 go over, in the sections O_1O_1 and O_2O_2 , into tubes with radii R_1 and R_2 . At top and bottom, the tubes are connected by common chambers. A third capillary with constant radius r_3 is connected in parallel with the first two. For simplicity, we assume that $r_1 = r_2 = r_3 = r$ and $R_1 = R_2 = R$. First, the entire system is filled from below with the test liquid, which is then slowly removed through tube 4. The nature of the level change in all three legs (1, 2, and 3) can be followed in Fig. 2 in relation to the amount of liquid withdrawn V . The level continues to fall simultaneously in all three legs until the level in the first leg reaches section O_1O_1 , where $V = V_1$, and, as in the maximum pressure method, a bubble of vapor (or gas) with radius $r_n = r$ has grown at the end of the capillary. At this moment, the bubble expands sharply and the level in the first leg falls abruptly; while in the second and third legs, on the other hand, it rises abruptly so that between them there is established a level difference equal to the capillary rise

$$h_k = 2\sigma\gamma^{-1} (1/r - 1/R).$$

Here, σ is the surface tension and γ is the specific weight of the liquid.

This difference of levels will be preserved until, as more liquid is withdrawn, the level in the second capillary reaches section O_2O_2 , and $V = V_2$; at this point, a second jump takes place.

The total volume change between the two jumps in tube R_2 (Fig. 2) will be $\Delta V = V_1 - V_2 = h_k\pi(R^2 + 2r^2)$. Eliminating h_k , we obtain

$$\sigma = \frac{\gamma\Delta V}{2\pi} \frac{1}{(R^2 + 2r^2)(1/r - 1/R)} = C\gamma\Delta V.$$

Thus, if the dimensions of the system and the density are known, in order to determine the surface tension, it is sufficient to measure ΔV or

a quantity proportional to it. The function of the third capillary is to fix the beginning and end of the working period. In principle, it is possible to employ both absolute and relative variants of the method.

The proposed method enables measurements to be made both in an inert gas atmosphere and in the saturated vapor of the test liquid.

It is very important to choose the dimensional relations correctly. The calculation formula does not impose limitations on the capillary dimensions. The only exception is the trivial case for $r_1 = R_1$ and $r_2 = R_2$.

An error analysis indicates that it is necessary to reduce the ratio r_2/R_1 . In addition, there are certain technical limitations.

1. The conditions of bubble formation must be the same in both legs; i.e., $r_1 = r_2$ and $R_1 = R_2$. This makes it possible to exclude the effect of the contact angle.

2. The drop in level for the first leg h_1 must not be less than $(2-4)R_1$, since otherwise there will not be a sharp enough jump and the bubble at the end of the first capillary will simply enlarge.

3. To get a reliable fix, the jump in the third capillary must be not less than several mm.

4. Reduction of the radii r_1 and r_2 involves serious technical difficulties. Writing the equilibrium conditions for the liquid in communicating tubes of different diameters before and after the first jump and also the mass balance condition at the instant of the jump, keeping in mind that

$$r_1 = r_2 = r; \quad R_1 = R_2 = R, \quad h_1' = nR \quad (n = 1, 2, 3...),$$

we obtain the following expressions:

$$\frac{r_3}{R} = \left[\frac{1}{h_k'/k_1 - 1} - \left(\frac{r}{R}\right)^2 \right]^{1/2},$$

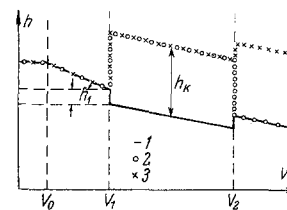


Fig. 2

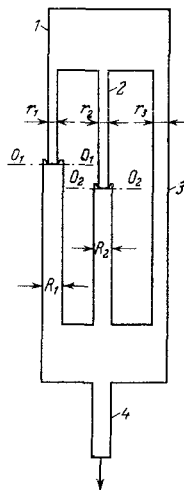


Fig. 1

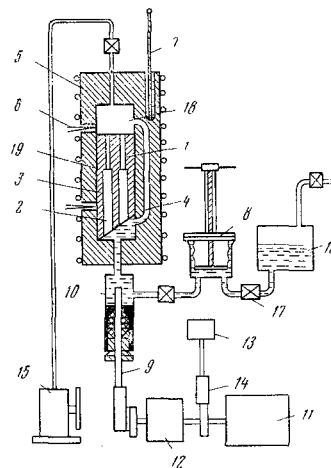


Fig. 3

Table 1

T, °C	N, rev	ρ , g/cm ³	σ , dyne/cm	T, °C	N, rev	ρ , g/cm ³	σ , dyne/cm
Doubly distilled water							
21.8	1481	0.997	72.08	150.0	1079	0.914	48.12
23.05	1486	0.996	72.23	150.8	1077	0.913	47.97
100.0	1252	0.963	58.86	151.0	1074	0.913	47.88
Ethyl alcohol-water system (96 vol %)							
16.5	590	0.810	23.33	86.70	458	0.746	16.69
20.0	580	0.806	22.79	90.0	445	0.742	16.11
37.2	557	0.792	21.52	132.0	363	0.693	12.30
39.3	552	0.790	21.28	134.2	361	0.691	12.15
59.9	516	0.770	19.38	148.3	324	0.670	10.59
65.5	507	0.766	18.94	148.8	320	0.669	10.44
83.5	467	0.750	17.08	152.5	315	0.660	10.15
Ethyl alcohol-water system (78 vol %)							
17.1	650	0.868	27.53	124.1	442	0.770	16.59
18.9	657	0.867	27.77	128.0	424	0.766	15.86
20.0	646	0.865	27.28	160.8	359	0.729	12.79
50.0	600	0.839	24.55	168.0	330	0.718	11.57
83.2	528	0.810	20.89	169.9	337	0.717	11.81
Ethyl alcohol-water system (51 vol %)							
19.5	697	0.929	31.63	103.4	557	0.855	23.23
20.0	702	0.928	31.77	110.6	541	0.850	22.45
21.5	688	0.927	31.14	131.3	506	0.830	20.50
22.0	698	0.926	31.53	147.7	477	0.811	18.89
42.5	663	0.910	29.43	160.7	448	0.798	17.47
74.2	607	0.883	26.16	170.3	425	0.784	16.25
Ethyl alcohol-water system (19 vol %)							
20.1	955	0.974	45.39	140.2	681	0.883	29.33
22.5	951	0.970	45.00	140.5	686	0.882	29.53
89.0	803	0.928	36.36	168.0	618	0.850	25.62
90.0	798	0.927	36.12	170.1	611	0.848	25.28
Ethyl alcohol-water system (6 vol %)							
19	1232	0.989	59.44	105.7	985	0.940	45.00
21.5	1218	0.989	58.80	122.5	938	0.926	42.36
63.7	1093	0.971	51.78	145.3	883	0.904	38.95
65.1	1096	0.970	51.88	148.5	868	0.901	38.16
100.0	1005	0.945	46.36	169.5	803	0.880	34.50
103.0	997	0.943	45.88	171.0	798	0.879	34.21

$$\frac{\Delta}{h_k} = \left[1 + \left(\frac{r}{R} \right)^2 + \left(\frac{r_3}{R} \right)^2 \right]^{-1},$$

$$h_k = \frac{2\sigma}{\gamma} \left(\frac{1}{r} - \frac{1}{R} \right)$$

$$h_k' = nR \quad (n = 1, 2, 3, \dots) \quad (1)$$

Here, Δ is the jump in the third leg.

Using these equations, we can calculate r_3/R and Δ for known values of σ , γ , n , and r/R . It is best to use graphs of functions (1) for this purpose. For alcohol, if $r = 0.25$ mm, the following are optimum: $R = 2$ mm, $r_3 = 1.5$ mm, and $\Delta = 5$ mm.

A diagram of the apparatus is shown in Fig. 3. The glass capillaries 1 and broader tubes 2 were sealed into stainless steel cylinder 3, which, in turn, was placed in airtight can 19. The third capillary 4 took the form of a gauge glass. The entire system was placed in a demountable copper block with an external electric heater. The tem-

perature was measured with two chromel-alumel thermocouples 6 and mercury thermometer 7 graduated in 0.1° C. The liquid level in the capillaries was roughly controlled by means of a siphon metering device 8 and could be smoothly varied by means of polished rod 9, which was displaced in chamber 10 by means of dc motor 11 with reducer 12.

The volume of liquid removed from the working space is proportional to the vertical displacement of the rod, i.e., to the number of revolutions of the motor. Since the relative variant of the method was used, it is possible to write the calculation formula in the form $\sigma = A\rho N$, where N is the number of revolutions of the motor between the two jumps, A is an instrument constant, and ρ is the density of the liquid.

The number of revolutions of the motor was determined with a TSB 1M-100 electromechanical pulse counter 13, which received six pulses from relay 14 per revolution of the shaft. The dimensions of

Table 2
Surface Tension of Aqueous Solution of Ethyl Alcohol (dyne/cm) or (erg/cm²)

T, °C	Alcohol concentration, vol. %										
	96	90	80	70	60	50	40	30	20	10	0
20	22.8	25.1	27.1	27.9	29.5	31.9	35.2	39.6	45.1	54.2	72.4
30	22.1	23.9	26.1	26.9	28.5	30.8	34.1	38.3	43.4	52.4	71.1
40	21.2	23.1	25.3	26.2	27.7	29.8	32.9	37.1	42.3	50.9	69.7
50	20.2	22.2	24.5	25.4	26.8	28.9	31.8	36.0	41.0	49.2	68.2
60	19.3	21.3	23.3	24.5	25.9	28.0	30.9	34.9	39.4	47.6	66.4
70	18.4	20.2	22.2	23.4	24.9	26.9	29.8	33.6	38.0	46.1	64.6
80	17.4	19.1	21.1	22.3	23.7	25.8	28.8	32.6	36.9	45.1	62.8
90	16.1	18.0	19.8	21.1	22.6	24.8	27.7	31.5	35.6	43.4	60.9
100	15.5	17.2	18.9	20.2	21.7	23.9	26.8	30.4	34.5	41.7	58.9
110	14.6	16.3	17.8	19.0	20.7	22.8	25.8	29.4	33.3	40.5	56.9
120	13.6	15.2	16.8	17.9	19.6	21.8	24.8	28.3	32.0	38.7	54.8
130	12.4	14.1	15.7	16.8	18.6	20.8	23.5	26.9	30.7	36.9	52.6
140	11.6	13.0	14.7	15.9	17.6	19.8	22.6	25.6	29.4	35.3	50.3
150	10.4	12.0	13.6	14.9	16.6	18.8	21.4	24.4	27.8	33.6	48.1
160	9.2	10.9	12.6	13.8	15.6	17.7	20.1	23.1	26.5	32.0	45.7
170	8.9	9.8	11.6	12.8	14.4	16.6	19.0	21.8	25.2	30.8	43.3

the rod were so selected that 600–1200 pulses were generated during the working stroke. Before being filled, the system was heated and evacuated to 10^{-3} mm Hg by means of a VN-2MG vacuum pump 15. Before being admitted to the system, the working liquid was degassed in reservoir 16, after which it was drawn into the system through valve 17. By means of the metering device, the liquid level was established slightly below the top of chamber 18. The subsequent displacement of the liquid was controlled with the rod 9.

Measurements were made only after a long period at constant temperature. Usually, the rate of temperature drop was not greater than 1 deg/hr. The liquid surface-level fell at a rate of about 0.01 cm/sec. In this case, the counter recorded from two to five pulses per second. The instrument constant was determined from experiments with 96% ethyl alcohol at temperatures from 20 to 170° C.

The surface tension and density of the alcohol were taken from [1–4]. A value of $A = 20.11 \pm 0.05$ was obtained. The surface tension of solutions of alcohol in water were measured at concentrations of 0.6, 19, 51, 78, and 96% by volume. The alcohol concentration was determined with a set of float densimeters. The results are presented in Table 1. Table 2 gives values of the surface tension of aqueous solutions of ethanol obtained by graphic interpolation. The scatter of the experimental data is 0.7% on the average and does not exceed 1.5%. The maximum possible error is estimated at 2.5%, to which

the chief contribution consists in the error in determining the number of pulses (up to 2%).

The experiments showed that the proposed method can be used for measuring the surface tension of aggressive liquids both in the saturated vapor and in an inert gas atmosphere. In the case of liquid metals, the jump can be registered electrically from the change in resistance of a third (metal) capillary inserted in a bridge circuit. This possibility was tested in experiments on liquid sodium at temperatures up to 800° C.

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10 November 1966

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