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Fundamental Studies on Interfacial Tensions in Flotation. II Surface-Tension Variation, Surface Activity, and Surface Orientation of Frothers at Air-water Interface*

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Synopsis

It has been found that the surface tension of cineol solutions varies appreciably with time during measurement by a tensiometer. This fact will have considerable influence on froth characteristics in flotation. Therefore time variation of surface tension of aqueous solutions of frothers has been theoretically considered and two equations are introduced according to the assumption whether or not the rate of diffusion of molecules to the surface from the body of a solution is small as compared with that of evaporation. It is verified experimentally that the equation obtained on the former assumption holds good in the aqueous solutions of cineol. The time variation of the concentration of a solution may also be obtained by the surface tension measurement using this equation.

The activity coefficients of pure as well as commercial frothers are calculated. An equation for the relation between surface pressure and the surface concentration of various frothers is introduced and it is concluded that the difference in the surface activity of frothers are mainly due to the ease of adsorption of the molecules of frothers to the surface from the body of a solution.

The relation between the surface pressure and the area occupied by a gram molecule is expressed by a formula, which coincides with that of Schofield and Rideal for higher surface pressure. The least area that a molecule can occupy and the reciprocal of the molecular cohesion in Schofield and Rideal's equation are calculated for each frother.

I. Introduction

There have been many notable contributions on the theoretical aspects of flotation process up to the present time. Of recent notable investigators may be mentioned Wark in Australia, Rebinder, Volkova, Shvedov, Lipetz, Held, Trapeznikov, Lubman, Klyachko and Eigeles in Russia, Gaudin, De Witt and Keck in America and Siedler in Germany. It is to be noted that in recent years the fundamental research works have become markedly active in Russia, but on the contrary it seems that those in Germany are on decline.

It is sure that further progress in flotation process will be made in promoting a more thorough understanding of the principles involved. However, it seems that there are many important and difficult problems to be solved, of which the following may be mentioned: (a) accurate calculation or measurement of the absolute values of the interfacial tension liquid-solid and gas-solid; (b) study of the preferential adsorption of various substances on mineral surfaces; (c) method of removal of adsorbed substances from mineral surfaces; (d) study on molecular films; (e) electron-beam diffraction analysis and surface studies; (f) establishment of the theory of the mechanism of adsorption at mineral surfaces.

In this report surface-tension variation, surface activity, and surface orientation of several pure or commercial frothers at air-water interface have been dealt with.

* The 8th report of the Research Institute of Mineral Dressing and Metallurgy. Some parts of this investigation were already published in Japanese. See *J. Mining Inst. Japan*, 60 (1944), 109-12; 65 (1949), 253-4.

II. Time Variation of Surface Tension of Aqueous Solutions of Frothers

1. *Previous results.* In continuing the preceding experiment⁽¹⁾ it has been found that the surface tension of cineol solutions varies appreciably with time during measurement by the tensiometer. It is considered, therefore, that this fact will have considerable influence on froth characteristics in flotation.

There are a number of literatures on the time variation of surface tension, a brief survey of which may be useful for reference. Pockels⁽²⁾ studied the change of surface tension with time and pointed out that when the fresh surface of a liquid has a higher surface tension than an older one, this must be due to the adsorption of vapours on the surface of liquid and when the freshly formed surface has a smaller tension than the older one the influence of dissolved salts is to be investigated.

Du Nouey⁽³⁾ found that after addition of a substance which lowers surface tension, the immediate drop in surface tension is frequently followed by a rise, which may be either rapid or slow, the final equilibrium value in some cases being practically identical with the original value, which is presumably due to adsorption of active molecules.

Schmidt and Steyer⁽⁴⁾ measured the time which was necessary to establish the final surface tension of pure water to be from 0.004 to 0.009 sec. and to depend upon the temperature, being shorter at higher temperatures and found no such phenomenon for nitrobenzene.

Dhar⁽⁵⁾ reported that hydrophilic colloids such as gelatin and egg albumin, with age decreases in surface tension.

Bigelow and Washburn⁽⁶⁾ undertook the research on the time variation of surface tension in capillary method with solutions of various solutes as sodium oleate, ethyl alcohol, etc., and concluded that the variation is due to a change in the concentration caused by the preferential evaporation of one component of the solution.

Trimble⁽⁷⁾ confirmed the conclusion of Bigelow and Washburn by measuring the capillary rise of solutions as carbon tetra-

chloride-toluene, etc.

Ghosh and Nath⁽⁸⁾ measured the variation in surface tension of a number of dyestuffs with a precision apparatus and classified the compounds in three groups; that is, true solutions where the equilibrium concentration at the surface is reached too rapidly to be measured, solutions containing mainly multi-molecular aggregates where the surface tension changes with time as equilibrium is established, and colloidal solutions where the surface tension varies with time in a somewhat irregular manner.

Doss⁽⁹⁾ found by the surface-pressure technique of Langmuir and Adam that the surface tension of an extended surface of a mol./500 solution of benzopurpurin decreases regularly with time, while the surface tension of a compressed surface increases with time.

Doss and Rao⁽¹⁰⁾ concluded that the method of maximum pull on a ring, by means of a herical silica spring, is not suitable for aging studies.

Bond and Puls⁽¹¹⁾ derived an equation for the change with time of the surface tension of a solution, on the assumption that the delay in reaching equilibrium is due to the time required for the solute to reach the surface and measured the dynamic surface tension for aqueous solutions of soap, alcohols, etc.

Kopaczewski⁽¹²⁾ studied the time changes in surface tension of liquids when stored in the dark in paraffined bottles.

Boutaric and Bertheir⁽¹³⁾ proposed the equation

$$H=L+(H_0-L)e^{-at}, \quad (1)$$

in which H_0 is the measured surface tension, L is the ultimate surface tension, perhaps requiring infinite time to be reached, a is a constant and t is the time that has elapsed since the free surface was formed and observed H_0 during the period of time between 2 and 120 min. for a solution containing between 0.05 and 1.0g. per 1. of saponin in a buffer mixture of HCl and disodium citrate, pH being 4.16.

Nutting, Long and Harkins⁽¹⁴⁾ followed the change with time of the surface tension of solutions of sodium cetyl sulphate and sodium lauryl sulphate in two min. intervals from 3 to 6 hours. In the cetyl sulphate

solutions without added electrolyte at concentrations below 6×10^{-4} N, a rapid fall in surface tension is found followed by a slow fall, linear with time, at the same rate for all solutions. In the lauryl sulphate solutions the initial fall is not so marked and is followed usually by a broad minimum surface tension.

As there are found no literatures on the time-variation of the surface tension of aqueous solutions of cineol, it is intended to investigate this problem in the following experiments.

2. *Equation for the time variation of surface tension of solutions.* After Bigelow and Washburn⁽⁶⁾ it is assumed that the time variation of surface tension is due to a change in the concentration caused by the preferential evaporation of one component of the solution in question.

Let us consider the rate of change of the concentration of an aqueous solution of a surface-active solute. The molecules of the solute are adsorbed at the surface of water, from which they evaporate preferentially.

Suppose that the concentration of the solute in the atmosphere is negligibly small as compared with that at the surface of water, the rate of diffusion of molecules to the surface from the body of solution is not small as compared with that of evaporation, and the area of the surface is constant.

Then the rate of change with time of the concentration at the surface may be expressed by an equation of the form

$$-du/dt = Ku, \quad (2)$$

where u is the surface concentration of the solute, t is the time and K is a constant.

Gibbs⁽¹⁵⁾ introduced the following equation expressing the relation among the quantity u of a solute adsorbed on a unit surface of a solution, the concentration c of the solute and the surface tension H of the solution after thermodynamical considerations:

$$u = -c/RT \cdot dH/dc, \quad (3)$$

where R is the gas constant and T is the absolute temperature.

By combining Gibbs' equation (3) with Szyszkowski's equation (4)⁽¹⁶⁾ written in the form

$$H_0 - H = bH_0 \ln(c/a + 1), \quad (4)$$

where H_0 is the surface tension of pure water, a and b are constants, we get

$$u = bH_0/RT \cdot c/(c+a). \quad (5)$$

Differentiating equation (5) with respect to c ,

$$du/dc = bH_0/RT \cdot a/(c+a)^2, \quad (6)$$

and eliminating u from equations (2), (5) and (6), we get

$$-dc/dt = K/a \cdot c(c+a). \quad (7)$$

By integrating equation (7)

$$t = 1/K \cdot \ln(a/c + 1) + C. \quad (8)$$

When boundary conditions $t = 0$, $c = c_1$ are put in,

$$C = -1/K \cdot \ln(a/c_1 + 1). \quad (9)$$

Consequently, the following equation for the time variation of the concentration of a solution is obtained:

$$t = 1/K \cdot \ln[(a+c)/c \cdot c_1/(a+c_1)]. \quad (10)$$

From equations (4) and (10) the equation for the time variation of the surface tension of a solution of surface-active substance is obtained:

$$H_0 - H = bH_0 \ln[1 - c_1/(a+c_1) - e^{-Kt}] \quad (11)$$

or it may be written in the form:

$$Kt = -\ln[(a+c_1)/c_1] - \ln[1 - e^{(H-H_0)/bH_0}]. \quad (12)$$

That is the relation between t and $\ln[1 - e^{(H-H_0)/bH_0}]$ is expressed by a linear equation.

In the above assumption, if we consider that the rate of diffusion of molecules to the surface from the body of solution is small as compared with that of evaporation from the surface layer, the evaporation will be controlled mainly by the first factor.

In this case the rate of change with time of the concentration of the solution may be put in the form:

$$-dc/dt = Kc \quad (13)$$

By integrating equation (13),

$$t = -1/K \cdot \ln c + C. \quad (14)$$

As $c = c_1$, when $t = 0$,

$$t = 1/K \cdot \ln(c_1/c). \quad (15)$$

This is the equation for the time variation of the concentration of a solution.

From equations (4) and (15), the equation for the time variation of the surface tension

Table 1. Time variation of the surface tension of aqueous solutions of cineol-No. 1.

A: Angle of twist in degree, *c*: Concentration in mol./1,000g. H₂O, *H*: Surface tension in dyne/cm., *R*: Residual, *t*: Time in min.

Temp. of water: 25.1°C, Flow of water: 3.13 cc./sec.

a: 0.005432, *b*: 0.2513, *c*₁: 0.000897, *K*: 0.0121.

No.	<i>t</i>	<i>A</i>	<i>H</i>	<i>H</i> ₀ - <i>H</i>	<i>t</i> _{<i>c</i>}	<i>R</i>
1	18.1	81.8	69.9	2.05	25.9	-7.8
2	20.8	81.8	69.9	2.05	25.9	-5.1
3	24.8	81.9	70.0	1.95	30.3	-5.5
4	27.4	82.0	70.0	1.95	30.3	-2.9
5	34.5	82.2	70.2	1.75	39.6	-5.1
6	40.6	82.1	70.1	1.85	34.8	5.8
7	51.2	82.6	70.5	1.45	55.8	4.6
8	61.3	82.5	70.5	1.45	55.8	5.5
9	68.9	82.7	70.6	1.35	53.5	15.4
10	74.3	82.7	70.6	1.35	53.5	20.8
Average:						7.9

Table 2. Time variation of the surface tension of aqueous solutions of cineol-No. 2.

A: Angle of twist in degree, *c*: Concentration in mol./1,000 g. H₂O, *H*: Surface tension in dyne/cm., *R*: Residual, *t*: Time in min.

Temp. of water: 25.5°C, Flow of water: 3.23 cc./sec.

a: 0.005432, *b*: 0.2513, *c*₁: 0.002063, *K*: 0.00910.

No.	<i>t</i>	<i>A</i>	<i>H</i>	<i>H</i> ₀ - <i>H</i>	<i>t</i> _{<i>c</i>}	<i>R</i>
1	5.3	78.1	66.4	5.5	7.1	-1.8
2	7.8	78.1	66.4	5.5	7.1	0.7
3	11.2	77.9	66.2	5.7	2.6	8.6
4	15.4	78.5	66.7	5.2	14.5	0.9
5	22.1	78.0	66.3	5.6	5.0	17.1
6	25.7	78.2	66.4	5.5	7.1	18.6
7	31.7	78.2	66.4	5.5	7.1	24.6
8	38.0	79.3	67.4	4.5	32.8	5.2
9	46.7	79.1	67.2	4.7	26.9	19.8
10	49.4	79.3	67.4	4.5	32.8	16.6
11	52.3	79.7	67.9	4.0	46.9	5.4
12	56.0	79.6	67.8	4.1	44.3	11.7
13	59.0	79.8	68.0	3.9	50.5	8.5
14	62.4	80.1	68.3	3.6	60.0	2.4
15	66.7	80.0	68.2	3.7	56.6	10.1
16	70.4	80.6	68.7	3.2	74.4	-4.0
17	74.0	80.6	68.7	3.2	74.4	-0.4
18	77.8	81.0	69.0	2.9	85.8	-8.0
19	80.5	81.1	69.1	2.8	90.3	-9.8
20	82.5	80.8	68.9	3.0	82.1	0.4
21	85.3	81.0	69.0	2.9	85.8	-0.5
22	87.8	81.1	69.1	2.8	90.3	-2.5
23	90.5	81.2	69.4	2.5	103.6	-13.1
24	93.4	81.5	69.6	2.3	113.7	-20.3
25	97.1	81.6	69.7	2.2	118.7	-21.6
26	98.7	81.5	69.6	2.3	113.7	-15.0
27	103.1	81.5	69.6	2.8	113.7	-10.6
28	106.2	82.0	70.0	1.9	136.2	-30.0
29	110.3	81.6	69.7	2.2	118.7	-8.4
30	113.3	81.6	69.7	2.2	118.7	-5.4
31	116.1	81.8	69.9	2.0	129.5	-13.4
32	118.0	81.9	70.0	1.9	136.2	-18.2
33	120.3	81.8	69.9	2.0	129.5	-9.2
34	124.7	81.9	70.0	1.9	136.2	-11.5
35	127.5	81.7	69.8	2.1	124.0	3.5
36	129.9	81.7	69.8	2.1	124.0	5.9
37	132.5	81.6	69.7	2.2	118.7	13.8
38	137.1	81.6	69.7	2.2	118.7	18.4
39	141.4	81.8	69.9	2.0	129.5	11.9
Average:						10.5

Table 3. Time variation of the surface tension of aqueous solutions of cineol-No. 3.

A: Angle of twist in degree, *c*: Concentration in mol./1,000g. H₂O, *H*: Surface tension in dyne/cm., *R*: Residual, *t*: Time in min.

Temp. of water: 25.9°C, Flow of water: 3.30cc./sec.

a: 0.005432, *b*: 0.2513, *c*₁: 0.003789, *K*: 0.0128.

No.	<i>t</i>	<i>A</i>	<i>H</i>	<i>H</i> ₀ - <i>H</i>	<i>t</i> _{<i>c</i>}	<i>R</i>
1	5.2	74.2	62.6	9.2	3.9	1.3
2	7.9	74.2	62.6	9.2	3.9	4.0
3	9.8	75.0	63.2	8.6	6.4	2.4
4	12.9	75.0	63.2	8.6	6.4	6.5
5	14.7	75.1	63.3	8.5	11.7	3.0
6	16.6	75.2	63.4	8.4	13.0	3.6
7	17.9	75.6	63.8	8.0	17.6	0.3
8	20.5	75.3	63.5	8.3	14.0	6.5
9	22.7	75.6	63.8	8.0	17.6	5.1
10	24.5	75.8	63.9	7.9	18.9	5.6
11	26.3	76.0	64.1	7.7	21.4	4.9
12	27.8	76.5	64.8	7.0	30.4	-2.6
13	31.1	76.2	64.6	7.2	27.8	3.3
14	34.5	76.6	64.9	6.9	31.9	2.6
15	36.3	77.0	65.3	6.5	37.3	-1.0
16	38.2	76.9	65.2	6.6	36.1	2.1
17	39.9	77.1	65.4	6.4	39.0	0.9
18	41.8	77.2	65.4	6.4	39.0	2.8
19	43.9	77.5	65.7	6.1	43.3	0.6
20	45.8	77.5	65.7	6.1	43.3	2.5
21	47.9	77.5	65.7	6.1	43.3	4.6
22	51.3	77.9	66.0	5.8	48.0	3.3
23	54.5	77.9	66.0	5.8	48.0	6.5
24	57.7	78.1	66.2	5.6	51.1	-6.6
25	60.4	78.2	66.3	5.5	52.6	7.8
26	64.3	78.6	66.6	5.2	57.9	6.4
27	67.4	78.9	66.9	4.9	63.2	4.2
28	69.8	79.0	67.0	4.8	65.0	4.8
29	73.0	79.0	67.0	4.8	65.0	8.0
30	76.3	79.5	67.7	4.1	79.1	-2.8
31	78.8	79.8	68.0	3.8	85.5	-6.7
32	81.3	79.8	68.0	3.8	85.5	-4.2
33	85.3	79.7	67.9	3.9	83.5	1.8
34	88.7	80.0	68.2	3.6	90.3	-1.6
35	90.5	80.1	68.2	3.6	90.3	0.2
36	93.7	80.1	68.2	3.6	90.3	3.4
37	96.2	80.2	68.3	3.5	92.9	3.3
38	99.5	80.3	68.4	3.4	95.1	4.4
39	103.1	80.4	68.5	3.3	97.8	5.3
40	105.7	81.0	69.0	2.8	111.9	-6.2
41	108.1	80.8	68.8	3.0	106.0	2.1
42	111.6	81.0	69.0	2.8	111.9	-0.3
43	114.3	81.0	69.0	2.8	111.9	2.4
44	118.1	81.0	69.0	2.8	111.9	6.2
45	122.2	81.1	69.1	2.7	114.8	7.4
46	128.4	81.5	69.6	2.2	132.1	-3.7
47	132.1	81.7	69.8	2.0	139.8	-7.7
48	135.5	81.8	69.9	1.9	144.6	-9.1
49	139.0	81.9	70.0	1.8	149.0	-10.0
50	141.5	82.0	70.1	1.7	145.8	-4.3
51	145.0	82.0	70.1	1.7	145.8	-0.8
52	150.1	82.1	70.2	1.6	158.6	-8.5
53	155.2	82.2	70.3	1.5	162.9	-7.7
54	159.4	82.2	70.3	1.5	162.9	-3.5
55	166.3	82.4	70.4	1.4	169.5	-3.2
56	175.3	82.7	70.7	1.1	189.5	-14.2
57	180.3	82.7	70.7	1.1	189.5	-9.2
58	185.8	82.7	70.7	1.1	189.5	-3.7
59	190.5	82.8	70.8	1.0	196.0	-5.5
60	194.7	82.9	70.8	1.0	196.0	-1.3
61	198.3	83.0	70.9	0.9	204.7	-6.4
62	200.4	83.1	71.0	0.8	214.5	-14.1
63	203.1	83.0	70.9	0.9	204.7	-1.6
64	206.0	83.0	70.9	0.9	204.7	1.3
Average:						4.5

Table 4. Time variation of the surface tension of aqueous solutions of cineol—No. 4.

A : Angle of twist in degree, c : Concentration in mol./1,000 g H_2O , H : Surface tension in dyne/cm.,
 R : Residual, t : Time in min. Temp. of water: 25.1°C, Flow of water: 3.26 cc./sec.
 a : 0.005432, b : 0.2513, c_1 : 0.007104, K : 0.0113.

No.	t	A	H	$H_0 - H$	t_c	R	No.	t	A	H	$H_0 - H$	t_c	R
1	5.0	68.7	57.5	14.5	5.4	-0.4	39	101.3	77.6	65.8	6.2	102.9	-1.6
2	9.7	69.0	57.8	14.2	8.1	1.7	40	103.8	77.4	65.6	6.4	99.5	4.3
3	13.7	70.0	58.7	13.3	16.4	-2.7	41	106.9	77.9	66.2	5.8	109.8	-2.9
4	15.8	70.0	58.7	13.3	16.4	-0.6	42	111.1	78.1	66.3	5.7	111.5	-0.4
5	17.9	70.1	58.8	13.2	17.3	0.6	43	116.8	78.3	66.5	5.5	115.4	1.4
6	20.8	70.3	59.0	13.0	19.2	1.6	44	118.5	78.7	66.8	5.2	121.1	-2.6
7	23.3	70.8	59.5	12.5	24.0	-0.7	45	121.1	78.4	66.6	5.4	117.2	3.9
8	25.8	71.1	59.7	12.3	26.0	-0.2	46	125.1	79.0	67.1	4.9	127.1	-2.0
9	28.7	71.2	59.8	12.2	27.0	1.7	47	128.0	79.0	67.1	4.9	127.1	0.9
10	32.5	71.7	60.3	11.7	32.0	0.5	48	131.1	79.0	67.1	4.9	127.1	4.0
11	35.9	72.0	60.6	11.4	35.2	0.7	49	135.2	79.4	67.4	4.6	133.3	1.9
12	37.3	72.1	60.7	11.3	36.2	1.1	50	140.8	79.3	67.4	4.6	133.3	7.5
13	40.7	72.8	61.3	10.7	42.6	-1.9	51	146.6	80.1	68.2	3.8	152.3	-5.7
14	42.2	73.0	61.4	10.6	43.7	-1.5	52	150.5	80.5	68.6	3.4	163.1	-12.6
15	44.8	73.0	61.4	10.6	43.7	1.1	53	161.0	80.5	68.6	3.4	163.1	-2.1
16	46.5	73.2	61.7	10.3	47.0	-0.5	54	165.3	80.8	68.8	3.2	169.3	-4.0
17	48.5	73.2	61.7	10.3	47.0	1.5	55	168.2	80.9	68.9	3.1	172.1	-3.9
18	50.8	73.8	62.2	9.8	52.8	-2.0	56	173.9	81.0	69.0	3.0	175.5	-1.6
19	53.8	73.8	62.2	9.8	52.8	1.0	57	182.8	81.2	69.2	2.8	182.1	0.7
20	55.3	74.1	62.5	9.5	56.3	-1.0	58	189.6	81.4	69.6	2.4	196.5	-6.9
21	57.5	74.1	62.5	9.5	56.3	1.2	59	192.3	81.6	69.7	2.3	201.0	-8.7
22	59.8	74.2	62.6	9.4	57.6	2.2	60	197.2	81.6	69.7	2.3	200.0	-2.8
23	60.3	74.4	62.7	9.3	58.8	1.5	61	203.0	81.9	70.0	2.0	213.6	-10.6
24	62.9	74.6	63.0	9.0	62.5	0.4	62	211.7	82.1	70.2	1.8	224.1	-12.4
25	63.5	74.8	63.2	8.8	65.1	-1.6	63	216.5	82.1	70.2	1.8	224.1	-7.6
26	66.8	75.0	63.4	8.6	67.7	-0.9	64	222.3	82.1	70.2	1.8	224.1	-1.8
27	70.0	75.4	63.7	8.3	71.5	-1.5	65	228.2	82.2	70.2	1.8	224.1	4.1
28	75.5	75.6	63.9	8.1	74.3	1.2	66	235.3	82.3	70.3	1.7	229.3	6.0
29	77.1	75.7	64.0	8.0	75.5	1.6	67	240.1	82.5	70.5	1.5	240.9	-0.8
30	80.3	76.0	64.2	7.8	78.3	2.0	68	245.5	82.6	70.6	1.4	247.3	-1.8
31	84.1	76.2	64.6	7.4	84.2	-0.1	69	251.1	82.6	70.6	1.4	247.3	3.8
32	86.3	76.7	65.0	7.0	90.0	-3.7	70	258.7	82.7	70.7	1.3	254.2	4.5
33	89.5	76.5	64.8	7.2	87.1	2.4	71	266.8	82.5	70.5	1.5	240.9	25.9
34	91.6	76.7	65.0	7.0	90.0	1.6	72	271.0	82.8	70.8	1.2	261.7	9.3
35	92.1	77.1	65.4	6.6	96.4	-4.3	73	276.0	82.8	70.8	1.2	261.7	14.3
36	95.8	76.9	65.2	6.8	92.5	3.3	74	279.7	83.0	70.9	1.1	269.8	9.9
37	97.6	77.2	65.4	6.6	96.4	1.2	75	282.0	82.9	70.8	1.2	260.4	21.9
38	99.6	77.5	65.7	6.3	101.2	-1.6							
												Average :	3.7

of a solution of surface-active substance is obtained:

$$H_0 - H = bH_0 \ln(c_1/a \cdot e^{-Kt} + 1), \quad (16)$$

or,

$$Kt = \ln(c_1/a) - \ln[e^{(H_0 - H)/bH_0} - 1]. \quad (17)$$

That is t is in a linear relation with $\ln[e^{(H_0 - H)/bH_0} - 1]$.

3. *Experimental results.* The sample of cineol is of the Shiono Chemical Industrial Works' make.* Its boiling point is measured to be 175.8°C (760 mm.).** After Earle⁽¹⁹⁾ the solubility of cineol in water is 0.35% in weight at 21°C.

Tables 1-4 show the results of the measurement of the time variation of the surface

tension of cineol solutions of various initial concentrations. The values of the initial surface tension of cineol solutions are obtained by the numerical extrapolation of the surface tension-time curves and the constants a and b in Szyszkowski's equation are calculated from the relation between the concentration and the surface tension of solutions in the initial state, that is $t = 0$, as shown in Table 5. The average residual of initial surface pressure is but 0.3 dyne/cm.

The results shown in Tables 1-4 indicate that the time t is not in a linear relation with $\ln[1 - e^{(H - H_0)/bH_0}]$ but with $\ln[e^{(H_0 - H)/bH_0} - 1]$ as shown in Fig. 1. That is, the second theoretical equation (16) holds true, but the first one (11) does not. Hence it may be concluded that the rate of evaporation of cineol is mainly controlled by the rate of

* By courtesy of the same works.

** The boiling point of cineol given in literatures: 176°C,⁽¹⁷⁾ 173-176°C after Penfold, 175-177°C after Wallach and 174.4°C after Simonsen.⁽¹⁸⁾

Table 5. Surface tension of aqueous solutions of cineol.

a : 0.005432 mol./kg. H_2O , 0.8373 g./kg. H_2O , b : 0.2513.

Temperature t , °C	Water flow V , cc./sec.	Concentration c		Surface tension H , dyne/cm.	Surface tension of water H_0 , dyne/cm.	Surface pressure, dyne/cm.		Residual R
		mol./kg. H_2O	g./kg. H_2O			F	F_c	
25.1	3.13	0.000897	0.1382	69.57	71.95	2.38	2.76	-0.38
25.5	3.23	0.002063	0.3180	66.27	71.90	5.63	5.82	-0.19
25.9	3.30	0.003789	0.5841	61.99	71.84	9.85	6.56	0.29
25.1	3.26	0.007104	1.095	56.60	71.95	15.35	15.07	0.28
Average :								0.29

diffusion of the molecules of cineol to the surface from the body of solution.

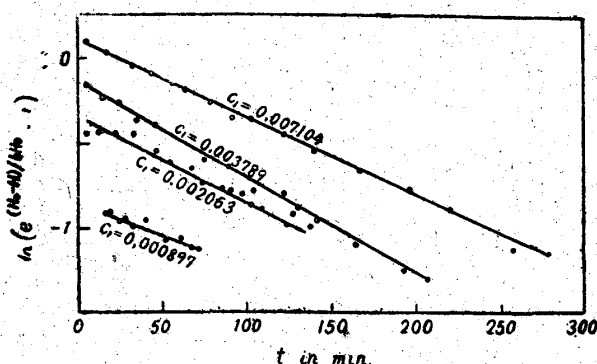


Fig. 1. Time variation of surface tension of aqueous solutions of cineol.

The constant K is calculated by putting the values of the initial concentration c_1 and the constants a and b obtained above in the equation (16). The value of K varies but little with experiment. It ranges from 0.00910 to 0.0128 and the average is 0.0113 at the average temperature of 25.4°C. By substituting the value of K thus computed in (15), the time variation of the concentration of a solution may be followed.

The average residual between the time t measured and that calculated ranges from 3.6 to 10.5 min. for the duration of experiment of 282 min. and 141 min. respectively, which is reasonably small for such kind of experiments.

According to Arrhenius⁽²⁰⁾ the constant K may be put in the form

$$K = ke^{-E/RT}, \quad (18)$$

where E is the energy of activation, and k is a new constant characteristic of the properties of frothers and the conditions of experiments.

In conclusion the equation for the time variation of the surface tension of aqueous solutions of surface-active substances which

are apt to volatilize, may be written in the form:

$$H_0 - H = bH_0 \ln(c_1/a \cdot e^{-kte^{-E/RT}} + 1). \quad (19)$$

III. Surface Activity of Frothers

The surface activity of surface-active substances may be conveniently defined as the slope of the surface tension-concentration curve at zero concentration. In terms of Szyszkowski's equation the surface activity at any concentration is expressed as follows:

$$A = -dH/dc = bH_0/(c+a). \quad (20)$$

In zero concentration, it becomes

$$A_0 = (-dH/dc)_0 = bH_0/a. \quad (21)$$

That is, the surface activity, defined as above, is proportional to b/a . The constant a varies widely, but the constant b varies but little from frother to frother. For the sake of convenience, the constant a is called the concentration coefficient, b the surface tension coefficient and b/a the activity coefficient according to their respective positions in equation (4).

The pure frothers are arranged in the order of decreasing activity coefficient in Table 6. If we take the activity coefficient of meta-cresol as a unit, those of other frothers are: α -terpineol 24.4, d-camphor 9.46, cineol 5.26, and iso-amyl alcohol 1.76 in the basis of kg. H_2O /mol. and 17.1, 6.73, 3.69, and 2.16 respectively in the basis of kg. H_2O /g. It is clear that α -terpineol is exceedingly surface active.

The surface activities of citronella oils are shown in Table 7. Both the activity coefficients are very large contrary to expectations and 78.7 for sulphuric-acid treated one and 19.8 for oxidized one in the basis of kg. H_2O /g. taking meta-cresol as a unit.

Table 6. Surface activities of pure frothers at air-water interface.

Frothers	Molecular weight	a , mol./kg. H ₂ O	a , g./kg. H ₂ O	b	b/a , kg. H ₂ O/mol.	b/a , kg. H ₂ O/g.
α -terpineol	154.14	0.0007043	0.1086	0.1513	214.8	1.39
d-camphor	152.13	0.001751	0.2664	0.1456	83.15	0.547
Cineol	154.14	0.005432	0.8373	0.2513	46.26	0.300
Iso-amyl alcohol	88.10	0.0120	1.057	0.186	15.50	0.176
Meta-cresol	108.06	0.02401	2.595	0.2112	8.792	0.0813

Table 7. Surface activities of treated citronella oils at air-water interface.

Citronella oils	t , °C	V , cc./sec.	a , g./kg. H ₂ O	b	b/a , kg. H ₂ O/g.
Sulphuric-acid treated	28.8	3.22	0.02085	0.1334	6.40
Oxidized	28.4	3.26	0.06284	0.1013	1.61

Table 8. Surface activities of commercial frothers at air-water interface.

Frothers	t , °C	V , cc./sec.	a , g./kg. H ₂ O	b	b/a , kg. H ₂ O/g.
Takasago's No. 5 flotation oil	27.5	3.25	0.147	0.142	0.966
Yarmor "F" S.D. pine oil	25.7	3.23	0.2460	0.1898	0.772
Shiono's No. 1 flotation oil	26.5	3.25	4.10	3.12	0.761
Du Pont's B-22 frother	26.4	3.25	0.5464	0.1616	0.296

The surface activities of commercial frothers are shown in the order of decreasing activity in Table 8. The activity coefficient of Takasago's No. 5 oil is the greatest and those of Yarmor "F" S. D. oil and Shiono's No. 1 oil follow it and these three rank between that of α -terpineol and of d-camphor. That of Du Pont's B-22 frother is the least contrary to expectations, and ranks between that of cineol and of iso-amyl alcohol. The activity coefficients in the basis of kg. H₂O/g., taking meta-cresol as a unit, are: Takasago's No. 5 oil 11.9, Yarmor "F" S. D. oil 9.50, Shiono's No. 1 oil 9.37, and Du Pont's B-22 frother 3.64.

IV. Surface Tension and Surface Concentration

By eliminating the concentration c in Szyszkowski's equation (4) with the equation (5), the surface-tension lowering, that is to say, the surface pressure F is expressed in terms of the surface concentration u .

$$F = H_0 - H = -bH_0 \ln(1 - uRT/bH_0). \quad (22)$$

Unlike Szyszkowski's original equation, the new equation expresses directly the relation between the surface pressure and the surface

concentration.

By differentiating the above equation with respect to surface concentration, the surface activity in terms of the latter is obtained:

$$A_u = -dH/du = bH_0/(bH_0/RT - u). \quad (23)$$

In the above equation there is not found the constant a , that is, only b , the surface tension coefficient, is significant in this case. As already shown, the values of b vary but little, namely, which range from 0.146 to 0.211 for pure frothers, from 0.101 to 0.133 for citronella oils and from 0.142 to 3.12 for commercial frothers. Only Shiono's No. 1 has a comparatively high value of b .

From the above fact it is clear that the differences in the surface activity of frothers are mainly due to the ease of adsorption of the molecules of frothers to the surface from the body of a solution. The surface pressure exerted by the surface film of the same surface concentration does not vary so much with the kind of frothers.

At zero surface concentration, the surface activity A_u reduces to

$$A_{u=0} = RT, \quad (24)$$

that is, it is a constant irrespective of the kind of frothers.

V. Surface Orientation of Frother Molecules

From equation (5), the area occupied by a gram molecule of a frother adsorbed on the surface may be calculated:

$$S = 1/u = RT/bH_0 \cdot (c+a)/c. \quad (25)$$

If the adsorbed molecules constitute a monomolecular layer, the area occupied by a molecule may be computed by dividing the area S by Avogadro-Loschmidt's number N .

$$N = 6.064 \times 10^{23},^{(21)}$$

that is

$$S/N = 1/Nu = RT/bH_0N \cdot (c+a)/c. \quad (26)$$

In (25), let the concentration of the solute be equal to the concentration coefficient, that is, $c = a$, then the equation reduces to the form,

$$u_a = bH_0/2RT. \quad (27)$$

Therefore, the concentration coefficient a corresponds to the concentration of a solute where the surface concentration of the solute

has a definite value expressed by the above equation.

Table 9 shows the values of u_a for various frothers examined hitherto. The frothers have the value of u_a between 1.47×10^{-10} and 3.65×10^{-10} moles per cm.^2 except Shiono's No. 1 flotation oil, which has an abnormally large value of 45.3×10^{-10} moles per cm.^2 . The corresponding area per molecule ranges from 112.1 to 45.2 \AA^2 except 3.64 \AA^2 for Shiono's No. 1 oil.

As the molecular weight of citronella oils and of commercial frothers are not measured, the values of the surface concentration and the area per molecule shown above have only the imaginary meaning.

The relation between the surface pressure F and the area occupied by a gram molecule is expressed by a $FS-F$ curve. From equations (25) and (4),

$$FS/RT = Fe^{F/bH_0}/bH_0(e^{F/bH_0} - 1). \quad (28)$$

According to the equation, the $FS-F$ curve at first turns gently upwards where F is

Table 9. Surface concentration (u_a) and area per molecule (S_a) of aqueous solutions of frothers when concentration is equal to concentration coefficient.

$N: 6.064 \cdot 10^{23}$. $R: 8.3136 \cdot 10^7$ ergs/degree·mol. $T: 273.18 + 25 = 298.18$. $H_0: 71.97$ dynes/cm.

Frothers	b	u_a , mol./cm. ² · 10 ⁻¹⁰	S_a/N , \AA^2
α -terpineol	0.1513	2.20	75.1
d-camphor	0.1456	2.12	78.0
Cineol	0.2513	3.65	45.2
Iso-amyl alcohol	0.186	2.70	61.1
Meta-cresol	0.2112	3.07	53.8
Sulphuric-acid treated citronella oil	0.1334	1.94	85.2
Oxidized citronella oil	0.1013	1.47	112.1
Takasago's No. 5 flotation oil	0.142	2.06	80.0
Yarmor "F" S. D. pine oil	0.1898	2.76	59.9
Du Pont's B-22 frother	0.1616	2.35	70.3
Shiono's No. 1 flotation oil	3.12	45.3	3.64

Table 10. Least area occupied by a gram molecule (B) and reciprocal of lateral molecular cohesion (α) of frothers at air-water interface.

Frothers	B , cm. ² per mol. · 10 ⁹	B/N , \AA^2 per molecule	α	Ratio of area per molecule S_a/B
α -terpineol	1.82	30.0	0.74	2.50
d-camphor	1.66	27.4	0.90	2.85
Cineol	0.76	13.1	0.99	3.45
Iso-amyl alcohol	1.30	21.4	0.87	2.86
Meta-cresol	1.13	18.6	0.92	2.89
Sulphuric acid-treated citronella oil	2.32	38.2	0.46	2.23
Oxidized citronella oil	2.29	37.7	0.91	2.97
Takasago's No. 5 flotation oil	1.78	29.3	0.84	2.73
Yamor "F" S. D. pine oil	1.40	23.1	0.75	2.59
Du Pont's B-22 frother	1.56	25.8	0.85	2.72
Shiono's No. 1 flotation oil	0.116	1.92	0.98	1.90

small and then rises straight diagonally upwards as F becomes large.

If we put $F = 0$ in the above equation,

$$FS/RT = 0/0, \quad (29)$$

that is, it reduces itself to an indeterminate form. But if we differentiate both the numerator and denominator of the right-hand term of (28) and put $F \rightarrow 0$,

$$\lim_{F \rightarrow 0} FS/RT = \lim_{F \rightarrow 0} (e^{F/bH_0} + F/bH_0 \cdot e^{F/bH_0}) / e^{F/bH_0} = 1, \quad (30)$$

where the state of molecules in the adsorbed layer approaches to that of a perfect gas. In this equation the value of FS/RT does not become smaller than 1, that is, the equation has no part turning downwards below the F -axis, where $FS/RT = 1$. Hence the equation is applicable to the molecules displaying gaseous state in the adsorbed layer.

The straight part of this equation is expressed by the equation of Schofield and Rideal.⁽²²⁾

$$FS/RT = FB/RT + x, \quad (31)$$

where B is the least area that a gram molecule can occupy, $1/x$ is the quantity relating to the degree of cohesion of molecules, and the smaller x is, the larger the cohesion is.

The value of B and x are calculated for frothers tested and shown in Table 10. The value of B/N ranges from 13.1 Å² to 38.2 Å² except 1.92 Å² for Shiono's No. 1 oil. The value of x ranges from 0.46 to 0.99 for all frothers tested. The ratio of the area S_a occupied by a molecule when the concentration c is equal to a to the least area B ranges from 1.90 to 3.45 and the average is 2.70.

Summary

(1) The time variation of surface tension due to the change in concentration caused by the preferential evaporation of one component of a solution is theoretically considered and two equations are introduced according to the assumption whether or not the rate of diffusion of molecules to the surface from the body of solution is small as compared with that of evaporation.

(2) It is verified experimentally that one of the equations, in which the rate of dif-

fusion of molecules to the surface from the body of solution is assumed to be small as compared with that of evaporation, holds good in the aqueous solutions of cineol.

$$H_0 - H = bH_0 \ln (c_1/a \cdot e^{-kte^{-E/RT}} + 1),$$

where H is the surface tension of solution, H_0 is that of pure water, t is the time, c_1 is the initial concentration, k is the time constant, a is the concentration coefficient, b is the surface tension coefficient, E is the energy of activation, R is the gas constant and T is the absolute temperature.

(3) Finding the value of K by the surface-tension measurement, the time variation of the concentration of a solution may be calculated from the equation

$$t = 1/K \cdot \ln (c_1/c),$$

where the constant K is expressed as

$$K = ke^{-E/RT}.$$

(4) The activity coefficients of pure frothers at air-water interface are: α -terpineol 1.4, d-camphor 0.55, cineol 0.3, iso-amyl alcohol 0.18 and meta-cresol 0.08 kg. H₂O/g. The activity coefficients of citronella oils are very large. Among the commercial frothers tested, the activity coefficient of Takasago's No. 5 oil is the greatest and those of Yarmor "F" S. D. pine oil, and Shiono's No. 1 oil follow it and these three rank between that of α -terpineol and of d-camphor. That of Du Pont's B-22 frother is the least and ranks between that of cineol and of iso-amyl alcohol.

(5) The relation between the surface pressure F and the surface concentration u is expressed as follows:

$$F = H_0 - H = -bH_0 \ln (1 - uRT/bH_0).$$

In this equation only the constant b is significant. As it varies but little with frothers, the differences in the surface activity of frothers are considered to be mainly due to the ease of adsorption of the molecules of frothers to the surface from the body of a solution.

(6) The relation between the surface pressure and the area S occupied by a gram molecule is expressed as follows:

$$FS/RT = Fe^{F/bH_0}/bH_0(e^{F/bH_0} - 1).$$

(7) The least area B that a gram molecule can occupy and the reciprocal of the

molecular cohesion α in Schofield and Rideal's equation are calculated for each frother. The least area that a molecule can occupy ranges from 1.9 Å² to 38.2 Å² and the value of α ranges from 0.46 to 0.99. The ratio of the area occupied by a molecule when the concentration is equal to α to the least area that a molecule can occupy ranges from 1.9 to 3.5, the average being 2.7.

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