

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE ACTIVITY COEFFICIENTS AND THE ADSORPTION OF ORGANIC SOLUTES. I. NORMAL BUTYL ALCOHOL IN AQUEOUS SOLUTION BY THE FREEZING POINT METHOD

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I. Introduction

Since, when this work was begun, no determinations of the activity coefficients of organic solutes in dilute solution had been made, it seemed important to determine the activities for at least one typical organic solute. Since the activity coefficients are essential for the calculation of the adsorption in the surface of the solution, it was advisable to choose a substance for whose aqueous solutions the surface tension values are known.

The substance used, *n*-butyl alcohol, has the further advantage that it can be purified with relative ease.

In the more concentrated solutions (0.25 molal and above) the results may be compared with those of Jones and Bury¹ on the organic acids, including butyric acid.

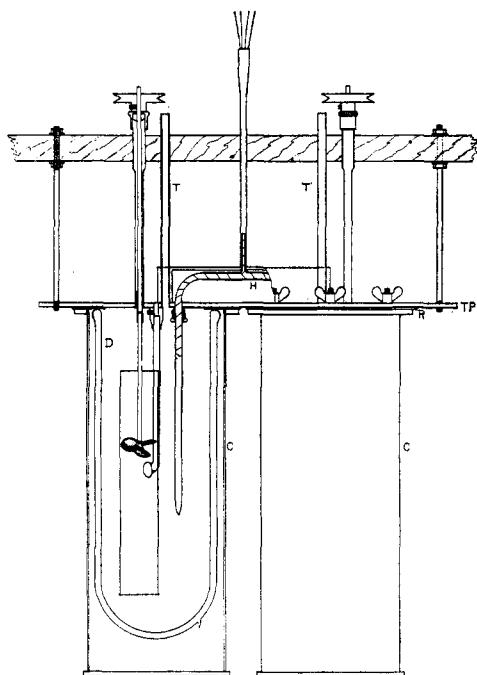


Fig. 1.

junctions each, was used for the determination of the temperature difference between ice-water in one Dewar, and ice-solution in the other. Five No. 30 double silk covered constantan wires in parallel were soldered to a single No. 35 double silk covered copper

II. Freezing Point Apparatus

The freezing point apparatus (Fig. 1) is a modification of that used by Adams² and by Harkins and Hall,³ and resembles that of Randall and Vanselow.⁴ Two one-liter Dewar vessels (D) are suspended from a gold-plated brass plate (TP), each in a brass cylinder (C). When in use these brass cylinders were kept immersed in ice in a metal box, which was well insulated thermally by wool felt.

A 24-junction copper-constantan thermel, made in halves of twelve

¹ Jones and Bury, *Phil. Mag.*, [7] 4, 841 (1927).

² Adams, *THIS JOURNAL*, 37, 481 (1915).

³ Hall and Harkins, *ibid.*, 38, 2658 (1916).

⁴ Randall and Vanselow, *ibid.*, 46, 2418 (1924).

wire. Only extremely uniform constantan wire, as tested by the method of White,⁵ was used. The dried thermel was made air tight and waterproof. The equation for the potential difference between its ends is: $E = 957.10 t - 1.1646 t^2 + 0.00115 t^3$ ($t = ^\circ\text{C}.$). Its performance was tested by the determination of the lowering of the freezing point produced by various small amounts of mannite in water, as was done by Hall and Harkins.

A Zeiss laboratory type interferometer, with an all glass 4-cm. cell, and a 2-cm. and an 8-cm. cell, was used to determine the concentration of the solutions. The interferometer was inclosed in a long thermostat kept at $25 \pm 0.01^\circ$. With the 4-cm. cell one interferometer scale division corresponds to approximately 0.00006 molal *n*-butyl alcohol. For the most dilute solutions the 8-cm. cell was used.

III. Preparation of Materials

The *n*-butyl alcohol was Eastman's best grade. It was first treated with sodium bisulfite. Then it was refluxed with 10% sodium hydroxide for four hours, the alcohol separated from the aqueous layer and washed several times with water to free the alcohol from the base. The remaining base was neutralized with hydrochloric acid, lime was added and the mixture allowed to stand overnight. The partly dried alcohol was again treated with freshly heated lime and refluxed for three hours. The third treatment with lime removed the last traces of water and the alcohol was distilled from the lime and collected in fractions. The alcohol was fractionated twice more, the first time from a distilling column 40 cm. long and finally from a more effective column.

The latter distilling apparatus consisted of a one-liter distilling bulb connected to the fractionating column by a ground-glass joint. The column was 1.6 meters tall and 28 mm. in diameter, and was filled with 6-mm. glass tubing cut in 6-mm. lengths. A layer of sheet asbestos was wrapped around the column, then No. 21 B. and S. gage nichrome wire, five to six turns to the inch, was wrapped over the asbestos. The windings were now covered with a single tightly wrapped layer of asbestos cord. When the heater coil was connected to the 110-volt circuit through a rheostat, the temperature could be controlled so that it just counteracted the heat lost by the vapors in mounting the column. At the top of the column, a small but very efficient condenser was connected by means of a side arm. The ratio of reflux to distillate could be controlled⁶ by means of a capillary stopcock connected to the side arm. The *n*-butyl alcohol obtained boiled at 117.70 to 117.74° (corrected).

The ice used in the determinations was frozen in the following manner. Distilled water was placed in a heavily nickel-plated copper vessel, 5 by 51 cm. at the bottom, 7.6 by 51 cm. at the top and 41 cm. high, and boiled for thirty minutes to remove the dissolved air. The tight fitting cover was then placed on the vessel, which was immersed in an ice and salt mixture to freeze. Solutions were made with distilled water that had just been boiled and cooled.

The problem of the air dissolved in the water and the solutions was made difficult in this case since the solute is volatile. The removal of the dissolved air by evacuation of the freezing point apparatus as used by Randall and Vanselow did not give a stable condition of equilibrium. After evacuating for thirty to sixty minutes, the water and the solution both being practically free from dissolved air at the outset, air was admitted through a soda lime tube and after twenty to thirty minutes, readings were taken. The temperature rose in every case and continued to rise slowly for a period of two to three hours, equilibrium never being reached. The method of saturating the solutions with air as used by Rodebush and Hovorka⁷ was not applicable, for the solubility of air in the

⁵ White, *THIS JOURNAL*, **36**, 2292 (1914).

⁶ Lovelace, *Ind. Eng. Chem.*, **18**, 826 (1926).

⁷ Rodebush and Hovorka, *THIS JOURNAL*, **47**, 1617 (1925).

solutions is different from that in water, especially in the more concentrated solutions. Rodebush and Hovorka⁷ make the statement that for salt solutions any error which might arise from this cause is less than the experimental error for solutions of 0.01 molal concentration. The method of removing dissolved air at the outset was adopted as the most advisable procedure.

IV. Experimental Procedure

The distilled water ice was cracked by crushing it through an iron grating. The finely divided ice was removed, leaving pieces from 7 to 10 mm. in diameter. The cracked ice was washed thoroughly with distilled water and finally twice with the distilled water that was used in making the solutions. Approximately 400 g. of ice was placed in each Dewar vessel and boiled distilled water was added so that the surface would be just 4 mm. above the edge of the stirrer tube. The top was placed in position and the apparatus placed in the ice thermostat. The stirrers were started and after about two hours readings were taken until no change in temperature was noted, thus showing that equilibrium had been established. In the meantime, the solution to be used was placed in an ice and salt mixture, where it was allowed to remain until ice started to freeze out. The water in the right-hand Dewar vessel was removed by suction and the solution was added to replace it. Stirring was continued for thirty to sixty minutes before readings on the potentiometer were taken. Thereafter, readings were taken every five minutes until four or five readings showed that equilibrium had been established. A sample of the solution was removed by suction directly into a 100-cc. volumetric flask. Ice water was added to replace the solution removed. By continuing in this manner, it was possible to make the determinations for as many as six to eight different concentrations in a day. As soon as the solutions were removed from the freezing point apparatus, they were brought to the correct temperature and their concentrations determined in the interferometer, thus avoiding any chance for evaporation or change in concentration due to any other cause. The more concentrated solutions were analyzed in two ways. First, they were checked against a solution of approximately the same concentration. Then, they were diluted by weight to a concentration around 0.04 to 0.05 molal and compared against the water used in making up the solutions.

V. Method of Calculation

The method of calculation of the activities is that given by Lewis and Randall.⁸ The equation for the activity of the solute is

$$d \ln a_2 = \frac{d\vartheta}{\lambda m} + 0.00057 \frac{\vartheta d\vartheta}{m} \quad (1)$$

In order to integrate the equation use is made of the quantity j which is defined by the equation

$$j = 1 - \frac{\vartheta}{\lambda m} \quad (2)$$

which, when differentiated, gives

$$\frac{d\vartheta}{\lambda m} - \frac{\vartheta dm}{\lambda m^2} = -dj \quad (3)$$

Substituting the value of ϑ/m derived from Equation 2 in Equation 3 and rearranging

⁸ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," 1st ed., McGraw-Hill Book Co., Inc., New York, 1923, p. 286.

$$\frac{d\vartheta}{\lambda m} = (1 - j) d \ln m - dj \quad (4)$$

Substituting in Equation 1 and subtracting $d \ln m$ from both sides

$$d \ln \frac{a_2}{m} = -j d \ln m - dj + 0.00057 \frac{\vartheta d\vartheta}{m} \quad (5)$$

Integrating from infinite dilution up to a given molality

$$\ln \frac{a_2}{m} = \int_0^m -j d \ln m - j + 0.00057 \int_0^m \frac{\vartheta}{m} d\vartheta \quad (6)$$

By means of the appropriate graphs, the area under the curves is ascertained and thence the activities.

VI. Discussion of Results

In Table I are given the freezing points for the different concentrations of *n*-butyl alcohol. The third column gives the molal freezing point lowering ϑ/m . In the fourth and fifth columns are, respectively, the values of j and j/m , while the activities are found in the last column. The values of j/m were obtained from a smooth curve of a plot of j/m against the molality. A graph of the freezing point lowering ϑ/m against the molalities m is shown in Fig. 2.

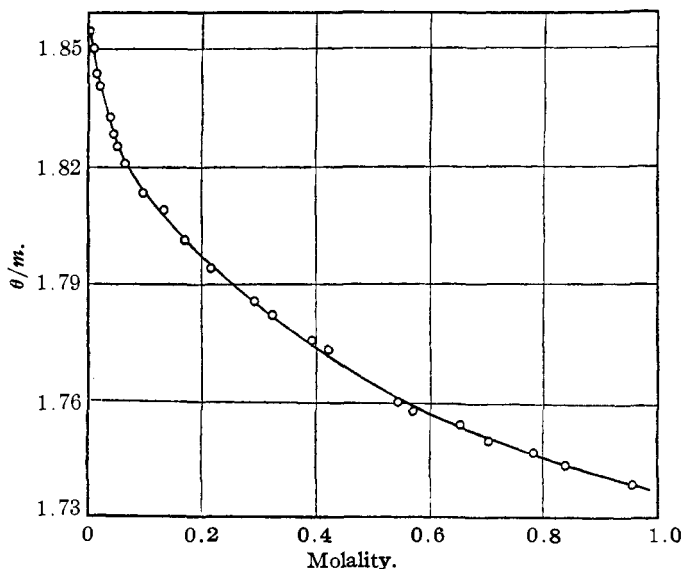


Fig. 2.—Molal freezing point lowering for *n*-butyl alcohol in water.

In Table II, the values of the activity coefficients are given for rounded values of the concentration. The values of the two integrals and $-j$ of Equation 6 are also given. The integral $\int_0^m -j d \ln m$ is designated as A .

TABLE I
 LOWERING OF THE FREEZING POINT (ϑ) PRODUCED BY *n*-BUTYL ALCOHOL OF MOLALITY
 m = Moles per 1000 g. of Water

m	ϑ	ϑ/m	j	j/m (interpolated)	a_2
0.95555	1.66128	1.7385	0.06428	0.0673	0.78711
.83881	1.46253	1.7436	.06158	.0725	.69802
.78227	1.26659	1.7469	.05932	.0760	.65472
.70353	1.23100	1.7497	.05830	.0804	.59362
.65318	1.14570	1.7540	.05595	.0842	.55428
.57148	1.00432	1.7574	.05416	.0916	.48982
.54338	0.95622	1.7598	.05287	.0941	.46748
.41966	.74425	1.7734	.04551	.1084	.36548
.39195	.69606	1.7759	.04420	.1128	.34492
.32265	.57504	1.7822	.04077	.1264	.28731
.29236	.52206	1.7857	.03892	.1331	.26187
.21532	.38634	1.7942	.03429	.1593	.19733
.16774	.30221	1.8016	.03032	.1837	.15452
.16409	.29556	1.8012	.03059	.1864	.15133
.13356	.24161	1.8091	.02636	.2076	.12434
.09748	.17680	1.8136	.02385	.2447	.09191
.08067	.14679	1.8195	.02062	.2686	.07657
.06894	.12554	1.8211	.01975	.2865	.06578
.06680	.12166	1.8211	.01986	.2928	.06381
.05206	.09505	1.8257	.01739	.3250	.05011
.05123	.09359	1.8269	.01674	.3268	.04933
.04631	.08470	1.8288	.01572	.3394	.04472
.03982	.07300	1.8332	.01430	.3590	.03859
.02420	.04452	1.8398	.00997	.4120	.02372
.019330	.035588	1.8411	.00832	.4304	.018999
.016049	.029569	1.8425	.00711	.4428	.015852
.014184	.026163	1.8445	.00638	.4488	.013999
.011403	.021116	1.8510	.00525	.4600	.011281
.004134	.007669	1.8550	.00201	.4870	.004117
.001027	.001818	1.7690	.00051	.4970	.001026

The directly calculated values of j/m are given in Figs. 4 and 5. The interpolated values are given above. At concentrations below 0.05 molal the mean difference between the two amounts to a temperature difference of about one fifty-thousandth of a degree.

while B represents the other integral $0.00057 \int_0^m \vartheta/m \, d\vartheta$. The activity coefficients γ , or a_2/m , are given in the fifth column (see Fig. 3 also).

The activity coefficient of butyl alcohol in its 1.0 molal solution (0.82) is approximately that of a 0.07 molal solution of potassium or sodium chloride. If the activity coefficient of butyl alcohol at 1 molal is considered to be unity, then that in a 0.25 m solution is 1.101, while the corresponding values of Jones and Bury are 1.160 for butyric, 1.091 for propionic, and 1.015 for formic acid. Thus the value for butyl alcohol is not very different from that for propionic acid. From this comparison it seems

TABLE II
VALUES OF THE ACTIVITY COEFFICIENT (a_2/m) OF *n*-BUTYL ALCOHOL IN ITS AQUEOUS SOLUTIONS

The values for the activity coefficient in the column marked (1) correspond to extrapolation along the heavy line, and (2) along the light line in Fig. 5.

Molality m	-A	j	B	$\log a_2/m$	Activity coefficient, a_2/m	
					(1)	(2)
0.001	0.000499	0.00050	0.999566	0.9990	0.9991
.003	.001485	.00147998717	.9971	.9974
.006	.002946	.00288997470	.9942	.9946
.010	.004840	.00465	0.00001	.995883	.9906	.9911
.020	.009308	.00856	.00004	.992246	.9823	.9833
.030	.013380	.01173	.00006	.989121	.9753	.9764
.040	.017100	.01432	.00008	.986389	.9691	.9702
.050	.020530	.01645	.00010	.983983	.9638	.9650
.070	.026612	.01995	.00013	.979834	.9546	.9558
.100	.034442	.02416	.00019	.974632	.9433	.9445
.150	.044273	.02928	.00028	.967361	.9276	.9288
.200	.054196	.03342	.00038	.961943	.9161	.9173
.250	.062971	.03667	.00046	.957032	.9058	.9070
.300	.069911	.03926	.00054	.952986	.8974	.8986
.400	.082011	.04490	.00071	.945321	.8817	.8829
.500	.092521	.05015	.00089	.938570	.8681	.8693
.600	.101901	.05465	.00106	.932636	.8563	.8574
.700	.110401	.05790	.00123	.927627	.8465	.8476
.800	.118201	.06050	.00141	.923192	.8379	.8390
.900	.125401	.06290	.00158	.919130	.8301	.8312
1.000	.132101	.06530	.00175	.915242	.8227	.8238

TABLE III
FILMS OF BUTYL ALCOHOL ON WATER

Molality	Activity	Surface tension	Moles per sq. cm. $\times 10^{10}$	Number of molecules per sq. cm.			Area per molecule adsorbed	Area per molecule, sq. Å.	Square root of area
				Ad-sorbed	Already present	Total			
0.00329	0.00328	72.80							
.00658	.00654	72.26							
.01320	.01304	70.82	1.26	0.76	0.04	0.80	132	120	11
.0264	.02581	68.00	2.15	1.31	.06	1.37	76	73	8.8
.0536	.05184	63.14	3.54	2.14	.10	2.24	47	45	6.7
.1050	.09892	56.31	4.72	2.86	.15	3.01	35	33	5.8
.2110	.19277	48.08	5.26	3.19	.23	3.42	31.4	29.2	5.4
.4330	.37961	38.87	5.69	3.45	.37	3.82	29.0	26.2	5.1
.8540	.71189	29.87	6.03	3.65	.56	4.22	27.4	23.7	4.9

Surface tensions at 25°. Activities at 0°. It is assumed that the relative activities at 25° are the same as at 0°.

probable that the activity coefficients of the acids vary somewhat more with the concentration than those of the alcohols, if the number of carbon atoms is the same.

TABLE IV
 ADSORPTION AND MOLECULAR AREA FOR ORGANIC ACIDS
 Temperature, 0°

Moles per 1000 g. of water	Area per molecule in Ångström units	
	Adsorbed	In film
Propionic Acid		
0.1008	70.8	63.8
.2420	47.2	41.8
1.0167	32.4	26.4
2.3110	28.8	21.7
Butyric Acid		
0.0211	98.0	93.0
.0503	62.5	59.3
.1049	43.2	40.4
.2510	34.6	31.5
.5088	30.2	26.6
1.095	26.5	22.2

It has usually been considered that the value of the function j/m is constant below 0.1 molal but Fig. 4 shows that it increases rapidly as the molality decreases, and, on the whole, more rapidly at the lower concentrations.

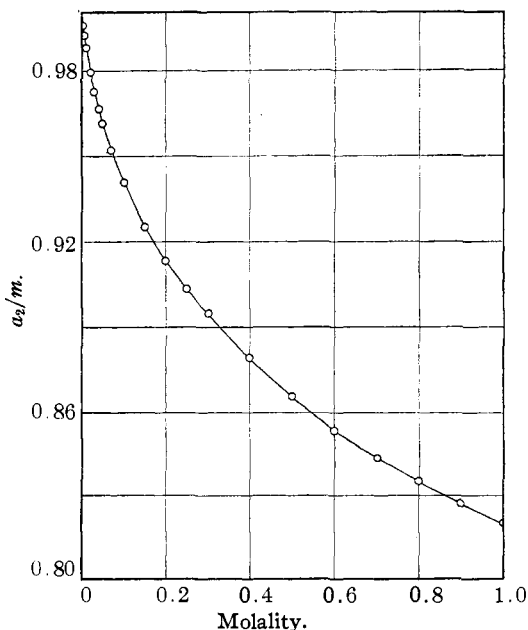


Fig. 3.—Activity coefficient of *n*-butyl alcohol in its aqueous solutions.

Figure 5 gives the values of j/m at molalities below 0.1 molal. The middle curve represents the smoothed values of j/m , while the upper and lower curves show the deviation produced in j/m by an error of 0.00005° in the temperature measurement. It is evident that the deviations from the mean are in general much less than a twenty-thousandth of a degree, and that below 0.05 molal the average deviation is about one fifty-thousandth of a degree.

In Table II the activity coefficients under (1) represent the extrapolation to zero concentration along the heavy line of Fig. 5, which corresponds better to the data at the lowest concentrations, while those under (2) correspond

to extrapolation along the light line, which seems better on the basis of the data at higher concentrations. The maximum difference produced in the activity is only 0.12%.

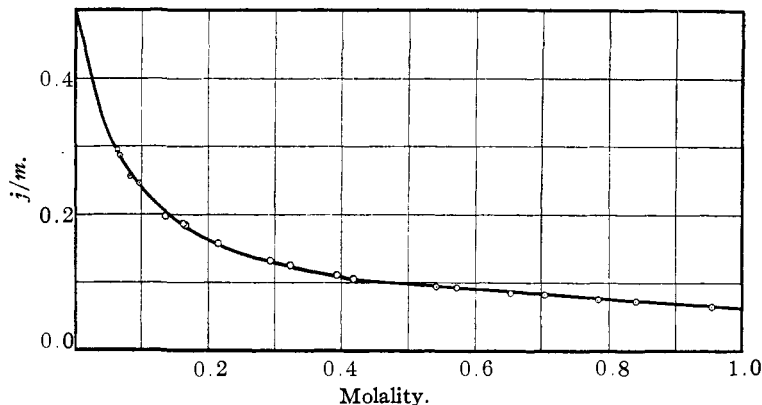


Fig. 4.—Variation of j/m with the molality of butyl alcohol.

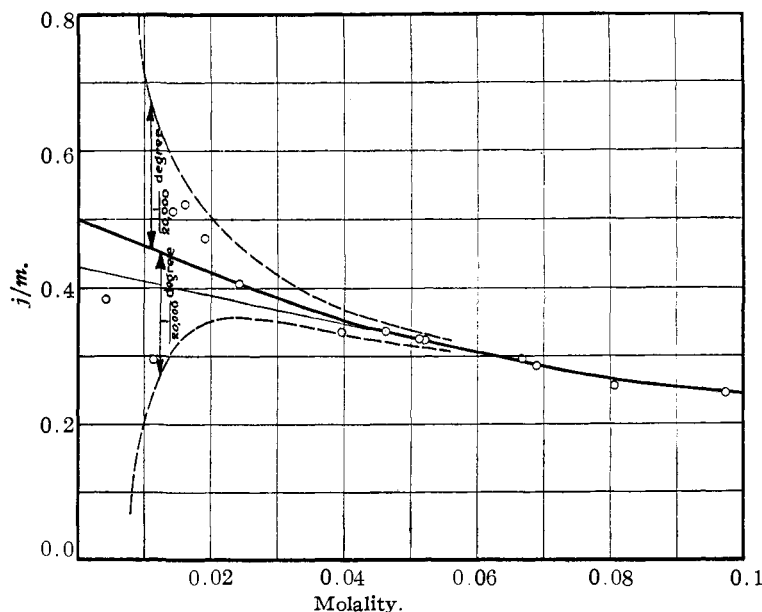


Fig. 5.—Variation of j/m with the molality of butyl alcohol.

VII. The Film of Butyl Alcohol on an Aqueous Solution

The adsorption (u) in the surface region of a solution is supposed to be given by the equation

$$u = - \frac{1}{RT} \frac{d\gamma}{d \ln a}$$

in which γ is the surface tension of the solution, a is the activity of the solute, T is the absolute temperature and R is the gas constant. Figure 6 gives the surface tension values for aqueous solutions of butyl alcohol as determined by King, plotted against the logarithm of the activity of the alcohol in its aqueous solutions as given earlier in this paper. The values for the adsorption, as calculated from these data are given in Table III. At the highest concentration (0.854 molal) the area of the surface per molecule adsorbed is 27.4 sq. Å. units of area.

The area per molecule for normal alcohols in insoluble films on water is about 21.6 sq. Å. units at zero compression. The value per adsorbed

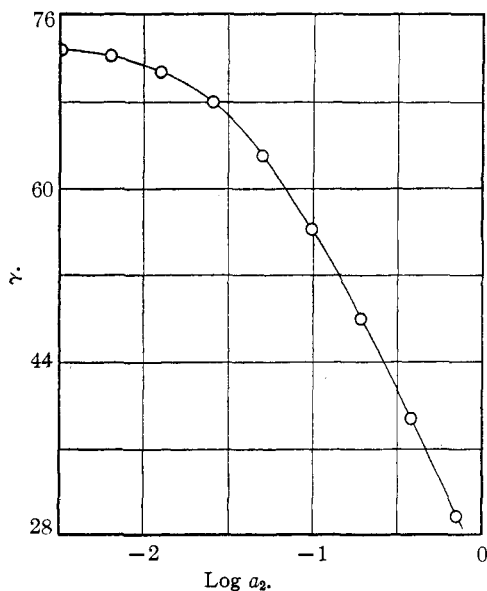


Fig. 6.—Surface tension and activity of butyl alcohol in water.

molecule of butyl alcohol (27.4) is about one-third larger, and this suggests that the film is monomolecular with respect to butyl alcohol.

The value of the adsorption (u) in the above equation gives the number of moles of solute which must be added to the whole solution in order to keep the activity of the solute constant when the area of the surface of the solution is increased by one sq. cm. While it is evident that some solute is present in the surface film of a solution if the adsorption (u) is zero, sufficient attention has not been given to this fact. For example, the value of u for a 0.854 *m* solution of butyl alcohol is 3.65×10^{14} molecules per sq. cm. of increase of surface. It is commonly assumed that this number of alcohol molecules moves into the surface film. However, if the number of molecules of butyl alcohol in the surface were to be determined an infinitesimal time after the formation of the surface, the number would not be negligible. It may be assumed that a plane surface, one sq. cm. in area, inside such a solution would cut 0.56×10^{14} molecules of butyl alcohol, since this number is equal to the two-thirds power of the number of alcohol molecules in one cc. of the solution. It will be assumed that this is the number of alcohol molecules "initially" present in the first surface layer. If all of the adsorbed molecules move into this same "layer" the total number present is 4.22×10^{14} , and the area per molecule of alcohol present in this layer is 23.7 sq. Å. units, or very nearly that (21.6)

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exhibited by alcohol molecules in insoluble films. For comparison the surface tension data of Reh binder and the activity data of Jones and Bury have been used to calculate the corresponding areas for propionic acid and butyric acid (Table IV). The minimum areas are 21.7 and 22.2 sq. Å., respectively. The first surface layer of solute molecules, as defined in this paper, does not include the entire surface *region* as defined in earlier papers by Harkins. The relation between the first surface layer, sometimes called the surface film, and the surface region, will be discussed in a later paper.

Summary

1. The activity values for solutions of *n*-butyl alcohol in aqueous solution were determined by the use of a specially designed apparatus for the determination of the lowering of the freezing point. This was a modified form of the apparatus used by Adams, and by Harkins and Hall. It was sensitive to 0.00901° when used with a White double combination potentiometer.

2. The *n*-butyl alcohol was purified carefully in a specially designed fractionating column. The material used distilled over within a range of 0.04° .

3. The activity coefficient of *n*-butyl alcohol in its 1 molal solution is 0.8227. At 0.5 *M* it is 0.8681, and at 0.1 *M*, 0.9433. Thus the deviation from normal behavior is of considerable magnitude with this organic solute. This indicates that the concentration of the solution cannot be used in place of the activity, in accurate calculations. It may be assumed that the deviations produced by the $-\text{COOH}$ group are somewhat larger and other active groups of this type give deviations of about the same general order of magnitude.

4. If the "adsorption equation" is correct, the film of butyl alcohol on its aqueous solutions is monomolecular. The area per molecule of alcohol in the film is 23.7 sq. Å., while the well-known value for longer alcohol molecules in insoluble films is 21.6 sq. Å.

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