

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Surface Tension Studies with *n*-Butyl Acetate

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The surface tension of a solution will change with the passage of time if some phenomenon brings about a change in the concentration of the solution at the surface. Du Noüy,¹ among others,² has studied the decrease in surface tension due to the adsorption and orientation of molecules of non-volatile surface active solutes in the surface layer.

The fact that the surface tension of a solution of a volatile, surface active solute in water, may increase while the solution is allowed to remain undisturbed in a capillaritymeter has been established.³ The theory was advanced that the increase in surface tension is due to the evaporation of the solute being more rapid than the diffusion of the solute molecules through the solution into the surface layer, while the solvent molecules are replenished about as rapidly as they evaporate, thus the surface layer becomes more nearly pure solvent with the elapse of time. That a change in the concentration of the surface layer, rather than the extremely small change in the gross concentration of the solution, is the cause of the change in surface tension, is indicated by the relatively large increase in surface tension which was observed during a short time interval. The fact that a slight agitation of the capillary meniscus after some increase in surface tension had taken place caused a return to near the original surface tension also leads to this conclusion.

The quantitative work on which this theory is based was carried out with aqueous solutions of ethyl acetate. The fact that ethyl acetate has a higher vapor pressure at 20° than water seems to have been responsible for the idea advanced by some workers that the solute must be more volatile than the solvent in order to have the surface tension increase to that of the solvent due to evaporation from the surface layer. Accordingly, this investigation with aqueous solutions of *n*-butyl acetate, a material with a lower vapor pressure than water at 25°, has been carried out.

Materials

Water.—Carefully redistilled water was used in checking the capillaritymeters, in preparing the solutions and in the final washings of all apparatus used in these measurements.

***n*-Butyl Acetate.**—Eastman's best grade of *n*-butyl acetate was repeatedly dried over phosphorus pentoxide, treated with sodium carbonate and distilled in an all-glass apparatus until further treatment caused no measurable change in the density or in the surface tension of the material; 450 g. of ester distilling over within a range of 0.15°.

(1) Du Noüy, "Surface Equilibria of Biological and Organic Colloids," American Chemical Society Monograph, Chemical Catalog Co., New York, 1926.

(2) Davis, Salisbury and Harvey, *Ind. Eng. Chem.*, **16**, 161 (1924); Johlin, *J. Phys. Chem.*, **29**, 270, 897 (1925).

(3) Bigelow and Washburn, *ibid.*, **32**, 321 (1928).

was obtained from 1 kg. of original material. The following constants were obtained for the purified ester; b. p. $125.8 \pm 0.08^\circ$; d_4^{25} 0.8769; n_D^{20} 1.39459.

Apparatus and Method.—The capillary rise method was used in the study of surface tension. Two capillarimeters were constructed from carefully selected capillary tubes and reference tubes which were 40 mm. or more in diameter. The uniformity of bore and the radii of the capillaries were established by the measurements of mercury threads and by the capillary rise of water. The capillary tube in capillarimeter "A" had an internal radius of 0.02715 ± 0.00005 cm.; while that of capillarimeter "B" was 0.01513 ± 0.00003 cm. Previously³ described methods of cleaning, drying and supporting of the capillarimeters were followed. The capillarimeters were immersed in an electrically heated and controlled bath at the desired temperature $\pm 0.1^\circ$ during the studies. The capillary rise was measured with a measuring microscope of 10 cm. range fitted with a scale and a graduated head which permitted readings to be made directly to 0.01 mm.

Experimental Results and their Interpretation.—The following experiments have been chosen as typical of several performed in each group. The tabulated or graphed surface tensions have been calculated from the formula, $\gamma = hrg(D - d)/2$, where h represents the measured capillary height plus $1/3$ of the radius of the capillary tube; the other symbols have their usual significance.

Surface Tension of Pure *n*-Butyl Acetate.—The surface tension of the pure ester was measured at 20.0, 25.0, 30.0, 35.0°. Two capillarimeters were used in these measurements and the results listed are the averages of several independent measurements. The maximum observed variation of any single result from the average at that temperature was ± 0.05 dyne/cm.

TABLE I

Temp., °C.	d_4^{25}	Surface tension, dyne/cm.	Eötvös constant	$\left[\frac{\text{Parachor}}{(D - d)} \gamma^{1/4} \right]$
20.0	0.8817	24.81	2.26	294.3
25.0	.8769	24.30	(Range, 20 to 35°)	294.3
30.0	.8720	23.77		294.4
35.0	.8673	23.23		294.3

The value for the Eötvös constant and the fact that the parachor agrees closely with the sum of the atomic and structural parachors⁴ seem to indicate that the ester is a "normal" liquid.

Surface Tensions of Aqueous Solutions.—Nearly saturated solutions were prepared by weighing out 4.6436 g. of ester and diluting to a liter. Other solutions were prepared from these by dilution. The very small changes in volume which accompany the addition of water to such water rich solutions were disregarded. The surface tensions of these solutions were measured in a capillarimeter which was closed with a glass stopper. Alteration of surface concentration by evaporation was prevented and thus it was possible to obtain a true equilibrium at the surface and to study the corresponding surface tension. The following results were obtained at $25.0 \pm 0.1^\circ$.

Changing Surface Tension with Time.—Studies made of the changing surface tension with time shown by aqueous solutions of *n*-butyl acetate in open capillarimeters and in capillarimeters which were at first open and

(4) Sugden, *J. Chem. Soc.*, **125**, 1177 (1924).

Concentration of ester, moles per liter of solution	Density d_4^{25}	Surface tension, dynes/cm. 25.0°
0.000	0.9970	72.0
.005	.9970	61.8
.010	.9970	56.5
.020	.9969	49.7
.030	.9969	45.2
.040	.9969	41.8

then closed gave results similar to those previously obtained with solutions of ethyl acetate.³ Although the partial pressure of *n*-butyl acetate from these dilute solutions at 25° is much less than that of water, still the surface layer of such a solution on exposure to air becomes more nearly pure water with the passage of time. The rate with which the surface tension increases due to this change in concentration of the surface layer varies with the diameter of the bore of the capillary and with the length of the capillary tube above the meniscus in a manner similar to that observed by Trimble⁵ with non-aqueous mixtures.

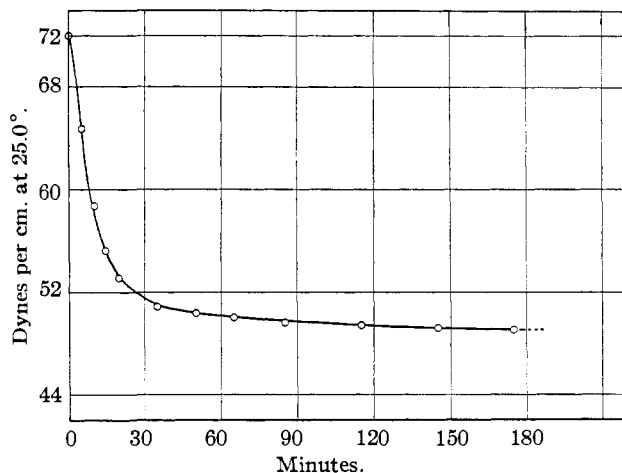


Fig. 1.—Water in capillarimeter, *n*-butyl acetate in side arm.

Experiments Giving Decreasing Surface Tension.—Figure 1 shows typical results obtained when pure water was placed in capillarimeter "B" with pure *n*-butyl acetate in a "U" tube side arm sealed to the tube above the capillary. As will be shown later, the actual amount of ester vapor which will diffuse through a capillary tube in an hour is very small yet is sufficient to cause the surface tension of water to decrease in that length of time to a value corresponding to a 0.019 *M* solution of the ester. It would seem that the ester must be concentrated in the surface layer and that the diffusion into the interior of the solution is very slow.

(5) Trimble, *J. Phys. Chem.*, **32**, 1211 (1928).

Extent of the Surface Layer.—It is possible to get some idea of the extent of the surface layer in a capillary tube from the rate at which a vapor diffuses through the capillary and the rate at which the surface tension falls due to diffusion and solution of the ester in the surface layer of water.

The capillary tube of capillarimeter "B" was broken 4 cm. from the upper end, this being the average distance of capillary through which the ester vapor diffused in determining the values plotted as Fig. 1. Some pure *n*-butyl acetate was placed in the side arm and the two upper ends sealed off in a flame. Then the only escape for the ester vapor was through the 4 cm. of capillary tubing. This side arm section of the capillarimeter with the enclosed ester was weighed from time to time throughout a period of seventy-four days. The observed decreases in weight indicated that 0.0000025 g. of ester diffused out of the capillary per hour. In the experiment referred to the surface tension of water decreased in one hour's time to a value corresponding to 0.019 molar ester solution. Because of the rapid decrease with time and because of the effect of a slight agitation of the meniscus it may be permissible to assume that nearly all of the ester is concentrated in the surface layer. Then by assuming different possible values for this surface area, it is possible to calculate the depth to which the surface layer must extend in order to include the volume of 0.019 *M* ester which 2.15×10^{-8} mole of ester could form. Three different assumptions were made in regard to the extent of surface. If the surface layer exists only in the meniscus, and if the meniscus is hemispherical in shape, it must be 0.76 cm. deep. Secondly, if the layer consists of the hemispherical meniscus and if it extends 1 cm. upward on the walls of the capillary, it would be 0.01 cm. thick. In the third case, if it extends to the top of the capillary, in the particular experiment cited, a height of 5.50 cm., the thickness would turn out to be 0.002 cm. Careful study of capillary phenomena⁶ has offered some evidence that the liquid extends on the capillary walls several millimeters above the meniscus. Whatever the extent of the surface may be, between the limits here assumed, the evidence indicates a layer far more than one molecule in thickness.

Summary

The surface tension of *n*-butyl acetate at 20.0, 25.0, 30.0, 35.0° has been determined. Values of the Eötvös constant and of the parachor indicate that the ester is a "normal" liquid.

The equilibrium values for the surface tensions of aqueous solutions of *n*-butyl acetate have been determined at 25.0°.

Semi-quantitative evidence seems to indicate that the surface layer in solutions of this type must be many molecules in thickness.

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(6) Bigelow and Washburn, *J. Phys. Chem.*, **32**, 345 (1928).