their other points should be expected. Their use of a straight line over the range 63–70% seems poorly justified, since there were no experimental points in this range. In the range 70–75% the straight line they used is supported by a number of points. The stock acid used in this work was in this range of concentration. It should be noted that while the difference in density figures at 65% is rather large, it corresponds to a difference in acid concentration of about 0.027%.

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON RECEIVED DECEMBER 10, 1940

A Note on the Phase Rule Diagram for a Mixture of Sodium Palmitate and Sodium Laurate with Water

BY J. W. MCBAIN AND S. A. JOHNSTON

The temperatures above which mixtures of soap and water in various proportions form isotropic solutions, T_i, and the temperatures below which they contain soap curd, T_c, have been determined for most of the single pure soaps. It is therefore of interest to see how these are affected when two such soaps are mixed. For this purpose a constant mixture of equal weights of sodium palmitate and sodium laurate has been examined with different percentages of water, using the materials and technique of previous communications.[1]

Briefly, this consisted in preparing sealed Pyrex tubes containing the mixture with varying amounts of water. The contents of the tubes were homogenized by heating to a high temperature, around 300° in this case. If the tube was then cooled slowly a temperature was reached at which another phase separated. This phase is frequently anisotropic and may be recognized even in minute quantities by observing the solution through crossed Polaroids. These points form the T_i curve. The tubes were then cooled to room temperature and heated slowly. The temperature at which the white curdiness disappeared was noted and these temperatures form what is usually called the T_c curve.

The results are given in Fig. 1 for the mixture where also the positions of middle soap, neat soap and curd are indicated. Figure 1 also compares these results with those of the separate single soaps, represented by faint lines. A comparison of the curves shows that the mixture tends to follow a behavior which would be an average of the individual curves. Probably the outstanding difference is that the peak for middle soap is higher than either of the individual peaks and if anything is nearer the peak for sodium palmitate. The T_c curve, on the other hand, adheres more closely to the curve for sodium laurate, as might be expected from previous experience.[1a,1c] Mixed micelles of smaller size, less orientation and greater solubility, must be produced by the occurrence of the shorter laurate molecules amongst the longer homologs, an example of mutual solubilization.

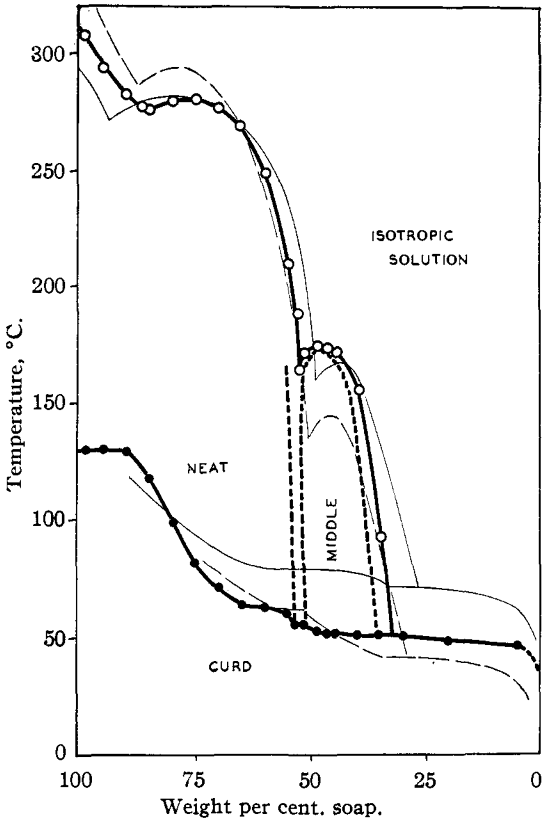

Fig. 1.—○, T_i curve; ●, T_c curve; ———, NaP; - - -, NaL.

STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIFORNIA RECEIVED NOVEMBER 12, 1940

---

[1] (a) McBain, Lazarus and Pitter, *Z. physik. Chem.*, **A147**, 87, 116 (1930); (b) McBain, Brock, Vold and Vold, THIS JOURNAL, **60**, 1870 (1938); (c) McBain, Vold and Jameson, *ibid.*, **61**, 30 (1939); (d) Vold, *J. Phys. Chem.*, **43**, 1213 (1939).

The Effect of Potassium Oleate upon the Solubility of Hydrocarbon Vapors in Water

BY J. W. MCBAIN AND J. J. O'CONNOR

Solubilization by colloidal electrolytes and other detergents is best studied in systems where there is no possibility of competing effects, such as mere emulsification or suspension. Likewise all possibility of salt formation should be excluded since we have found that base exchange may be an important factor in detergent action.[1]

We have therefore studied the solubility of the indifferent hydrocarbons, isobutane, butadiene and propylene in water and in solutions of potassium oleate.

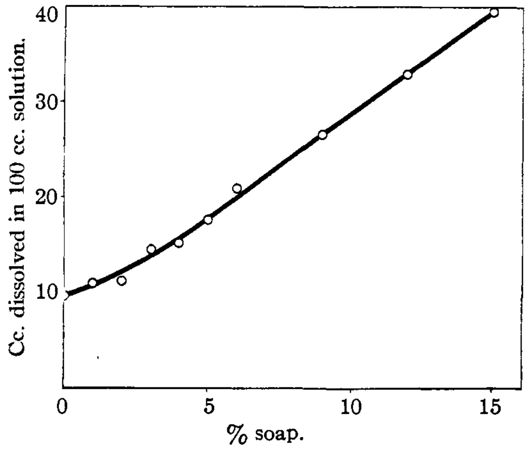

Fig. 1.

Experimental

The following simple but effective method was employed. The liquid was placed in a weighed tube sealed at one end and closed with a stopcock at the other. The liquid is degassed by evacuation and the tube reweighed. The connection between the tube and a gas buret containing the hydrocarbon vapor was evacuated and then opened to the hydrocarbon vapor. After admitting a suitable volume of hydrocarbon vapor, the tube was shaken in a thermostat at 25.0° for several hours. Thereupon an ordinary buret filled with mercury was attached through an evacuated connection to the stopcock, the tube being held vertically with stopcock underneath. Mercury was admitted to establish atmospheric pressure and the tube weighed to determine its amount and therefore the volume of gas remaining undissolved. From this, making all corrections for hydrostatic and vapor pressure, etc., the equilibrium pressure was calculated together with the amount of hydrocarbon dissolved.

Soap solution does not froth at all when evacuated and degassed.

The hydrocarbons were supplied through the kindness of the Shell Development Company. The propylene was made by dehydrogenation of isopropyl alcohol with subsequent fractionation. A similar sample, a portion of whose vapor was analyzed, contained 0.3% propane. However, it is probable that the liquid contained more propane and that appreciable fractionation occurred between first and last use of the cylinder as was shown by definitely decreased solubility.

The potassium oleate was made from Merck oleic acid of molecular weight 288.4 and iodine value 93, by neutralizing in 80% ethyl alcohol with Baker's stick potash containing about 4% carbonate; however, before use, half of each stick was first washed away and discarded.

The results may be presented in graphical form, plotting the total volume of hydrocarbon, corrected to 0° and 760 mm., which was dissolved in 100 g. of liquid, against the equilibrium pressure.

Figure 1 shows the effect of the addition of soap to water in enhancing the solubility of propylene when the final equilibrium pressure is adjusted in every case to 400 mm. It is seen that the solubility which in water was 9.8 cc./100 cc. is raised to 39 cc. by the presence of 15% potassium oleate.

Figure 2 shows that isobutane is about as soluble in 1% potassium oleate as was propylene in water. The work was broken off through call to duty as Ordnance Officer of one of us (J. J. O'C.) before the solubility of the isobutane in water was determined. Figure 2 also shows the enhancement of the solubility of butadiene by 1% potassium oleate.

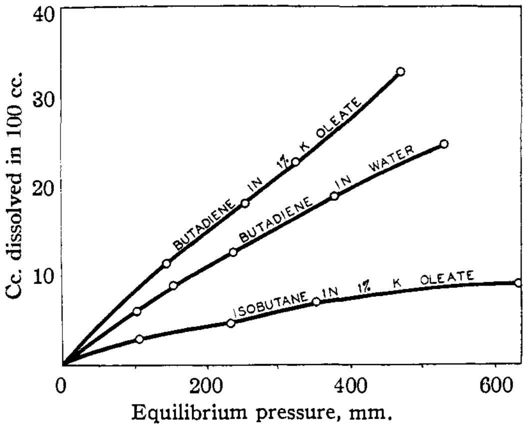

Fig. 2.

Figure 3 shows, first, by points marked in circles, the solubility of propylene in water and the increased solubility due to 1% and 5% of potassium oleate. An earlier series of measurements with the freshly opened cylinder of propylene is marked with crosses, showing a distinctly higher solubility, and also its enhancement by 1% potassium oleate.

Since McBain and Woo[2] had obtained a pronounced effect upon 5% sodium oleate solutions by the addition of 0.2% of silica in the form of

---

(1) McBain, Lee, Merrill and O'Connor, *Chem. Prod.* (*London*), communicated October, 1940.

(2) McBain and Woo, *Kolloid-Z.*, **87**, 76 (1939).

"O" brand, originally containing 29.4% SiO_2 and 9.3% Na_2O, ratio 3.15, a similar addition was made to the 5% potassium oleate here. This made no influence upon the result, as shown by the three triangles which fall upon the original curve in Fig. 3. In Woo's experiments the oleate was not only solubilizing Yellow AB, but to a still greater extent was suspending and protecting colloidal particles of Yellow AB, and we have since shown that solubilizing and protective or suspending actions are wholly separate processes. The present experiments are designed to exclude the protective factor. The foam in 1 atmosphere of propylene with and without silicate was not very different; possibly the one containing silicate was creamier after standing a short time. The effect of the silicate upon the solubility in water was not measured for lack of time. However, in such dilution it would have been negligible.

The soap is exerting its expected action, namely, definite solubilization, overriding other factors. Electrolytes as such would be expected slightly to reduce the solubility by salting out. An additional small influence in the same direction would be caused by hydration of the soap. This is illustrated by the slight but distinct negative sorption of propylene on cotton thread. One gram of cotton thread added to 50 g. of water (the two square points on Fig. 3, corresponding to the crosses for pure water) caused this small decrease in the apparent solubility of the propylene, showing that the cotton preferentially sorbed the water.

In the previous work with the less volatile hexane and methylcyclopentane the amount taken up from the saturated vapor was approximately one mol of hydrocarbon to one mol of soap. It is quite possible that the solubility of the present hydrocarbons would be of comparable magnitude if measured at similarly high relative vapor pressures. It is thought that if the excess solubility above that in water alone were plotted against relative vapor pressure of hydrocarbon, the general curve would be sigmoid in character. The first part would, as here, be concave downward, and pass through a point of inflection before rising to much higher values. The isobutane and propylene are here studied only at the left-hand part of the curve; the butadiene extends further and indicates a further stage of the S-shaped curve, whereas the previous less volatile hydrocarbons were studied on the right-hand portion near saturation. According to this working hypothesis, the soap itself is strongly modified by the larger amounts of solubilized hydrocarbon.

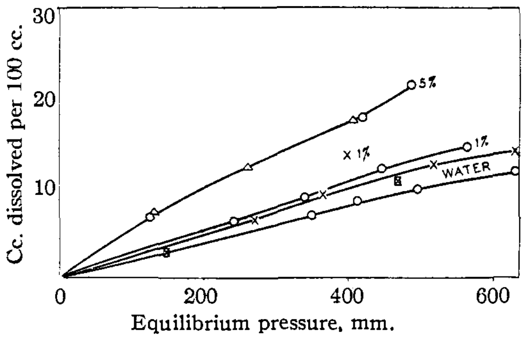

Fig. 3.

Comparing the amount of extra hydrocarbon dissolving in the presence of soap with that dissolving in an equal amount of olein, the only comparable material for which we have data,[3] we find that the potassium oleate dissolves only about one quarter as much as would an equal weight of olein. In general, solubilization appears to involve several factors other than mere solution in hydrocarbon groups, if any.

The most extensive series of studies of the solubility of gases as affected by other dissolved substances are those of Findlay and collaborators, 1910–1915. They found that proteins sometimes increased the solubility of gases such as carbon dioxide, and that polysaccharides did not. They likewise observed departures from Henry's law similar to those found here.

Summing up, the solubility of the hydrocarbons, propylene, isobutane and butadiene, is enhanced by presence of potassium oleate acting as solubilizer. This is one, but only one, of the important factors in detergent action.

---

[3] Berthelot, *Ann. chim. phys.*, **43**, 276 (1855).

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
CALIFORNIA

RECEIVED DECEMBER 10, 1940

Heavy Oxygen (O^{18}) as a Tracer in the Study of Photosynthesis

BY SAMUEL RUBEN, MERLE RANDALL, MARTIN KAMEN AND JAMES LOGAN HYDE

It is generally agreed that the net reaction for green plant photosynthesis can be represented by the equation

$$CO_2 + H_2O + h\nu \xrightarrow{\text{Chlorophyll}} O_2 + (1/n)(C{\cdot}H_2O)n \qquad (1)$$