*Measurement of Solubilities of Sparingly Soluble Liquids in Water and Aqueous Detergent Solution Using Non-ionic Surfactant**

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Introduction

During the past few years, numerous studies were reported with regard to the solubilization of various substances into the aqueous solutions of surface active agents. But in the region of concentration below cmc., little is known as to the behavior of solutes in solution. To know such characteristics of the surface active agents in aqueous solution, particularly their interactions with the solutes, it is necessary to begin with the determination of the solubility of solutes in water as well as in aqueous solutions of detergents, since we have unfortunately no reliable data available up to the present. This lack of correct data may come partly from the roughness of the method itself, and partly from the fact that the sparingly soluble substances usually show a tendency to be dispersed as colloidal particles, which make obscure the true solubility determination. Formerly, one of the present authors also determined the solubility of iso-amyl alcohol in water taking account of this fact[1]. In the present paper we determined the solubility of iso-amyl alcohol, *n*-butyl alcohol and benzene in water, making use of the influence on solubility of these substances produced by the addition of non-ionic surfactant, Tween 80.

Experiment

(a) Materials.—The surfactant used in this experiment was a kind of non-ionic surfactant, Tween 80, of Atlas Powder Co., which was kept in vacuum until a constant weight was attained.

For the purification of iso-amyl alcohol and *n*-butyl alcohol, they were boiled with a concentrated sodium hydroxide solution, washed with water, dried with anhydrous potassium carbonate and distilled over calcium oxide. Distillation was repeated over calcium metal, and the fractions distilled at 131°C for the former and 118°C for the latter were collected. Benzene was purified by the ordinary method, that is, it was shaken repeatedly with concentrated sulfuric acid, boiled with mercuric oxide, recrystallized several times and distilled over sodium metal.

(b) Principle and Apparatus.—A definite amount of iso-amyl alcohol is added to a varying amount of Tween 80 solution of known concentration in the cylindrical tube with a well-ground stopper. The mixture is then shaken vigorously, and is stood in the thermostat for about fifteen minutes. If the alcohol concentration is higher than its solubilization limit, the system becomes turbid due to emulsification. The turbidity decreases and finally disappears with an increasing amount of Tween 80 solution added. The diagram is drawn between the turbidity and the concentration (wt. %) of iso-amyl alcohol in the mixture taking the concentration of Tween 80 constant as shown in Fig. 1. From these curves

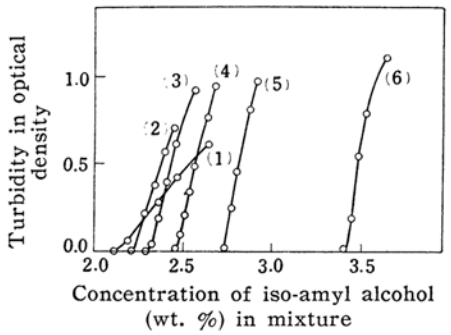

Fig. 1. Relation between turbidity and iso-amyl alcohol concentration in Tween 80 solution of concentration: (1) 0.0998%, (2) 0.228%, (3) 0.52%, (4) 1.046%, (5) 2.00%, (6) 3.86%.

we can estimate the limit of solubilization by extrapolating the linear parts of these curves to zero turbidity. The values of solubilization thus obtained are plotted against the concentration of Tween 80, which is shown as f(c) in Fig. 2. In this figure the point A represents the solubility of iso-amyl alcohol in pure water which is determined as follows. The saturate solution of iso-amyl alcohol in water is prepared and is titrated using Tween 80 solution of the concentration corresponding to the point C in Fig. 2. Hereby, turbidity increases, passes through a maximum, and then decreases gradually, when plotted against the concentration of Tween 80 added, as in Fig. 3. The decreasing portion of the curve is linear. From the extrapolation of this portion to zero turbidity, we can obtain the concentration of Tween 80 (D) required just to dissolve alcohol, which in turn corresponds to the ordinate of the

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1) S. Mitsui and T. Sasaki, *J. Chem. Soc. Japan*, **63**, 1766 (1942).

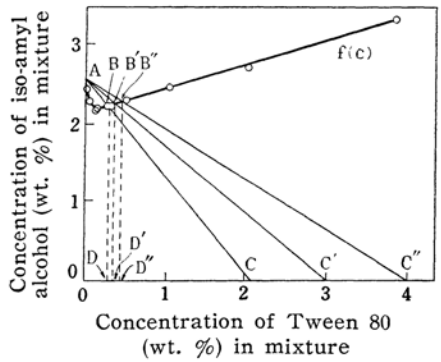

Fig. 2. Solubility of iso-amyl alcohol in aqueous Tween 80 solution. Concentration of Tween 80 in aqueous solution: C=2.061%, C′=2.988%, C″=3.99%; D=0.272%, D′=0.346%, D″=0.436%; A, Saturate solution of iso-amyl alcohol in water; B, B′, B″, End point of titration of saturate solution A.

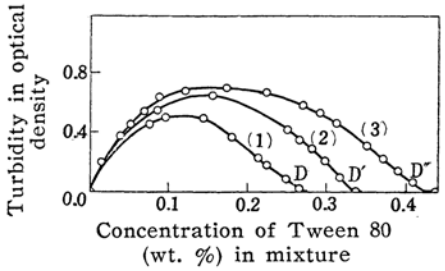

Fig. 3. Turbidities of saturate iso-amyl alcohol solution when titrated with aqueous Tween 80 solution. Concentration of Tween 80 solution used: (1) 2.061%, (2) 2.988%, (3) 3.99%.

point of intersection (B) made by the curve f(c) and the straight line AC in Fig. 2. Inversely, the point B can be determined from D and f(c); thus we can determine the point A, namely the solubility of iso-amyl alcohol, by extrapolating the straight line BC. The turbidity was measured by the photocell type photometer, and expressed in terms of the optical density of transmitted light. The monochromatic light (550 mμ) from a 50 watt lamp with an interference filter was used as a light source.

The temperature of the cell containing solution was regulated within 30.1±0.1°C by the thermostatted water circulating through a water mantle surrounding it.

(c) Experimental Procedure and Results.— For the determination of f(c) of iso-amyl alcohol, about 0.7 g. of it was accurately weighed and mixed with known weight (about 20 g.) of Tween 80 solution of the concentration from 0.0998 to 3.86%. For the determination of the steeply inclined portion of f(c) near the point A, aqueous iso-amyl alcohol was usen instead of pure alcohol. For the preparation of saturate solution, about 7 g. of iso-amyl alcohol and about 200 cc. of water were well shaken together at a temperature lower than that of the measurement (30.1°C), and then stood in the thermostat for about twenty-four hours. After the excess solute particles cleared up, a transparent saturate solution was obtained which was taken out from the bottom of the vessel by a siphon. A known amount of this solution (about 20 g.) was titrated with Tween 80 solution corresponding to C(2.061%), C′(2.988%) and C″(3.99%) as indicated in Fig. 2, under the constant temperature (30.1°C). The points D, D′ and D″ were thus obtained and the corresponding points B, B′ and B″ were found on f(c) of Fig. 2. The extrapolation of the straight lines BC, B′C′ and B″C″ gave nearly the same values of solubility corresponding to the point A in Fig. 2, which were also listed in Table I.

The solubility of *n*-butyl alcohol could be obtained similarly.

In the case of benzene, however, the above method could not be applied directly as the turbidity plotted aginst the concentration of benzene was not linear as shown in Fig. 4. This fact made the extrapolation inaccurate. In this case, however, the addition of ethyl alcohol enabled us to overcome this difficulty. Fig. 5 shows the opacity curve of benzene emulsion using the ethyl alcohol solution of Tween 80 (1.67%) instead of Tween 80 alone as the solubilizer. Further procedures were the same as in the case of iso-amyl.

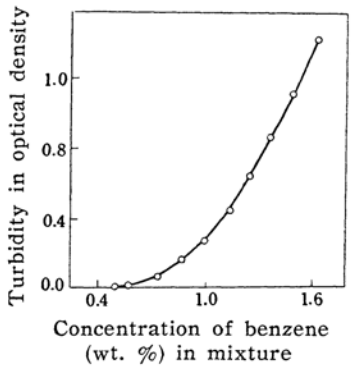

Fig. 4. Relation between turbidity and benzene concentration in 1.07% Tween 80 aqueous solution.

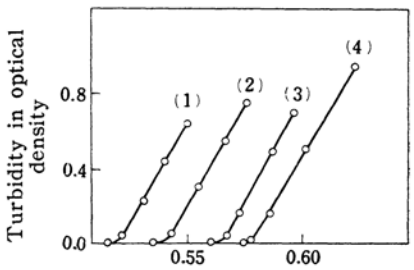

Fig. 5. Relation between turbidity and benzene concentration in aqueous solution of Tween 80-ethyl alcohol mixture. Concentration of 1.67% Tween 80-ethyl alcohol mixture in total mixture: (1) 25.8%, (2) 26.8%, (3) 28.0%, (4) 28.6%.

alcohol. The curve g(c) was thus obtained and shown in Fig. 6.

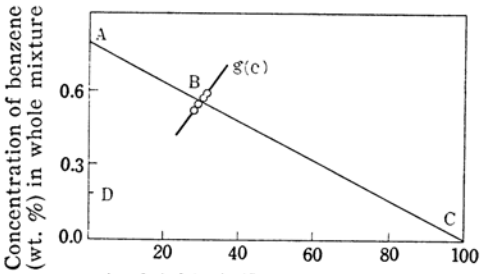

Fig. 6. Solubility of benzene in aqueous solution of Tween 80-ethyl alcohol mixture.
A, Heterogeneous benzene-water mixture obtained by the addition of benzene to the saturate solution
B, End point of titration of heterogeneous system A
C, 1.67% alcohol solution of Tween 80
D, Saturate solution of benzene in water

The saturate solution of benzene expressed as D in Fig. 6 was prepared by the same method as iso-amyl alcohol except for the temperature of shaking being higher than that of the measurement. Actually 0.5244 g. of benzene was added to 92.9926 g. of the saturate solution thus obtained, so as to bring the system in favorable conditions for titration. The point A in Fig. 6 represents the composition of the heterogeneous system thus obtained which was titrated with the solution C, namely 1.67% alcohol solution of Tween 80 containing no water. Now, the titration easily went on just as in the case of iso-amyl alcohol and the point A was obtained similarly. From the composition of A, the solubility of benzene in water could be obtained by subtracting the excess concentration of benzene added to the saturate solution. Solubility data for *n*-butyl alcohol and benzene were also listed in Table I.

TABLE I

Substance	Temperature	Solubility in Water (wt. %)		Reference	
Iso-amyl alcohol	30.1°C	2.587 2.565 2.577	2.57±0.01	2.56 2.31	(30°C)[5] (29°C)[6]
Benzene	20.0°C	0.137		0.179	(25°C)[2]
	25.0°C	0.180		0.174	(25°C)[3]
				0.1865	(25°C)[4]
n-Butyl alcohol	30.0°C	7.01		7.08	(30°C)[7]

2) R. L. Bohn and W. F. Claussen, *J. Am. Chem. Soc.*, 73, 1571 (1951).
3) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, 71, 3645 (1949).
4) Landolt-Börnstein, "Physikalische-Chemisch Tabellen", IIIA, 667 (1935).
5) I. A. Kablukov and V. T. Malischeva, *J. Am. Chem. Soc.*, 47, 1553 (1925).
6) F. Fontein, *Z. physik. Chem.*, 73, 212 (1910).
7) Int. Crit. Table, III, p. 388 (1928).

Discussion

As shown in the earlier part of this paper, we proposed a new method of determining a sparlingly soluble solute in water. This method offers advantages in that the process of preparing a saturate solution and that of the determination of a saturate concentration were separated, whereas in other methods such as the determination of the amount of a solute added to a solvent before the turbidity appears, the above two processes are not separated from each other, so the errors are inevitably introduced due to the inaccuracy of the judgement of saturation, especially in the case where the solute shows a tendency to be dispersed colloidally. The accuracy of our method is satisfactory compared with that of the other method as shown in Table I. We should like further to draw attention to the curve f(c) in Fig. 2 which shows a distinct minimum in solubility of iso-amyl alcohol in Tween 80 solution. Such a behavior is interesting in relation to the mechanism of surfactant in solution from the standpoint of solubilizate versus surfactant interaction. But we need further study for a more precise discussion.

Summary

1. The solubility of iso-amyl alcohol, *n*-butyl alcohol and benzene were determined by the titration using the surfactant, Tween 80.

2. In the case of iso-amyl alcohol and *n*-butyl alcohol, the relation between the turbidity and the quantity of solute in surfactant solution is linear, and the solubility limits are both lower than the solubilities in pure water in the dilute region of the surfactant. This makes the determination of their solubility easy and accurate both in pure water and aqueous solution of the detergent.

3. The above method cannot be applied directly for the determination of the solubility of benzene. Ethyl alcohol–Tween 80 mixture is used instead of Tween 80 to overcome this difficulty.

4. The solubilities obtained by this method are accurate enough compared with other methods, in the case of iso-amyl alcohol and *n*-butyl alcohol, possible error being estimated to be 0.4%. In benzene, the error is somewhat larger, but is in good agreement with the values of the literature.

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