SHORT COMMUNICATIONS

Solubility of Alcohols in Water Determined by the Surface Tension Measurements

By Kyoji KINOSHITA, Hidehiko ISHIKAWA and KŌZŌ SHINODA

(Received September 11, 1958)

The solubility data of alcohols in water are very important and useful for the study in colloid chemistry. Surface active molecules, like higher alcohols, aliphatic amines or fatty acids, have an habitual tendency to form supersaturated solution and the solubility determination encounters some difficulties by the use of the usual method[1]. However, the surface tension in aqueous solutions of these substances monotonously decreases up to their saturation concentration and then remains constant in the heterogeneous region. Therefore, it is possible to determine the solubility of surface active substance in water from the surface tension —logarism of concentration curve without the disturbance from supersaturation as it is in some other cases. As the surface tensions change over the common range, namely from 74 to 30 dynes/cm., the accuracy of this method is nearly equal for any alcohol of markedly different solubility. This principle of determining the solubility by surface tension method was proposed already by several authors[2-4]. But, there are few reports expect for those by Addison and Hutchinson[3,6] who determined the solubility of alcohols from the measurement of surface tension by vibrating-jet or vertical plate method.

Experimental. — *n*-Butanol, *n*-pentanol, *n*-hexanol, *n*-octanol, *n*-nonanol and *n*-decanol were purified by vacuum distillation through 50~100cm. column. The boiling points were 11°C, 138°C, 155.7~156°C, 96°C at 16 mmHg, 113~114.5°C at 20 mmHg and 101°C at 5 mmHg, respectively. Heptanol was of Kahlbaum pure grade material. Pentanol and nonanol were synthesized from *n*-propanol and nonanoic acid, respectively. Surface tension was measured by the drop weight method, using a tip of 6 mm. in diameter. The measurements were carried out in a water thermostat at 25±0.05°C. From the surface tension—logarism of concentration curves the saturation points are determined as the intersections of the curves with the horizontal straight lines passing through the lowest experimental points[7]. The experimental error by this method is about 4% or less.

Results and Discussion. — The results are summarized in Table I and plotted in Fig. 1.

TABLE I
THE SOLUBILITY OF ALCOHOLS IN WATER DETERMINED BY SURFACE TENSION MEASUREMENT AT 25°C

Substance	moles/l.	weight %	weight %
Butanol	0.97	7.4	7.35[8] 7.3[9]
Pentanol	0.25	2.2	2.2[9]
Hexanol	0.059	0.60	0.62[9]
Heptanol	0.0146	0.17	0.18[9]
Octanol	0.0038	0.049	0.059[9]
Nonanol	0.00097	0.014	—
Decanol	0.000234	0.0037	0.0037[6]*

* Solubility measured at 20°C.

The logarithms of the solubility of *n*-aliphatic alcohols in water as a function of hydrocarbon chain length showed a linear relationship and is expressed as follows,

$$\log C = -1.39m + 5.53 \qquad (1)$$

Here C is the solubility of alcohol in mole per liter and m the number of carbon atoms in the alcohol molecule studied.

We have, however, no reliable data of the temperature dependence of the solubility of alcohols in water. We may estimate the heat term, at least, the difference of heat of solution due to the change in

---

[1] T. Sasaki, "Koshitsugaku Ronso" No. 1, 45 (1943).

[2] S. Motylewski, *Z. Anorg. Chem.*, **38**, 410 (1904).

[3] A. Taubamann, *Z. Physik. Chem.*, **A161**, 141 (1932).

[4] H. K. Zimmermann Jr., *Chem. Rev.*, **51**, 25 (1952).

[5] C. C. Addison, *J. Chem. Soc.* **1945**, 98.

[6] C. C. Addison and S. K. Hutchinson, ibid., **1949**, 3387.

[7] K. Shinoda, T. Yamanaka and K. Kinoshita, *J. Phys. Chem.*, to be published.

[8] A. E. Hill and W. M. Walisoff, *J. Am. Chem. Soc.*, **48**, 918 (1926).

[9] J. A. V. Butler, D. W. Thomson and W. H. Maclennan, *J. Chem. Soc.*, **1933**, 674.

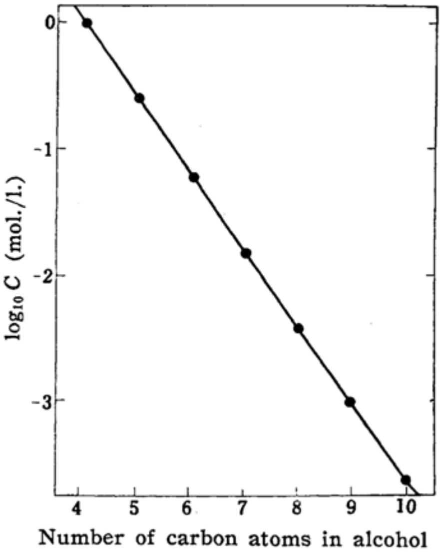

Fig. 1. The relation between the logarithum of the solubility (mole/l.) and the number of carbon atoms in alcohol.

hydrocarbon chain length, by the aid of the following equation[10],

$$0 \cong \ln a_2 = \ln X_2 + \phi_1^2 (m\omega + c_2)/\boldsymbol{k}T \qquad (2)$$

Where a_2 is the activity of solute, X_2 the solubility of solute expressed in mole fraction, ϕ_1 the volume fraction of solvent, ω the heat of solution (or the energy) required for passing one methylene group from hydrocarbon medium into water, c_2 the experimental constant, $\boldsymbol{k}$ the Boltzmann constant and T the absolute temperature.

Replacing the solubility values of alcohols in equation 2, we obtain, as the heat of solution, 4.8 $\boldsymbol{k}T$ for R_4OH, 5.6 $\boldsymbol{k}T$ for R_5OH, 6.9 $\boldsymbol{k}T$ for R_6OH, 8.2 $\boldsymbol{k}T$ for R_7OH, 9.6 $\boldsymbol{k}T$ for R_8OH, 11.0 $\boldsymbol{k}T$ for R_9OH and 12.4 $\boldsymbol{k}T$ for $R_{10}OH$. From the difference of these values, the heat (or the energy if there is no volume change) required for passing one methylene group from hydrocarbon medium into water was calculated to be about 811 cal./mole (1.37 $\boldsymbol{k}T$). (This value is of course very close to the values 823 cal./mole obtained from the slope in Fig. 1, neglecting the change in volume fraction of solute.) This value shows excellent agreement with the value 824 cal./mole obtained by Sasaki and his collaborator[11] for the energy required passing one methylene group from paraffin surface into water.

In connection with this, we draw further attention to the fact that the energy obtained passing one methylene group from water to air-water interface was also determined as 656 cal./mole by the same authors[11]. This value again shows excellent agreement with the value 652~640 cal./mole obtained by Davies[12] and one of us[13,14].

We wish to thank Mr. T. Masumizu for his exploratory work and the Department of Education for the Scientific Research Expenditure.

Department of Chemistry
Faculty of Engineering
Yokohama National University
Minami-ku, Yokohama

---

[10] J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes", Reinhold Publishing Corporation, (1950), p. 131.

[11] T. Sasaki and M. Tsunoda, 11th Annual Meeting of the Chemical Society of Japan (1958).

[12] J. T. Davies, *Trans. Faraday Soc.*, **48**, 1052 (1952).

[13] K. Shinoda, *J. Phys. Chem.*, **58**, 1136 (1954).

[14] K. Shinoda, ibid., **59**, 432 (1955).