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A New Method of Solubility Determination of Hydrolyzing Solute — Solubility of Benzyl Chloride in Water

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A method of determining the solubility of a solute with a considerable rate of hydrolysis and small solubility in water was devised. The method consists of measurements of the hydrolysis rate below or at saturation solubility, the rate constants and order of reaction, and analysis of kinetic data. The solubility of benzyl chloride in water was found to be 33.1 mg/100 m*l* at 4.5°C, 49.3 at 20°C, and 55.5 at 30°C. Solubility of benzal chloride and benzotrichloride was calculated to be 25 mg/100 m*l* at 30°C and 5.3 at 5°C, respectively, by utilizing the kinetic data given in literature

In a course of a study on the relative reactivity of benzyl chloride, benzal chloride and benzotrichloride,[1] it became necessary to obtain the solubility of the compounds in water. The only datum is the solubility of benzyl chloride at 30°C obtained by means of extraction with ether from the saturated aqueous solution.[2] However, since chlorine compounds having small solubility in water hydrolyze fairly fast during extraction, the extraction method does not seem to be reliable. We therefore attempted to determine the solubility by analyzing the kinetic data of hydrolysis. The rate, the rate constant, and the order of the hydrolysis reaction of benzyl chloride were measured at 4.5, 20, and 30°C and the solubility was determined by a new method. The solubility of benzal chloride and benzotrichloride determined by the same method using known kinetic data is also reported.

Principle of Kinetic Determination of Solubility

Let us express the rate V of a hydrolysis reaction by the equation

$$V = \sum_i k_i[S]^i \tag{1}$$

where i is the order of reaction, k_i the rate constant of ith order reaction, and $[S]$ the concentration of a solute.

First, a sufficiently large amount of a solute is dissolved in water forming a liquid phase of a solute, the concentration of the solute in water being kept constant at constant temperature with the saturation solubility S_s. The rate V_s at saturation solubility can be measured keeping the solute concentration constant during the rate measurement. The rate V is then measured at various solute concentrations below saturation solubility, and k_i and i are determined from the data by the usual method. Saturation solubility S_s is now obtained from the observed V_s, k_i, and i by the following equation.

$$V_s = \sum_i k_i[S_s]^i \tag{2}$$

The principle of this method is simple and can be applied to the solubility measurement of a solute whose solubility is so small and solvolysis rate so great that the application of usual methods is difficult. However, there are several restrictions for the measurement. 1) The solubility of a solute must be so small that the phase of the solute can exist together with the solvent phase. 2) The rate of dissolution of a solute into a solvent must be sufficiently fast in comparison with that of solvolysis. 3) The solubility or the rate of solvolysis must not be influenced by any product of solvolysis. If the influence cannot be neglected, correction of the influence should be made. 4) The rate of solvolysis in solute phase must be negligibly small compared with that in solvent phase. If not, correction should be made.

Experimental

Since benzyl chloride decomposes in water to form benzyl alcohol and hydrogen chloride,[1,2] the reaction was followed by observing the increase in proton concentration.

As soon as benzyl chloride was added to water in a glass reaction vessel equipped with a tefron-coated magnetic stirrer and placed in a water bath, the mixture was vigorously stirred in order to dissolve the benzyl chloride and start the reaction immediately. The pH change of the solution due to hydrolysis was measured with a Hitachi-Horiba M-5 type pH meter (accuracy: 0.03 pH) whose glass electrode was dipped in the solution. The temperature of the reaction mixture was maintained at 20±0.01°C, 30±0.01°C, and 4.5±0.2°C. In the measurement of V, the amount of benzyl chloride

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[1] K. Tanabe, *Nippon Kagaku Zasshi*, **87**, 629 (1966).

[2] S. C. J. Olivier, *Rec. Trav. Chim.* **53**, 891 (1934).

which is smaller than that of the saturation solubility was used for the reaction, while a sufficiently large amount above S_s was used for the measurement of V_s.

An approximate value of the saturation solubility necessary to undertake experiments at solute concentration below saturation solubility was obtained by the following method. A certain amount (a mg) of benzyl chloride is dissolved in a certain amount (b m*l*) of acetone which can dissolve both benzyl chloride and water and in which benzyl chloride does not solvolyze. Some amount (c m*l*) of water is then added dropwise from a burette into the solution until the solution shows white turbidity. An approximate value of the solubility in acetone-water is thus calculated by the equation, $a/(b+c)\times 100$ (mg/100 m*l*). An approximate solubility in pure water is obtained by extrapolating the plots of $a/(b+c)\times 100$ against the volume %, $(c/b+c)\times 100$, of added water.

Benzyl chloride (extra pure reagent of Wako Junyaku Co., Ltd.) was distilled in a vacuum. Deionized water was used.

Results and Discussion

Rate V_s at Saturation Solubility. The pH change due to the hydrolysis of benzyl chloride in the saturated aqueous solution plotted against reaction time is shown in Fig. 1. The change is fast in the initial stage of the reaction but slow later. Since the increase in the amount of added benzyl chloride above saturation solubility value caused an increase in the amount of the first sharp pH change but did not change the inclination of the straight line at the later stage, the sharp pH change is considered to be due to the hydrolysis of impurities such as benzal chloride and benzotrichloride whose rate constants,3) (292±2) × 10^{-5} sec^{-1} at 30°C and (387±5) × 10^{-5} sec^{-1} at 5°C, are much larger than that of benzyl chloride, (58.3±0.1) × 10^{-5} sec^{-1} at 60°C. The amount of impurities was estimated to be 0.1 mol% from the amount of the sharp pH change. The rate V_s was thus obtained from the inclination of the straight line appearing later, the values being listed in Table 1. The fact that V_s was almost constant independent of the amount of added benzyl chloride indicates that the hydrolysis in the phase of benzyl chloride can be neglected. All calculations were made by employing the method of least square.

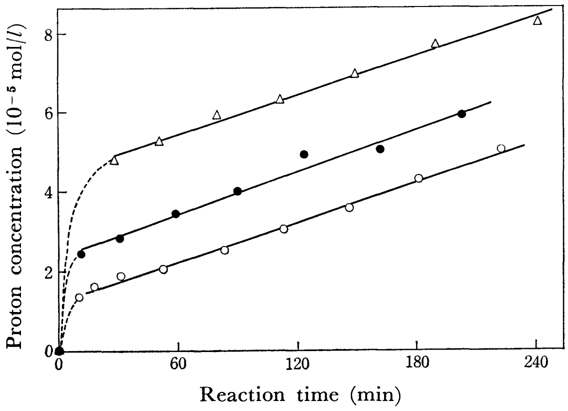

Fig. 1. Proton concentration *vs.* reaction time at 4.5°C.
-○- 0.5 m*l* of benzyl chloride in 300 m*l* of water
-●- 1 m*l*/300 m*l* -△- 2 m*l*/300 m*l*

Rate Constant k_i and Order of Reaction i. An approximate value of the solubility of benzyl chloride was 15 mg/100 m*l* of water at room temperature (Experimental). The reactions were carried out at several concentrations of benzyl chloride below the approximate solubility, and the initial rates $(dx/dt)_0$ were calculated from the curves obtained by plotting proton concentration against reaction time, where x is the concentration of proton formed by the hydrolysis at time t. The initial rates thus obtained at various initial concentrations a and at several temperatures are given in Table 2.

By plotting $\log(dx/dt)_0$ against $\log a$, the order of reaction was obtained to be 1.00 at 30°C, 1.11 at 20°C, and 1.17 at 4.5°C. At 20 and 4.5°C, second order reaction seems to take place together with first order reaction as represented by the equation

$$\left(\frac{dx}{dt}\right)_0 = k_1a + k_2a^2 \tag{3}$$

where k_1 and k_2 are the rate constants of the first and second order reactions, respectively. Eq. (3) was justified by the fact that the plot of $(dx/dt)_0/a$ *vs.* a gave straight lines as shown in Fig. 2. The values of k_1 and

Table 1. Rate V_s at staturation solubility

Temp. (°C)	Volume (m*l*)		V_s (M/min)	Averaged values of V_s (M/min)
	Benzyl chloride	Water		
4.5	0.5	300	$(1.64\pm0.42)\times10^{-7}$	$(1.65\pm0.04)\times10^{-7}$
	1	300	$(1.77\pm0.10)\times10^{-7}$	
	2	300	$(1.62\pm0.07)\times10^{-7}$	
	5	100	$(1.56\pm0.12)\times10^{-7}$	
20	1	300	$(1.62\pm0.03)\times10^{-6}$	$(1.67\pm0.04)\times10^{-6}$
	1	300	$(1.63\pm0.04)\times10^{-6}$	
	2	300	$(1.86\pm0.07)\times10^{-6}$	
	2	300	$(1.71\pm0.06)\times10^{-6}$	
	5	100	$(1.80\pm0.05)\times10^{-6}$	
30	0.44	400	$(5.81\pm0.23)\times10^{-6}$	$(5.59\pm0.07)\times10^{-6}$
	0.55	400	$(5.65\pm0.11)\times10^{-6}$	
	1	400	$(5.57\pm0.10)\times10^{-6}$	
	10	200	$(5.23\pm0.24)\times10^{-6}$	

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3) P. M. Laughton and R. E. Robertson, *Can. J. Chem.*, **37**, 1491 (1959).

Table 2. Initial rate

Temp. (°C)	a (M)	$(dx/dt)_0$, (M/min)
4.5	2.54×10^{-3}	$(1.59\pm0.04)\times10^{-7}$
	1.91×10^{-3}	$(1.09\pm0.03)\times10^{-7}$
	1.29×10^{-3}	$(6.42\pm0.24)\times10^{-8}$
	6.08×10^{-4}	$(2.81\pm0.13)\times10^{-8}$
20	2.63×10^{-3}	$(1.01\pm0.01)\times10^{-6}$
	2.53×10^{-3}	$(9.62\pm0.13)\times10^{-7}$
	1.58×10^{-3}	$(5.48\pm0.09)\times10^{-7}$
	1.27×10^{-3}	$(4.26\pm0.08)\times10^{-7}$
	5.95×10^{-4}	$(1.85\pm0.01)\times10^{-7}$
	2.77×10^{-4}	$(8.55\pm0.31)\times10^{-8}$
30	1.76×10^{-3}	$(2.02\pm0.09)\times10^{-6}$
	9.30×10^{-4}	$(1.11\pm0.05)\times10^{-6}$
	4.31×10^{-4}	$(5.65\pm0.44)\times10^{-7}$
	$3{\cdot}48\times10^{-4}$	$(3.92\pm0.26)\times10^{-7}$

k_2 obtained by Eq. (3) are given in Table 3. The activation energies and frequency factors calculated from the data are also given in Table 3.

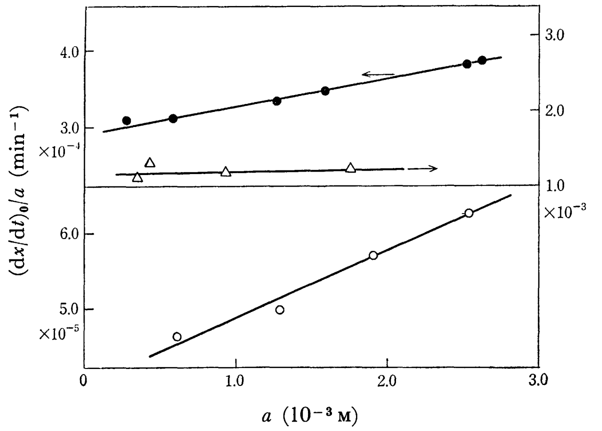

Fig. 2. Plots of $(dx/dt)_0/a$ against a.
-○- 4.5°C, -●- 20°C, -△- 30°C

Table 3. k_1 and k_2 and activation parameter

Temp. (°C)	k_1, (min^{-1})	k_2, (M^{-1} min^{-1})
4.5	$(3.98\pm0.17)\times10^{-5}$	$(8.9\pm2.5\ )\times10^{-3}$
20	$(2.90\pm0.02)\times10^{-4}$	$(3.6\pm0.10)\times10^{-2}$
30	$(1.16\pm0.09)\times10^{-3}$	$(2.7\pm7.1\ )\times10^{-2}$
Activation energy (kcal/mol)	21.2 ± 1.1	14.6 ± 1.3
Frequency factor (sec^{-1})	12.2 ± 0.8	9.4 ± 1.0

Table 4. Solubility of benzyl chloride

Temp. (°C)	Solubility	
	M	mg/100 m*l*
4.5	$(2.61\pm0.09)\times10^{-3}$	33.1
20	$(3.89\pm0.08)\times10^{-3}$	49.3
30	$(4.4\ \pm1.0\ )\times10^{-3}$	55.5

Determination of Solubility. Solubility S_s of benzyl chloride is now calculated from the values of V_s, k_1, and k_2 according to the following equation.

$$V_s = k_1S_s + k_2S_s^2 \tag{4}$$

The results are given in Table 4. The solubility value at 30°C is a little larger than 46.5 mg/100 m*l* obtained by Olivier.[2] The heat of dissolution calculated from the data in Table 4 was 4.05±0.44 kcal/mol.

Equation (4) allows us to calculate the degree of contribution of second order reaction to total hydrolysis reaction. The fractions of second order reaction, $k_2S_s^2/(k_1S_s+k_2S_s^2)$, are 36.9% at 4.5°C, 32.6 at 20°C, and 9.25 at 30°C, the values being higher at lower temperature.

The solubility of benzal chloride and benzotrichloride was calculated similarly by the present method, utilizing the kinetic data obtained by Ohnishi,[4] Tanabe and Sano,[5] and Laughton and Robertson,[3] and is shown in Table 5. Tables 4 and 5 reveal that with the increase of the number of chlorines of chlorinated phenylmethanes, their hydrolysis rate increases, but solubility decreases.

Table 5. Solubility of benzal chloride and benzotrichloride

	Temp. (°C)	V_s (M/min)	i	k_1 (sec^{-1})	S_s, mg/100 m*l*
Benzal chloride	30	2.77×10^{-4} a)	1	297×10^{-5} c)	25
Benzotrichloride	5	$6.3\ \times10^{-5}$ b)	1	387×10^{-5} c)	5.3

a) From Ref. 4, b) From Ref. 5, c) From Ref. 3.

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[4] R. Ohnishi, unpublished data.

[5] K. Tanabe and T. Sano, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **13**, 110 (1966).