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Equilibrium Solubilities of Iodine Vapor in Water

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Equilibrium solubilities of iodine vapor in water were measured by introducing iodine vapor, in equilibrium with solid iodine, into water and by circulating it in a closed system, and Henry's law constants were determined. Equilibrium distributions of iodine vapor between a gas phase and an aqueous phase were also measured by another method, and partition coefficients were determined. The solubilities of iodine vapor in water estimated from both the Henry's law constants and the partition coefficients are compared with those of solid iodine reported in the literature. Thermodynamic parameters for the hydration of iodine vapor are evaluated experimentally.

A large number of papers have been published on solubilities of iodine in water.[1] All of them are concerned with saturated solutions prepared through direct contact of solid iodine with water. On the other hand, in the field of nuclear power plant, there are some publications on the partition study of iodine vapor between air and water.[2,3,4] The experimentally determined partition coefficients, however, differ from literature to literature. Both the solubility of solid iodine in water and the iodine vapor pressure are known at a given temperature, so the partition coefficient can be predicted provided the iodine vapor behaves ideally.[5] However, the partition coefficients reported in the literature are not consistent with the prediction.

In our previous paper we reported a method of preparing solutions saturated with solute by use of solute vapor. The method has successfully been applied to determining Henry's law constants of metallic mercury and some liquid aromatic hydrocarbons.[6,7] The present paper is concerned with an extension of the method to such solutes as iodine which exists in the solid state at ordinary temperatures. Another technique was also employed for estimation of partition coefficients of iodine vapor between the gas phase and the aqueous phase.

Experimental

Materials. The iodine used as solute was of analytical reagent grade and used without further purification. Deionized-redistilled water was used as solvent. Analytical reagent grade carbon tetrachloride was used for solvent extraction and for the preparation of iodine standard solutions.

Apparatus and Procedures. The apparatus, used to prepare aqueous solutions saturated with iodine vapor, is shown in Fig. 1. It is composed of a separatory funnel (100 cm^3), A, two condensers, B and C, a bottle (300 cm^3), D, and a Viton diaphragm pump (Iwaki Type AP-32 Z), P. Gas inlet-type adaptors are mounted in A and D. Teflon and glass pipes, both of ϕ=8 mm, are used for connection. Solid iodine is packed in the upper condenser B (ϕ 8 mm×200 mm), the top end of which is equipped with a coarse sintered glass disk and the bottom part is plugged with glass wool. We will hereinafter refer to condenser B packed with solid iodine and separatory funnel A containing *ca.* 50 cm^3 water as the "solute reservoir" and "solubility flask," respectively. Lower condenser C and bottle D serve to trap water droplets and to keep the air and the solute reservoir in thermal equilibrium. The temperature of the solubility flask is held constant by circulating water through a surrounding jacket from a thermostated bath. The temperature of the solute reservoir is also maintained constant in the same way by using another thermostated bath. These thermostats are controlled within ±0.02 °C. The assembled apparatus was placed in a chamber, the temperature of which was kept higher than that of the solute reservoir in order to prevent the iodine vapor from condensing inside the apparatus. Aqueous solutions saturated with iodine vapor were prepared as follows: after the desired temperatures for the solubility flask and solute reservoir were attained, the pump was started, and the iodine vapor, which had been generated by allowing air to flow through the solute reservoir, was introduced into the solubility flask *via* a sintered glass ball, and circulated as indicated in Fig. 1. The iodine vapor pressure inside the solubility flask can be fixed at any desired value by controlling the temperature of solute reservoir. At the beginning of this study, iodine crystals purified by sublimation were packed in the solute reservoir. However, the fine crystals tended to pack together inside the column so tightly during the course of continuous air-circulation as to make the further aeration through the column difficult. Then, we used coarse iodine crystals. The circulation rate, which could be changed by means of a Variac, was set at 0.8 dm^3 min^{-1} in most instances. After the

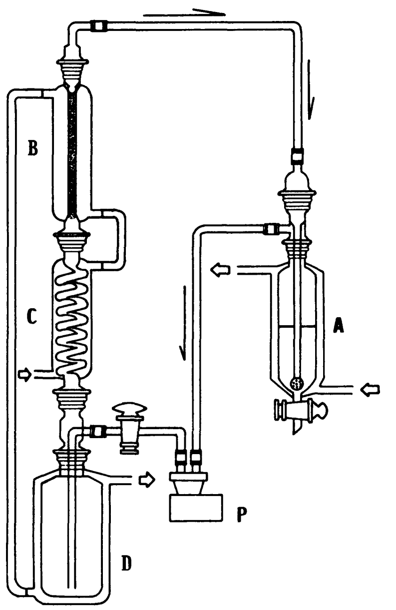


Fig. 1. Solubility apparatus.
The solid arrows indicate the direction of air-circulation.

solubility equilibrium was attained, a stopcock on the bottom of the solubility flask was opened. The first portion of *ca.* 10 cm^3 was discarded and the following 10 cm^3 portions were transferred successively into three cylindrical separatory funnels, in which 10 cm^3 CCl_4 had previously been placed. Each separatory funnel had been calibrated so that the volume of an aqueous solution poured into it might be read out. Mixtures in the separatory funnels were hand-shaken and allowed to stand for 30 min, and then, after dehydrating the CCl_4 phase with anhydrous sodium sulfate, absorbances were measured at 514 nm using a Hitachi Model 100-50 spectrophotometer against a blank extract as the reference. Standard solutions were prepared by weighing out of suitable quantities of solid iodine, followed by dilution with CCl_4 in volumetric flasks. Calibration curves were constructed by using iodine standard solutions of the order of 10^{-3} mol dm^{-3} in the same way as described in our previous paper.[7)]

The apparatus, used to determine partition coefficients of iodine vapor between air and water, is shown in Fig. 2. A large separatory funnel of *ca.* 5 dm^3 capacity, to be called the "partition flask," was connected to a Viton diaphragm pump of the same type as pump P shown in Fig. 1 through Teflon tubes (ϕ=8 mm) and two glass adaptors, one of which was attached to a sintered glass ball and was long enough to reach nearly the bottom of the partition flask. The temperature inside the partition flask was kept constant by circulating water through a surrounding jacket from a thermostated bath. A particular attention was paid in assembling the apparatus so as to minimize the section exposed out of the jacket, down to a volume as small as 42.5 cm^3. Aqueous iodine solutions were prepared by using the apparatus shown in Fig. 1 with the solubility flask replaced by one of 300 cm^3 capacity. An aliquot of the iodine solution thus prepared was poured into the partition flask and another aliquot was used to determine the iodine concentration. The pump was operated at a flow rate less than 0.1 dm^3 min^{-1} and the air was circulated at least 10 min. The iodine concentration in the aqueous phase after this air-circulation was measured. The time required to attain the equilibrium partition was preliminarily investigated with a result that 10 min-circulation is sufficient. The air-circulation, however, needed to be made intermittently, lest the temperature of the aqueous phase should decrease owing to the heat of evaporation of the solvent water. From preliminary experiments the best way of the air-circulation was found to be as follows: the air was circulated for 1 min, then the solution was allowed to stand for another 1 min, and finally the operation was repeated at least 10 times.

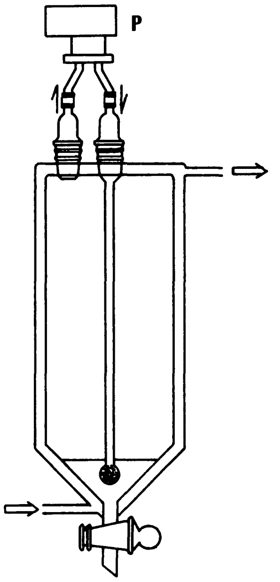


Fig. 2. Partition apparatus.
The solid arrows indicate the direction of air-circulation.

Results

The Time Required for Attaining the Solubility Equilibrium. The time required to attain the equilibrium solubility was checked by taking a small amount of aqueous solution from the bottom of the solubility flask directly into a cuvette and by measuring the absorbance at 460 nm without solvent extraction. The results are shown in Fig. 3. The absorbance readings begin to rise, reach a maximum after 30—90 min according to the rate of air-circulation, and thereafter remain constant. On the basis of this observation, subsequent experiments were carried out at a constant circulation rate of 0.8 dm^3 min^{-1} and iodine concentrations in sample solutions withdrawn after 60 min-circulation were measured.

Solubility as a Function of Iodine Vapor Pressure. It is an essential requirement, as we have emphasized in our previous paper,[7)] to keep the temperature of solubility flask ≧ the temperature of solute reservoir < the room temperature. For this reason, the solubility runs were made by raising the temperature of solute reservoir up to that of solubility flask while the latter was maintained constant. The results are given in Table 1. The vapor pressure of iodine at a given temperature of solute reservoir was estimated from the equation $\log PT^{3/2}=16.945-3464/T$, where P is vapor pressure in Pa and T is absolute temperature. This equation was derived by reference to literature.[8,9)] The equilibrium solubilities are plotted against iodine vapor pressure in Fig. 4, from which we can see that the solubility obeys Henry's law at respective temperatures of water. In Fig. 4 are also shown the results obtained under conditions such that the temperature of solute reservoir was set higher than that of solubility flask. Under such circum-

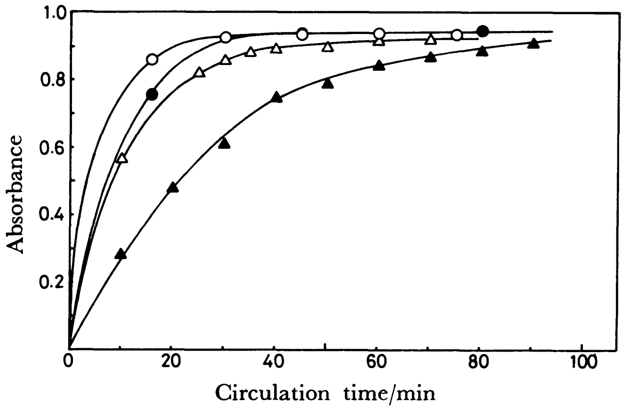


Fig. 3. Absorbance changes of iodine dissolved in water *vs.* circulation time.
Air-circulation rate: 0.8 (○), 0.5 (●), 0.3 (△), 0.2 dm^3 min^{-1} (▲).

Table 1. Solubilities of iodine as a function of its vapor pressure

Temperature of solid I_2 / °C	Vapor pressure of I_2[a)] / Pa	Solubility[b)] / 10^{-4} mol dm^{-3}
Temperature of water: 15.00 °C		
5.00	6.68	3.88, 3.91, 3.74
10.00	10.79	5.90, 5.81, 5.81, 5.78
15.00	17.14	9.12, 9.12, 9.09
Temperature of water: 20.00 °C		
5.00	6.68	2.51, 2.52, 2.52
10.00	10.79	4.51, 4.61, 4.50
15.00	17.14	6.90, 6.84, 6.88
20.00	26.78	10.5, 10.6, 10.7
Temperature of water: 25.00 °C		
10.00	10.79	3.33, 3.32, 3.22
15.00	17.14	5.18, 5.22, 5.21
20.00	26.78	8.11, 8.14, 8.09
25.00	41.20	12.1, 12.1, 12.1
Temperature of water: 30.00 °C		
5.00	6.68	1.53, 1.53
10.00	10.79	2.53, 2.51, 2.51
15.00	17.14	3.93, 3.94, 3.93
20.00	26.78	6.42, 6.40, 6.39
25.00	41.20	9.44, 9.59
30.00	62.48	13.8, 13.9
Temperature of water: 35.00 °C		
5.00	6.68	1.11
10.00	10.79	1.64
15.00	17.14	2.88
20.00	26.78	4.62
25.00	41.20	7.04
29.32	59.09	10.6
31.33	69.63	12.3
35.00	93.43	16.1

a) The vapor pressure of iodine, P (in Pa), was estimated by $\log PT^{3/2} = 16.945 - 3464/T$, where T is absolute temperature. b) A set of two or more solubility values indicates that experiments were carried out under the same conditions on different days.

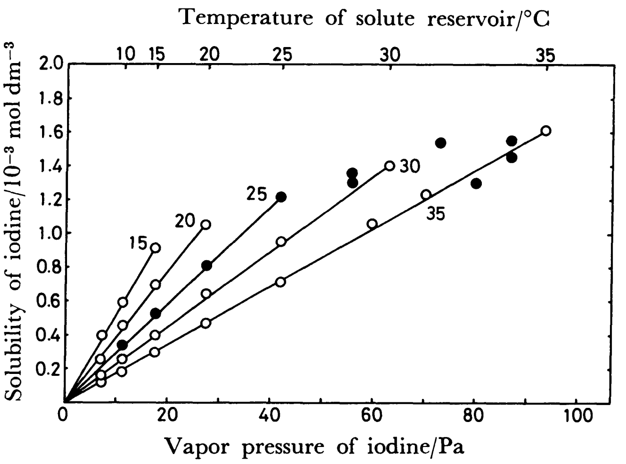


Fig. 4. Equilibrium solubility of iodine *vs.* iodine vapor pressure.
The figure near each solid line indicates the temperature of water. The solid circles are the results obtained under conditions such that the temperature of water was held constant at 25 °C while the temperature of solid iodine was raised beyond 25°C.

stances, iodine vapor condenses inside the solubility flask, and the solid appears in the aqueous phase mostly in the bottom and a little on the surface. Solutions thus prepared were allowed to stand for at least 3 h without air-circulation, and aliquots were pipetted off from the middle part of the aqueous phase to measure iodine concentrations. The results varied widely and the reproducibility was poor as can be seen in Fig. 4.

Gas-Water Partition Coefficients of Iodine. The partition coefficient, K_P, is defined according to literature as follow:[3,4] K_P=(concentration of I_2 in aqueous phase in mol dm^{-3})/(concentration of I_2 in gaseous phase in mol dm^{-3}). In the present study, the concentration of iodine in the gaseous phase was not measured but estimated from the iodine concentrations in the aqueous phase before and after equilibrium, C_B and C_A (in mol dm^{-3}), respectively, by $K_P = C_A(10^3 \times V - v)/v(C_B - C_A)$, where v is the volume of aqueous phase (cm^3) and V is the volume of partition flask (V=4.9165 dm^3). The results are given in Table 2.

Discussion

Solubilities of Iodine in Aqueous Solutions. The primary purpose of the present study is to determine whether the method proposed here can be used for preparing aqueous solutions of desired iodine concentration. The most important problem is whether an aqueous solution is saturated with iodine vapor. It was experimentally confirmed that equilibrium solubilities obey Henry's law. However, this does not necessarily mean that solutions are saturated actually 100% with iodine vapor. Thus, solutions saturated, say, 90% can be expected to obey Henry's law in appearance provided the imperfect saturation is maintained constant throughout the range of iodine vapor pressure investigated. In this study, therefore, we employed the partition method, too, in which the problem of imperfect saturation need not be considered so long as the gas-water partition equiliblium is attained. The partition coefficients determined here are tabulated in Table 3, together with some available literature values. Though the data reported so far in the literature are scanty, our present results seem to be in reasonable agreement with those reported by Eguchi *et al.*[3]

The Henry's law constant, K_H, is expressed in the following well-known equation

$$K_H = P/X_2, \tag{1}$$

where P is the partial pressure of iodine vapor in Pa and X_2 is the mole fraction of dissolved iodine in water. Based on the definition of partition coefficient and on the assumption that the iodine vapor in the gaseous phase is ideal, the partition coefficient can be written as

$$K_P = 55.51\,X_2/(PR^{-1}\,T^{-1}), \qquad (2)$$

where the factor 55.51 is the mole number of 1 dm^3 water and R and T have their usual significances, R being 8.3145×10^3 dm^3 Pa K^{-1} mol^{-1}. From Eqs. 1 and 2, we can derive the Henry's law constant from the partition coefficient as

$$K_H{}^* = 4.615\times10^5\,T/K_P. \qquad (3)$$

We will specify as $K_H{}^*$ the Henry's law constant as derived from the partition coefficient. In Table 4 are listed the values of K_H and $K_H{}^*$, the former being determined by applying the least-squares method to the data given in Table 1. The solubilities of iodine vapor in water were estimated from Eq. 1. Table 4 shows that the solubilities of iodine vapor are somewhat lower than those of solid iodine. Is there any essential difference between the solubilities of vapor and solid? They should both be equal to each other in principle if there is no possibility of any alteration, in physicochemical properties of the solid interface, to occur during the contact of the solid iodine with water, such as formation of hydrated iodine crystals (water molecule-included iodine crystals). It is supposed that an imperfect saturation with iodine vapor may give rise to the lower solubilities. However, this explanation seems to be unlikely since the values of K_H are lower than those of $K_H{}^*$ over the temperature range studied. At present we cannot offer any satisfactory explanations for the difference observed between the solubilities of iodine vapor and solid iodine.

It should be mentioned that the present method for determining partition coefficients, though rapid and simple, suffers from three inherent disadvantages, and therefore the $K_H{}^*$ values estimated seem to be less reliable than those of K_H. Firstly, iodine concentrations in the gaseous phase were estimated indirectly. Secondly, a part of the aqueous phase was caused to splash inside the partition flask during the course of air-bubbling. The partition equilibrium between the droplets and the gaseous phase might require much longer time, and therefore the volume of the aqueous phase initially taken, v, should be corrected for these droplets. Thirdly, in deriving Eq. 2, the iodine vapor in gase-

TABLE 2. GAS-WATER PARTITION OF IODINE VAPOR

Temperature °C	Volume of aqueous phase cm^3	Concentration of iodine in aqueous phase 10^{-4} mol dm^{-3} Before equilibrium	After equilibrium$^{a)}$	Partition coefficient $K_P{}^{b)}$
15.00	50	2.29	1.27	121
	100	4.57	3.28	122
	200	1.99	1.67	123
20.00	50	0.897	0.445	95.8
	100	3.99	2.60	90.1
	200	8.24	6.56	92.1
25.00	50	9.73	4.12	71.5
	100	3.40	2.02	70.5
	100	4.35	2.57	69.5
	100	4.72	2.89	76.1
	100	5.23	3.02	65.8
	100	7.82	4.59	68.4
	100	8.86	5.24	69.7
	100	5.00	3.55$^{c)}$	118
	100	8.18	5.37$^{d)}$	92.2
	100	6.05	3.63$^{e)}$	72.0
	100	6.92	4.17$^{e)}$	72.9
	100	10.5	6.30$^{e)}$	71.8
	100	0.724	0.423$^{f)}$	67.6
	100	5.83	3.51$^{f)}$	72.7
	200	9.02	6.74	69.7
30.00	50	3.92	1.36	51.7
	100	1.78	0.931	52.8
	200	6.49	4.47	52.2
35.00	50	5.20	1.60	43.3
	100	2.88	1.37	43.7
	200	1.19	0.774	43.9
40.00	50	5.86	1.60	36.6
	100	12.1	5.24	36.8
	200	5.73	3.48	36.5
45.00	100	0.486	0.186	29.9
	100	4.16	1.55	28.6
	100	4.42	1.65	28.7
	100	5.44	2.09	30.0
	100	7.38	2.83	30.0
50.00	100	2.74	0.895	23.4
	100	3.55	1.17	23.7
	100	4.13	1.37	23.9

a) The air-circulation time was 10 min unless otherwise noted. b) Partition coefficients, K_P, were calculated by $K_P = C_A(10^3\times V - v)/v(C_B - C_A)$, where C_B and C_A are concentrations of iodine before and after equilibrium, respectively, v is the volume of aqueous phase (cm^3), and V is the volume of the partition flask (4.9165 dm^3). c) The air-circulation time was 0.5 min. d) The air-circulation time was 1 min. e) The air-circulation time was 5 min. f) The air-circulation time was 30 min.

TABLE 3. PARTITION COEFFICIENTS OF IODINE VAPOR, K_P

Temperature °C	This work	Literature a)	b)	c)
15	122			
20	92.7	122		
25	70.2±2.9$^{d)}$		70	103—114
30	52.2			
35	43.6			
40	36.6		35	32.0—37.6
45	29.4			
50	23.7			
60	15.8$^{e)}$		17	
70	10.0$^{e)}$			16.4—18.4

a) Ref. 2. b) Ref. 3. c) Ref. 4. d) In calculating the mean value, the data obtained at air-circulation times of 0.5, 1, and 5 min were omitted. e) Estimated by extrapolation of $\log K_P$ vs. $1/T$, where T is absolute temperature.

TABLE 4. HENRY'S LAW CONSTANTS AND SOLUBILITIES OF IODINE

Temperature	Henry's law constant		Solubility of iodine vapor		Solubility of solid iodine	
	10^6 Pa		10^{-4} mol dm^{-3} Estimated from		10^{-4} mol dm^{-3} Literature values	
°C	K_H	K_H* a)	K_H	K_H* a)	b)	c)
15.0	1.03±0.04	1.09	9.23±0.36	8.73		9.717
20.0	1.39±0.06	1.46	10.7 ±0.5	10.2	10.2	11.27
25.0	1.86±0.03	1.96	12.3 ±0.2	11.7	13.2	13.11
30.0	2.44±0.06	2.68	14.2 ±0.3	12.9	15.2	15.28
35.0	3.19±0.02	3.26	16.3 ±0.1	15.9		17.87
40.0		3.95		19.4	20	20.07
45.0		4.99		22.3		24.63
50.0		6.29		25.5	28	29.03

a) Derived from the partition coefficient, K_P, by $K_H^* = 4.615 \times 10^5\, T/K_P$, where T is absolute temperature. b) Taken from Ref. 1. c) Taken from Ref. 14.

TABLE 5. THERMODYNAMIC PARAMETERS OF IODINE CORRESPONDING TO SOLUTION, VAPORIZATION, AND HYDRATION PROCESSES AT 25 °C

	Solution process	Vaporization process	Hydration process		
			Calcd$^{a)}$	Exptl$^{b)}$	Lit$^{c)}$
ΔG / kJ mol^{-1}	26.40	19.360	7.040	7.20 (7.32)	6.987
ΔH / kJ mol^{-1}	22.70	62.421	−39.72	−41.7 (−38.3)	−39.52
ΔS / J K^{-1} mol^{-1}	−12.41	144.428	−156.8	−164 (−153)	−156.0

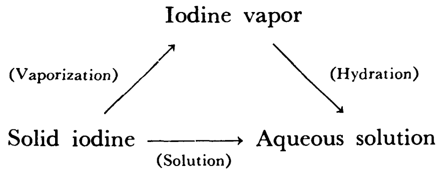
a) Calculated by subtracting the value for vaporization from that for solution process. b) Estimated from the temperature dependence of Henry's law constant. The values designated in parentheses were estimated from partition coefficients. In both cases the temperature dependence of ΔH was neglected. c) Taken from Ref. 12.

ous phase was postulated to be ideal. This assumption, however, may be permissible because of its low pressure. These disadvantages might lead to relatively large deviations for the measured K_P values and, therefore, for the estimated K_H* values, as compared with the K_H values. However, it is difficult to explain why, at respective temperatures of water, the value of K_H* is lower than that of K_H, the difference amounting to as much as *ca.* 10% in the extreme case.

In the beginning of this work, we used aqueous solutions acidified with perchloric acid, 10^{-4} mol dm^{-3}, as well as pure water. However, the difference in the two results could not be regarded as significant, and according to the literature,$^{10)}$ the hydrolysis constant of the reaction $I_2 + H_2O \rightarrow HIO + H^+ + I^-$ has been reported to be in the order of 10^{-13} at 25 °C. These facts, therefore, suggest that the hydrolysis may be neglected over the iodine concentration range concerned in the present study. Indeed, it has been pointed out from partition experiments that the hydrolysis of iodine does occur at very low iodine concentrations less than *ca.* 4×10^{-5} mol dm^{-3}.$^{11)}$ This concentration range is much lower than those of solutions saturated with iodine.

The method described in this paper is considered to be useful to prepare aqueous solutions of desired iodine concentrations below saturation. The method is suitable for studying possible interactions between iodine and hydrophobic substances in aqueous environment by measuring solubility increments.

Thermodynamic Parameters of Hydration of Iodine Vapor. While it has previously been shown that thermodynamic parameters of hydration of iodine vapor can be evaluated from solubility data of solid iodine,$^{12)}$ it is considered desirable to confirm them experimentally. The temperature dependence of Henry's law constants has led to an estimation of thermodynamic parameters which correspond to the hydration of iodine vapor. The results are given in Table 5, together with literature values. The solution of solid iodine in water can be divided into two processes: vaporization and hydration. This is shown in Scheme 1.



Scheme 1.

Thermodynamic parameters for each process are related to one another as follows:

$$\Delta G\,(\text{solution}) = \Delta G\,(\text{vaporization}) + \Delta G\,(\text{hydration}),$$
$$\Delta H(\text{solution}) = \Delta H(\text{vaporization}) + \Delta H(\text{hydration}),$$
$$\Delta S\,(\text{solution}) = \Delta S\,(\text{vaporization}) + \Delta S\,(\text{hydration}).$$

Values of ΔG, ΔH, and ΔS for the vaporization process are available from literature,$^{13)}$ and those for the solution process are reported in literature.$^{14)}$ Using these literature values, we have calculated the values of ΔG, ΔH, and ΔS for the hydration process. The results are given in Table 5. The agreement between the experimental and the calculated values is fairly good.

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5) For instance, at 25 °C, the partition coefficient can be predicted to be 79.4 provided that the solubility of solid iodine in water is 13.2×10^{-4} mol dm^{-3} and that the vapor pressure of iodine is 41.20 Pa.

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