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Hydrates of Organic Compounds. I. Solid-Liquid Phase Equilibria in the Water+1,4-Dioxane System and Some Properties of 1,4-Dioxane Hydrate

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The solid-liquid phase diagram for the water +1,4-dioxane system has been determined by the ordinary cooling curve method and with the aid of a differential scanning calorimeter (DSC). The diagram shows the existence of a hydrate which is stable in rather narrow ranges of temperature (−15.8∼−13.5 °C) and of composition (37.0∼46.5 wt% dioxane). From the phase relations and an analysis of the calorimetric data, the composition and the heat of formation (from the liquid states of both components) of the hydrate have been estimated to be $C_4H_8O_2 \cdot mH_2O$ with $m=36\sim39$ and $\Delta H_1=-51.3$ (for $m=36$)∼−55.6 (for $m=39$) kcal/mol respectively. This hydrate seems to be the same as that recently reported by Rosso *et al.*, though the compositions and the temperature ranges are very different.

In our previous papers,[1-3] from the thermodynamic measurements (heat of mixing, vapour pressure, volume change on mixing, and so forth) for aqueous solutions of various ethers, the dissolution states of ether molecules in water have been discussed. The main conclusion from these results is that the most important factor which characterizes the properties of these solutions is the structural modifications of water around the solute. In the present paper, an attempt will be made to examine some properties of the crystalline hydrates of cyclic ethers. It is conceivable that, in an aqueous solution, the local order of the water molecule induced around the solute is very similar to the state of a hydrogen-bonded water which surrounds a guest molecule in a clathrate. The propriety of such an analogy has been pointed out by a number of investigators.[4]

By various experimental techniques (such as X-ray diffraction,[5-7] phase diagram,[8,9] and dielectric absorption,[10,11]) it is now apparent that the crystalline hydrates of several cyclic ethers (such as propylene oxide, trimethylene oxide, and tetrahydrofuran) are clathrate hydrates. However, the phase diagrams[9,12,13] for the binary system of water and 1,4-dioxane, a typical cyclic ether, show no indication of a hydrate; furthermore, it has been pointed out that this rather abnormal behavior is closely associated with the unusual behavior of dilute aqueous solutions of 1,4-dioxane.[9] Very recently, nevertheless, from the phase diagram studies as well, Rosso and others[14] have reported a hitherto unknown 1,4-dioxane hydrate which contains

1) H. Nakayama and K. Shinoda, *J. Chem. Thermodynamics*, **3**, 401 (1971).
2) H. Nakayama, This Bulletin, **45**, 1371 (1972).
3) H. Nakayama, *ibid.*, **43**, 1683 (1970).
4) J. L. Kavanau, "Water and Solute-Water Interactions," Holden-Day, Inc., San Francisco (1964).
5) M. von Stackelberg and B. Meuthen, *Z. Elektrochem.*, **62**, 130 (1958).
6) R. K. McMullan and G. A. Jeffrey, *J. Chem. Phys.*, **42**, 2725 (1965).
7) D. F. Sargent and L. D. Calvert, *J. Phys. Chem.*, **70**, 2689 (1966).
8) J. Erva, *Suomen Kemistilehti*, **29B**, 183 (1956).
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10) D. W. Davidson, M. M. Davies, and K. Williams, *J. Chem. Phys.*, **40**, 3449 (1964).
11) R. E. Hawkins and D. W. Davidson, *J. Phys. Chem.*, **70**, 1889 (1966).
12) F. Hovorka, R. A. Schaefer, and D. Dreisbach, *J. Amer. Chem. Soc.*, **58**, 2264 (1936).
13) J. R. Goates and R. J. Sullivan, *J. Phys. Chem.*, **62**, 188 (1958).
14) J. C. Rosso and L. Carbonnel, *C. R. Acad Sci. Paris, Ser. C*, **272**, 136 (1971).

34 moles of water to one mole of dioxane. The temperature and composition ranges in which it can exist are −12.3 °C(peritectic)∼−14.2 °C(eutectic) and 31.5∼33.5 wt% dioxane. However, there are two notable features in their results. First, their phase diagram is appreciably different from those hitherto reported[6,12,13] over almost the entire range of composition. Secondly, as has been mentioned above, the estimated composition of the hydrate is expressed as $C_4H_8O_2 \cdot 34H_2O$; this is very different from the characteristic composition of the cubic Structure II hydrate (Structure II clathrate has 17 moles of water to one mole of the guest species). All the experimental data at present available show that the hydrates of low molecular-weight cyclic ethers, except ethylene oxide, are normal Type II hydrates.

In order to clarify these ambiguous points, the present work has first been undertaken in order to re-examine the solid-liquid phase equilibria in this binary system. Furthermore, from the phase diagram obtained and from the heat changes observed at peritectic and eutectic temperatures, the composition of a hydrate and the heat reaction accompanying its formation from liquid water and liquid dioxane have been estimated.

Experimental

Reagent-grade 1,4-dioxane was further purified by both crystallization and fractional distillation from sodium. The freezing points were always determined from the cooling curves. The apparatus to measure the freezing points was, for the most part, conventional. It consisted of a Pyrex tube (2.5×15 cm) sealed inside an outer jacket connected to a vacuum. The thermocouple, coated with Teflon, was inserted directly into the freezing tube, and its out-put was connected to a 1 mV recorder. Stirring was established with either a motor-driven glass stirrer or a Teflon disk-vibrator that moved vertically at high periods. A flexible Teflon sleeve was used to seal the opening between the cap and the stirring mechanism. A dry ice+acetone mixture was used as a coolant.

In order to measure the amount of heat absorbed when a hydrate melted and/or was decomposed, a differential scanning calorimeter (DSC) was employed (Shimadzu Seisakusho, SC-20). A small amount (10—20 mg) of the 1,4-dioxane+water mixture of a known composition, sealed in an aluminium pan, was cooled to about −40 °C. After being annealed at this temperature for about two hours, the sample was slowly heated at the rate of 0.5 °C/min. Pure water was used as the reference sample. The correction for the temperature and for the amount of heat was established by comparing, under the same experimental conditions, the melting point and the heat of fusion of pure water (1.436 kcal/mol[15] at 0 °C). The determination of a peritectic temperature was carried out from temperature reading on a DSC chart since, in the cooling-curve method, the change in the curve at such a temperature is somewhat ambiguous.

Results and Discussion

The Existence of a 1,4-Dioxane Hydrate. The solid-liquid phase diagram for the 1,4-dioxane+water system is shown in Fig. 1, in which most of the peritectic temperatures are obtained from DSC measurements. This phase diagram obviously shows the existence of a 1,4-dioxane hydrate in the temperature range of −13.5°C (peritectic temperature)——15.8 °C (eutectic temperature) and in the composition range of 37.0—46.5 wt% dioxane. This phase diagram is in fair agreement with the other data[6,12,13] over the major part of the composition, yet all the data except ours overlook the existence of a hydrate in a rather narrow composition range. As has been mentioned above, the measurements of Rosso and Carbonnel[14] deviate appreciably from all the data, including ours, though their report was the first to point out the existence of a hydrate. The compositions and temperatures of characteristic points in the phase diagram for this binary system are summarized in Table 1, together with the values available in the literature.

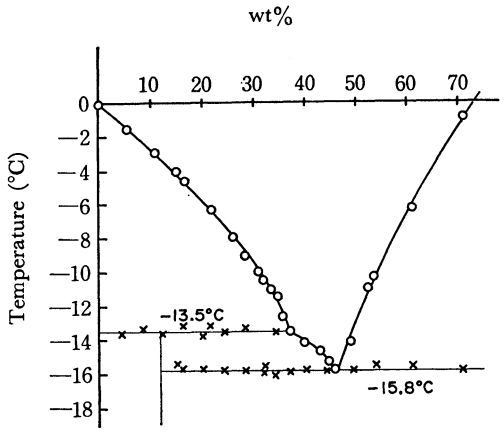

Fig. 1. The solid-liquid phase diagram for the 1,4-dioxane+water system.

Table 1. Characteristic points in the phase diagram of 1,4-dioxane+water system

Points	This work	Other work
Peritectic point		
composition(X_p)[a]	0.107	0.086[14]
temperature(T_p)[b]	−13.5	−12.3[14]
Eutectic point		
composition(X_e)	0.151	0.146,[12] 0.148,[13] 0.093[14]
temperature(T_e)	−15.8	−15.1,[9] −14.9,[12] −15.6,[13] −14.2[14]

a) X is the mole fraction of dioxane. b) in °C.

The composition of the hydrate cannot be clearly determined solely from the phase diagram since it exhibits a peritectic decomposition at −13.5 °C and since, unfortunately, the concentration dependence of the peritectic-halt length in cooling curves is quite uncertain. Thus, the composition of the hydrate was estimated by analyzing the heat change observed in the DSC measurements (Section (2)).

Typical results of the DSC measurements are illustrated in Fig. 2 as a function of the dioxane content. As may be seen from this figure, two characteristic peaks are observed around −13 °C and −16 °C.

15) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water", Oxford University Press, London, (1969).

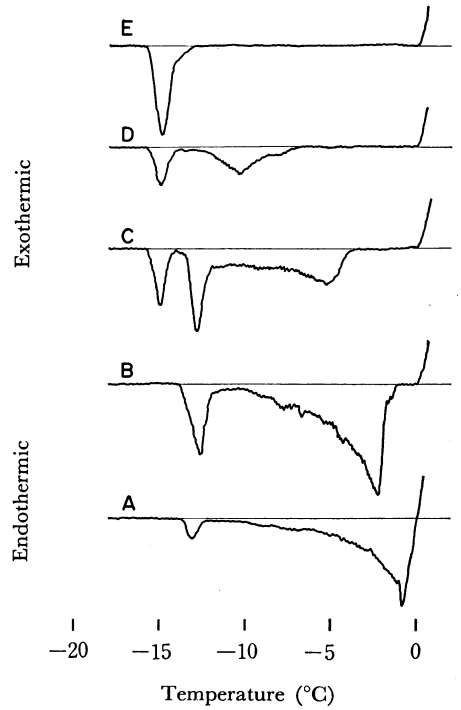

Fig. 2. Representative DSC charts for the 1,4-dioxane+water system as a function of weight per cent of 1,4-dioxane. A: X=0.009 (4%), B: X=0.027 (12%), C: X=0.061 (24%), D: X=0.088 (32%), E: X=0.143 (45%).

It is reasonable to ascribe the endothermic peak near −13 °C to the peritectic decomposition of a hydrate, thus presenting further support for the existence of a 1,4-dioxane hydrate. The other peak, near −16 °C, is unquestionably due to the melting of solids (hydrate and/or solid dioxane) at the eutectic temperature. The remarkably exothermic peak near 0 °C is due to the melting of pure water sealed in a reference pan.

Estimation of the Composition and of the Heat of Formation of the 1,4-*Dioxane Hydrate.* It is obvious that the hydrate has a hydration number greater than 17, which is the typical composition of the Type II clathrate hydrate, since, in the above phase-diagram experiments (Figs 1 and 2), the eutectic halt (at −15.8 °C) has been clearly observed at mole fractions lower than 1/18. In order to determine the probable composition of the hydrate and, at the same time, the heat of reaction, ΔH_i, accompanying its formation from liquid water and liquid dioxane, *i.e.*,

$$\text{1,4-dioxane}(l) + m\text{H}_2\text{O}(l) \rightarrow \text{1,4-dioxane}\cdot m\text{H}_2\text{O}(s), \quad (1)$$

the heat changes observed in the DSC measurements were analyzed as follows.

We assume that the composition of the hydrate can always be expressed as a stoichiometric compound, $C_4H_8O_2\cdot m H_2O$, in which m is a constant. The observed heat changes can be classified into the following four groups. The notations X_p, X_e, T_p, and T_e have the same meanings as in Table 1.

(a) The Heat Change, ΔH_p, at T_p and in the Composition Range between 0 and X_i. X_i denotes the mole fraction of dioxane in the solid hydrate, *i.e.*, $X_i=1/(m+1)$. The ΔH_p corresponds to the enthalpy change when, on heating, all the hydrate decomposes

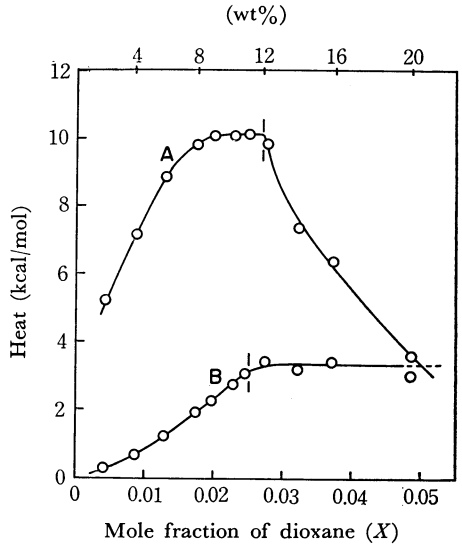

Fig. 3. The concentration dependence of the value of the left-hand side of Eq. (2) (curve A), and of Eq. (3) (curve B).

into a mixture of ordinary ice and a solution whose concentration is X_p. Thus, ΔH_p can be given by the following relation:

$$\frac{\Delta H_p}{n_2} = -\Delta H_i + \left(\frac{1}{X_p} - m - 1\right)\cdot\Delta H_{f,w} + \frac{\Delta H_M}{X_p} \quad (2)$$

where n_2 is the total number of moles of dioxane contained in the sample, $\Delta H_{f,w}$ is the heat of fusion of ordinary ice at T_p, and ΔH_M is the hypothetical heat of mixing (per mole of mixture) of liquid dioxane with water at T_p and X_p. If m is a constant, as is supposed above, the right-hand side of Eq. (2) should be constant. In Fig. 3 the observed values of $\Delta H_p/n_2$ are plotted against the mole fraction of dioxane (X). At first, it increases with an increase in X; then it reaches an almost constant value of 10.1 kcal/mol near X=0.02, after which it decreases drastically above $X>0.027$. The concentration dependence at a low mole fraction ($X<0.02$) reflects the situation that there is a minimum concentration necessary to make the hydrate stable. The marked decrease above $X>0.027$ presumably shows that Eq. (2) can not hold over X=0.027; *i.e.*, X_i is close to 0.027.

(b) The Heat Change, $\Delta H_p'$, at T_p and in the Composition Range between X_i and X_p. The $\Delta H_p'$ corresponds to the enthalpy change when the hydrate, after having been in equilibrium with an aqueous solution of dioxane, decomposes into a mixture of ordinary ice and an X_p solution. Simple calculation leads to the following equation:

$$\frac{\Delta H_p'}{(n_1+n_2)X_p - n_2} = -\frac{\Delta H_i}{mX_p-(1-X_p)} - \frac{1}{X_p}\cdot\Delta H_{f,w} + \left\{\frac{m+1}{mX_p-(1-X_p)} - \frac{1}{X_p}\right\}\cdot\Delta H_M \quad (3)$$

where n_1 is the number of moles of water in the sample. From the DSC measurements, unfortunately, only approximate values of $\Delta H_p'$ can be obtained (especially in the concentration range above X=0.05 (about 20 wt%)), because great difficulty is experienced in separating the peak corresponding to $\Delta H_p'$ from that due to the heat change at T_e and also from those of

subsequent reactions occurring in the temperature range between T_e and T_p. In Fig. 3, the observed values of $\Delta H_p'/\{(n_1+n_2)X_p-n_2\}$ are also plotted against X. At first it increases with an increase in X and reaches an almost constant value (about 3 kcal/mol) above $X=0.025$. It seems reasonable to consider that the inconstancy of the values of $\Delta H_p'/\{(n_1+n_2)X_p-n_2\}$ at low mole fractions ($X<0.025$) is due to the fact that Eq. (3) cannot hold in this region; *i.e.*, X_i is approximately equal to 0.025.

Therefore, from the concentration dependences of Eqs. (2) and (3), we arrive at the conclusion that $X_i=0.025-0.027$; that is, $m=36-39$. The change in m from 36 to 39 corresponds to a variation in dioxane content of less than one per cent (11.1~12.0 wt%).

(c) The Heat Change, ΔH_e, at T_e and in the Composition Range between X_i and X_e. This enthalpy change corresponds to the melting of solid dioxane and of a part of the hydrate, and to the establishment of an equilibrium between the rest of the hydrate and an X_e solution. The ΔH_e must satisfy the following equation:

$$\frac{\Delta H_e}{n_2-n_1/m} = -\frac{1-X_e}{(m+1)X_e-1}\cdot\Delta H_i + \Delta H_{f,d} + \frac{m}{X_e(m+1)-1}\cdot\Delta H_M' \quad (4)$$

is which $\Delta H_{f,d}$ is the heat of fusion of pure dioxane at T_e and $\Delta H_M'$ is the hypothetical heat of mixing (per mole of mixture) of dioxane with water at T_e and X_e. The temperature dependence of the ΔH_i is neglected. The average value of the left-hand side of Eq. (4) over six solutions of different compositions is found to be 11.6 kcal/mol.

(d) The Heat Change, $\Delta H_e'$, at T_e and in the Composition Range between X_e and $X=1$. This $\Delta H_e'$ is an enthalpy change when all of the hydrate and a part of a solid dioxane melt and when the rest of the solid dioxane comes to be in equilibrium with an aqueous solution of X_e. Thus, $\Delta H_e'$ is expressed as:

$$\frac{\Delta H_e'}{n_1} = -\frac{\Delta H_i}{m} + \left(\frac{X_e}{1-X_e}-\frac{1}{m}\right)\cdot\Delta H_{f,d} + \frac{\Delta H_M'}{1-X_e} \quad (5)$$

in which all the notations are the same as above. The average value of the experimental data for $\Delta H_e'/n_1$ is 1.74 kcal/mol.

In order to calculate the most probable pair of values of m (as has been concluded above, $m=36-39$) and ΔH_i from these experimental results, the following numerical values are employed: $X_p=0.107$ (Table 1), $X_e=0.151$ (Table 1), $\Delta H_{f,w}=1.436$ kcal/mol,[16] $\Delta H_{f,d}=3.632$ kcal/mol,[17] $\Delta H_M=-0.150$ kcal/mol,[18] and $\Delta H_M'=-0.165$ kcal/mol.[18] As a result of calculation, it has been found that the most plausible pairs of m and ΔH_i, which meet above four equations simultaneously, are $m=36$ and $\Delta H_i=-51.3$ kcal/mol, $m=37$ and $\Delta H_i=-52.7$ kcal/mol, $m=38$ and $\Delta H_i=-54.1$ kcal/mol, and $m=39$ and $\Delta H_i=-55.6$ kcal/mol. Tentatively, if we insert $m=37$ and $\Delta H_i=-52.7$ kcal/mol into Eqs. (2)—(5), the following values are obtained: Eq. (2)=10.1 kcal/mol, Eq. (3)=3.3 kcal/mol, Eq. (4)=11.8 kcal/mol, and Eq. (5)=1.78 kcal/mol. These values are in good agreement with the experimental results presented above.

From these results, the following two features are worth noting: (a) The determined composition of the 1,4-dioxane hydrate ($C_4H_8O_2\cdot(36—39)H_2O$) differs greatly from that characteristic of the Structure II hydrate. This suggests, therefore, that the 1,4-dioxane hydrate has a structure either new or one of those described by Jeffrey and his co-workers.[19] (b) The estimated values of ΔH_i happen to be very close to $-\Delta H_{f,w}\cdot m$, irrespective of the choice of m (the differences between the two are 0.4—0.5 kcal/mol). The reason for this can be considered to be as follows. The reaction of Eq. (1) can be divided into the following three hypothetical processes: $m_2HO(l)\rightarrow mH_2O(s,\alpha)\rightarrow mH_2O(s,\beta)$ and a dissolution of liquid dioxane into the vacant $H_2O(s,\beta)$ lattice. The $H_2O(s,\alpha)$ means an ordinary ice I, and $H_2O(s,\beta)$ means the metastable clathrate lattice (the β-modification of water). The heat change in the first process is simply equal to $-\Delta H_{f,w}\cdot m$, *i.e.*, $-1.436\cdot m$ kcal/mol, if the temperature dependence of the heat of fusion of ice is neglected. The heat change in the second process can be approximately taken as zero (Eucken's assumption), as has been verified for several gas hydrates.[20,21] Finally, if, in the hydrate, there is no specific interaction, such as hydrogen bonding, between the dioxane molecule and the water host lattice, the heat change in the third process may also be slight, because this heat change[22] can be approximately expressed as $\Delta H_{vap}-\sqrt{\Delta H_{vap}\cdot\Delta H_{ice}}$, in which ΔH_{vap} is the heat of vaporization of liquid dioxane and ΔH_{ice} is the heat of sublimation of ice, and because the numerical value of ΔH_{ice} (8.0 kcal/mol[20]) is very close to the ΔH_{vap}. Thus, we may expect that the heat change in Eq. (1), that is, ΔH_i, will be close to $-1.436\cdot m$ kcal/mol provided the above assumptions are appropriate. In conclusion, we may expect that there are no specific interactions, such as hydrogen bonding, between dioxane (guest molecule) and water (host lattice).

16) This value is the heat of fusion of water at 0 °C (Ref. 15). Temperature correction is not made because of the experimental accuracy in DSC measurements.

17) C. J. Jacobs and G. S. Parks, *J. Amer. Chem. Soc.*, **56**, 1513 (1934). The value 3.632 kcal/mol is the sum of the heat of fusion at its melting point (3.070 kcal/mol) and the heat of transition at −0.3 °C (0.562 kcal/mol). In this case also temperature correction is not made.

18) These values are obtained from a long extrapolation of the experimental data (K. W. Morcom and R. W. Smith, *Trans. Faraday Soc.*, **66**, 1073 (1970)) for the temperature dependence of the heat of mixing of the 1,4-dioxane+water system.

19) P. T. Beurskens and G. A. Jeffrey, *J. Chem. Phys.*, **40**, 906 (1964), and earlier papers.

20) R. M. Barrer and W. I. Stuart, *Proc. Roy. Soc. Ser. A*, **243**, 172 (1957).

21) J. C. Platteeuw and J. H. van der Waals, *Mol. Phys.*, **1**, 91 (1958).

22) This heat change is a sum of two types of heat; heat of vaporization of liquid dioxane (ΔH_{vap}) and cohesive energy between gaseous dioxane and vacant $H_2O(s,\beta)$ lattice. The latter heat (exothermic) can be expressed, as a first approximation, as a geometrical mean of cohesive energies of both components, *i.e.*, $-\sqrt{\Delta H_{vap}\cdot\Delta H_{ice}}$, provided that there are no specific interactions between dioxane and H_2O lattice.