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# Solubility of Some Organic Mercury(II) Halides in Water[1)]

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The solubilities of methylmercury(II) chloride (MMC), methylmercury(II) bromide (MMB), methylmercury(II) iodide (MMI), ethylmercury(II) chloride (EMC), and ethylmercury(II) bromide (EMB) in water have been determined over the temperature range of 10—55 °C (20—40 °C for MMC and EMC). The temperature dependence of the solubilities expressed as mole fractions $x_2$ was given by the following equations:

$$\log x_{2(\mathrm{MMC})} = -1059/T + 0.176 \quad (20\text{—}40\,^\circ\mathrm{C})$$
$$\log x_{2(\mathrm{MMB})} = -1094/T - 0.263 \quad (10\text{—}55\,^\circ\mathrm{C})$$
$$\log x_{2(\mathrm{MMI})} = -463/T - 3.246 \quad (10\text{—}25\,^\circ\mathrm{C})$$
$$\log x_{2(\mathrm{MMI})} = 5.498 \times 10^6(1/T)^2 - 3.711 \times 10^4(1/T) + 57.814 \quad (25\text{—}55\,^\circ\mathrm{C})$$
$$\log x_{2(\mathrm{EMC})} = -1048/T - 0.612 \quad (20\text{—}40\,^\circ\mathrm{C})$$
$$\log x_{2(\mathrm{EMB})} = -179/T - 4.293 \quad (10\text{—}25\,^\circ\mathrm{C})$$
$$\log x_{2(\mathrm{EMB})} = 5.389 \times 10^6(1/T)^2 - 3.603 \times 10^4(1/T) + 55.322 \quad (25\text{—}55\,^\circ\mathrm{C})$$

The thermodynamic parameters for the transfer process from solid to saturated aqueous solution were also determined.

Few papers have been published on the study of the organic mercury(II) compounds from the standpoint of pure chemistry. Waugh *et al.*[2)] obtained the solubility product of MMC only at 25 °C from the dissociation constant and solubility in water. Schwarzenbach and Schellenberg[3)] reported formation constants and the thermodynamic values of $CH_3Hg^+$ with several ligands, and Budevsky *et al.*[4)] studied an interaction of $CH_3Hg^+$ with $Cl^-$. Hepler and Olofsson[5)] also reviewed the thermodynamic properties, chemical equilibria, and standard potentials of the organic mercury(II) compounds. However, neither detailed solubility data with water over a wide temperature range nor thermodynamic parameters have been found in the literature.

As pointed out in the preliminary communication,[1)] the determination of the solubility of the organic mercury(II) compounds in water is considered to be an urgent need. Accordingly, the present paper describes the solubilities of five organic mercury(II) compounds in water and the partial molal enthalpy and entropy of these compounds for the dissolution process, in which MMC is confirmed as the causal agent of the so-called "Minamata Disease".[6—8)] The heat of fusion, one of the very important fundamental properties, was also measured.

## Experimental

*Materials.* MMC, MMB, MMI, EMB, and ethylmercury(II) iodide (EMI)[9)] were obtained from Wako Co., Ltd., and EMC from Tokyo Kasei Co., Ltd. They were recrystallized from hot ethanol. Before recrystallization, inorganic mercury(II) as an impurity was detected by spot test of TLC with dithizone. After recrystallization, no color spot due to inorganic mercury(II) was observed. Other impurities were measured quantitatively by a gas chromatograph equipped with an electron capture detector (Yanagimoto, G-80), and then the degree of purity was evaluated. The results are listed in Table 1, together with the melting points. Water was carefully purified twice by distillation with potassium permanganate.

TABLE 1. PURITY AND MP

| Substance | Purity<br>% | Mp[a)]<br>°C |
|---|---|---|
| MMC | 99.1 | 168 (ref. values; 167,[10)] 168,[10)] 174[8)]) |
| MMB | 99.0 | 160 (ref. values; 160,[11)] 160—161[12)]) |
| MMI | 93.9 | 148 (ref. values; 148,[11)] 150[10)]) |
| EMC | 99.3 | 192 (ref. value; 192[13)]) |
| EMB | 98.9 | 192 (ref. value; 192[11)]) |

a) Different melting points have been reported in the literature, and it is our belief that some of these substances may have impurities.

*Solubility Measurement.* The solubility was determined by density measurements of the saturated aqueous solutions at a given temperature. The saturated aqueous solutions were prepared using two thermostated baths for all experiments. The temperature of the first bath was maintained higher by 3 °C than the desired temperature by continuous stirring, a saturated solution at higher temperature was thus primarily

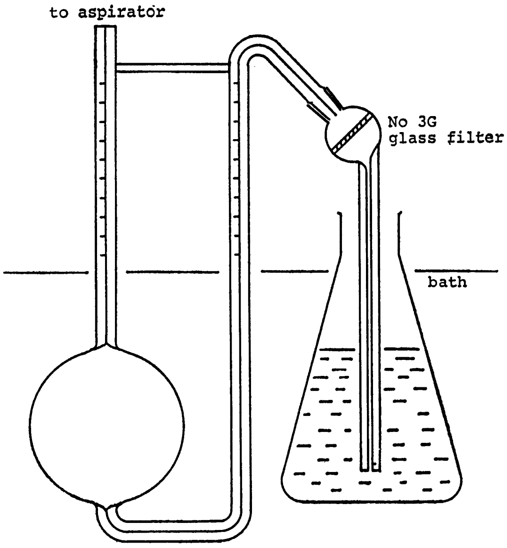

Fig. 1. Handling of solution.

obtained. The constant temperature of this first bath was controlled by a Pt–Hg regulator with ±0.05 °C accuracy. This solution was then immersed in the second bath controlled at the desired temperature with a Pt–toluene–Hg regulator having an accuracy of ±0.01 °C. Great care must be paid to deposition of the solutes with decreasing temperature of the solution and to the handling of such vigorous toxicant. Therefore, the apparatus in Fig. 1 was used to lead the saturated solution directly into the pycnometer (*ca.* 20 ml capacity for MMC and EMC, 45 ml for MMB, MMI, and EMB) without taking out the sample solution from the bath. The pycnometer was joined *via* a glass filter (G-4, 5—10 μ) to the flask containing the thermostated solution and then filled with the solution by aspiration.

*Measurement of Heat of Fusion.* TG–DTA analysis (Rigakudenki, 8076 E1) was carried out in order to obtain the heat of fusion. For determining the instrumental constant, benzoic acid (mp=122.28 °C, heat of fusion=17.3 kJ mol$^{-1}$), indium (mp=156.84 °C, heat of fusion=3.3 kJ mol$^{-1}$), and stannum (mp=231.94 °C, heat of fusion=7.07 kJ mol$^{-1}$) were used as the standard substances, because the melting points of the organic mercury(II) compounds studied (from 148 °C (MMI) to 192 °C (EMC and EMB) were included in the range of these three standard substances, and these standard substances have no solid-solid phase transition near their melting points. The mean value of the instrumental constant was estimated using $k=M\Delta H/A$ ($M$: sample weight, $\Delta H$: heat of fusion, $A$: endothermic peak area) as 2.12.

## Results and Discussion

The concentration of a solute is often determined by spectrophotometry. The present solutes, however, have no absorption maxima in the 200—300 nm region. Direct gravimetry could not be applied because of the volatility and high toxicity of the solutes studied. Therefore, the determination of the concentration was performed in this experiment by density measurements of the solutions at a given temperature. The error in density, mainly due to the weighing error of the pycnometer, was ±0.00005 g/cm$^3$. The relations between the mole fraction $x_2$ and the density of solution are illustrated in Figs. 2—6. All the figures showed good linearity, with a correlation coefficient of 0.999 at every experimental temperature. Table 2 shows the experimental solubility data expressed as mole fractions at various temperatures. The logarithm of the solubility against the reciprocal temperature is given in Fig. 7, which shows that all the solubilities increased with increasing temperature. From these data, the following solubilities

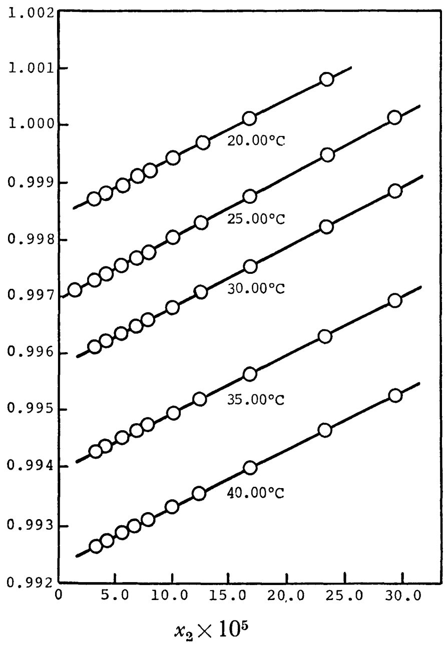

Fig. 2. Relation between mole fraction and density of MMC.

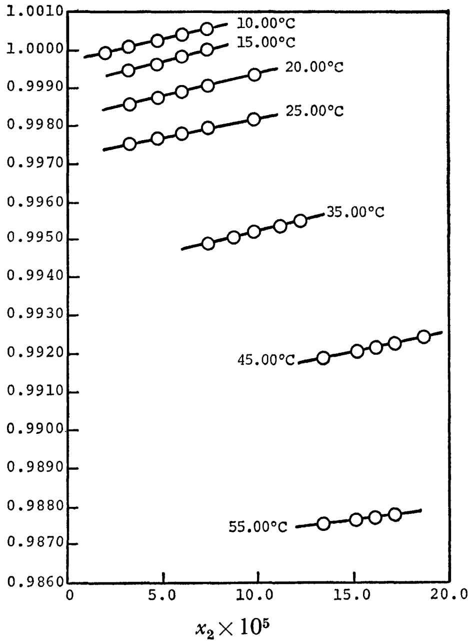

Fig. 3. Relation between mole fraction and density of MMB.

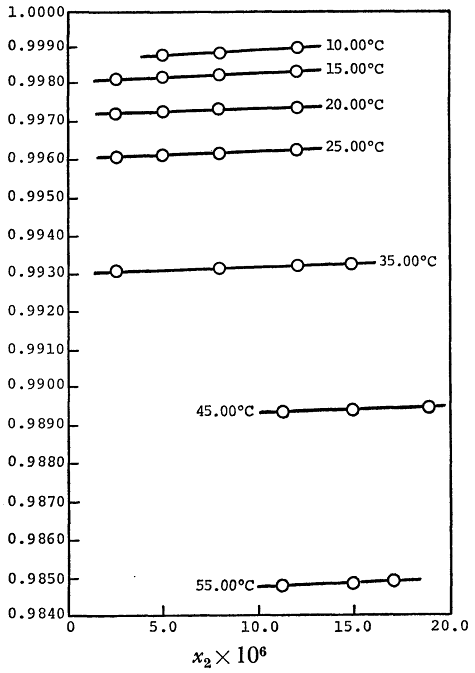

Fig. 4. Relation between mole fraction and density of MMI.

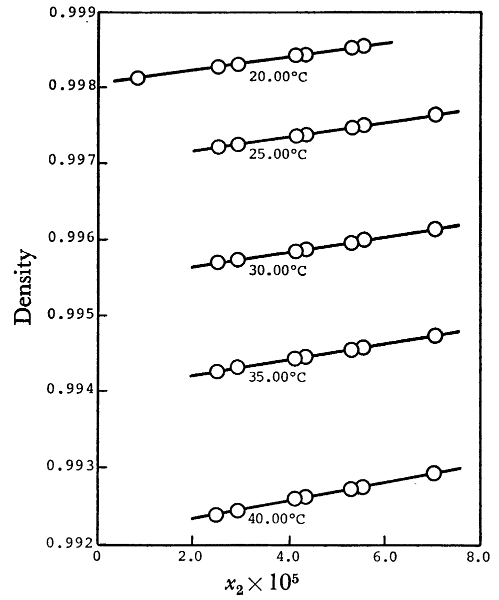

Fig. 5. Relation between mole fraction and density of EMC.

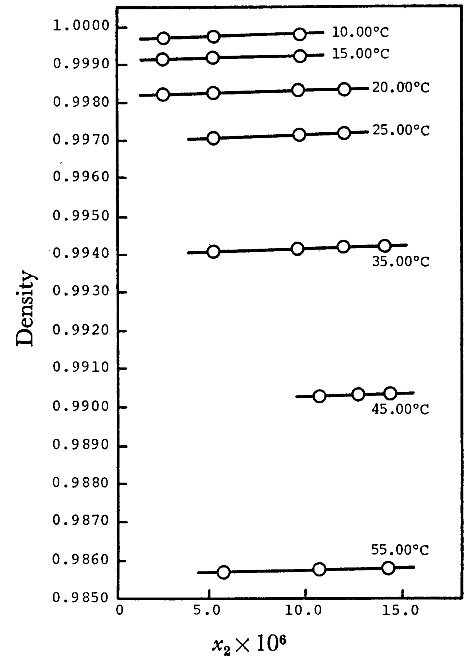

Fig. 6. Relation between mole fraction and density of EMB.

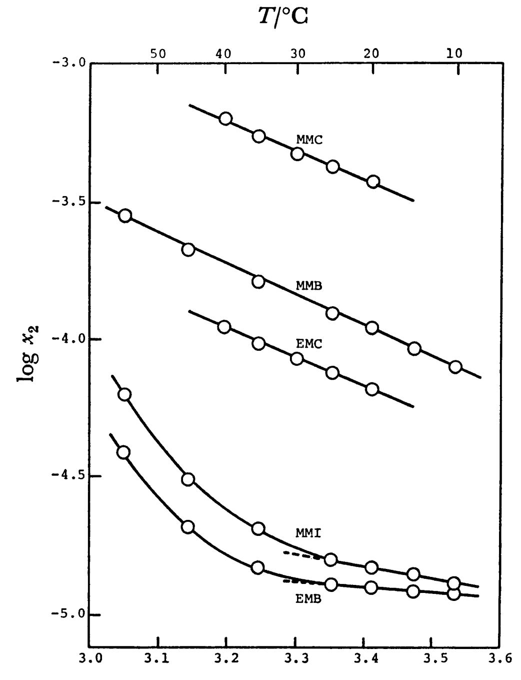

Fig. 7. Temperature dependence of solubility.

were obtained from the least squares fits:

$$\log x_{2(\mathrm{MMC})} = -1059/T + 0.176 \quad (20\text{—}40\ ^\circ\mathrm{C})$$
$$\log x_{2(\mathrm{MMB})} = -1094/T - 0.263 \quad (10-55\ ^\circ\mathrm{C})$$
$$\log x_{2(\mathrm{MMI})} = -463/T - 3.246 \quad (10-25\ ^\circ\mathrm{C})$$
$$\log x_{2(\mathrm{MMI})} = 5.498 \times 10^6(1/T)^2 - 3.711 \times 10^4(1/T) + 57.814 \quad (25\text{—}55\ ^\circ\mathrm{C})$$
$$\log x_{2(\mathrm{EMC})} = -1048/T - 0.612 \quad (20\text{—}40\ ^\circ\mathrm{C})$$
$$\log x_{2(\mathrm{EMB})} = -179/T - 4.293 \quad (10\text{—}25\ ^\circ\mathrm{C})$$
$$\log x_{2(\mathrm{EMB})} = 5.389 \times 10^6(1/T)^2 - 3.603 \times 10^4(1/T) + 55.322 \quad (25-55\ ^\circ\mathrm{C})$$

As can be seen from Fig. 7, the solubility features of MMI and EMB are different from those of MMC, MMB, and EMC: the former exhibits an abrupt curvature above 25 °C, while the latter shows linearity over the temperature range studied.

For a discussion of the thermodynamic behavior of the dissolution process of the solute, the heat of fusion of the solute was determined. As a typical example, the TG–DTA curve of MMI is shown in Fig. 8. As can be

Table 2. Temperature dependence of solubility

| $T$/K | MMC<br>$x_2 \times 10^5$ | MMB<br>$x_2 \times 10^5$ | MMI<br>$x_2 \times 10^5$ | EMC<br>$x_2 \times 10^5$ | EMB<br>$x_2 \times 10^5$ |
|---|---|---|---|---|---|
| 283.16 | | 8.16±0.01 | 1.31±0.04 | | 1.19±0.01 |
| 288.16 | | 9.22±0.04 | 1.40±0.01 | | 1.22±0.06 |
| 293.16 | 37.3±0.5 | 10.95±0.01 | 1.50±0.15 | 6.5±0.2 | 1.26±0.05 |
| 298.16 | 42.4±0.5 | 12.14±0.13 | 1.58±0.01 | 7.6±0.3 | 1.28±0.03 |
| 303.16 | 46.8±0.1 | | | 8.5±0.1 | |
| 308.16 | 54.8±0.1 | 15.80±0.02 | 2.03±0.01 | 9.4±0.2 | 1.49±0.03 |
| 313.16 | 63.4±0.1 | | | 11.2±0.2 | |
| 318.16 | | 20.65±0.05 | 3.02±0.01 | | 2.05±0.01 |
| 328.16 | | 28.16±0.03 | 6.24±0.01 | | 3.84±0.03 |

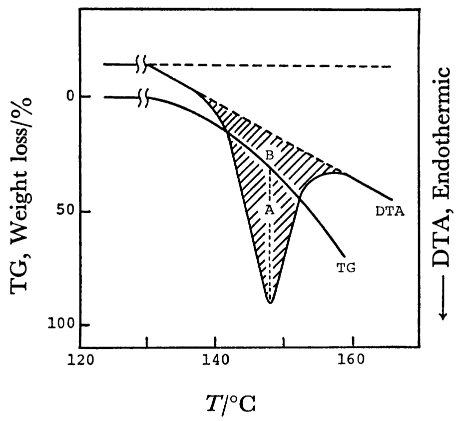

Fig. 8. TG–DTA curve of MMI.

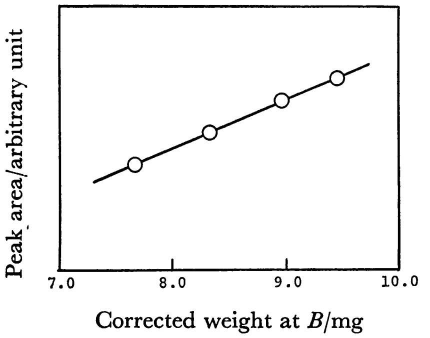

Fig. 9. Plot of corrected weight at *B* in Fig. 8 *vs.* peak area.

Table 3. Enthalpy and entropy of fusion

| Substance | $H^\circ_2 - H^s_2$ cal mol$^{-1}$ | $S^\circ_2 - S^s_2$ cal K$^{-1}$ mol$^{-1}$ |
|---|---|---|
| MMC | 2300 | 5.1 |
| MMB | 2900 | 6.6 |
| MMI | 3500 | 8.3 |
| EMC | 2500 | 5.5 |
| EMB | 3000 | 6.5 |
| EMI9) | 3200 | 6.9 |

seen from this TG curve, in general, the organic mercury(II) compounds sublime gradually before melting. Accordingly, it was required in this experiment to determine a heat purely due to fusion and not to sublimation. The relation between a sample weight corrected by the TG curve at the melting point (B) and an endothermic peak area (A) was examined repeatedly. The results gave a fine linear relation, as illustrated in Fig. 9. The values of the enthalpy and entropy of fusion, thus obtained, are listed in Table 3, where $H^\circ_2$ and $H^s_2$ ($S^\circ_2$ and $S^s_2$) denote the enthalpy (entropy) of solution of supercooled liquid and solid, respectively, of the 2nd component.

For the transfer process from solid to saturated solution, the values of partial molal enthalpy and entropy of solution are estimated from the data of the temperature dependence of the solubility by using the following equation,

$$(\bar{H}_2 - H^s_2)/T = \bar{S}_2 - S^s_2 \cong R(\partial \ln x_2/\partial \ln T)_{\mathrm{sat}}$$

where $\bar{H}_2$ ($\bar{S}_2$) represents the enthalpy (entropy) of a solute in a solution. The thermodynamic parameters calculated from the data of the solubility and fusion are summarized in Table 4. Here the values of $(\bar{H}_2 - H^\circ_2)$ and $(\bar{S}_2 - S^\circ_2)$ mean the enthalpy and entropy changes for mixing of the solute in supercooled liquid and water, and they are related as:

$$(\bar{H}_2 - H^\circ_2) = (\bar{H}_2 - H^s_2) - (H^\circ_2 - H^s_2)$$
$$(\bar{S}_2 - S^\circ_2) = (\bar{S}_2 - S^s_2) - (S^\circ_2 - S^s_2)$$

The values in Table 4 were calculated by assuming that a molal heat capacity of a supercooled liquid ($C^l_P$) and that of a solid ($C^s_P$) are equal at a constant pressure, namely, $\Delta C_P = C^l_P - C^s_P = 0$.

The above discussion was made with the assumption that these solutes are non-electrolytes. Schwarzenbach and Schellenberg,3) however, reported in detail the interactions of $CH_3Hg^+$ with $Cl^-$, $Br^-$, and $I^-$ in water at 25 °C ($[CH_3Hg^+][Cl^-]/[CH_3HgCl] = 5.62 \times 10^{-6}$ mol dm$^{-3}$; $[CH_3Hg^+][Br^-]/[CH_3HgBr] = 2.40 \times 10^{-7}$ mol dm$^{-3}$; $[CH_3Hg^+][I^-]/[CH_3HgI] = 2.51 \times 10^{-9}$ mol dm$^{-3}$). MMC, MMB, and MMI thus seem to be very weak electrolytes. In order to estimate the effect of these slight dissociations, the thermodynamic values for the dissociation process were calculated by using the above constants. However, no influence was observed on the values of $(\bar{H}_2 - H^s_2)$ and $(\bar{S}_2 - S^s_2)$ in Table 4. Although the values of dissociation of EMC and EMB were not found in the literature, it can be assumed that

Table 4. Thermodynamic parameters

| Substance | Temperature (°C) | $\bar{S}_2 - S^s_2$ (cal K$^{-1}$ mol$^{-1}$) | $\bar{H}_2 - H^s_2$ (cal mol$^{-1}$) | $\bar{S}_2 - S^\circ_2$ (cal K$^{-1}$ mol$^{-1}$) | $-R \ln x_2$a) (cal K$^{-1}$ mol$^{-1}$) | $\bar{H}_2 - H^\circ_2$ (cal mol$^{-1}$) |
|---|---|---|---|---|---|---|
| MMC | 20—40 | 15.8 | 4700 | 10.7 | 15.4 | 2400 |
| MMB | 10—55 | 16.5 | 4900 | 9.9 | 17.9 | 2000 |
| MMI | 10—25 | 7.3 | 2200 | −1.0 | 22.0 | −1300 |
| | 35 | 20.7 | 6400 | 12.4 | 21.5 | 2900 |
| | 45 | 36.3 | 11500 | 28.0 | 20.7 | 8000 |
| | 55 | 51.5 | 16900 | 43.2 | 19.2 | 13400 |
| EMC | 20—40 | 15.6 | 4600 | 10.1 | 18.8 | 2100 |
| EMB | 10—25 | 2.9 | 900 | −3.6 | 22.4 | −2100 |
| | 35 | 15.2 | 4700 | 8.7 | 22.1 | 1700 |
| | 45 | 30.6 | 9700 | 24.1 | 21.4 | 6700 |
| | 55 | 45.6 | 15000 | 39.1 | 20.2 | 12000 |

a) $x_2$ at 25 °C.

dissociations of EMC and EMB are less effective than those of MMC, MMB, and MMI. Further, it should be discussed whether the association of the solute can be neglected or not. However, no presence of, for example, an aggregate has been reported in the literature.

When the solubility behavior of these organic mercury(II) compounds in water is argued, the characteristics of "water" as a solvent should be considered necessarily. Frank and Evans[14] showed that, in spite of the small solubility of hydrocarbons such as higher alcohols in water, the heat of solution was small and the entropy of solution was negative. In order to rationalize this rather unusual situation, they postulated the formation of an "ice" which surrounds dissolved hydrocarbon molecules and they proposed to call this phenomenon an "iceberg" formation. In water, these phenomena are now considered to be usual.[15] This argument will show that, by dissolution of some kind of solute in water, the freedom of the water molecules surrounding the solute is restricted to some extent in the solution, compared with that of pure water.

In this study, the solubility behaviors could be classified into two groups according to the resemblances of the solubility features. In the first, the solubility increased abruptly above 25 °C (MMI and EMB). A behavior similar to this group was reported in the literature for the dissolution of aromatic hydrocarbons[16] such as benzene, toluene, *m*- and *p*-xylene, and ethylbenzene into water. In the cases of the solutes of MMI and EMB, the solubility curve could be divided into two parts: one was that in the 10—25 °C range and the other was that above 25 °C. In the range of 10—25 °C, because of negligibly weak interactions between solvent and solute, water molecules surrounding the solute were ice-like in structure. The tendency toward the formation of this ice-like structure in the 10—25 °C range, however, was considered to be relatively weak, because, as tabulated in Table 4, both the entropy and enthalpy changes for mixing were very small and negative as $-1.0$—$-3.6$ cal K$^{-1}$ mol$^{-1}$ and 1—2 kcal mol$^{-1}$ (exothermic) respectively. Upon increasing the temperature above 25 °C, the ice-like structure of the water molecules surrounding the solute was obstructed, and thus the solutes could move more freely in the solution than could those in the 10—25 °C range. This breaking of the ice-like structure, that is, the abrupt increasing of the solubility above 25 °C, can be recognized by the large positive entropy and large endothermic enthalpy changes in Table 4.

In the cases of the solutes of MMC, MMB, and EMC as the second group, the formation of an ice-like structure may have been obstructed owing to the solvent-solute interaction, which was, however, considered to be weak. This interpretation seems to be consistent with the large positive entropy and endothermic enthalpy changes in Table 4. Similar behavios to this second group were reported for iodine,[17] naphthalene and biphenyl.[16] After all, the difference of the solubility features above 25 °C was considered to be mainly due to a delicate variance of the solvent-solute interactions. Although an interpretation for the different solubility features with respect to the kinds of alkyl group and halogen was attempted, it failed because the solubility of a solute having propyl or butyl group could not be measured in our experimental conditions owing to their small solubilities in water.

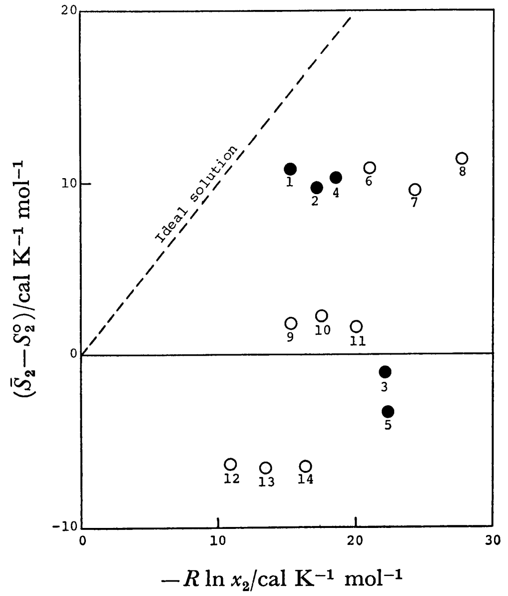

Fig. 10. Plot of $-R \ln x_2$ *vs.* $(\bar{S}_2-S_2^\circ)$.
1: MMC, 2: MMB, 3: MMI, 4: EMC, 5: EMB, 6: iodine,[19] 7: naphthalene,[16] 8: biphenyl,[16] 9: benzene,[16] 10: toluene,[15] 11: ethylbenzene,[16] 12: methane,[15] 13: ethane,[15] 14: propane.[15]

On the basis of the above discussion, so far as a non-polar solute is concerned, an argument of iceberg "making" or "breaking" should not be made as if it were a basic property possessed by a solute itself, but should be done in relation to the temperature studied.

Figure 10 shows the relation of the values of $(\bar{S}_2-S_2^\circ)$ against $-R \ln x_2$. If the solution is an ideal one, both values are identical as dotted line in the figure. For the comparison, besides the organic mercury(II) compounds studied, we plot the thermodynamic values of aromatic hydrocarbons[16] and of alkanes in the liquid state[15] obtained after converting the values in the gaseous state.[18] All the values of $-R \ln x_2$ are adopted as those at 25 °C. The solutes including the reference ones could be roughly classified. That is, the first group contained the solutes having the large positive values of $(\bar{S}_2-S_2^\circ)$, and their temperature dependence of the solubilities was shown to be linear (MMC, MMB, EMC, iodine, naphthalene, and biphenyl). Accordingly, the solutes having almost no ability to form an ice-like structure at the temperature studied were positioned in the vicinity of the ideal line. The second group (MMI, EMB, benzene, toluene, ethylbenzene, methane, ethan, and propane) largely deviated from the ideal line, showing nearly zero or negative $(\bar{S}_2-S_2^\circ)$ values, and the temperature dependence of the solubilities was curved.

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