CHEMISTRY LETTERS, pp. 201-204, 1978. Published by the Chemical Society of Japan

SOLUBILITY OF CHLOROALKYL MERCURY(II) IN WATER

Kooji TAJIMA* and Fumiaki KAI**#
* Kumamoto Municipal Institute of Public Health,
1-13-16 Kuhonji, Kumamoto 862
** Department of Chemistry, Faculty of Science, Kumamoto University,
2-39-1 Kurokami, Kumamoto 860

The solubilities of chloromethyl mercury(II) (MMC) and chloroethyl mercury(II) (EMC) in water were determined at 20 ∿ 40°C. The solubilities in mole fraction, χ_2, were given by the equations: $\log \chi_{2(MMC)} = -1059/T + 0.176$; $\log \chi_{2(EMC)} = -1048/T - 0.612$. For the process from solid to saturated aqueous solution, the thermodynamic parameters of MMC and EMC were obtained as follows: $\Delta\bar{H}_{2(MMC)}$ = 4711 cal/mole; $\Delta\bar{S}_{2(MMC)}$ = 15.8 e.u.; $\Delta\bar{H}_{2(EMC)}$ = 4642 cal/mole; $\Delta\bar{S}_{2(EMC)}$ = 15.6 e.u.

It is well known that a trace amount of organic mercury(II) compounds is seriously toxic to mammal, especially to the human, and an increasing attention is being paid to these compounds found even in natural occurence, *e.g.*, in river- and sea-water. Several problems, however, still remain unsolved. For example, a good attention should be paid against re-dissolution of these compounds into natural water after reclamation of contaminated soil or dredge of harbors etc. Accordingly a fundamental study on the solubility of organic mercury(II) compounds is an urgent need for finding clue to solution of these problems.

Several workers reported the studies on the reaction of CH_3Hg^+ and $C_2H_5Hg^+$ with various ligands. Waugh *et al.*[1] described the solubility product of MMC at only one temperature of 25°C from the dissociation constant and solubility in water. Schwarzenbach and Schellenberg,[2] and Budevsky *et al.*[3] reported the formation constants and thermodynamic parameters of CH_3Hg^+ with several ligands. However, the solubilities of MMC and EMC in wide temperature range and thermodynamic parameters of aqueous solution do not seem to have appeared in literatures.

The present study was initiated to obtain the values of solubilities and partial molal enthalpy and entropy of MMC and EMC. In particular MMC has been confirmed to be the causal agent of so-called "Minamata Disease" and is primarily analysed among the organic mercury(II) compounds. EMC was taken up as a related compound.

MMC was obtained from Wako Co., Ltd., and was recrystallized from ethanol: mp = 168°C (ref. values; 167,[4] 168,[5] 174°C[6]); purity = 99.1%.[7] EMC was purchased from Tokyo Kasei Co., Ltd., and was recrystallized from ethanol: mp = 192°C (ref. value; 192°C[8]); purity = 99.3%.[7] Water was carefully purified twice by distillation with $KMnO_4$. The density of aqueous solution was determined with a pyknometer (capacity = 20 ml).

The relation between the density (ρ) of solution and mole fraction (χ_2) of MMC and EMC was obtained in order to determine the concentration of saturated solution (Fig. 1). Linear relations were obtained at each experimental temperature from 20 to 40°C (±0.01°C). The error in density, mainly due to the weighing error of pyknometer, was ±0.00005 g/cm^3. The solubilities of these solutes were estimated by using these linear relations between ρ and χ_2. In Table 1 are presented the experimental values for the solubilities of MMC and EMC in water at 20 ∿ 40°C region. The solubilities of both solutes are increased with increasing temperature.

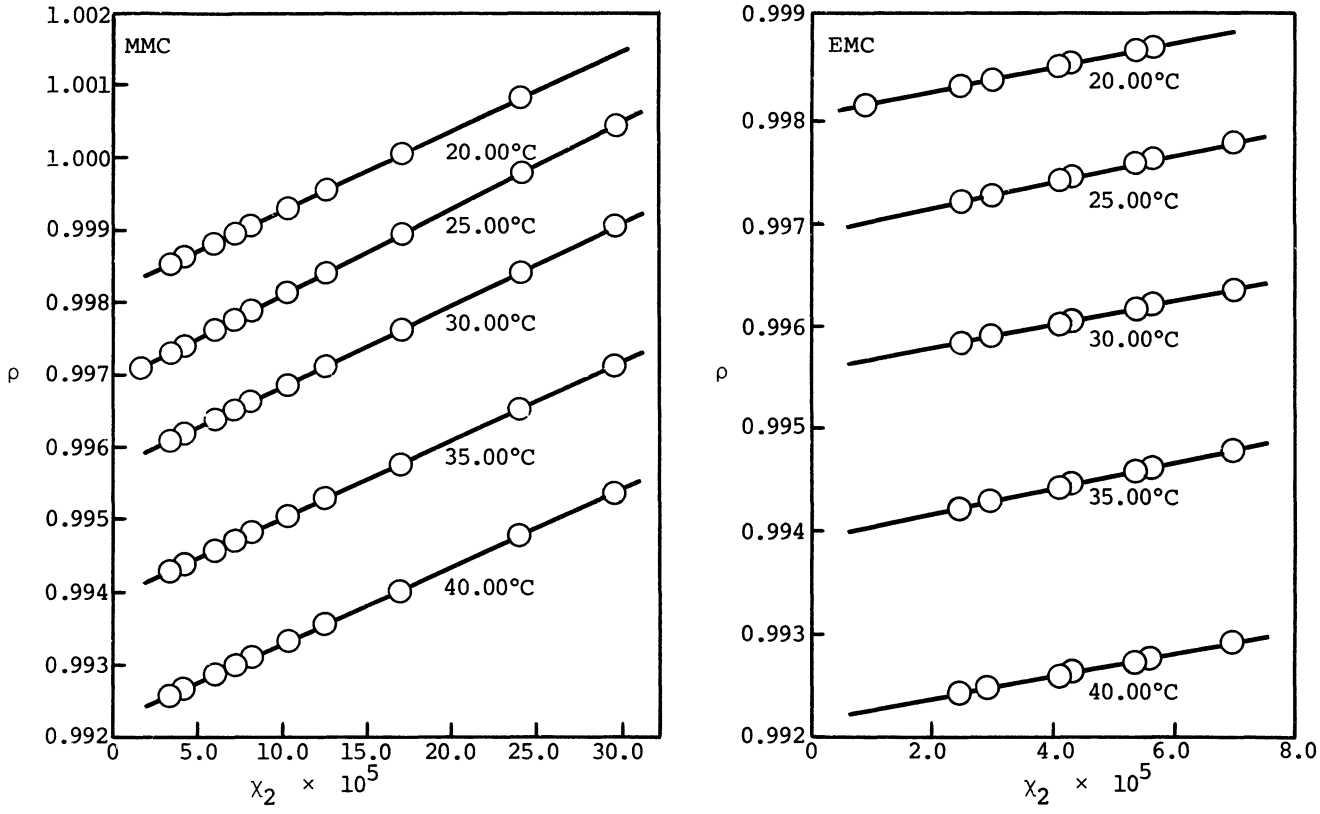

Fig. 1. Relations between mole fraction (χ_2) and density (ρ) at various temperature

Table 1. Temperature dependence of solubility

T°K	MMC $\chi_2 \times 10^5$	EMC $\chi_2 \times 10^5$
293.16	37.3 ± 0.5	6.5 ± 0.2
298.16	42.4 ± 0.5[a)]	7.6 ± 0.3
303.16	46.8 ± 0.1	8.5 ± 0.1
308.16	54.8 ± 0.1	9.4 ± 0.2
313.16	63.4 ± 0.1	11.2 ± 0.2

a) The previous value [0.02 mole per liter at 25°C, ref. 1)] corresponds to $\chi_2 = 36.0 \times 10^{-5}$.

After least-square adjustments, these mole fractions were given by the following equations:

$$\log \chi_{2(\mathrm{MMC})} = -1059/T + 0.176$$

$$\log \chi_{2(\mathrm{EMC})} = -1048/T - 0.612$$

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

$$\Delta\bar{S}_2 = \Delta\bar{H}_2/T \cong R(\partial \ln\chi_2/\partial \ln T)_{\mathrm{sat.}}$$

where $\Delta\bar{S}_2$ and $\Delta\bar{H}_2$ represent partial molal entropy and enthalpy of solution respectively. These values for MMC and EMC were calculated as $\Delta\bar{H}_{2(\mathrm{MMC})}$ = 4711 cal/mole, $\Delta\bar{H}_{2(\mathrm{EMC})}$ = 4642 cal/mole, $\Delta\bar{S}_{2(\mathrm{MMC})}$ = 15.8 e.u. and $\Delta\bar{S}_{2(\mathrm{EMC})}$ = 15.6 e.u. respectively.

The above discussion was made with the assumption that both MMC and EMC are non-electrolyte. Schwarzenbach[2] reported that MMC dissociates slightly in water with the dissociation constant of 5.62×10^{-6} at 20°C. In order to estimate the effect of dissociation, the thermodynamic values for dissociation process were calculated by using the above constant. However, no influence is observed for the $\Delta\bar{H}_{2(\mathrm{MMC})}$ and $\Delta\bar{S}_{2(\mathrm{MMC})}$ values obtained in this experiment. Although the value of dissociation constant for EMC was not found in literatures, it can be assumed that a dissociation of EMC is less effective than that of MMC.

Frank and Evans[9] described that, in spite of small solubility of such hydrocarbons as higher alcohols in water, heat of solution was small and entropy of solution was negative. In order to interpret this phenomenon, they postulated the formation of "ice" which surrounds dissolved hydrocarbon molecules and they proposed to call this phenomenon as "iceberg" formation. In addition Clausen and Polglase[10] also reported that the non-polar hydrocarbons such as methane, ethane, propane and n-butane behaved similarly. In "water", these phenomena are now considered to be general,[11] whereas such behavior is anomalous for solutes in other solvents.

Though the entropy of fusion, ΔS_2^f, of solid MMC and EMC was not obtained in this experiment, the entropy of mixing, $-R\ln\chi_2$, was calculated at 25°C as 15.4 e.u. for MMC and 18.8 e.u. for EMC. On the other hand, the values of entropy of solution were obtained in this experiment as 15.8 e.u. for MMC and 15.6 e.u. for EMC. As the result, an apparent value of the entropy of fusion seemed nearly to zero. However, it is generally considered that an actual value of ΔS_2^f has large positive one. Accordingly the following equation can be derived,

$$\Delta S_2^f \cong n\Delta\bar{S}_i^f - n'\Delta\bar{S}_h^f > 0$$

where $n\Delta\bar{S}_i^f$ is the partial molal entropy change of MMC and EMC due to the iceberg formation of n moles water which surround the dissolved solute, and $n'\Delta\bar{S}_h^f$ means the partial molal entropy change due to the hydrogen bond breaking, namely iceberg breaking.

On the basis of the above discussion, the present solutes seemed to form possibly "iceberg".

One of the authors (K. T.) wishes to express his thanks to Dr. H. Sassa, Chief of the Institute, for his encouragement throughout the work.

References and Notes

To whom all correspondence should be addressed.

1) T. D. Waugh, H. F. Walton and J. A. Laswick, *J. Phys. Chem.*, 59, 395(1955).

2) G. Schwarzenbach and M. Schellenberg, *Helv. Chim. Acta*, 48, 28(1965).

3) O. Budevsky, F. Ingman and D. H. Liem, *Acta Chem. Scand.*, 27, 1277(1973).

4) P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, 62, 1423(1966).

5) J. H. S. Green, *Spectrochim. Acta*, 24A, 863(1968).

6) K. Irukayam, F. Kai, M. Fujiki and T. Kondo, *Kumamoto Med. J.*, 15, 57(1962).

7) 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 the gas chromatograph equipped with an electron capture detector (Yanagimoto, G-80), and then the degree of purity was evaluated.

8) M. M. Kreevoy and R. L. Hansen, *J. Amer. Chem. Soc.*, 83, 626(1961).

9) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, 13, 507(1945).

10) W. F. Clausen and M. F. Polglase, *J. Amer. Chem. Soc.*, 74, 4817(1952).

11) K. Shinoda, *J. Phys. Chem.*, 81, 1300(1977).

(Received September 2, 1977)