2406 © 1993 The Chemical Society of Japan NOTES *Bull. Chem. Soc. Jpn.*, **66**, 2406—2408(1993) [Vol. 66, No. 8

Effect of Pressure on the Solubility of Sodium Bromide in Water

Seiji SAWAMURA,* Shigeo YASUHARA, Shigeru SUGI, and Nobuaki EGOSHI
Department of Chemistry, Faculty of Science and Engineering, Ritsumeikan University, Tojiin, Kita-ku, Kyoto 603-77

(Received February 17, 1993)

Synopsis. The solubility (m_s) of sodium bromide ($NaBr{\cdot}2H_2O$) in water was measured at 283.15—313.15 K and 0.1—300 MPa. The m_s decreases with increasing pressure and the coefficient, θ $(=(\partial m_s/\partial p)_T/m_s)$, is -10×10^{-5} MPa^{-1} at 298.15 K and 0.1 MPa. This sign of θ is opposite to that (7×10^{-5} MPa^{-1}) calculated using a thermodynamic equation.

High-pressure techniques have recently been applied to two industrial fields. One is high-pressure crystallization as a separation process.[1] The other is the high-pressure disinfection of food.[2] High-pressure solubility data have been increasingly important, accompanied by the development of such industries.

In order to estimate the pressure coefficient (θ) of the solubility of electrolytes, such as alkali halides in water, the following equation, which is thermodynamically precise, has been used;[3—8]

$$\theta = \frac{1}{m_s}\left(\frac{\partial m_s}{\partial p}\right)_T = \frac{-\Delta V}{\nu RT(1+(\partial\ln\gamma/\partial\ln m)_{p,T})}\frac{A}{(A-m_s n)}, \quad (1)$$

where m is the molality of solution, ΔV the volume change accompanying the dissolution of the electrolyte crystal in equilibrium with its saturated solution, γ the mean ionic activity coefficient, ν the stoichiometric number of ions produced per molecule of electrolyte, A the quantity of 1 kg of water in mole unit (=55.51), and n the number of water molecules per molecule of hydrated electrolyte crystal. Subscript S indicates an saturated concentration. Using Eq. 1, van Hook thermodynamically calculated a positive θ value of 7×10^{-5} MPa^{-1} for sodium bromide ($NaBr{\cdot}2H_2O$) at 298.15 and 0.1 MPa.[7] This means that the solubility of sodium bromide in water increases with increasing pressure. On the other hand, our direct measurement of the solubility in the present work shows a decrease upon increasing the pressure. We describe the details in the present article.

Sodium bromide crystal which is in equilibrium with saturated solution takes several hydrate forms at 0.1 MPa, depending on the temperature, that is, $NaBr{\cdot}5H_2O$ below 249.2 K, $NaBr{\cdot}2H_2O$ at 249.2—324.0 K, and NaBr (anhydride) above 324.0 K.[10] Therefore, in the temperature range of 283—313 K in the present work, $NaBr{\cdot}2H_2O$ coexists with the saturated solution at 0.1 MPa.

Experimental

Sodium bromide (NaBr, Nacalai Tesque Co.) was dissolved in water at 318 K and recrystallized in the form of $NaBr{\cdot}2H_2O$ by cooling the solution slowly. The obtained crystal and saturated solution were used as a sample to be placed in a pressure vessel. Figure 1 shows the pressure vessel (made of 17-4PH stainless-steel) for preparing a saturated solution at high pressure. The sample was put into a sample room (B) with a Teflon ball (D) for stirring. The vessel was pressurized using a hydraulic pump through an 1/8″-flexible stainless-steel tube (I), and shaken on a seesaw in a water bath. After several hours, the sample solution was slowly dropped out through the glass filter (H) from the outlet (K) by releasing a valve (J) and pushing a piston (E) with a hydraulic pump to hold the sample in the cylinder (A) at high pressure. The initial ca. 3 cm^3 of the solution was discarded; the remaining 10 cm^3 of the sample was used to determine the solubility. The solution was dried in an electric oven and the residue was weighed. Because the solution in the pressure vessel took 20—30 h for saturation, we shook the vessel for over 40 h. The pressure was monitored with a gauge of the Bourdon-tube type (Heise Co., fullscale 400 MPa, 0.5 MPa divisions). The water bath was regulated at 283.15, 293.15, 298.15, 303.15, and 313.15 K (±0.05 K), respectively, calibrated by a platinum-resistance thermometer.

Results and Discussion

There have been several solubility data concerning $NaBr{\cdot}2H_2O$ in water at 0.1 MPa and at temperatures between 253 K and 324 K.[11—18] Most of the data fit well to Eq. 2 within ±0.5%;

$$(m_s/\mathrm{mol\,kg^{-1}}) = 33.756 - 23.567\times10^{-2}(T/\mathrm{K}) + 51.389\times10^{-5}(T/\mathrm{K})^2. \quad (2)$$

Our values using a high-pressure vessel at 0.1 MPa were 8.30 $mol\,kg^{-1}$ at 283.15 K, 9.17 $mol\,kg^{-1}$ at 298.15 K, and 10.36 $mol\,kg^{-1}$ at 313.15 K; the deviations from

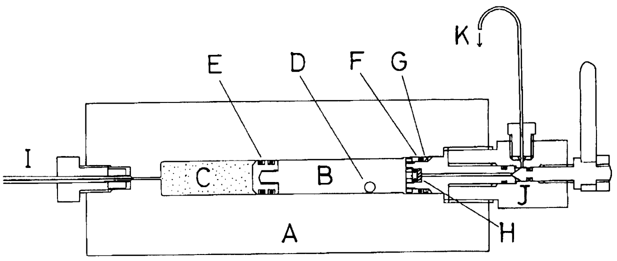

Fig. 1. High-pressure vessel for solubility measurements. A, cylinder; B, sample room; C, pressure-transmitting oil (kerosine); D, Teflon ball; E, piston; F, O-ring; G, copper-packing; H, glass filter; I, 1/8″-flexible tube (to a hydraulic pump and a pressure gauge); J, valve; K, outlet.

Eq. 2 are at most ±0.7%, suggesting a reasonable accuracy for our measurement using the pressure vessel.

Figure 2 shows the solubilities at high pressure. They do not increase, but decrease, with increasing pressure at all temperatures. Because no breaking point is observed in each curve, we can conclude that a crystal which coexists with the saturated solution is $NaBr{\cdot}2H_2O$ without any phase change in our measurement ranges of temperature and pressure. Since the degrees of the solubility decreasing are almost linear to pressure, we can present a fitting curve as follows:

$$\begin{aligned}(m_s/\mathrm{mol\,kg^{-1}}) &= 33.756 - 23.567\times10^{-2}(T/\mathrm{K}) \\ &+51.389\times10^{-5}(T/\mathrm{K})^2 \\ &-[15.77-15.48\times10^{-2}(T/\mathrm{K}) \\ &+35.248\times10^{-5}(T/\mathrm{K})^2]\times10^{-3}(p/\mathrm{MPa}). \qquad (3)\end{aligned}$$

The dotted values in Fig. 2 coincide with the lines of Eq. 3 within ±0.7%. From this equation, the pressure coefficients (θ) at 298.15 K and 0.1 MPa is estimated to be -10×10^{-5} $\mathrm{MPa^{-1}}$.

It is nothing to say that ν and $A/(A-m_s n)$ are positive in Eq. 1. Though $(\partial\ln\gamma/\partial\ln m)_{p,T}$ is negative at low concentration, following the Debye–Hückel theory, it generally becomes positive at high concentration, such as a saturated solution.[19] For sodium bromide in a saturated solution at 298.15 K and 0.1 MPa, $(\partial\ln\gamma/\partial\ln m_s)_{p,T}$ was estimated to be 1.4 based on the numerical table of Archer,[20] and 1.2 from that of Hamer and Wu.[21] The latter was cited by van Hook.[7] Because these values are positive and do not differ greatly from each other, θ would not change in sign even if the other different $(\partial\ln\gamma/\partial\ln m_s)_{p,T}$ values are cited. Therefore, the sign of θ in Eq. 1 is thought to depend on that of ΔV.

The ΔV in Eq. 1 for $NaBr{\cdot}2H_2O$ is presented as

$$\Delta V = \overline{V}(\mathrm{NaBr})_s + 2\overline{V}(\mathrm{H_2O})_s - V_c, \qquad (4)$$

where $\overline{V}(\mathrm{NaBr})_s$ and $\overline{V}(\mathrm{H_2O})_s$ are the partial molar volumes of sodium bromide and water for a saturated solution, respectively; V_c is the molar volume of solid $NaBr{\cdot}2H_2O$. V_c is estimated to be 64.38 ± 0.05 $\mathrm{cm^3\,mol^{-1}}$ from X-ray data.[22] $\overline{V}(\mathrm{NaBr})_s$ and $\overline{V}(\mathrm{H_2O})_s$ are usually estimated by extrapolation of $\overline{V}(\mathrm{NaBr})$ and $\overline{V}(\mathrm{H_2O})$ to saturated concentrations, respectively. Though van Hook did not report these values, the ΔV, at least, can be presumed to be -0.5 $\mathrm{cm^3\,mol^{-1}}$ from his θ and $(\partial\ln\gamma/\partial\ln m_s)_{p,T}$ values at 298.15 K and 0.1 MPa using Eq. 1. In a similar way, our θ value of -10×10^{-5} $\mathrm{MPa^{-1}}$ leads us to $\Delta V=+0.7$ $\mathrm{cm^3\,mol^{-1}}$. The difference of the ΔV amounts to 1.2 $\mathrm{cm^3\,mol^{-1}}$ and is only 2% of V_c of $NaBr{\cdot}2H_2O$. Therefore, the sign of θ may depend on the estimation of ΔV or the extrapolation of $\overline{V}(\mathrm{NaBr})$ and $\overline{V}(\mathrm{H_2O})$. It should be noted that the calculation of θ using Eq. 1 with an unreliable ΔV value may changes the sign. In such a case, a direct measurement of the high-pressure solubility is desired for a criticism of the sign of θ.

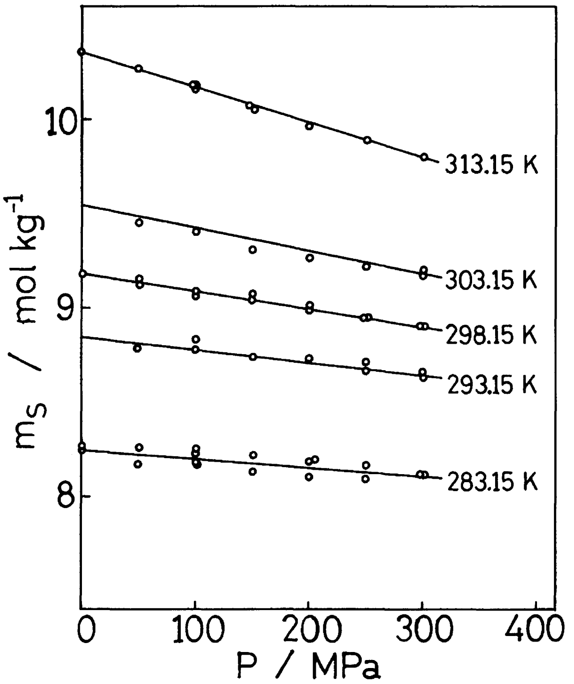

Fig. 2. Pressure dependence of the solubility of sodium bromide ($NaBr{\cdot}2H_2O$) in water.

We thank Mr. Toshio Yumiyama in the Machining Center of Ritsumeikan University for his excellent technical assistance concerning the construction of high pressure vessels.

References

1) M. Moritoki, K. Kitagawa, K. Onoe, and K. Kaneko, "Industrial Crystallization '84," Elsevier, Amsterdam (1984), p. 377; M. Moritoki, "Kouatsu Ryutai Gijutsu (Techniques for High-Pressure Fluid)," ed by T. Makita and M. Nishihara, Maruzen, Tokyo (1992), Chap. 11.

2) R. Hayashi, "Use of High Pressure in Food," San-Ei Publ. Co., Kyoto (1989); R. Hayashi, "Pressure-Processed Food Research and Development," San-Ei Publ. Co., Kyoto (1990); R. Hayashi, "High Pressure Science for Food," San-Ei Publ. Co., Kyoto (1991).

3) L. H. Adams, *J. Am. Chem. Soc.*, **53**, 3769 (1931).

4) L. H. Adams, *J. Am. Chem. Soc.*, **54**, 2229 (1932).

5) L. H. Adams and R. E. Gibson, *J. Am. Chem. Soc.*, **54**, 4520 (1932).

6) R. E. Gibson, *J. Am. Chem. Soc.*, **56**, 865 (1934).

7) W. A. van Hook, *Fluid Phase Equilib.*, **4**, 287 (1980).

8) A. T. Williamson, *Trans. Faraday Soc.*, **40**, 421 (1944).

9) A. K. Lyashchenko and B. R. Churagulov, *Zh. Neorg. Khim.*, **28**, 456 (1983).

10) K. -H. Hellwege, "Landolt–Börnstein," Springer-Verlag, Berlin (1964), Vol. II/2b.

11) A. F. Scott and E. J. Durham, *J. Phys. Chem.*, **34**, 1424 (1930).

12) R. G. Larson and H. Hunt, *J. Phys. Chem.*, **43**, 417 (1939).

13) R. D. Eddy and A. W. C. Menzies, *J. Phys. Chem.*, **44**, 207 (1940).

14) G. S. Klebanov and E. P. Basova, *Zhur. Prikla. Khim. (Leningrad)*, **12**, 1601 (1939).

15) L. Roger, *Ann. Chim.*, **19**, 362 (1944).

16) N. A. Vlassov and A. G. Bergman, *C. R. Acad. Sci. URSS*, **38**, 211 and **39**, 141 (1943).

17) J. E. Ricci, *J. Am. Chem. Soc.*, **66**, 1015 (1944).

18) A. F. Scott and W. R. Frazier, *J. Phys. Chem.*, **31**, 459 (1927).

19) P. W. Atkins, "Physical Chemistry," 2nd ed, Oxford Univ. Press, Oxford (1982), Chap. 11.

20) D. G. Archer, *J. Phys. Chem. Ref. Data*, **20**, 509 (1991).

21) W. J. Hamer and Y. -C. Wu, *J. Phys. Chem. Ref. Data*, **1**, 1047 (1972).

22) W. R. Haaf and G. B. Carpenter, *Acta Crystallogr.*, **17**, 730 (1964).