JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Up to 4 Orders of Magnitude Enhancement of Crown Ether Complexation in an Aqueous Phase Coexistent with Ice

Yuiko Tasaki[†] and Tetsuo Okada*[,‡]

[†]Research Institute of Environmental Management Technology, National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8569, Japan

[‡]Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8551, Japan

S *Supporting Information*

ABSTRACT: Ice chromatography measurements have revealed anomalous enhancements of crown ether complexation in a liquid phase coexistent with ice. The 4 orders of magnitude enhancement was confirmed for the complexation of dibenzo-24-crown-8 in sub-μm-sized liquid inclusions formed in ice doped with <1 mM NaCl or KCl. This enhancement became less pronounced with increasing dopant concentration.

The chemistry of ice has been a subject of great importance in a wide variety of scientific fields because it is involved in various natural and artificial processes.[1,2] Ice, for example, plays crucial roles in the global environment. It is known that some reactions of environmental interest are promoted in the presence of ice.[2] A typical example is ozone layer depletion: ice adsorbs gas molecules such as HCl and CCl_4, and then a series of reactions causing this hazardous phenomenon are initiated.[3] Since naturally occurring ice contains impurities and has properties different from those of pure ice, their effects should be taken into account for the interpretation of ice-related phenomena. A salt is the most common impurity possibly found in natural ice and even in ice prepared in laboratories.[4]

Salt-doped ice undergoes phase separation upon freezing. The phase diagram of a salt/water binary system predicts that a concentrated salt solution is included in the solid ice matrix at temperatures between the freezing and eutectic points (t_{eu}) when a relatively dilute salt solution is frozen. Also, recent studies have indicated that a small amount of the liquid phase still remains unfrozen even below t_{eu}.[4−6] The liquid phase surrounded by solid ice can be a microreactor in which water molecules are placed in circumstances different from those in the bulk liquid and some reactions are possibly influenced. We have devised "ice chromatography", in which water-ice particles are used as a stationary phase for liquid chromatography, and shown that it can be an efficient tool for obtaining a comprehensive understanding of ice-related phenomena.[7−10] In the course of ice chromatography investigations using salt-doped ice as the stationary phase, we have found anomalous retention behaviors of crown ethers. This paper discusses the unusual crown ether complexation in the liquid phase formed in salt-doped ice as studied by ice chromatography.

Crown ethers are absorbed on the ice surface from hexane by forming 2−3 hydrogen bonds between the ethereal oxygen atoms and the −OH dangling bonds.[9] Of the three crown ethers studied in this work, dibenzo-24-crown-8 (DB24C8) was most strongly adsorbed on the ice surface; the adsorption became weaker in the order DB24C8 > benzo-18-crown-6 (B18C6) > benzo-15-crown-5 (B15C5), reflecting the decreasing number of ethereal oxygen atoms in each molecule. When a salt is doped into the ice stationary phase, the ice chromatographic retention is governed not only by the adsorption but also by the partitioning into the liquid water phase coexistent with ice (WPI).[11,12] In such cases, the retention factor (k) is represented by

$$k = k_{\mathrm{ads}}^{\mathrm{ice}} + k_{\mathrm{par}}^{\mathrm{WPI}} \tag{1}$$

where $k_{\mathrm{ads}}^{\mathrm{ice}}$ and $k_{\mathrm{par}}^{\mathrm{WPI}}$ denote the contributions from the adsorption and partitioning mechanisms, respectively. The latter term is given by

$$k_{\mathrm{par}}^{\mathrm{WPI}} = \frac{V^{\mathrm{WPI}}}{V^{\mathrm{mob}}} K_{\mathrm{d}}^{\mathrm{WPI}} \tag{2}$$

where V^{WPI} and V^{mob} are the volumes of the WPI and mobile phase in the column, respectively, and $K_{\mathrm{d}}{}^{\mathrm{WPI}}$ $(=c_{\mathrm{s}}{}^{\mathrm{WPI}}/c_{\mathrm{s}}{}^{\mathrm{mob}})$ is the partition coefficient of a solute between these phases. Our previous work indicated that $k_{\mathrm{par}}^{\mathrm{WPI}}$ can be precisely evaluated for some solutes, such as resorcinol and hydroquinone, using partition coefficients determined by the usual solvent extraction experiments with bulk solvents ($K_{\mathrm{d}}{}^{\mathrm{bulk}}$). The volumes V^{WPI} and V^{mob} can be determined from the freezing-point depression curve and the holdup volume, respectively. The $k_{\mathrm{ads}}^{\mathrm{ice}}$ term was regarded as constant during the development of the WPI with increases in either the dopant concentration or temperature, because V^{WPI} is so small that the effective ice surface area is unchanged.[12] Thus, in some cases, $K_{\mathrm{d}}^{\mathrm{bulk}}$ reasonably can replace $K_{\mathrm{d}}^{\mathrm{WPI}}$ in eq 2.

Figures 1 and 2 show the dependences of k on the concentration of NaCl (c_{NaCl}) and KCl (c_{KCl}), respectively, in an unfrozen original solution. The left panel of each figure illustrates the enlargement of the lower salt concentration range. As noted above, the retention of hydroquinone and resorcinol can be explained by substituting $K_{\mathrm{d}}^{\mathrm{bulk}}$ into eq 2, as shown by the black dotted curves in Figure 1 for NaCl doping, which agree well with the experimental plots. In contrast, crown ethers exhibit much larger dependences on the salt

Received: February 28, 2012
Published: April 2, 2012

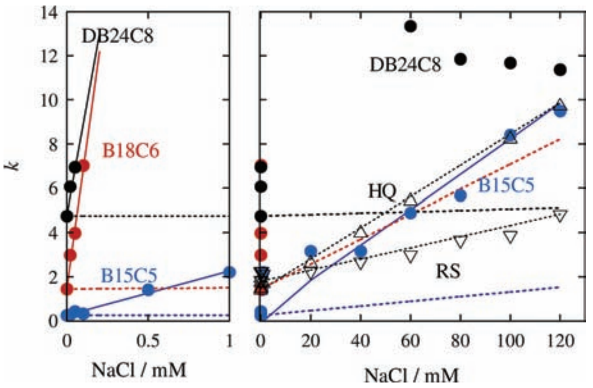

Figure 1. Effect of doped NaCl concentration (c_{NaCl}) on the retention factors (k) of various solutes at −10 °C. Dotted lines are the predictions of the simple partition model. Solid lines for crown ethers represent the results of linear regression.

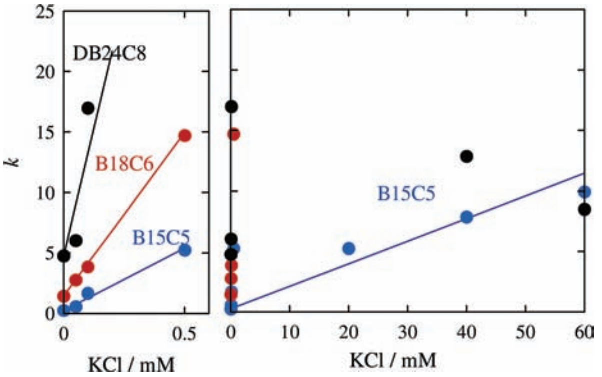

Figure 2. Effect of doped KCl concentration (c_{KCl}) on the retention factors (k) of various solutes at −10 °C. Lines represent the results of linear regression.

concentration than those predicted by eq 2, as depicted in Figure 1 by dotted curves in the same color as the associated symbols . As naturally expected, this is mainly caused by the complexation of the crown ether with a dopant cation, as discussed in detail later. Even though the complexation is taken into consideration, unusual behaviors can be seen in Figures 1 and 2. Although k for B15C5 appears to increase with increasing c_{NaCl} and c_{KCl} (c_{salt}), similar to hydroquinone and resorcinol, the slopes of k versus c_{salt} are obviously different in the lower and higher c_{salt} ranges; the slope in the lower concentration range is ca. 30 times larger than that in the higher range. The behavior DB24C8 is more marked. Its retention steeply increases with c_{salt} below 0.5 mM, and it is not eluted from the ice column prepared from 0.5−20 mM salt solutions within an appropriate measurement time. Interestingly, however, the elution of DB24C8 is detected at higher c_{salt} ($c_{NaCl} \geq 60$ mM and $c_{KCl} \geq 40$ mM), and its retention time decreases with the further increases in c_{salt}.

The deviation of crown ether retention from the predictions of eq 2 with K_d^{bulk} should be explained by crown ether complexation and/or different partition properties of the WPI relative to bulk liquid water. In the present study, we considered the former to be the main cause for the unusual retention behaviors of crown ethers for the following reasons. First, the large increase in k with increasing c_{salt} was not confirmed for low LiCl doping (<1 mM); in many instances, crown ether complexation with Li^+ is much weaker than that with Na^+ or K^+. Second, as shown above, the retention behaviors of some solutes can be quantitatively explained using K_d^{bulk}, suggesting that the WPI possibly has partition properties similar to usual liquid water. For these reasons, the results shown in Figures 1 and 2 were analyzed on the basis of the complexation of crown ethers with a cation added to the ice stationary phase.

In the present system, complexation in the WPI or at the interface between the WPI and the mobile phase is possible. The interfacial tension between hexane and concentrated aqueous KCl or NaCl was almost independent of the crown ether concentration (data not shown), indicating that interfacial complexation does not occur. Thus, the complexation should primarily occur in the WPI phase. The complexation constants of crown ethers in water ($\log K_c^{bulk}$) have been reported as 0.45 for B15C5−Na^+,[13] 0.38 for B15C5−K^+,[13] 0.81−1.38 for B18C6−Na^+,[14,15] 1.66−1.74 for B18C6−K^+,[14,15] −0.3 to 1.1 for DB24C8−Na^+,[16] and 0.63−0.91 for DB24C8−K^+.[16] As is well-known, the complexation of crown ethers is suppressed in water relative to that in polar organic solvents because of the strong hydration to cations.[17] Therefore, the above values are, in general, 2−3 orders of magnitude smaller than the corresponding ones determined in a polar organic solvent such as methanol. However, the ice chromatographic retention of crown ethers can be influenced even by weak complexation because the concentration of the cation in the WPI is very high; the freezing-point depression curves of the NaCl/water and KCl/water systems indicate that the concentrations of Na^+ and K^+ in the WPI are 2.73 and 2.86 M at −10 °C, respectively.[18]

As shown in the Supporting Information (SI), when the crown ether complexation occurs in the WPI, eq 2 is modified as follows:

$$k = k_{ads}^{ice} + \frac{V^{WPI}}{V^{mob}} K_d^{WPI} \left(1 + K_c^{WPI} [M^+]^{WPI}\right) \tag{3}$$

where K_c^{WPI} is the complexation constant for the crown ether in the WPI and $[M^+]^{WPI}$ is the concentration of Na^+ or K^+ therein. Substitution of V^{WPI}, V^{mob}, and K_d^{bulk} into eq 3 and fitting to the experimental data allow us to determine K_c^{WPI}. The fitting results are illustrated in Figures 1 and 2 by solid curves. The numerical values of K_c^{WPI} determined as the fitting parameters are also summarized in Table 1 together with the bulk complexation constants K_c^{bulk} determined by solvent extraction experiments as well as the corresponding literature values. The

Table 1. Complexation Constants of Crown Ethers in the WPI

	$\log K_c$[a]			
	B15C5		B18C6	DB24C8
	0−1 mM[b]	>20 mM[b]	0−1 mM[b]	0−1 mM[b]
Na^+	1.85	0.38	2.54	3.70
	0.23[c]		0.9[c]	−0.18[c]
	(0.45)[d]		(0.81−1.38)[d]	(−0.3−1.1)[d]
K^+	2.54	0.78	2.30	4.00
	0.35[c]		1.56[c]	0.33[c]
	(0.38)[d]		(1.66−1.74)[d]	(0.63−0.91)[d]

[a]Determined from the dependence of k on c_{salt} in the ice stationary phase. [b]Range of c_{salt} used for the determination of K_c. [c]Determined by solvent extraction at −10 °C. [d]Literature values[13−16] determined at 25 °C are shown in parentheses.

solvent extraction experiments were conducted under conditions modeled on the WPI (i.e., in 2.73 M NaCl or 2.86 M KCl at −10 °C; see the SI),[18] whereas the literature values were determined in water (with varying ionic strengths) at 25 °C. The general agreement between the K_c^{bulk} values determined in different ways and under different conditions suggest that the temperature (at least in the studied range) and ionic strength are not essential factors in governing the crown ether complexation. Although the activity of ions in the WPI is also important for rigorous discussions, the activity coefficients for the cation and the complex are involved in the denominator and numerator in K_c, respectively, and therefore, their effects largely cancel out. Also, comparison of the results obtained in the WPI with those in water containing the same concentration of a salt confirms that the activity coefficients influence the complexation in these media in the same manner.

The K_c^{WPI} values for B15C5 determined from the ice chromatographic retention data in the high-c_{salt} range (>20 mM) almost agree with the corresponding K_c^{bulk} values. In contrast, the K_c^{WPI} values determined in the low-c_{salt} range (≤1 mM) are appreciably larger than the corresponding K_c^{bulk} values; $\Delta \log K_c$ (=$\log K_c^{WPI} - \log K_c^{bulk}$ at −10 °C) is equal to ca. 1.5 for both Na^+ and K^+ complexation. A similar trend can be seen in the K_c^{WPI} values for B18C6 determined in the low-c_{salt} range, although its complexation could not be evaluated in the high-c_{salt} range because of extremely high retention, as stated above.

The most striking results are found for the complexation of DB24C8. The intrinsic complexation of this crown ether with either Na^+ or K^+ is very weak in water because its cavity size is too large; a substantial energetic expenditure is necessary to change the molecular conformation to form coordination bonds with a centered cation. This intrinsically poor complexation is enhanced in the WPI by nearly 4 orders of magnitude relative to that in bulk water. In addition, similar to the B15C5 complexation in the WPI, the marked enhancement is seen in the low-c_{salt} range. Decreases in k in the high-c_{salt} range imply that the enhancement of its complexation in the WPI is gradually reduced with increasing c_{salt} above 20 mM.

The volume of the WPI increases almost linearly with increasing c_{salt}, as shown in Figure S1 in the SI. The above results may suggest that the volume of the WPI is an important factor in governing its properties and is related to the enhanced complexation of crown ethers. Our previous study indicated that the liquid inclusions formed in salt-doped ice are discretely distributed in the ice matrix and that their sizes can be determined from the fluorescence intensity of a probe dissolved in the WPI.[19] Figure 3 illustrates the dependence of the radius of a liquid inclusion on c_{KCl}; the result for NaCl doping (not shown) was almost the same as that for KCl doping. The size of a liquid inclusion decreases with decreasing c_{KCl} but is in the sub-μm range even for $c_{KCl} = 10^{-6} - 10^{-4}$ M. These sizes are obviously larger than the dimension in which the anomalous properties of water have mostly been reported; a number of studies of water properties have been attempted in the nanometer range and have confirmed its unusual properties.[20−23] However, some researchers have found phenomena that cannot be interpreted in terms of either bulk or nanometer-sized water and have named this intermediate dimension "extended nanospace".[24−26] The higher viscosity and lower permittivity of water in extended nanospaces relative to bulk water have been explained by the extensive interaction of water molecules with the silica wall surrounding the space. In the present case, effects of the interaction between liquid water molecules and those fixed on the ice wall become more pronounced as the size of a liquid inclusion decreases. The structural correlation between liquid-water and frozen-water molecules is much better than that between water and silica gel walls. However, the size of the liquid inclusion in ice doped with 0.1 mM KCl is in the sub-μm range; this dimension is possibly too large to assume the extended wall effects. Another factor to be taken into account is the ionic strength, because the WPI always contains a salt of very high concentration. However, as noted above, the ionic strength is not an essential factor affecting the crown ether complexation. In addition, $[M^+]^{WPI}$ is constant at constant temperature irrespective of c_{salt}, and the c_{salt}-dependent change in K_c^{WPI} cannot be explained by the ionic strength of an aqueous phase.

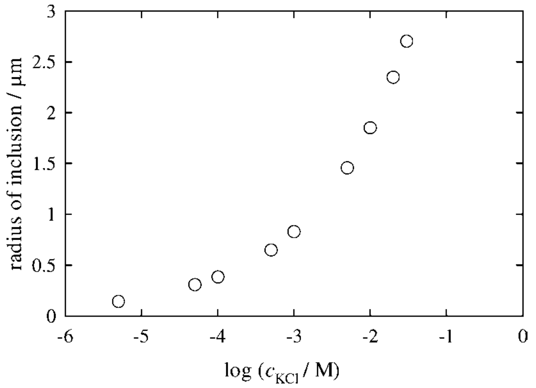

Figure 3. Dependence of the size of a liquid inclusion on the concentration of KCl doped in ice (c_{KCl}) at −10 °C.

If the hydration structure of a cation is perturbed in the WPI, crown ether complexation should be enhanced. A recent simulation study has indicated that the structure of ambient water itself is possibly perturbed between two states, i.e. high- and low-density liquid water (HDL and LDL water, respectively).[27] These two states of liquid water were pointed out from the polyamorphism of ice.[28] This has led to the possibility of the existence of a second critical point coming from phase transfer between HDL and LDL water, and experimental evidence has been extensively sought utilizing water confined in various nanospaces. Although the natures of these liquid phases have not been well-known, the water molecules adopt structures different from those in usual liquid water, and therefore, these liquid phases are expected to have different solvent properties. Theoretical simulations have pointed out that the hydrophobic hydration in LDL water can be thermodynamically preferable.[29] Also, Raman spectroscopy studies of LiCl water glass have suggested that ions are dissolved in HDL-like water rather than in LDL water.[30,31] If it is assumed that the perturbed water structure in the WPI is different from the bulk-water structure, the hydration of a cation and crown ether should be different from that in bulk water. This results in the enhanced complexation of crown ethers in the WPI.

In conclusion, ice chromatography has effectively probed anomalous phenomena occurring in the WPI. Compiled retention data and their comparison with the interaction and partition constants determined in bulk solutions will help us understand the nature of the WPI and eventually the properties of water itself. We believe that supportive evidence on the present unusual phenomena explored by ice chromatography measurements will be provided by spectroscopic and theoretical studies in the near future.

ASSOCIATED CONTENT

Supporting Information

Experimental details, partition data, equation derivations, and the dependence of V^{WPI} on c_{salt}. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

tokada@chem.titech.ac.jp

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work has been partially supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science and by SENTAN from the Japan Science and Technology Agency.

REFERENCES

(1) Simpson, W. R.; Von Glasow, R.; Riedel, K.; Anderson, P.; Ariya, P.; Bottenheim, J.; Burrows, J.; Carpenter, L. J.; Frieß, U.; Goodsite, M. E.; Heard, D.; Hutterli, M.; Jacobi, H.-W.; Kaleschke, L.; Neff, B.; Plane, J.; Platt, U.; Richter, A.; Roscoe, H.; Sander, R.; Shepson, P.; Steffen, J.; Wagner, T.; Wolff, E. *Atmos. Chem. Phys.* **2007**, *7*, 4375–4418.

(2) O'Driscoll, P.; Minogue, N.; Takenaka, N.; Sodeau, J. *J. Phys. Chem. A* **2008**, *112*, 1677–1682.

(3) Huthwelker, T.; Ammann, M.; Peter, T. *Chem. Rev.* **2006**, *106*, 1375–1444.

(4) Koop, T.; Kapilashrami, A.; Molina, L. T.; Molina, M. J. *J. Geophys. Res.* **2000**, *105*, 26393–26402.

(5) Cho, H.; Shepson, P. B.; Barrie, L. A.; Cowin, J. P.; Zaveri, R. *J. Phys. Chem. B* **2002**, *106*, 11226–11232.

(6) Harada, M.; Tasaki, Y.; Qu, H.; Okada, T. *RSC Adv.* **2012**, *2*, 461–466.

(7) Tasaki, Y.; Okada, T. *Anal. Chem.* **2006**, *78*, 4155–4160.

(8) Tasaki, Y.; Okada, T. *J. Phys. Chem. C* **2008**, *112*, 2618–2623.

(9) Tasaki, Y.; Okada, T. *Anal. Chem.* **2009**, *81*, 890–897.

(10) Shamoto, T.; Tasaki, Y.; Okada, T. *J. Am. Chem. Soc.* **2010**, *132*, 13135–13137.

(11) Tasaki, Y.; Okada, T. *Anal. Sci.* **2009**, *25*, 177–181.

(12) Tasaki, Y.; Okada, T. *Anal. Chem.* **2011**, *83*, 9593–9599.

(13) Takeda, Y.; Tanaka, M.; Yamada, H.; Katsuta, S. *J. Coord. Chem.* **2002**, *55*, 459–468.

(14) Takeda, Y.; Kohno, R.; Kudo, Y.; Fukada, N. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 999–1003.

(15) Takeda, Y.; Tanaka, M.; Katsuta, S.; Fukada, N. *J. Coord. Chem.* **2005**, *58*, 373–379.

(16) Katsuta, S.; Tachibana, H.; Takeda, Y. *J. Solution Chem.* **2002**, *31*, 499–510.

(17) Izatt, R. M.; Bradshaw, J. S.; Nielsen, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85*, 271–399.

(18) Cohen-Adad, R.; Vallee, P.; Lorimer, J. W. *Solubility Data Ser.* **1991**, *47*, 225–243.

(19) Hashimoto, T.; Tasaki, Y.; Harada, M.; Okada, T. *Anal. Chem.* **2011**, *83*, 3950–3956.

(20) Major, R. C.; Houston, J. E.; McGrath, M. J.; Siepmann, J. I.; Zhu, X.-Y. *Phys. Rev. Lett.* **2006**, *96*, No. 177803.

(21) Goertz, M. P.; Houston, J. E.; Zhu, X.-Y. *Langmuir* **2007**, *23*, 5491–5497.

(22) Mallamace, F.; Corsaro, C.; Broccio, M.; Branca, C.; González-Segredo, N.; Spooren, J.; Chen, S.-H.; Stanley, H. E. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 12725–12729.

(23) Alexiadis, A.; Kassinos, S. *Chem. Rev.* **2008**, *108*, 5014–5034.

(24) Hibara, A.; Saito, T.; Kim, H.-B.; Tokeshi, M.; Ooi, T.; Nakao, M.; Kitamori, T. *Anal. Chem.* **2002**, *74*, 6170–6176.

(25) Tsukahara, T.; Mizutani, W.; Mawatari, K.; Kitamori, T. *J. Phys. Chem. B* **2009**, *113*, 10808–10816.

(26) Tsukahara, T.; Mawatari, K.; Kitamori, T. *Chem. Soc. Rev.* **2010**, *39*, 1000–1013.

(27) Huang, C.; Wikfeldt, K. T.; Tokushima, T.; Nordlund, D.; Harada, Y.; Bergmann, U.; Niebuhr, M.; Weiss, T. M.; Horikawa, Y.; Leetmaa, M.; Ljungberg, M. P.; Takahashi, O.; Lenz, A.; Ojamäe, L.; Lyubartsev, A. P.; Shin, S.; Pettersson, L. G. M.; Nilsson, A. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 15214–15218.

(28) Mishima, O. *Proc. Jpn. Acad., Ser. B* **2010**, *86*, 165–175.

(29) Paschek, D. *Phys. Rev. Lett.* **2005**, *94*, No. 217802.

(30) Suzuki, Y. *Chem. Phys. Lett.* **2001**, *335*, 357–362.

(31) Mishima, O. *J. Chem. Phys.* **2007**, *126*, No. 244507.