Crystalline Complex of 18-Crown-6 with Water and a Phase Diagram of the Binary System as studied by Raman Spectroscopy

Hiroatsu Matsuura,* Koichi Fukuhara, Kaori Ikeda, and Miyuki Tachikake

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Naka-ku, Hiroshima 730, Japan

The formation of a crystalline complex of 18-crown-6 with water has been shown for the first time by Raman spectroscopy; the Raman spectral observations, incorporated with the measurement of the liquidus, lead to a phase diagram of this binary system, indicating that the molar ratio of 18-crown-6 to water in the complex is approximately 1 : 4—6.

The importance of water in complexation by crown ethers has been discussed by various authors[1] and a number of complexes in which metal ions and water molecules, or neutral organic molecules and water molecules, are simultaneously bound to the crown ether ligand have been reported.[2—8] Exclusive inclusion of water molecules in the complex has also been found for several macrocyclic polyethers.[9—11] It is surprising, however, that no crystalline complex of a binary system of 18-crown-6 and water has been reported.[5,11] We report here the first experimental evidence by Raman spectroscopy for the formation of a stable complex of 18-crown-6 with water. Raman spectroscopy[12] is a powerful technique for studying the structure of molecules in various states of aggregation; the spectra are particularly sensitive to the conformation of the molecule. The nature of the normal vibrations responsible for the Raman spectra of 18-crown-6 and other oxyethylene compounds has been investigated in detail in our previous studies.[13,14] The results have been utilized in the present work to identify the conformation of 18-crown-6 in the complex. A phase diagram of the 18-crown-6–water system is also presented in this communication on the basis of the Raman spectral observations and measurements of the liquidus (freezing curve).

Components of the 18-crown-6–water system with various compositions were prepared and maintained at appropriate temperatures between 40 and −195 °C. After equilibrium had been reached, Raman spectra were measured on the crystalline solid phase at fixed temperatures. The spectra observed at various compositions and temperatures were examined with reference to the spectra of 18-crown-6 and a number of its complexes whose structures have been established by *X*-ray diffraction studies; typical examples are uncomplexed 18-crown-6 with C_i molecular symmetry[15] and complexes with KSCN, $LiSCN{\cdot}H_2O$, and urea with a ring symmetry of D_{3d}, C_s, and C_i (of different conformation from the uncomplexed 18-crown-6), respectively.[16—18]

Of the various compositions of the 18-crown-6–water system studied, we discuss the phase behaviour and Raman spectral observations for several selected compositions, which

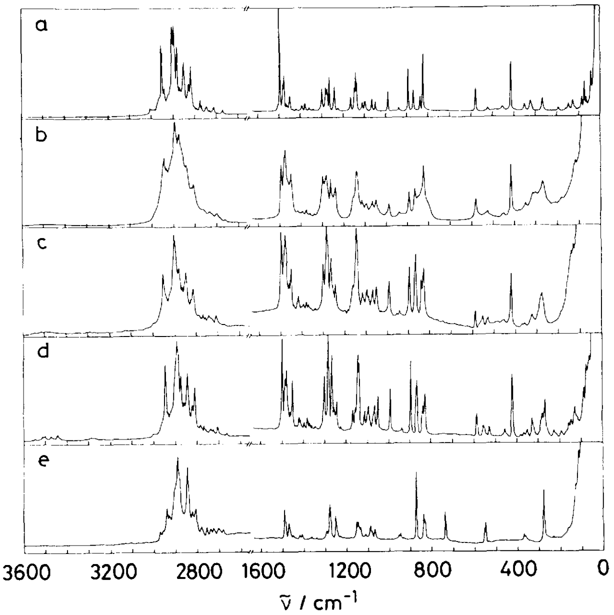

Figure 1. Raman spectra of the crystalline solid of the 18-crown-6–water system (b—d) and related substances: (a) uncomplexed neat 18-crown-6 crystal at −195 °C; (b) 92 wt% composition at 25 °C; (c) 92 wt% composition at 0 °C; (d) 92 wt% composition at −195 °C; (e) KSCN complex of 18-crown-6 at −195 °C.

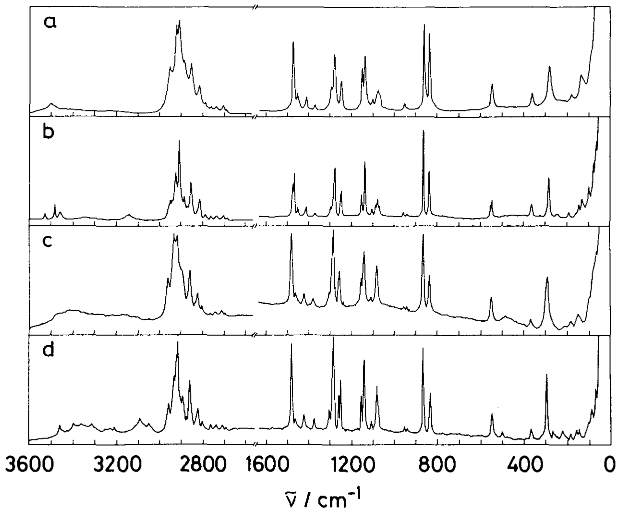

Figure 2. Raman spectra of the crystalline solid of the 18-crown-6–water system: (a) 70 wt% composition at 22 °C; (b) 70 wt% composition at −195 °C; (c) 49 wt% composition at 0 °C; (d) 49 wt% composition at −195 °C.

suffice for construction of the phase diagram and hence confirmation of the hydration complex formation. The Raman spectra for these compositions at various temperatures are shown in Figures 1 and 2.† When the liquid substance of the binary system with a 92 wt% composition of 18-crown-6 was gradually cooled, crystals began to grow at 28 °C and the coexistence of the liquid and crystalline solid phases persisted down to 23 °C. Below this temperature, the liquid phase disappeared and transformed completely into the crystal. The Raman spectra of the crystalline solid for this composition show interesting features depending on the temperature. Although the crystal is partly melted, the spectrum at 25 °C (Figure 1b) coincides completely with that of the uncomplexed neat 18-crown-6 crystal (Figure 1a). The Raman bands at 416 and 582 cm^{-1} are characteristic only of the C_i conformation.[14] It is indicated, therefore, that the 18-crown-6 molecule in the crystalline solid phase in equilibrium with the liquid phase takes the C_i conformation. The spectra observed below 23 °C (Figures 1c and d) are essentially the same, but are appreciably different from the spectra observed above 23 °C; namely, the lower temperature spectra give several new bands which are not found at higher temperatures. Spectral examination indicates that these additional bands coincide entirely with the bands observed for the KSCN complex with the D_{3d} conformation (Figure 1e) but do not agree with the bands for any other complexes with different conformations. These spectral observations demonstrate that, at the 92 wt% composition of the 18-crown-6–water system, the molecules in the C_i and D_{3d} conformations coexist in the solid phase at temperatures below 23 °C.

In the 18-crown-6–water systems with compositions of 70 and 49 wt%, crystallization started at 24 and 15 °C, respectively, when the substance was cooled. The crystallization was completed at −2 °C. The Raman spectra of the crystalline solid phase are substantially the same irrespective of the composition and temperature (Figures 2a—d) and are in agreement with the spectrum of the KSCN complex (Figure 1e). The molecule in the crystal is thus shown to have the D_{3d} conformation. The Raman bands observed at 285, 365, and 549 cm^{-1} are consistent only with the D_{3d} conformation.[14] It is noteworthy that these spectra exhibit distinctive Raman bands in the region above 3450 cm^{-1}, assignable to the O–H stretching vibrations of water molecules bound firmly to the ether oxygens of 18-crown-6. For temperatures below −2 °C, the spectra show the O–H stretching bands due to ice I[19] in the region 3050—3350 cm^{-1}. These spectral observations for the 70 and 49 wt% compositions indicate that, in the higher temperature region down to −2 °C, the 18-crown-6–water complex with the D_{3d} conformation is in equilibrium with the liquid phase, while in the lower temperature region, this hydration complex coexists with ice.

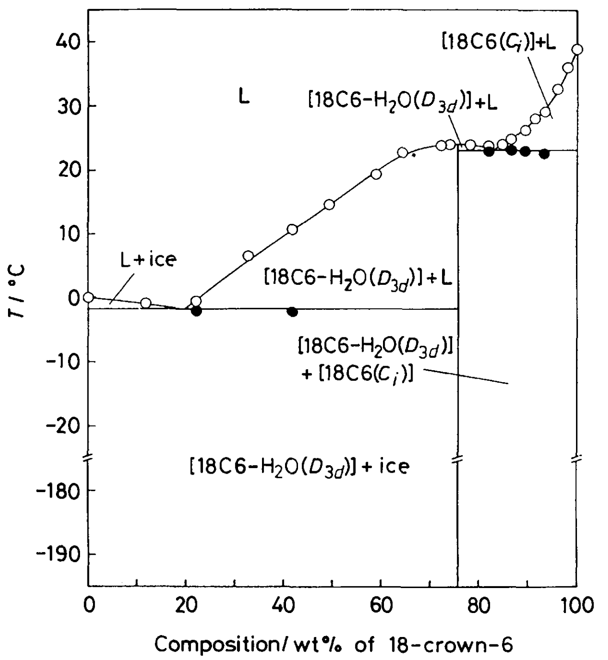

Figure 3. Approximate phase diagram of the binary system of 18-crown-6 and water. L: liquid (aqueous solution of 18-crown-6); 18C6 (C_i): solid of uncomplexed 18-crown-6 with the C_i conformation; 18C6-H_2O(D_{3d}): solid of the 18-crown-6–water complex with the D_{3d} conformation. ○: experimental points of liquidus (freezing curve); ●: experimental points of solidus (melting curve).

Measurements of the liquidus are essential for determining the molar ratio of the component compounds in the complex. The results for the 18-crown-6–water system show a maximum freezing temperature (congruent melting point) at a composition of 70—80 wt%; the ill-defined maximum makes sharp determination of the exact composition difficult. The phase behaviour thus observed and characterized by the Raman spectra and the liquidus leads to a phase diagram as shown in Figure 3. This is typical of phase diagrams for condensed two-component systems with stable compound formation (*e.g.*, the *p*-toluidine–phenol system).[20] At a composition of 70—80 wt%, the stable crystalline solid of the hydration complex solely exists at temperatures below the congruent melting point (approximately 24 °C). This composition corresponds to a molar ratio of 18-crown-6 to water of 1 : 4—6. Although the exact stoicheiometry is undetermined in the present work, the formation of a real hydration complex of 18-crown-6 is now proved by the existence of the congruent melting point.[20] In the phase region denoted by [18C6–H_2O(D_{3d})] + [18C6(C_i)] in Figure 3, the solid of the hydration complex 18-crown-6–water with the D_{3d} conformation and the solid of uncomplexed 18-crown-6 with the C_i conformation

---

† The observed wavenumbers and the results of normal co-ordinate calculations for 18-crown-6 and various complexes are available from one of the authors (H. M.) on request.

coexist, while in the region [18C6–$H_2O(D_{3d})$] + ice, the hydration complex and ice coexist. In the latter region, all the 18-crown-6 molecules are complexed with a surplus of water molecules, but in the former region, there are insufficient water molecules to complex all of the 18-crown-6 molecules. The Raman spectra have thus presented clear evidence for the D_{3d} conformation of 18-crown-6 in the complex.

According to the Monte Carlo calculations,[21] the D_{3d} conformation of the 18-crown-6 molecule is most stabilized in an aqueous environment. The present experimental finding of the D_{3d} conformation in the crystalline complex agrees nicely with this theoretical prediction. The previously evaluated four co-ordinating water molecules for both faces of the macrocyclic ring[21] also conform with our results.

Received, 24th July 1989; Com. 9/03105G

References

1 F. de Jong, D. N. Reinhoudt, and C. J. Smit, *Tetrahedron Lett.*, 1976, 1371; 1375.

2 M. Dobler, 'Ionophores and Their Structures,' Wiley, New York, 1981, p. 121.

3 I. Goldberg, 'Inclusion Compounds,' eds. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, Academic Press, London, 1984, vol. 2, p. 261.

4 J. D. J. Backer-Dirks, J. E. Cooke, A. M. R. Galas, J. S. Ghotra, C. J. Gray, F. A. Hart, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1980, 2191.

5 A. Elbasyouny, H. J. Brügge, K. von Deuten, M. Dickel, A. Knöchel, K. U. Koch, J. Kopf, D. Melzer, and G. Rudolph, *J. Am. Chem. Soc.*, 1983, **105**, 6568.

6 D. A. Grossie, W. H. Watson, F. Vögtle, and W. M. Müller, *Acta Crystallogr., Sect. B*, 1982, **38**, 3157.

7 W. H. Watson, J. Galloy, D. A. Grossie, F. Vögtle, and W. M. Müller, *J. Org. Chem.*, 1984, **49**, 347.

8 M. R. Caira, W. H. Watson, F. Vögtle, and W. Müller, *Acta Crystallogr., Sect. C*, 1984, **40**, 491.

9 I. Goldberg, *Acta Crystallogr., Sect. B*, 1978, **34**, 3387.

10 G. R. Newkome, F. R. Fronczek, and D. K. Kohli, *Acta Crystallogr., Sect. B*, 1981, **37**, 2114.

11 G. R. Newkome, H. C. R. Taylor, F. R. Fronczek, T. J. Delord, D. K. Kohli, and F. Vögtle, *J. Am. Chem. Soc.*, 1981, **103**, 7376.

12 D. A. Long, 'Raman Spectroscopy,' McGraw-Hill, New York, 1977.

13 H. Matsuura and K. Fukuhara, *J. Polym. Sci., Part B, Polym. Phys.*, 1986, **24**, 1383.

14 K. Fukuhara, K. Ikeda, and H. Matsuura, *J. Mol. Struct.*, in the press.

15 E. Maverick, P. Seiler, W. B. Schweizer, and J. D. Dunitz, *Acta Crystallogr., Sect. B*, 1980, **36**, 615.

16 P. Seiler, M. Dobler, and J. D. Dunitz, *Acta Crystallogr., Sect. B*, 1974, **30**, 2744.

17 P. Groth, *Acta Chem. Scand., Ser. A,* 1982, **36**, 109.

18 S. Harkema, G. J. van Hummel, K. Daasvatn, and D. N. Reinhoudt, *J. Chem. Soc., Chem. Commun.*, 1981, 368.

19 M. J. Taylor and E. Whalley, *J. Chem. Phys.*, 1964, **40**, 1660.

20 E. A. Moelwyn-Hughes, 'Physical Chemistry,' Pergamon, Oxford, 1961, 2nd rev. edn., p. 1051.

21 G. Ranghino, S. Romano, J. M. Lehn, and G. Wipff, *J. Am. Chem. Soc.*, 1985, **107**, 7873.