Composition Dependence of Thermodynamic Properties of Xenon Hydrate

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Heat capacities in the range 150-230 K and enthalpy of dissociation at 273.15 K and 1 bar have been determined for a clathrate hydrate of xenon of composition Xe-6.29H₂O. The results together with those for Xe-5.90H₂O reported previously give a composition dependence of the changes in heat capacity and enthalpy for the process ice \rightarrow empty lattice which is greater than that predicted by the ideal solid-solution theory.

Introduction

The ideal solid-solution theory of clathrates¹ assumes that the guest-guest interactions contribute negligibly to the free energy of the system and thus can be neglected. The heat capacities of Ar,² CH₄,³ Kr,⁴ O₂,⁵ and CO^{5,6} and the enthalpies of formation of CH₄,³ Ar,⁷ and O₂⁷ hydroquinone clathrates were found to be linear with composition, thereby attesting to the ideality of the solid solution. For the clathrate hydrates, the sorption isotherms of Ar, Kr, and Xe in the small cages of structure II CHCl₃ hydrate were also found to obey the Langmuir equation.⁸ The typical range of distance between neighboring cage centres is about 600-900 pm in hydroquinone and water clathrates. If the equilibrium position of the guest molecule is at the cage center, then at such distances the interaction between the molecules, together with the fact that some shielding will be provided by the cage walls, is negligible especially in the case of nonpolar molecules which interact via short-range dispersion forces only. However, if the molecules are polar, the long-range electrostatic interactions between guests can contribute significantly to the free energy of the system as is indicated by the phase transitions the guests undergo in the case of HCN,⁹ CH₃OH,¹⁰ and H₂S¹¹ hydroquinone clathrates and the structure I clathrate hydrate of trimethylene oxide.^{12,13} Between the two extremes noted above, interactions of intermediate magnitude can be expected to be operative in cases where the guest is slightly polar or has a large polarizability. Recent theoretical investigations¹⁴⁻¹⁷ appear to show that the incorporation of the guest-guest interactions in the ideal solidsolution theory leads to improved predictions of cage occupancy and phase equilibria even in cases where guests are rare gases.

Hydroquinone clathrates of variable composition are easily prepared and thus the composition dependence of thermodynamic properties has been mainly studied in such systems. In contrast, the clathrate hydrates exist over a very narrow range of composition, the composition itself is difficult to determine, and therefore determination of composition dependence of thermodynamic properties of clathrate hydrates puts severe limits on the precision with which the composition should be determined. Recently a calorimetric technique¹⁸ has been developed for precise determinations of composition, enthalpy of dissociation, and heat capacities of gas hydrates. This technique has been used to determine thermodynamic properties of $Xe \cdot nH_2O$ where *n* pertains to the equilibrium composition at 273.15 K. These results when combined with those obtained from a parallel study¹⁸ on a sample prepared under a pressure about 25 times the equilibrium pressure and of composition Xe-5.90H₂O give, for the first time, meaningful evidence for the composition dependence of thermodynamic properties of a clathrate hydrate and for the nonideality of the guest-host solution.

Experimental Methods

The details of preparation of the equilibrium sample are given elsewhere.¹⁸ The reaction vessel (Parr Instrument Co.) was equipped with stainless steel rods and a 34 bar full-scale pressure

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transducer (Setra, Model 204). The hydrate was prepared from ice and xenon gas (Air Products, 99.995 mol %) by grinding, intermittently, the components between 263 and 272 K for 5 days. The starting pressure of 10.10 bar at 263.9 K had fallen to a value of 4.25 bar at 273.2 K at the end of 5 days. The pressure was then reduced to 2.05 bar and the vessel was kept in an ice bath for 3 days. The final equilibrium pressure was (1.545 ± 0.005) bar at 273.15 K. For the hydrate-ice-gas equilibrium, the pressure at 273.15 K reported by Aaldijk¹⁹ is 1.528 bar. The sample was recovered from the reaction vessel and loaded into the calorimeter as described before.18

A Tian-Calvet heat-flow calorimeter (Setaram, Model BT) was used. The details of the calorimeter and the operating technique have been described elsewhere.²⁰ Briefly, about 6 g of the sample was placed in the calorimeter at 78 K and heated through 273 \boldsymbol{K} in the presence of xenon gas such that the gas pressure was always higher than the dissociation pressure. From the enthalpy of melting measured at 273.15 K, the ice content of the hydrate was found to be about 0.1% by mass. This ice was slowly converted into hydrate by subjecting it to freeze-thaw cycles under a xenon pressure of 2-3 bar until no melting was detected around 273 K. The sample was then cooled to 78 K, gradually removing the gas in the system but always maintaining a pressure greater than the dissociation pressure. Care was taken to avoid any condensed phase of xenon in the calorimeter. By the time the calorimeter reached 78 K, the gas pressure was reduced to less than 0.01 bar. The sample was then heated to room temperature at 10 K h^{-1} . The composition, enthalpy of dissociation, and heat capacities were calculated from the calorimetric runs as described before.¹⁸

Results and Discussion

The results reported below are based on measurements on three

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samples. The reproducibility of the results is represented by the errors quoted for composition and enthalpy of dissociation and by the standard deviation of the fit for heat-capacity results.

The composition of the equilibrium sample at 1.545 bar and 273.15 K was found to be $n = 6.29 \pm 0.03$. For a sample prepared at 253 K under an excess pressure of 20 bar, a value of $n = 5.90 \pm 0.05$ was obtained¹⁸ which is in accord with the fact that the cage occupancy increases with pressure. Other literature values of *n* pertaining to the equilibrium conditions at 273.2 K obtained by direct analysis are 6.0 by Aaldijk¹⁹ and 6.5 by Cady.²¹

The standard state (273.15 K and 1 bar) enthalpy of dissociation of the hydrate into ice and gas $\Delta H^{\circ}(h \rightarrow i + g)$ was determined to be (25.43 ± 0.17) kJ mol.⁻¹ It compares well with the value (25.79 ± 0.41) kJ mol⁻¹ obtained from the hydrate-ice-gas phase-equilibrium results in the range 263-273 K reported by Aaldijk.¹⁹ A somewhat lower value of 24.0 kJ mol⁻¹ is obtained from similar results in the range 211-268 K reported by Barrer and Edge.⁸ The procedure to obtain standard-state enthalpy of dissociation from the calorimetric results and from the phase equilibrium results has been described in detail previously.¹⁸ For Xe•5.90H₂O, $\Delta H^{\circ}(h \rightarrow i + g) = (26.50 \pm 0.17)$ kJ mol⁻¹ was reported previously.¹⁸

For Xe-6.29 H_2O , the heat capacities in the range 150–230 K are given by

$$C_p/(\mathrm{J} \mathrm{K}^{-1} \mathrm{mol}^{-1}) = 36.0 + 0.77505(T/\mathrm{K})$$
 (1)

with a standard deviation of 0.28 J K^{-1} mol⁻¹.

For analysis of the results for n, ΔH° , and C_p in terms of the ideal solid-solution theory, we shall take accuracy in each of the experimental results to be $\pm 1\%$,^{18,20} though the precision in the results reported here and previously¹⁸ is better than $\pm 1\%$. The cage occupancies for the small and the large cages, $\theta_{\rm S}$ and $\theta_{\rm L}$, for Xe-5.90H₂O²² and Xe-6.29H₂O²³ were obtained from *n* obtained

calorimetrically and θ_S/θ_L obtained from ¹²⁹Xe NMR by using the relation $n = 23/(\theta_S + 3\theta_L)$. Assuming the guest-host interactions to be spherically symmetrical 12-6 Lennard-Jones type and ignoring the guest-guest interactions, the theory predicts for the reaction

empty cage + guest molecule \rightleftharpoons occupied cage (2)

values of $\Delta H(e + g \rightarrow h)$ of (-31.995 ± 0.049) kJ mol⁻¹ for Xe-5.90H₂O and (-32.076 ± 0.035) kJ mol⁻¹ for Xe-6.29H₂O. The calculations were performed in the manner described before.²² These results when combined with the calorimetric enthalpies of dissociation yield, for the process ice \rightarrow empty lattice, values of $\Delta H(i \rightarrow e)$ of (0.93 ± 0.03) kJ (mol H₂O)⁻¹ for Xe-5.90H₂O and (1.06 ± 0.03) kJ (mol H₂O)⁻¹ for Xe-6.29H₂O. The difference between the two values is outside their combined errors and thus points to the inadequacy of the theory to account for the composition dependence of $\Delta H(e + g \rightarrow h)$ within the present limits of accuracy.

In a previous treatment of the heat capacities of Xe-5.90H₂O in terms of the ideal solid-solution theory,¹⁸ it was concluded that in the temperature range 100–270 K the heat capacity of the empty lattice is nearly the same as that of ice. The molar heat capacity of enclathrated guest C_g can then be obtained by subtracting from the molar heat capacity of Xe-*n*H₂O the heat capacity of *n* moles of ice.²⁰ In the range 150–230 K, the value of C_g is (21 ± 2) J K⁻¹ mol⁻¹ for Xe-5.90H₂O and (14 ± 2) J K⁻¹ mol⁻¹ for Xe-6.29H₂O. The difference between the two values is again greater than their combined errors and is perhaps due to the nonideality of the guest-host solution.

The evidence for nonideality presented in this report is based on results for two compositions only. Results on hydrate system(s) in which the composition can be varied over a large extent shall be desirable in establishing the nonideality of the guest-host solutions.

Registry No. Xe-xH₂O, 60212-94-4; water, 7732-18-5.

Chain-Length-Dependent ¹³C NMR Chemical Shifts of *n*-Alkanes in the Urea Inclusion Compounds

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¹³C NMR chemical shifts of *n*-alkanes ($C_7H_{16}-C_{20}H_{42}$, 7-20) in the urea inclusion compounds were measured by the ¹³C CPMAS NMR method. The ¹³C chemical shifts of the methyl and α - and β -methylene carbon atoms for 9-20 are independent of the chain lengths of the *n*-alkane molecules, whereas those for the γ -methylene carbon atoms move downfield with increasing chain length. The ϵ - and η -methylene ¹³C resonance signals of some odd *n*-alkanes were detected as an isolated line. Additivity parameters for the ¹³C chemical shifts of 9-20 and characteristic features for those of 7 and 8 are discussed.

Introduction

It is well-known that simple additivity rules hold for the ¹³C NMR chemical shifts of alkanes in solutions,^{1,2} where many

conformational isomers are populated statistically. *n*-Alkanes, however, take an extended all-trans conformation when they are

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