Double clathrate hydrate of propane and hydrogen

Sergey S. Skiba · Eduard G. Larionov ·
Andrej Yu Manakov · Boris A. Kolesov ·
Aleksei I. Ancharov · Eugeny Ya Aladko

Abstract Formation of the only cubic structure II double hydrate of propane and hydrogen occurs in the propane–hydrogen–water system. The decomposition curves of the double hydrate at low pressures are situated at 3–4° above the decomposition curve of propane hydrate; at pressures 2000–2500 bar double hydrate decompose at 20° above propane hydrate.

Keywords Clathrate hydrate · Propane · Hydrogen · High pressure · Phase diagram · Double hydrate

It is recognized at present that hydrogen, as an ecologically safe and high-energy fuel, can become one of the basic energy carriers of the future. One of the important questions of hydrogen power engineering is the storage of hydrogen in the form suitable for its further technological use and under technologically acceptable P-T conditions. Several methods of hydrogen storage are under consideration at present (in high-pressure cylinders, in liquefied form, adsorbed on various materials, or bound in the form of hydrides of some metals) [1, 2]; each of these methods

S. S. Skiba · E. G. Larionov · A. Y. Manakov (✉) ·
B. A. Kolesov · E. Y. Aladko
Nikolaev Institute of Inorganic Chemistry SD RAS, Lavrentieva ave. 3, Novosibirsk 630090, Russian Federation
e-mail: manakov@che.nsk.su

A. Y. Manakov · B. A. Kolesov · A. I. Ancharov
Novosibirsk State University, Pirogova str. 2, Novosibirsk 630090, Russian Federation

A. I. Ancharov
Institute of Solid State Chemistry SD RAS, Kutateladze str. 18, Novosibirsk 630128, Russian Federation
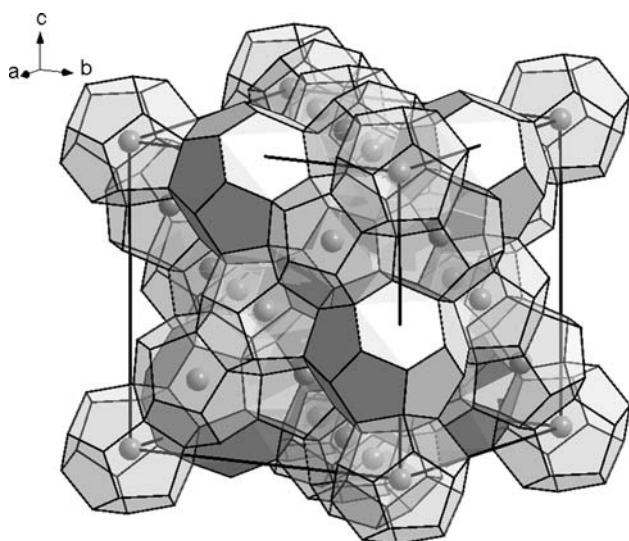
has its own advantages and shortcomings. The method involving hydrogen storage in the form of clathrate hydrates has been proposed not long ago [3, 4]. However, development of this method is only at the initial stage and requires further investigation.

Clathrate hydrates are inclusion compounds in which the host framework is formed by hydrogen-bonded water molecules, while the guest molecules (a gas or a readily volatile liquid) are situated in the polyhedral cavities of this framework [5]. Various aspects of the structural chemistry and physical chemistry of gas hydrates were considered in detail [5]. Many studies are dedicated to investigations of gas hydrates of hydrogen [3, 4, 6–9]. Unfortunately, the gas hydrates of pure hydrogen can hardly be used to store hydrogen because this requires very high pressure and/or low temperature. It is known that, as a rule, decomposition temperatures of the hydrates formed from mixtures of gases noticeably differing in size are higher than decomposition temperatures of the hydrates of individual components of these mixtures [10, 11]. The same situation takes place in the case of mixtures of the guest species forming cubic structure-II gas hydrate with hydrogen. Host framework of the cubic structure II is shown in Fig. 1. Florusse et al. [12] showed that the decomposition temperature of hydrogen hydrate can be increased substantially if the large cavities in the hydrate of cubic structure II are filled with tetrahydrofuran molecules. It seemed interesting for us to investigate the case when the initial gas mixture contains molecules smaller than THF in addition to hydrogen molecules. We chose the system H_2–C_3H_8–H_2O as the subject of investigation. The data concerning the phase diagram of the propane–water system in a wide range of pressures are presented in [1, 13].

Phase diagrams were investigated by means of differential thermal analysis at high pressure; high-pressure

Fig. 1 Framework of the cubic structure II gas hydrate. H cavities are depicted as solid polyhedra; the centres of small dodecahedral cavities (transparent) are shown by spheres

equipment used in the work has been described in detail in [14]. Pressure was measured with Bourdon pressure gauge (measurement error 0.5%). Temperature was measured with a Chromel-Alumel thermocouple. Reproducibility of measured decomposition temperatures within one set of experiments was about 0.3 °C. Scattering of results in different sets will be considered below. Gases with a purity not <99.9% and distilled water were used in experiments. Gas mixtures were prepared by volume (the error being not more than 1 mol.%); gas mixtures were loaded into the experimental cell at a small (5–10%) excess with respect to water. For each experimental curve (10–30 experimental points within the range 10–2500 bar), approximating polynomials best corresponding to the data set were chosen with the help of a least squares procedure. Scattering of experimentally determined temperatures with respect to calculated values, turned out to be close to Gaussian with a mean square deviation of a single measurement of 0.7 °C. We consider this value as the most correct estimate of the reliability of our results. It includes errors in measuring temperature, pressure, approximation error, and scatter of results between sets of experiments. This value is somewhat larger than the scatter obtained by us in investigating single-component systems. We explain this by the rather diffuse shape of the differential signals characteristic of gas hydrates with several components.

Hydrate samples for the investigation by means of powder diffraction and Raman spectroscopy were prepared as follows. Finely crushed ice powder was placed into a high-pressure cell. Then hydrogen and propane were supplied to the cell sequentially. The sample was kept for 2–3 weeks in a freezing chamber at a temperature of

−14 °C. The formation of the hydrate was monitored on the basis of pressure drop in the bomb. Then the bomb was cooled to liquid nitrogen temperature and the hydrate was removed. The X-ray diffraction study was performed using synchrotron radiation at the fourth beamline of the VEPP-3 storage ring (Siberian synchrotron and terahertz radiation center, Budker Institute of Nuclear Physics SB RAS), at $\lambda = 0.3685$ Å. The Debye-Scherrer scheme was applied. An MAR345 imaging plate detector (pixel dimension 100 µm) was used to record the diffraction pattern. The distance from the sample to the detector was determined using the diffraction patterns of a standard substance (NaCl). A fine-ground hydrate sample was placed in an aluminum cell with two foam-coated holes for the primary beam and the outlet of diffracted radiation. Raman spectra were recorded with a Triplemate SPEX spectrometer equipped with a multi-channel detector, LN-1340 PB, Princeton Instruments, in a back-scattering geometry. The spectral resolution was 1 cm^{-1}. The 514 nm line of a 50 mW Ar ion laser was used for spectral excitation. All the spectra were recorded in-situ at the temperature close to 0 °C using specially designed pressure chamber supplied with sapphire window.

Numerical data on the decomposition curves of double propane–hydrogen hydrate formed at different compositions of the initial gas mixture are shown in Table 1, experimental points are presented in Fig. 2. Decomposition curves of double hydrate at low pressures are situated at 3–4° above decomposition curve of propane hydrate h_1 (Fig. 2); at highest pressures 2000–2500 bar the double hydrate decomposes at 20° above decomposition curve of the propane hydrate h_2 (Fig. 2). This observation may be explained by the increase in hydrogen content in the hydrate with increase of pressure. No bending pointes occurs at the decomposition curves; in temperature-composition projections of the phase diagram (taken at constant pressures and water : gas mixture molar ratios) the liquidus curves are shaped as a cupola with flattened top. These

Table 1 The coefficients of equations T (°C) $= A + B \times P + C \times P^2 + D \times \ln P$ (P, bar) that approximate the lines of liquidus in the hydrogen–propane—water system within pressure up to 2500 bar with the gas in excess

CH$_2$	Pressure range (bar)	A	B	C	D
40	30–2500	−4.2162	5.76×10^{-3}	-5.208×10^{-7}	2.950
50	10–2500	−0.0151	9.27×10^{-3}	-1.431×10^{-6}	1.997
60	10–2500	1.4826	11.67×10^{-3}	-2.066×10^{-6}	1.375
70	20–2500	−0.3215	12.50×10^{-3}	-2.447×10^{-6}	1.641
80	15–2500	−1.0687	11.33×10^{-3}	-2.000×10^{-6}	1.637

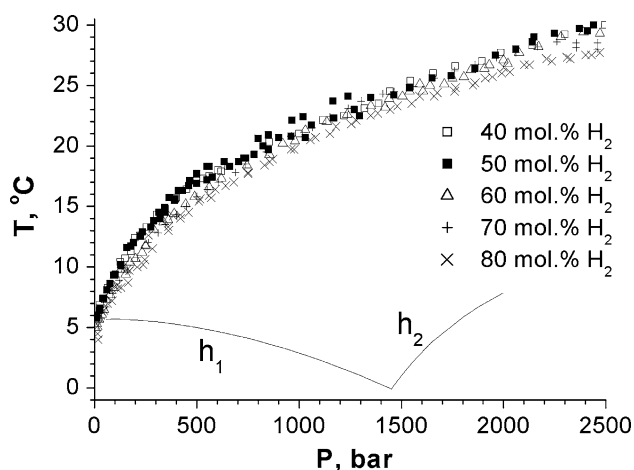Hydrogen concentration CH$_2$ is indicated for the initial gas mixture

Fig. 2 Decomposition curves of propane + hydrogen double clathrate hydrates. Hydrogen contents in the initial gas mixture are indicated in the figure. Decomposition curves of clathrate hydrates formed by pure propane are shown by solid lines. h_1—cubic structure II propane hydrate, h_2—propane hydrate with unknown structure [13]

observations show formation of the only gas hydrate in the system.

Powder diffraction patterns were obtained from the sample of quenched double hydrate synthesized from the gas mixture with 66.7 mol.% of hydrogen at $P = 24$ bar and $T = -14$ °C. Composition of the sample corresponded to the mixture of cubic structure II hydrate with the unit cell parameter 17.1 Å at -150 °C and ice Ih (Fig. 3). Positions of reflections corresponding to ice Ih were calculated from the data of [15]. Composition of the clathrate hydrate was confirmed by Raman spectrometry. In-situ Raman spectra of the double hydrate recorded at $P = 24$ bar and $T = -10$ °C, initial composition of the propane–hydrogen
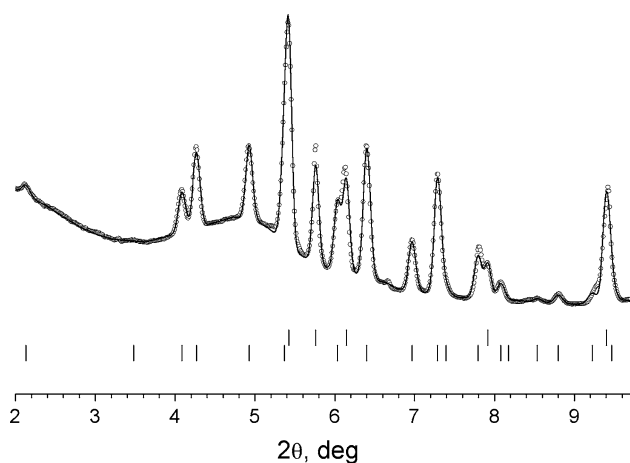

Fig. 3 Powder diffraction patterns of the sample of quenched propane–hydrogen double hydrate synthesized from the gas mixture with 66.7 mol.% of hydrogen at $P = 24$ bar and $T = -14$ °C taken at -150 °C. Tick marks correspond to expected positions of diffraction peaks for ice Ih (top) and cubic structure II hydrate (bottom)
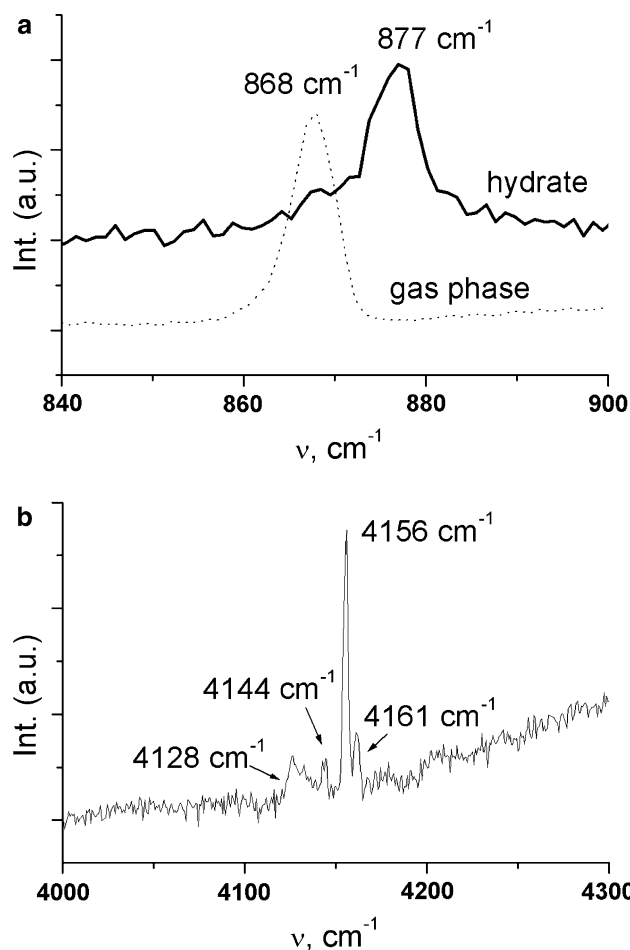

Fig. 4 Raman spectra of the double propane–hydrogen hydrate recorded at $P = 24$ bar and $T = -10$ °C, initial composition of the propane–hydrogen mixture corresponded to 66.7 mol.%. a Raman bands corresponding to C–C vibrations of propane in hydrate and gas phases, b Raman bands corresponding to H–H vibrations of H_2 molecule; bands at 4144, 4156 and 4161 cm^{-1} correspond to hydrogen in gas phase, wide band at 4128 cm^{-1} correspond to hydrogen molecule in small pentagondodecahedral cavity

mixture corresponded to 66.7 mol.% of hydrogen are shown in Fig. 4. One can see that the positions of the bands corresponding to vibrations of hydrogen and propane molecules in the clathrate and gaseous phases differ significantly. The Raman band observed at 877 cm^{-1} (Fig. 4a) corresponds well with the expected position for C–C vibrations in the propane hydrate. According to the data of [16] in cubic structure II propane hydrate position of this band corresponds to 878 cm^{-1}. Several Raman bands are visible in the interval 4000–4300 cm^{-1}. The data presented in [17] allow us to assign wide band at 4128 cm^{-1} to H–H vibrations of hydrogen molecules in small pentagondodecahedral cavities; other bands may be assigned to gaseous hydrogen. Low intensity of the band at 4128 cm^{-1} shows low occupation of D-cavities by hydrogen molecules.

We conclude that formation of double hydrates in this system is very similar to the situation observed in the tetrahydrofuran - hydrogen - water system [18]. Cubic structure II double hydrate exists in the propane–hydrogen–water system at pressures up to 2500 bar. This hydrate can be synthesized from the initial gas mixtures with hydrogen contents from 40 to 80 mol.%. Stabilization of the double hydrate takes place due to occupation of vacant small cavities in the cubic structure II hydrate framework with hydrogen molecules.

References

1. Schlapbach, L., Zuttel, A.: Hydrogen-storage materials for mobile applications. Nature **414**(15), 353–358 (2001). doi:10.1038/35104634
2. Zuttel, A.: Hydrogen storage methods. Naturwissenschaften **91**, 157–172 (2004). doi:10.1007/s00114-004-0516-x
3. Mao, W.L., Mao, H.-k.: Hydrogen storage in molecular compounds. Proc. Natl. Acad. Sci. USA **101**, 708–710 (2004). doi:10.1073/pnas.0307449100
4. Mao, W.L., Mao, H.-k., Goncharov, A.F., Struzhkin, V.V., Guo, Q., Hu, J., Shu, J., Hemley, R.J., Somayazulu, M., Zhao, Y.: Hydrogen clusters in clathrate hydrate. Science **297**, 2247–2249 (2002). doi:10.1126/science.1075394
5. Sloan, E.D.: Clathrate hydrates of natural gases, 2nd edn. Marcel Dekker, New-York (1998)
6. Vos, W.L., Finger, L.W., Hemley, R.J., Mao, H.: Novel H_2–H_2O clathrate at high pressures. Phys. Rev. Lett. **71**(19), 3150–3153 (1993). doi:10.1103/PhysRevLett.71.3150
7. Dyadin, Y.A., Larionov, E.G., Manakov, A.Y., Zhurko, F.V., Aladko, E.Y., Mikina, T.V., Komarov, V.Y.: Clathrate hydrates of hydrogen and neon. Mendeleev Commun. 209–210 (1999). doi:10.1070/mc1999v009n05ABEH001104
8. Lokshin, K.A., Zhao, Y., He, D., Mao, W.L., Mao, H.-k., Hemley, R.J., Lobanov, M.V., Greenblatt, M.: Structure and dynamics of hydrogen molecules in the novel clathrate hydrate by high pressure neutron diffraction. Phys. Rev. Lett. **93**(12), contr. 125503 (2004)
9. Barkalov, O.I., Klyamkin, S.N., Efimchenko, V.S., Antonov, V.E.: Formation and composition of the clathrate phase in the H_2O–H_2 system at pressures to 1.8 kbar. JETP Lett. **82**(7), 413–415 (2005). doi:10.1134/1.2142867
10. Glew, D.N., Mak, H.D., Rath, N.S.: Aqueous non-electrolyte solutions: Part VII. Water shell stabilization by interstitial non-electrolytes. In: Covington, A.K., Jones, P. (eds.) Hydrogen-Bonded Solvent Systems, pp. 185–195. Taylor and Francis, London (1968)
11. Larionov, E.G., Manakov, A.Y., Zhurko, F.V., Dyadin, Y.A.: CS-II double clathrate hydrates at pressures up to 15 kbar. J. Struct. Chem. **41**(3), 476–482 (2000). doi:10.1007/BF02742008
12. Florusse, L.J., Peters, C.J., Schoonman, J., Hester, K.C., Koh, C.A., Dec, S.F., Marsh, K.N., Sloan, E.D.: Stable low-pressure hydrogen clusters stored in a binary clathrate hydrate. Science **306**, 469–471 (2004). doi:10.1126/science.1102076
13. Dyadin, Y.A., Larionov, E.G., Aladko, E.Y., Zhurko, F.V.: Clathrate formation in propane-water and methane-propane-water systems under pressures of up to 15 kbar. Dokl. Phys. Chem. **376**(4–6), 23–26 (2001). doi:10.1023/A:1018860413545
14. Dyadin, Y.A., Larionov, E.G., Mirinskij, D.S., Mikina, T.V., Aladko, E.Y., Starostina, L.I.: Phase diagram of the Xe–H_2O system up to 15 kbar. J. Incl. Phenom. **28**, 271–285 (1997)
15. Rottger, K., Endriss, A., Ihringer, J., Doyle, S., Kuhs, W.F.: Lattice constants and thermal expansion of H_2O and D_2O ice Ih between 10 and 265 K. Acta Crystallogr. B **50**, 644–648 (1994). doi:10.1107/S0108768194004933
16. Sum, A.K., Burrus, R.C., Sloan, E.D.: Measurement of clathrate hydrates via Raman Spectroscopy. J. Phys. Chem. B **101**, 7371–7377 (1997). doi:10.1021/jp970768e
17. Hashimoto, S., Sugahara, T., Sato, H., Ohgaki, K.: Thermodynamic stability of H_2+ tetrahydrofuran mixed gas hydrate in nonstoichiometric aqueous solutions. J. Chem. Eng. Data **52**, 517–520 (2007). doi:10.1021/je060436f
18. Anderson, R., Chapoy, A., Tohidi, B.: Phase relations and binary clathrate hydrate formation in the system H_2–THF–H_2O. Langmuir **23**, 3440–3444 (2007). doi:10.1021/la063189m