

Research Article

Preservation of Methane Hydrates Prepared from Dilute Electrolyte Solutions

Hiroshi Sato,¹ Takanori Tsuji,¹ Tetsunari Nakamura,¹ Koichi Uesugi,¹ Takahiro Kinoshita,¹ Masahiro Takahashi,² Hiroko Mimachi,² Toru Iwasaki,² and Kazunari Ohgaki¹

¹ Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

² Chiba Technology Center, Research & Development Department, Mitsui Engineering and Shipbuilding Co., Ltd, 1 Yawatakaigandori, Ichihara, Chiba 290-8601, Japan

Correspondence should be addressed to Kazunari Ohgaki, ohgaki@cheng.es.osaka-u.ac.jp

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The anomalous or self-preservation of methane hydrate at atmospheric pressure and temperatures below the ice point was investigated to determine whether this phenomenon might have applications in the storage and transportation of natural gas. Particular attention was paid to the effects of dilute electrolytes, as the presence of impurities in water is unavoidable in commercial transportation processes. The presence of electrolytes had a marked effect on the decomposition kinetics of methane hydrate at temperatures between 243 and 269 K. It was also found that chloride and sulfate ions may exhibit greater effects than do sodium and magnesium ions.

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1. Introduction

Gas hydrates are crystalline solids that are formed by association of water and a gas under conditions of relatively high pressure and low temperature. An important practical feature of gas hydrates is that, depending on the gas, a given volume of gas hydrate can contain up to about 150 times the mass of gas present in an equivalent volume of the pure gas in the standard state. The storage and transportation of natural gas in the form of its hydrate has therefore been recently suggested as a practical measure [1–4].

As a general rule, gas hydrates must be stored in conditions under which they are thermodynamically stable. In practice, however, when methane hydrate is subject to temperatures of between about 243 and 270 K at atmospheric pressure, it becomes metastable and continues to exist for a certain time at temperatures that are 50–80 K above its nominal equilibrium temperature (193 K) [5]; however, at temperatures above or below this anomalous region of stability, methane hydrate decomposes at rates that are

orders of magnitude greater than those in the anomalous region.

It has been postulated that a thin film of ice may form on the surface of the hydrate during its partial decomposition, and that this film serves as a barrier to subsequent gas diffusion [6–9]; however, Stern et al. speculated that anomalous preservation is not primarily the result of encapsulation by ice [5, 10].

Recently, an “ultrastability” of methane and natural gas hydrates prepared from dilute aqueous surfactant solutions has been reported by Zhang and Rogers [11], who claimed that only 0.04% of stored gas in a methane + ethane + propane hydrate was evolved during 256 hours at 268 K and atmospheric pressure. According to these authors, ice shielding is not the primary mechanism of anomalous preservation and the enhancement of preservation by the use of additives may be a practical possibility. Because waters that contain various amounts of impurities, such as river water, are likely to be used for the commercial production of natural gas hydrates for the purpose of

transportation, we examined the effects of dilute electrolytes on the kinetics of decomposition of methane hydrate.

2. Experimental Section

In this study, sodium chloride (Wako), sodium sulfate (Wako), and magnesium chloride hexahydrate (Aldrich) were used as electrolytes. These salts were dissolved in distilled water (Wako).

Methane hydrate was prepared in a high-pressure cell with internal mixing baffles that moved vertically across the gas-liquid interface. The cell was essentially the same to that reported previously [12]. The walls of the cell were equipped with a circulating water jacket to maintain the cell temperature at 280 K. Pure water or aqueous electrolyte solution was introduced into the cell, which was then pressurized with methane. Mixing was started, and the pressure gradually decreased as methane hydrate formed. The pressure was maintained in the range 5.8–6.2 MPa by intermittently supplying methane. The hydrate crystals were formed at the gas-liquid interface and on the cell wall. The crystals interfered with the mixing motion and the motion finally stopped. The consumption of methane greatly slowed on this occasion.

When the consumption of methane had almost ceased, the residual liquid in the cell was discharged through a tap at the bottom of the cell. The cell pressure decreased to around 5.8 MPa and hence methane was supplied to the cell. The volume of the discharged water was about one sixth of the supplied water and the electrolyte concentration of the discharged water was 120–140% of the supplied water. The electrolytes were primarily excluded from the hydrate crystals and the remaining electrolytes located probably on the surface and grain boundary of the final hydrate product [13].

The remaining contents of the cell were kept at the same pressure and temperature for a further 2–3 days before the cell was further cooled to 253 K for 1 day and then depressurized to atmospheric pressure. The methane hydrate that was produced by this procedure was partly granular and partly compact. No differences were found by visual observation between hydrates prepared from pure water and those prepared from dilute electrolytes, as well as the amount and rate of methane consumption recorded during the sample preparation.

The decomposition experiments were conducted under conditions that simulated the transportation of hydrate powder in a bulk cargo carrier. The experimental apparatus is shown in Figure 1. Powdered methane hydrate with an average diameter of about 0.5–1 mm, prepared by grinding the multicrystalline aggregates at 253 K and atmospheric pressure, was used as an initial material in all the experiments for the purpose of eliminating the probable dependency of grain size on the decomposition kinetics. Immediately after grinding, about 2–4 g of the resulting powder was packed into a bag that was placed in a glass vessel. The temperature of the vessel was controlled at the experimental temperature (243–269 K).

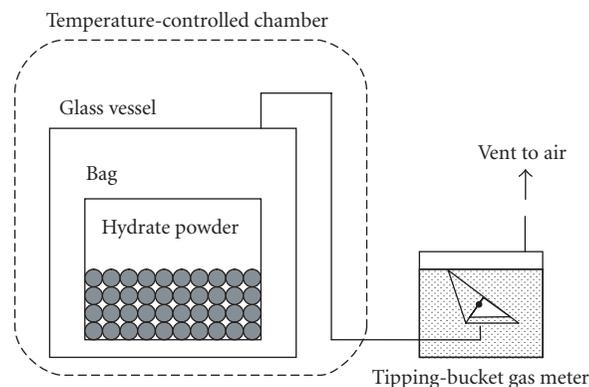


FIGURE 1: Schematic of the experimental apparatus for the decomposition of methane hydrate.

The bag became swollen by methane that evolved as a result of decomposition of the sample; this caused an identical volume of air to be discharged through a vent in the vessel. The volume of the discharged air was measured by means of a tipping-bucket-type gas meter (Japan Flow Control MGC). In order to get the total gas content of the sample, the residual hydrate was decomposed completely at the end of each isothermal experiment (normally of 336 hours duration) by raising the temperature above the ice point.

3. Results and Discussion

Figure 2 shows the temporal variations in the residual fraction of methane in samples kept at various constant temperatures. The residual fraction is based on the total gas occluded at the start of the isothermal decomposition experiments; this eliminates any losses incurred during collection from the high-pressure cell and grinding at 253 K. In all the experiments, the decomposition slowed as time elapsed. To check the reproductively of the experiments, two runs were conducted for the case of 1.0 mol/m³ sodium chloride at 263 K. A significant difference is seen on the decomposition rate and thus minor fluctuations on the results cannot be discussed based on the present experiments.

In the case of methane hydrates prepared from pure water, the rate of decomposition decreased on reducing the temperature from 269 to 258 K (Figure 2(a)). Note that an exceptionally rapid decomposition occurred at 253 K, but this slowed again as the temperature approached 243 K. Such nonmonotonous temperature dependency of the decomposition kinetics has already been reported by Stern et al. [5], but the details of their results were different from ours. They found two minima in the decomposition rate at 269 and 249 K, and one broad maximum at around 255 K. Apart from the differing temperature dependencies, the ranges of the mean decomposition rates unexpectedly match ours. The times required for the samples to evolve 50% of their gas content were reported to vary from 3 hours (256 K) to 30 day (269 K) and those for our results were between 33 hours (253 K) and 28 day (258 K) from extrapolation

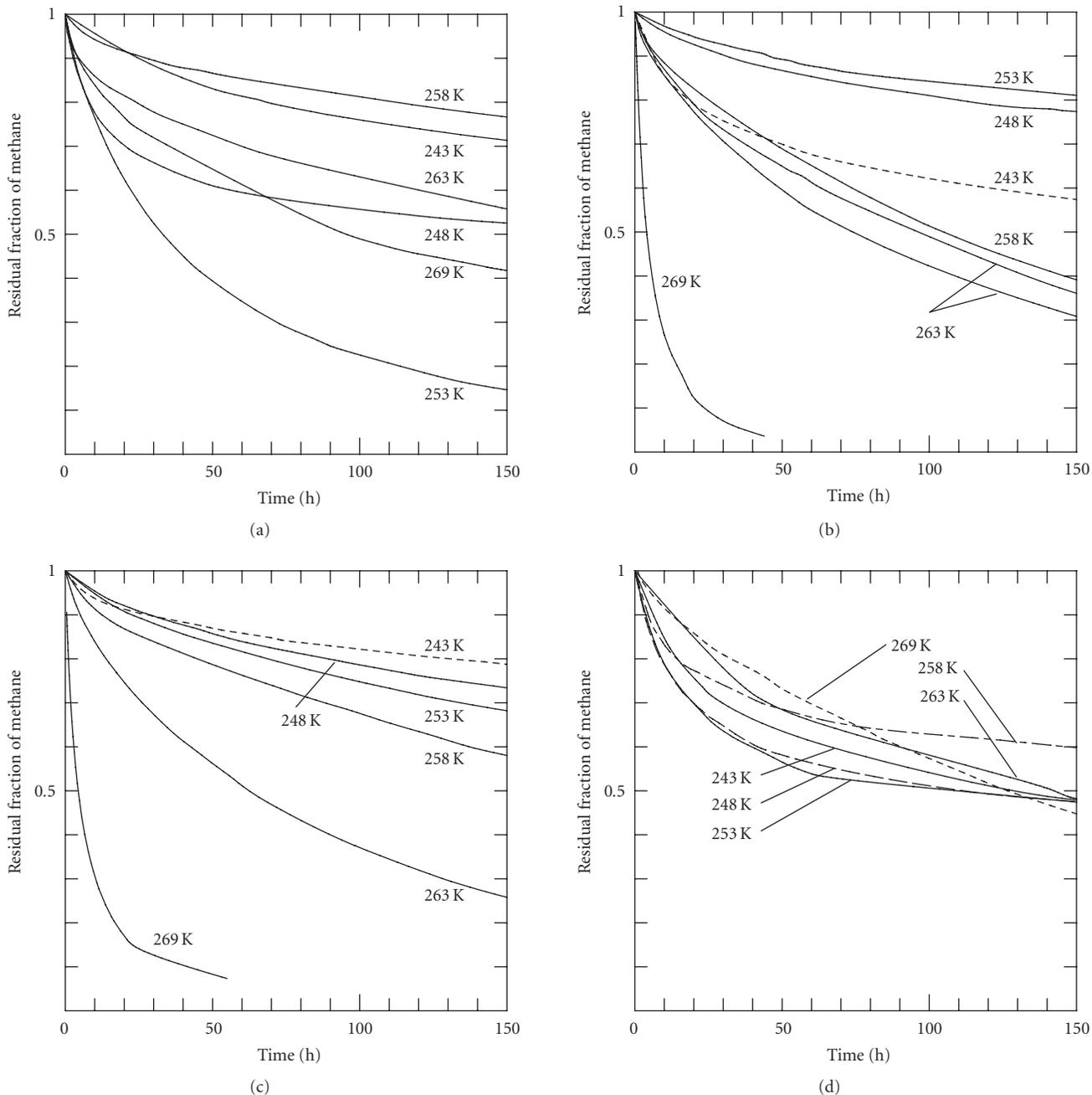


FIGURE 2: Decomposition behavior of methane hydrate samples prepared from various solutions. (a) Pure water. (b) 1.0 mol/m^3 aqueous sodium chloride. (c) 0.50 mol/m^3 aqueous magnesium chloride. (d) 0.50 mol/m^3 aqueous sodium sulfate.

based on the mean rate between 150–300 hours. We have not yet clarified the cause of this discrepancy, but at present we regard it as arising from differences in experimental conditions, such as the size of the hydrate granules or the purity of the water that was used.

Figure 2(b) shows the results for the methane hydrates prepared from 1.0 mol/m^3 aqueous sodium chloride. The rate of decomposition decreased with decreasing temperature from 269 to 253 K, but this trend reversed at 253 to 243 K. On the other hand, methane hydrates prepared

from 0.50 mol/m^3 aqueous magnesium chloride showed a monotonous decomposition behavior with the rate of decomposition increasing with increasing test temperature (Figure 2(c)). A peculiar feature of the results for samples of hydrate prepared from 0.50 mol/m^3 aqueous sodium sulfate solution is a very weak temperature dependency (Figure 2(d)). Note that the residual fractions at various temperatures converge at around 150 hours, except for the case of a temperature of 258 K, whereas the initial rates of decomposition differ from one other. These results clearly

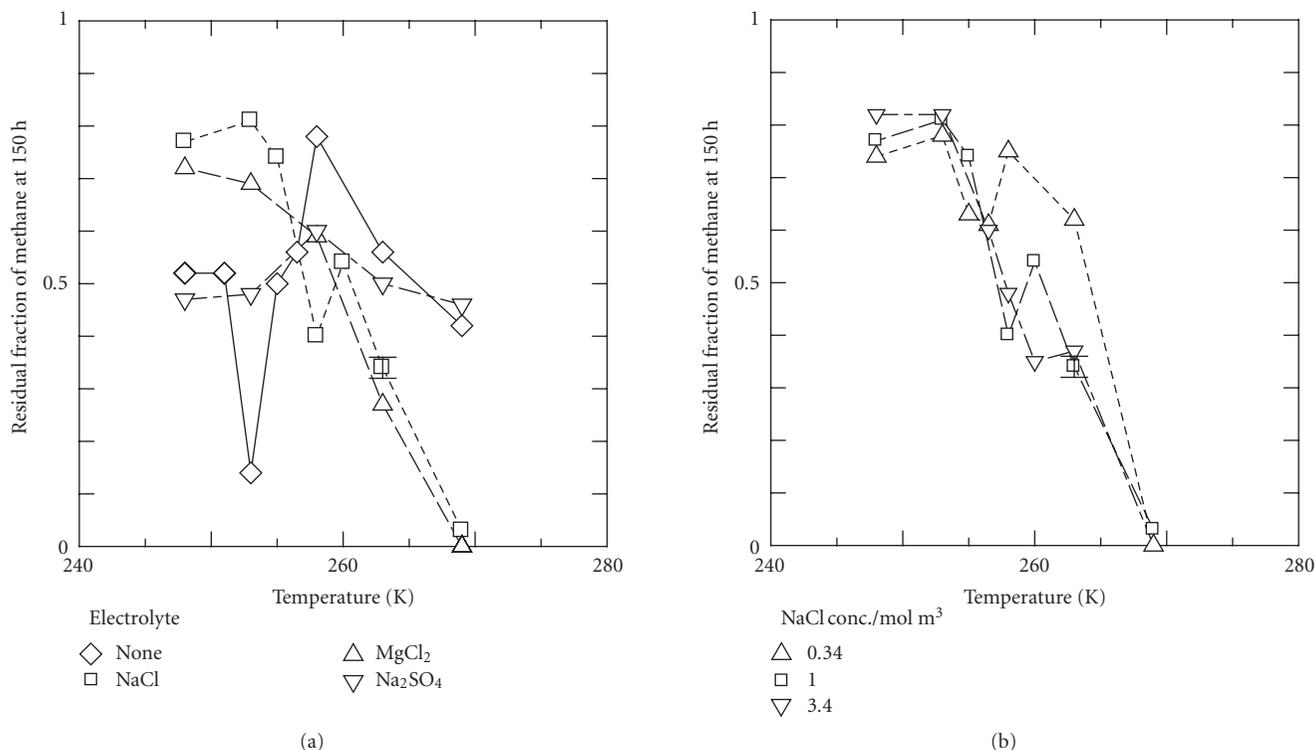


FIGURE 3: Residual fraction of methane in hydrate samples after an isothermal hold for 150 hours. (a) Samples prepared from pure water, 1.0 mol/m³ aqueous sodium chloride, 0.50 mol/m³ aqueous magnesium chloride, or 0.50 mol/m³ aqueous sodium sulfate. (b) Samples prepared from sodium chloride solutions of various concentrations.

show that decomposition of methane hydrate is significantly affected by the presence of dilute electrolytes, but this effect is not monotonous.

Figure 3(a) shows the fractions of methane preserved for 150 hours at various temperatures in samples prepared from pure water, 1.0 mol/m³ sodium chloride, 0.50 mol/m³ magnesium chloride, and 0.50 mol/m³ sodium sulfate solutions. An error bar corresponding to the case of sodium chloride at 263 K displays the difference between the results of two runs. The exceptionally rapid decomposition of the methane hydrates from pure water at 253 K was markedly suppressed by the addition of any of the salts. On the other hand, the decomposition at the highest temperature (269 K) was accelerated by the presence of sodium chloride or magnesium chloride. In comparison with the sodium sulfate system, the values for the samples from sodium chloride and magnesium chloride solutions at the same temperature show a passable resemblance to one another; we therefore surmise that chloride and sulfate ions have a greater effect on the decomposition of methane hydrate than do sodium and magnesium ions.

Figure 3(b) shows the residual methane fraction after 150 hours for samples prepared from three sodium chloride solutions of differing concentrations. The temperature dependencies of the residual fractions for the three concentrations show a marked similarity to one another. Whereas minor reverses are seen for all concentrations, the residual fractions generally increase with decreasing temperature from 269

to 253 K with a maximum at about 253 K for each of the concentrations. These results suggest that the effects of ion concentration on the decomposition kinetics are rather weak at low concentrations.

To summarize, the anomalous longevity of methane hydrates is markedly affected by the presence of low concentrations of ions in the water from which they are formed. These findings have both practical and scientific implications. From the point of view of practical applications, they show that it is possible to enhancing the longevity of gas hydrates by preparing them from dilute electrolyte solutions. Another result of the study is that an expanded examination of the effects of various additives could give further insights into the mechanism of anomalous preservation. Virtually no changes have been found on the properties of the hydrates other than the decomposition kinetics (e.g., phase equilibria, gas content, formation rate, and visual appearance) and thus the author has no trustworthy explanation at present for the mechanism of the effect of dilute electrolytes on anomalous preservation.

4. Conclusion

The decomposition behavior of methane hydrates prepared from pure water or dilute electrolyte solutions was studied under isothermal conditions between 243 and 269 K at atmospheric pressure. In the case of samples prepared from pure water, the decomposition rate showed a complicated

dependence on the temperature, as previously reported. The temperature dependence was altered by the presence of low concentrations of sodium, magnesium, chloride, and sulfate ions. The effect of these ions was not monotonous. In particular, the temperature dependence was almost eliminated in the case of sodium sulfate, and it is suggested that chloride and sulfate ions may exhibit greater effects than do sodium and magnesium ions.

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References

- [1] J. Gudmundsson and A. Borrehaug, "Frozen hydrate for transport of natural gas," in *Proceedings of the 2nd International Conference of Natural Gas Hydrates*, pp. 415–422, Toulouse, France, 1996.
- [2] H. Shirota, I. Aya, S. Namie, P. Bollavaram, D. Turner, and E. D. Sloan, "Measurement of methane hydrate dissociation for application to natural gas storage and transportation," in *Proceedings of the 4th International Conference of Gas Hydrates*, pp. 972–977, Yokohama, Japan, 2002.
- [3] T. Takaoki, T. Iwasaki, Y. Katoh, T. Arai, and K. Horiguchi, "Use of hydrate pellets for transportation of natural gas—I, Advantage of pellet form of natural gas hydrate in sea transportation," in *Proceedings of the 4th International Conference on Gas Hydrates*, pp. 982–986, Yokohama, Japan, 2002.
- [4] C. Giavarini and F. Maccioni, "Self-preservation at low pressures of methane hydrates with various gas contents," *Industrial & Engineering Chemistry Research*, vol. 43, no. 20, pp. 6616–6621, 2004.
- [5] L. A. Stern, S. Circone, S. H. Kirby, and W. B. Durham, "Anomalous preservation of pure methane hydrate at 1 atm," *The Journal of Physical Chemistry B*, vol. 105, no. 9, pp. 1756–1762, 2001.
- [6] V. S. Yakushev and V. A. Isotomin, "Gas-hydrates self-preservation effect," in *Physics and Chemistry of Ice*, N. Maeno and T. Hondoh, Eds., pp. 136–140, Hokkaido University Press, Sapporo, Japan, 1992.
- [7] T. Komai, S.-P. Kang, J.-H. Yoon, Y. Yamamoto, T. Kawamura, and M. Ohtake, "In situ Raman spectroscopy investigation of the dissociation of methane hydrate at temperatures just below the ice point," *The Journal of Physical Chemistry B*, vol. 108, no. 23, pp. 8062–8068, 2004.
- [8] W. F. Kuhs, G. Genov, D. K. Staykova, and T. Hansen, "Ice perfection and onset of anomalous preservation of gas hydrates," *Physical Chemistry Chemical Physics*, vol. 6, no. 21, pp. 4917–4920, 2004.
- [9] W. Shimada, S. Takeya, Y. Kamata, et al., "Texture change of ice on anomalously preserved methane clathrate hydrate," *The Journal of Physical Chemistry B*, vol. 109, no. 12, pp. 5802–5807, 2005.
- [10] L. A. Stern, S. Circone, S. H. Kirby, and W. B. Durham, "Temperature, pressure, and compositional effects on anomalous or "self" preservation of gas hydrates," *Canadian Journal of Physics*, vol. 81, no. 1-2, pp. 271–283, 2003.
- [11] G. Zhang and R. E. Rogers, "Ultra-stability of gas hydrates at 1 atm and 268.2 K," *Chemical Engineering Science*, vol. 63, no. 8, pp. 2066–2074, 2008.
- [12] T. Sugahara, T. Makino, and K. Ohgaki, "Isothermal phase equilibria for the methane + ethylene mixed gas hydrate system," *Fluid Phase Equilibria*, vol. 206, no. 1-2, pp. 117–126, 2003.
- [13] G. D. Pavlov and I. N. Medvedev, "Gas hydrating process of water desalination," in *Proceedings of 1st International Symposium on Water Desalination*, vol. 3, pp. 123–127, Washington, DC, USA, 1967.



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