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# Equilibrium Data of Neohexane + Hydrogen Sulfide and Neohexane + Methane Clathrate Hydrates

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**ABSTRACT:** Experimental hydrate dissociation pressures for the hydrogen sulfide + neohexane (2,2-dimethylbutane) + water and methane + neohexane + water systems are reported in the temperature ranges of (287.2 to 293.2) K and (275.5 to 286.8) K, respectively. The experimental data were generated using an isochoric pressure-search method. The hydrate dissociation data for the methane + neohexane + water system are compared with some selected experimental data from the literature, and the acceptable agreement confirms the reliability of the experimental method used in this work. The experimental data for both measured systems are finally compared with the corresponding experimental data in the absence of neohexane reported in the literature to study the hydrate promotion effects of neohexane.

## 1. INTRODUCTION

Gas hydrates (or clathrate hydrates) are crystalline water-based solids physically resembling ice, which are formed through a combination of water and small guest molecule(s) like methane, nitrogen, and so forth.<sup>1</sup> In the clathrate hydrate lattice, water molecules form hydrogen-bonded cage-like structures, encapsulating the guest molecule(s).<sup>1</sup> Gas hydrates normally form three crystalline structures, namely, structure I (sI), structure II (sII), and structure H (sH), where each structure is composed of a certain number of cavities formed by water molecules.<sup>1</sup> The formation of structure H and also structure II of some heavy molecules requires the presence of large and small guest molecules. Large molecules occupy large cavities while small molecule(s) (called help gas) fill the remaining cavities.<sup>1</sup> It has been reported that neohexane (2,2-dimethylbutane) generally forms structure H of clathrate hydrates with a help gas like methane, xenon, and krypton.<sup>1–3</sup> However, information on other help gases is limited. To the best of our knowledge, there is no information on the clathrate hydrate formation of neohexane with hydrogen sulfide as a help gas.

In this work, gas hydrate dissociation data for the hydrogen sulfide + neohexane + water and methane + neohexane + water systems are reported in the temperature ranges of (287.2 to 293.2) K and (275.5 to 286.8) K, respectively. The experimental data were generated using an isochoric pressure-search method.<sup>4–7</sup> As gas hydrate dissociation data for the methane + neohexane + water system have already been reported in the literature, therefore, we first generated and report experimental data for the latter system and compare them with some selected experimental data from the literature<sup>8–10</sup> to confirm the reliability of the experimental method used in our work. We then report hydrate dissociation data for the hydrogen sulfide + neohexane + water system. The experimental data for the studied systems are finally compared with some selected experimental data from the literature for the methane + water<sup>11–13</sup> and hydrogen sulfide + water<sup>4,14–16</sup> systems to study the hydrate promotion effects of neohexane.

## 2. EXPERIMENTAL SECTION

**2.1. Chemicals.** Table 1 reports the purities and suppliers of the chemicals used in this work.

**2.2. Experimental Apparatus.** Figure 1 shows the schematic diagram of the apparatus used in this work. Briefly, the main part of the apparatus is a cylindrical vessel made of Hastelloy, which can withstand pressures up to 20 MPa. The volume of the vessel is approximately 30 cm<sup>3</sup>. A stirrer installed in the vessel is used to agitate the fluid(s) and hydrate crystals inside it. Two platinum resistance thermometers (Pt100) inserted into the vessel are used to measure temperature and check for the equality of temperatures within the temperature measurement uncertainty, which is estimated to be less than 0.1 K. This temperature uncertainty estimation comes from calibration against a 25  $\Omega$  reference platinum resistance thermometer. The pressure in the vessel is measured with a Druck pressure transducer (Druck, type PTX611 for pressures up to 16 MPa). The pressure measurement uncertainty is estimated to be less than 5 kPa, as a result of calibration against a dead weight balance (Desgranges and Huot, model 520).

**2.3. Experimental Method.** The liquid water + liquid hydrocarbon + hydrate + gas/vapor equilibrium conditions were measured with an isochoric pressure-search method.<sup>4–7,17</sup> The vessel containing liquids (approximately 0.1 volume fraction of the vessel was filled by water and 0.1 volume fraction by neohexane) was immersed into the temperature-controlled bath, and the gas was supplied from a cylinder through a pressure-regulating valve into the vessel. Note that the vessel was evacuated (down to 0.8 kPa for at least 2 h) before introducing any liquid and gas. After obtaining temperature and pressure stability (far enough from the hydrate formation region), the valve in the line connecting the vessel and the cylinder was closed. Subsequently, the temperature was slowly decreased to a set point temperature (at which hydrate formation is expected) with a cooling rate of 5 K/h. Hydrate formation in the vessel was observed when a pressure drop at the set point temperature was detected by the data acquisition unit. The temperature was then increased with steps

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of 0.1 K. At every temperature step, the temperature was kept constant with enough time (at least 4 h) to obtain an equilibrium state in the equilibrium cell. Therefore, a pressure–temperature diagram was sketched for each experimental run, from which we determined the hydrate dissociation point.<sup>4–7,17</sup> The pressure is gradually increased by increasing the temperature during the dissociation of the hydrate crystals inside hydrate formation region. However, a slighter pressure increase is observed during the increase of temperature outside this region.<sup>4–7,17</sup> Consequently, the real hydrate dissociation point can be determined when the slope of the pressure–temperature diagram changes suddenly.<sup>4–7,17</sup>

### 3. RESULTS AND DISCUSSION

All of the experimental data are reported in Table 2 and are plotted in Figures 2 and 3. As mentioned earlier, we first measured the hydrate dissociation conditions for the methane + neohexane + water system. As can be observed in Figure 2, the

**Table 1. Purities and Suppliers of Chemicals<sup>a</sup>**

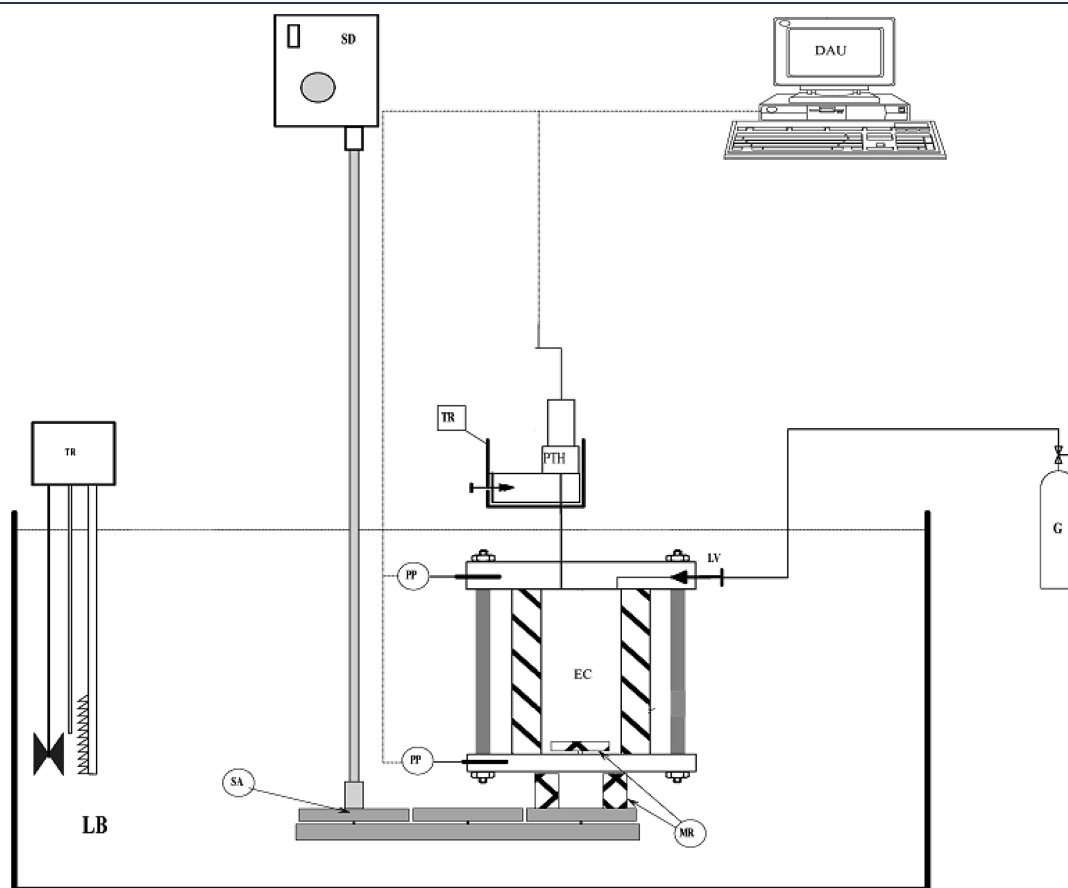
| chemical                       | supplier         | purity, mole fraction |
|--------------------------------|------------------|-----------------------|
| hydrogen sulfide               | Air Liquide      | 0.999                 |
| methane                        | Messer Griesheim | 0.99995               |
| neohexane (2,2-dimethylbutane) | Aldrich          | ≥ 0.99 (GC)           |

<sup>a</sup> Deionized water was used in all experiments.

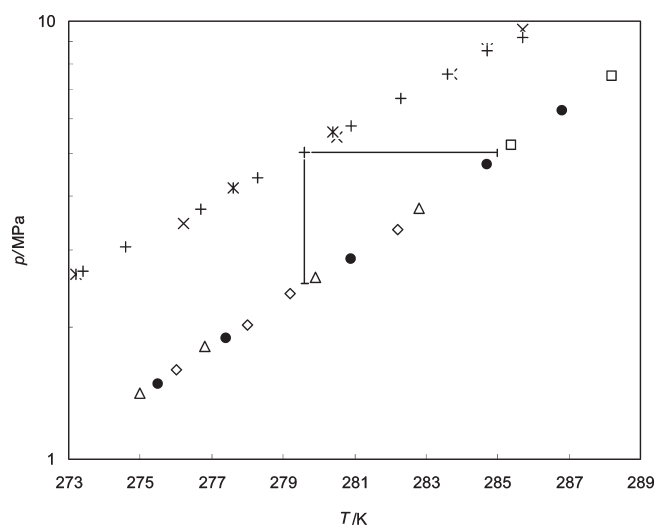
experimental data measured in this work for the latter system are in good agreement with the experimental data reported in the literature,<sup>8–10</sup> demonstrating the reliability of the experimental method used in our work. In both figures, we have shown some selected experimental data from the literature for the

**Table 2. Experimental Hydrate Dissociation Data for the Methane + Neohexane + Water and Hydrogen Sulfide + Neohexane + Water Systems**

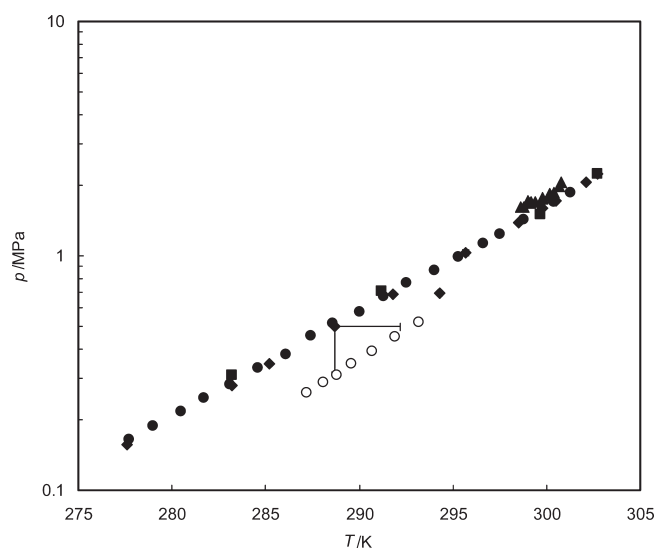
| T/K   | p/MPa |
|---|-------|
| Methane + Neohexane + Water System          |       |
| 275.5                                       | 1.48  |
| 277.4                                       | 1.88  |
| 280.9                                       | 2.87  |
| 284.7                                       | 4.71  |
| 286.8                                       | 6.23  |
| Hydrogen Sulfide + Neohexane + Water System |       |
| 287.2                                       | 0.261 |
| 288.1                                       | 0.288 |
| 288.8                                       | 0.311 |
| 289.6                                       | 0.346 |
| 290.7                                       | 0.391 |
| 291.9                                       | 0.451 |
| 293.2                                       | 0.523 |



**Figure 1.** Schematic diagram of the experimental apparatus. DAU, data acquisition unit; EC, equilibrium cell; G, gas cylinder; LB, liquid bath; LV, loading valve; MR, magnetic rod; PP, platinum probe (temperature sensor); PTH, pressure transducer; SA, stirring assembly; SD, stirring device with variable speed motor; TR, temperature controller.



**Figure 2.** Experimental hydrate dissociation conditions for the methane + neohehexane + water and methane + water systems. Symbols represent experimental data. Methane + water system: \*, ref 13; +, ref 12; ×, ref 11. Methane + neohehexane + water system: ●, this work; ◇, ref 10; □, ref 9; △, ref 8. Pressure band: 2.5 MPa; temperature band: 5.4 K.



**Figure 3.** Experimental hydrate dissociation conditions for the hydrogen sulfide + neohehexane + water and hydrogen sulfide + water systems. Symbols represent experimental data. Hydrogen sulfide + water system: ■, ref 16; ◆, ref 15; ▲, ref 14; ●, ref 4. Hydrogen sulfide + neohehexane + water system: ○, this work. Pressure band: 0.18 MPa; temperature band: 3.5 K.

methane + water<sup>11–13</sup> and hydrogen sulfide + water systems,<sup>4,14–16</sup> respectively, to study the hydrate promotion effects of neohehexane. It should be mentioned that hydrate promotion results in a shift of the dissociation conditions of methane or hydrogen sulfide hydrates due to the presence of neohehexane in the system to low pressures/high temperatures. As can be seen in Figure 2, the presence of neohehexane increases the hydrate dissociation temperature of the methane + water system by approximately 5.4 K at given pressures in the temperature ranges shown in this figure. In other words, it reduces the hydrate dissociation pressure of the methane + water system by approximately 2.5 MPa at given

temperatures indicating the promotion effect of neohehexane is relatively considerable for the methane + water system in terms of pressure reduction. In Figure 3, it is observed that the presence of neohehexane reduces the hydrate dissociation pressure of the hydrogen sulfide + water system by approximately 0.18 MPa at given temperatures. In other words, it increases the hydrate dissociation temperature by approximately 3.5 K at given pressures. This hydrate promotion effect has not been reported for the hydrogen sulfide + neohehexane + water system; however, it is not very considerable in terms of pressure reduction.

In Figures 2 and 3, the slope of the logarithm of hydrate dissociation pressure versus temperature changes when neohehexane exists in the system, indicating a possible change in clathrate hydrate structure due to the presence of neohehexane.<sup>1</sup> It is known that the clathrate hydrates of neohehexane + methane form sH structures.<sup>1</sup> It is likely the neohehexane + hydrogen sulfide clathrate hydrates also form sH structures. However, the final proof for the stable hydrate structure and also the exact compositions of the latter clathrate hydrate at various temperatures require direct measurements by suitable physical techniques (e.g., NMR, X-ray, or Raman spectroscopy).

#### 4. CONCLUSION

Presented here are hydrate dissociation pressures for the hydrogen sulfide + neohehexane + water and methane + neohehexane + water systems in the temperature ranges of (287.2 to 293.2) K and (275.5 to 286.8) K, respectively. An isochoric pressure-search method<sup>4–7,17</sup> was used to perform all of the measurements. The measurements were first performed for the methane + neohehexane + water system, and the comparisons between the experimental data measured in this work and the literature data<sup>8–10</sup> showed acceptable agreement confirming the reliability of the isochoric pressure-search method<sup>4–7,17</sup> used in this study. We then reported hydrate dissociation data for the hydrogen sulfide + neohehexane + water system, for which there is no information in the literature. The comparison of the hydrate dissociation data for the above-mentioned ternary systems with the experimental data reported in the literature for the binary systems of methane + water<sup>11–13</sup> and hydrogen sulfide + water<sup>4,14–16</sup> showed that neohehexane reduces hydrate dissociation pressures. Although the hydrate promotion effect of neohehexane on the methane + water system is not ignorable, it is not very considerable on the hydrogen sulfide + water system in terms of pressure reduction.

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