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Comments on "Solubility of Liquid CO_2 in Synthetic Sea Water at Temperatures from 278 K to 293 K and Pressures from 6.44 MPa to 29.49 MPa, and Densities of the Corresponding Aqueous Solutions" (Teng, H.; Yamasaki, A. *J. Chem. Eng. Data* 1998, *43,* 2−5)

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Teng and Yamasaki (1998) recently reported measurements of the CO_2 solubility in seawater and the density of CO_2-saturated seawater under high pressures. They provided a set of solubility/density data, which may contribute to the research and development of the technology of CO_2 disposal in the ocean. However, there is an ambiguity as to what the *solubility* they measured was. This issue is discussed below.

The pressure/temperature region covered by Teng and Yamasaki's measurements partially falls in the hydrate-formation region. In fact, the authors wrote that they observed CO_2 hydrate formation in some of their experiments. It is now well acknowledged that, in the hydrate-formation pressure/temperature region for any hydrate-forming substance (CO_2 in the present case), the concentration of the substance in a water-rich liquid phase in equilibrium with the hydrate, x_{gh}, is different from x_g, the solubility of the same substance in the water-rich liquid phase in the *metastable* state in the absence of the hydrate. Under a constant pressure, x_{gh} decreases and x_g increases as the temperature decreases beyond T_{tri}, the critical temperature at which the three phases—a water-rich liquid phase, a hydrate phase, and a hydrate-former-rich fluid phase—can be equilibrated. This fact has been confirmed both experimentally (Kimuro et al., 1994; Yamane and Aya, 1995; Makogon, 1996) and theoretically (e.g., Zatsepina and Buffett, 1997; Tabe et al., 1998).

Nevertheless, it seems that Teng and Yamasaki did not discriminate between x_{gh} and x_g. In principle, the *solubility* that the authors measured in the presence of CO_2 hydrate in their sapphire tube can be neither x_{gh} nor x_g. How the *solubility* they measured is close to x_{gh} or x_g is dependent on the experimental operation, the details of which cannot be known from their paper. If the two liquid columns in the sapphire tube were almost saturated with each other before the hydrate formation at the liquid−liquid interface, the *solubility* determined from the change in the liquid-CO_2 column volume in the sapphire tube would be close to x_g because of the reason described below.

Once a hydrate phase formed in the form of a film intervening between the two liquid columns in the sapphire tube, the seawater column should have become supersaturated with CO_2 because of the excess of x_g over x_{gh}, thereby causing a diffusion of CO_2 molecules excessively dissolved in the bulk of the seawater column to the hydrate film. However, the CO_2 molecules thus transferred to the hydrate film would have been consumed to grow the hydrate film, causing no change in the volume of the liquid-CO_2 column on the opposite side of the hydrate film.

On the basis of the suspicion described above, we compare in Figure 1 three sets of CO_2-in-seawater solubility data reported by different research groups after standardizing them to be expressed in the common solubility unit, the CO_2 mass fraction in CO_2-dissolved seawater. Evi-

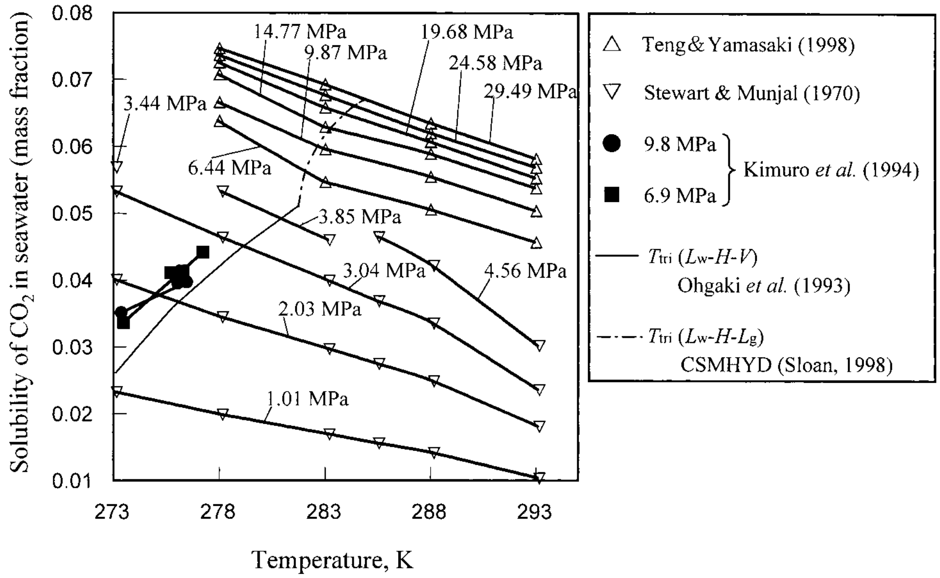

Figure 1. Comparison of CO_2-in-seawater solubility data from three different sources. Note the temperature dependencies exhibited by the isobaric solubility curves (thick solid lines) fitted to the data. Fine solid and chain lines superposed on the solubility curves are three-phase equilibrium lines due to Ohgaki et al. (1993) and the CSMHYD program given in Sloan (1998), respectively. L_w denotes water-rich liquid, H hydrate, V vapor, and L_g CO_2-rich liquid.

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dently, Teng and Yamasaki's data show, even in the temperature range below T_{tri} at each pressure level, a negative temperature dependency similar to that exhibited by Stewart and Munjal's x_g data (1970) obtained at lower pressures. On the other hand, the x_{gh} data obtained by Kimuro et al. (1994) showing a positive temperature dependency are in qualitative agreement with relevant data obtained by other research groups with CO_2/freshwater and methane/freshwater systems (Yamane and Aya, 1995; Makogon, 1996). Thus, we can conclude that the *solubility* that Teng and Yamasaki measured in the CO_2-hydrate-formable pressure/temperature region does not represent the CO_2 concentration in seawater in equilibrium with CO_2 hydrate but approximates the solubility in the metastable absence of CO_2 hydrate.

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