Improved Thermodynamic Parameters for Prediction of Structure H Hydrate Equilibria

Ajay P. Mehta and E. Dendy Sloan
Center for Hydrate Research, Chemical Engineering and Petroleum-Refining Dept., Colorado School of Mines,
Golden, CO 80401

An improved set of all the thermodynamic and molecular properties required for the prediction of the existing 20 systems of Structure H (sH) hydrate phase equilibrium data is presented. The statistical thermodynamics model was based on the van der Waals and Platteeuw theory, and the spherical core Kihara potential was used for guest-water interactions. Optimized Kihara parameters and reference thermodynamic properties were derived from experimental data of over 20 sH hydrate forming systems. The model could fit all the existing sH hydrate data within an accuracy of ± 6%. Inhibitor predictions were also shown to fit recent data with no adjustable parameters. The feasibility of using hydrate cage occupancies to derive refined Kihara parameters of the guest molecules was investigated. Possible existence of sH hydrates at cryogenic temperatures was also established based on the model.

Introduction

Clathrate hydrates are ice-like crystalline inclusion compounds formed in the presence of molecules such as methane, ethane, or propane, via a hydrogen-bonding network of water molecules. The two commonly occurring hydrate structures are known as Structure I (*s*I) and Structure II (*s*II) hydrates, and these have been studied extensively. Generally, small molecules such as methane form *s*I hydrate, while larger molecules such as propane form *s*II hydrate. However, the smallest hydrate formers such as argon, krypton, and nitrogen, form *s*II hydrate. Sloan (1990) provides a detailed summary of the crystal features, phase equilibria, kinetics, and inhibition of both these hydrate structures.

Until the discovery of *s*H, molecules larger than *n*-butane were assumed to be nonhydrate formers (Katz et al., 1959). Structure H (*s*H) hydrate—the newest member of the clathrate hydrate family—was discovered by Ripmeester et al. (1987). *s*H hydrate is unique due to its ability to encapsulate fairly large (≤ 9 Å diameter) molecules like adamantane and methylcyclohexane, in the presence of smaller help guest molecules such as methane or hydrogen-sulfide. While hydrates are a widely recognized problem in the natural gas industry due to their tendency to plug pipelines, the existence of *s*H hydrate poses a potential problem for the petroleum industry since several *s*H formers, such as isopentane (2-methylbutane), neohexane (2,2-dimethylbutane), and methylcyclopentane, constitute a small fraction of crude oil.

Initial phase equilibrium data of *s*H hydrate was reported from our laboratory for methane + adamantane by Lederhos et al. (1992). Subsequently, several researchers have reported phase equilibrium measurements of *s*H hydrate for a wide range of liquid hydrocarbons. Becke et al. (1992) measured the high-pressure *s*H equilibria of methane + methylcyclohexane (Mehta and Sloan, 1993, 1994a; Thomas and Behar, 1994) for a series of methane + liquid hydrocarbon systems, and Danesh et al. (1994) measured for *s*H hydrates from methylcyclopentane with methane and nitrogen as help guests. The temperature and pressure conditions of *s*H hydrate stability were found to be consistent with those of hydrocarbon production, processing, and transportation facilities. Sassen and MacDonald (1994) have recently provided the first evidence of the natural occurrence of *s*H hydrate in the continental slope of the Gulf of Mexico.

The statistical thermodynamics model for hydrate equilibria was developed by van der Waals and Platteeuw (1959) and generalized by Parrish and Prausnitz (1972) for the prediction of the hydrate dissociation pressures of gas mixtures. Mehta and Sloan (1994b) extended the model to enable the prediction of *s*H hydrate equilibria and reported preliminary optimized values of the thermodynamic and molecular parameters. However, at the time that model was developed,

---

Correspondence concerning this article should be addressed to E. Dendy Sloan.
Current address of A. P. Mehta: Shell E&P Technology Co., Westhollow Technology Center, Houston, TX 77251.

*s*H hydrate equilibrium data for only four systems were available. Subsequently, as stated earlier, *s*H hydrate equilibria has been reported for over 20 liquid hydrocarbon systems.

In this work, all the available *s*H hydrate equilibrium data were utilized to generate improved thermodynamic reference properties and molecular parameters for the successful prediction of *s*H equilibria. Predictions of *s*H equilibria in the presence of salt were performed, with no new adjustable parameters. In addition, the feasibility of using hydrate cage occupancies to derive refined molecular parameters was investigated following the premises of Avlonitis (1994). Finally, we explored the possibility of the formation of *s*H hydrate at cryogenic temperatures, and evidence for the probable occurrence of such a phenomenon is also provided.

Theoretical Background

The statistical thermodynamics model for hydrate equilibria developed by van der Waals and Platteeuw (1959) relates the chemical potential of water in the hydrate phase μ_w^H, to the chemical potential of water in a hypothetical empty hydrate lattice μ_w^β, as

$$\Delta \mu_w^H = \mu_w^\beta - \mu_w^H = -RT \sum_i \nu_i \ln\left(1 - \sum_k \theta_{ki}\right) \tag{1}$$

where ν_i is the number of type i cages per water molecule, and θ_{ki} is the fractional occupancy of type i cages with type k guest molecules. The fractional occupancy is given by an expression similar to the Langmuir isotherm

$$\theta_{ki} = \frac{C_{ki} f_k}{1 + \sum_i C_{ki} f_k} \tag{2}$$

where C_{ki} is the Langmuir constant of guest molecule k in cage i, and f_k is the fugacity of guest k. The Langmuir constant describes the potential interaction between the encapsulated guest molecule and the water molecules surrounding it inside each cage and is evaluated by assuming a spherically symmetrical potential as

$$C_{ki} = \frac{4\pi}{kT} \int_0^R \exp\left(\frac{-\omega(r)}{kT}\right) r^2 dr \tag{3}$$

where $\omega(r)$ is the potential function of guest k in cage i, and R is the radius of the cage.

The Kihara spherical core pair potential was used to determine the guest-water interaction. Mckoy and Sinanglu (1963) summed up all the guest-water binary interactions to yield an overall cell potential $\omega(r)$ given by

$$\omega(r) = 2z\epsilon \left[\frac{\sigma^{12}}{R^{11} r} \left(\delta^{10} + \frac{a}{R} \delta^{11} \right) - \frac{\sigma^6}{R^5 r} \left(\delta^4 + \frac{a}{R} \delta^5 \right) \right] \tag{4}$$

where

$$\delta^N = \frac{2}{N} \left[\left(1 - \frac{r}{R} - \frac{a}{R}\right)^{-N} - \left(1 + \frac{r}{R} - \frac{a}{R}\right)^{-N} \right] \tag{5}$$

where z is the coordination number (the number of water molecules at the periphery of each cage), a is radius of the spherical core, σ is the distance between core surfaces corresponding to zero potential energy (note that the collision diameter measured as the distance between molecular centers at zero potential energy is $\sigma + 2a$), and ϵ is the depth of the intermolecular potential well.

The Kihara parameters for each guest molecule are found by fitting the expression for the chemical potential difference given by Eq. 1 to that derived from classical thermodynamics by Marshall et al. (1964), and simplified by Holder et al. (1980) and Menten et al. (1981) as

$$\frac{\Delta \mu_w^H}{RT} = \frac{\Delta \mu_w^0}{RT_0} - \int_{T_0}^{T} \left(\frac{\Delta h_w}{RT^2}\right) dT + \int_0^P \left(\frac{\Delta v_w}{RT}\right) dP - \ln \gamma_w x_w \tag{6}$$

where $\Delta \mu_w^0$ is the reference difference in the chemical potential of water between the hypothetical empty hydrate lattice and ice at a reference temperature T_0 (273.15 K) and zero absolute pressure; Δh_w and Δv_w are the enthalpy and volume differences between the empty hydrate and pure ice/liquid water phases; and γ_w is the activity coefficient of water.

Detailed discussions and derivations for all of the above expressions are given by Marshall et al. (1964), Parrish and Prausnitz (1972), Holder et al. (1980, 1988), and for *s*H hydrate by Mehta and Sloan (1994b). The crystal features of *s*I and *s*II hydrates are known from the single crystal X-ray diffraction data of Stackelberg and Muller (1954), while those of *s*H hydrates have been calculated indirectly from the ^{129}Xe NMR and X-ray powder diffraction data of Ripmeester and coworkers (1987, 1988, 1990). A summary of these geometrical features for all the hydrate structures is given in Table 1,

Table 1. Geometry of Cages

Hydrate Structure	I		II		H		
Cavity Type	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^3 5^6 6^3$	$5^{12}6^8$
Radius (Å)	3.95	4.33	3.91	4.73	3.91	4.06	5.71
Cavities/Unit Cell	2	6	16	8	3	2	1
Coordination No.*	20	24	20	28	20	20	36
H_2O molec./Unit cell	46		136		34		
Crystal Type	Cubic		Cubic		Hexagonal		
Lattice Const. (Å)**	$a = 12$		$a = 17.3$		$a = 12.26$, $c = 10.17$		

*Number of oxygen atoms at the periphery of each cavity.
**Lattice constants for *s*I and *s*II hydrates from Parrish and Prausnitz (1972), for *s*H from Davidson et al. (1986).

and these were the values used in the development of this model.

Optimization of Parameters

In this work, we have derived the optimum Kihara parameters for the large sH hydrate formers. The Kihara parameters for the small guest molecules methane and nitrogen were taken directly from Sloan (1990). The core radius a of the large sH former was determined from the virial and viscosity correlations of Tee et al. (1966).

Multidimensional minimization techniques (Mehta and Sloan, 1994b) were used to regress the experimental data and fit the two expressions given by Eqs. 1 and 6. The optimized reference properties and Kihara core parameters are listed in Tables 2 and 3. Table 2 also lists the reference properties of sI and sII hydrates, as reported by Sloan (1990). It should be noted that more accurate reference properties of sI and sII hydrates have been measured experimentally by Dharamwardhana et al. (1980), Ripmeester et al. (1987), and theoretically deduced by Handa and Tse (1986). The sI and sII reference properties listed in Table 2 were used in the Colorado School of Mines Hydrate prediction program CSMHYD (1990). The Kihara parameters reported by Sloan (1990) were regressed from several sets of single and multicomponent data with the above reference properties (Table 2) and could fit most pure and binary sI and sII equilibrium data within an error of ±5%. Since one of the objectives of this work was to incorporate the parameters for sH equilibria directly into this existing program, the original reference properties of sI and sII hydrates were retained.

The optimized value of the reference chemical potential difference $\Delta\mu_w^0$ for sH hydrate reported in Table 2 is significantly different from that reported by us earlier (Mehta and Sloan, 1994b). The justification for this new value of $\Delta\mu_w^0$ is that it has been optimized using a much larger database of sH equilibria. Retaining the old value of $\Delta\mu_w^0$ and using it directly for optimizing the Kihara parameters for the newer sH systems lead to errors exceeding ±15% for some cycloalkanes. The previous value of $\Delta\mu_w^0$ had been optimized by regressing the only sH equilibrium data available at that time for four systems (16 experimental data points), whereas in the current work we have used all the existing sH equilibrium data for over 20 systems (over 150 experimental data points). Consequently, due to an order of magnitude difference in the available experimental data, we believe that the value of $\Delta\mu_w^0$ reported here will serve as a better reference for the prediction of sH equilibria. Holder et al. (1994) have recently introduced the concept of a varying $\Delta\mu_w^0$ as a function of the size of the guest molecule to account for lattice distortion or stretching. Such an approach could be especially useful for sH hydrates since there is a wide size range (7.5–9 Å diameter) of guest molecules that can stabilize the large sH cavity.

Table 2. Reference Properties

Hydrate Structure	I	II	H
$\Delta\mu_w^0$ (J/mol)*	1,263.60	883.82	1,187.52
Δh_w^0 (J/mol)**	1,389.08	1,025.08	846.57
Δv_w^0 (cm^3/mol)†	3.0	3.4	3.85
$\Delta C_{pw}^{\alpha-L}$ (J/mol·K)‡	$38.12-0.141\,(T-273.15)$		

*Values for sI and sII are from CSMHYD (Sloan, 1990).
**In the liquid water region subtract 6,012.35 J/mol from Δh_w^0.
†In the liquid water regions add 1.6 cm^3/mol to Δv_w^0.
‡Parrish and Prausnitz (1972).

Table 3. Optimized Kihara Core Parameters and Critical Constants

Guest Molecule	a (Å)	σ (Å)	ϵ/κ (K)	T_c (K)	P_c (MPa)	ω
Methane*	0.3834	3.1650	154.54	190.6	4.60	0.008
Xenon	0.2357	3.3390	190.50	289.7	5.84	0.002
Nitrogen*	0.3526	3.0124	125.15	126.2	3.39	0.040
Oxygen	0.2676	3.2499	128.97	154.6	5.05	0.021
2-Methylbutane (isopentane)	0.9868	3.2955	307.09	460.4	3.38	0.227
2,2-Dimethylbutane (neohexane)	1.0481	3.2317	367.70	488.8	3.08	0.232
2,3-Dimethylbutane	1.0790	3.4194	287.57	500.0	3.13	0.247
2,2,3-Trimethylbutane	1.1288	3.1178	420.94	531.2	2.95	0.250
2,2-Dimethylpentane	1.2134	3.0820	357.69	520.5	2.77	0.287
3,3-Dimethylpentane	1.2219	3.1474	364.31	537.4	2.91	0.296
Methylcyclopentane	1.0054	4.5420	353.66	532.7	3.78	0.231
Ethylcyclopentane	1.1401	3.4045	304.71	569.5	3.40	0.271
Methylcyclohexane	1.0693	3.1931	407.29	532.7	3.78	0.236
cis-1,2-Dimethylcyclohexane	1.1494	3.4232	314.79	606.0	2.96	0.236
1,1-Dimethylcyclohexane	1.1440	3.0532	487.49	591.0	2.96	0.238
Ethylcyclohexane	1.1606	3.2929	281.11	609.0	3.00	0.243
Cycloheptane	1.0575	3.5012	312.44	604.2	3.81	0.237
Cyclooctane	1.1048	3.6337	277.80	647.2	3.56	0.236
Adamantane	1.3378	3.1030	471.43	680.0	2.81	0.297
2,3-Dimethyl-1-butene	1.0175	3.2459	339.80	501.0	3.24	0.221
3,3-Dimethyl-1-butene	0.7773	3.3876	353.99	490.0	3.25	0.121
Cycloheptene**	1.0301	3.1441	453.06	598.3	3.95	0.231
cis-Cyclooctene**	1.1150	3.2451	401.47	641.4	3.62	0.246
3,3-Dimethyl-1-butyne**	0.7961	3.4028	318.47	490.8	3.41	0.133

*These parameters were used directly from CSMHYD (Sloan, 1990).
**Critical properties of these guests were determined by group contribution techniques outlined by Reid et al. (1987).

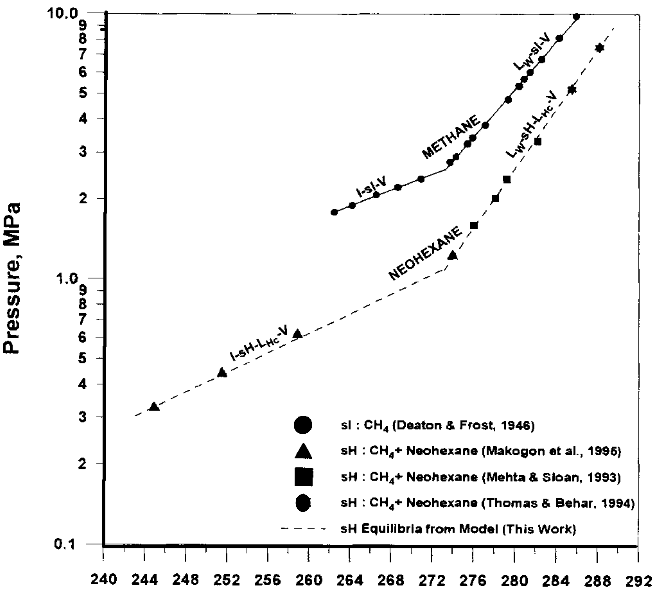

Figure 1. Experimental data vs. model for methane+ neohexane.

The coexisting phases along each equilibrium line are marked explicitly.

The parameters for the large guest molecules are listed in Table 3, and were used to determine the *s*H hydrate equilibrium pressure at various temperatures. Employing these parameters all the *s*H equilibrium data could be fit within an accuracy of ±6%. Since experimental data for methane+neohexane had been measured both above and below the ice point, it was selected as the initial standard against which the model was tested. In Figure 1, the experimental data of pure *s*I methane hydrates, and *s*H hydrates of methane+neohexane are shown with the pressures determined from this model. The model could fit this *s*H equilibrium data within an error of ±2%. Figures 2 and 3 show the fit of the model for other methyl-substituted alkanes.

Since independently measured *s*H equilibrium data has been reported for methane+methylcyclopentane (Thomas and Behar, 1994; Mehta and Sloan, 1994a) and nitrogen+methylcyclopentane (Danesh et al., 1994), the Kihara parameters for methylcyclopentane were derived by performing a simultaneous optimization using both these systems. As shown in Figure 4, the model could fit the experimental data of methane+methylcyclopentane and the high-pressure nitrogen+pressure nitrogen+methylcyclopentane data within an accuracy of ±3%.

Figures 5, 6, and 7 show the results of the model for cycloalkanes, and Figures 8 and 9, for methyl-substituted alkenes and alkynes. It should be noted that the guest molecules ethylcyclopentane, ethylcyclohexane, cyclooctane, and cycloheptane were assumed to be *s*H hydrate formers by Thomas and Behar (1994) based upon their equilibrium measurements. These four molecules were not listed among the 24 guests identified by Ripmeester and Ratcliffe (1990) as *s*H formers using ^{129}Xe NMR spectroscopy. In the absence of NMR and X-ray diffraction data, the formation of *s*H hydrate with these guests should be regarded as tentative.

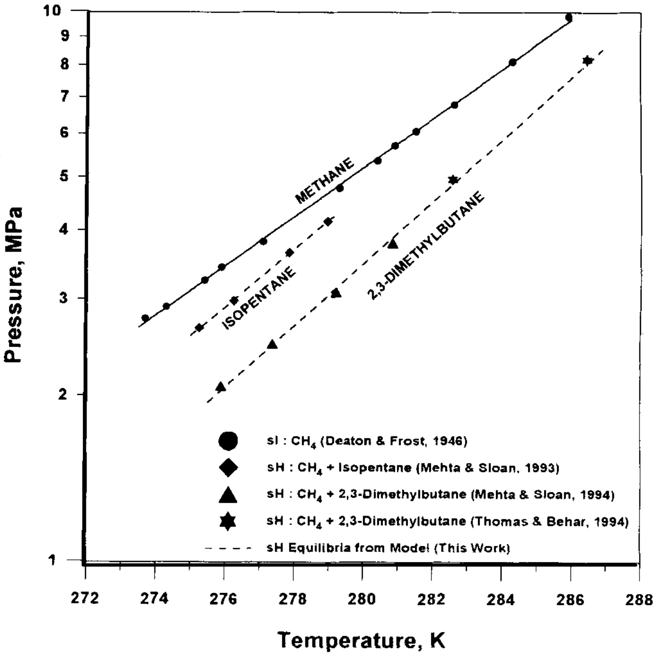

Figure 2. *s*H hydrate equilibrium data vs. model for methyl-substituted butanes.

As a further validation of the model, it was tested against the most recently reported *s*H hydrate equilibrium data of Hutz and Englezos (1995). The optimized properties reported in Tables 2 and 3 were not modified to predict the *s*H equilibrium data of methane with adamantane, isopentane, and neohexane. As shown in Figure 10, the model could predict the *s*H equilibrium data within an accuracy of ±5%.

Hutz and Englezos (1995) have also reported the first experimental measurements of *s*H equilibria in the presence of

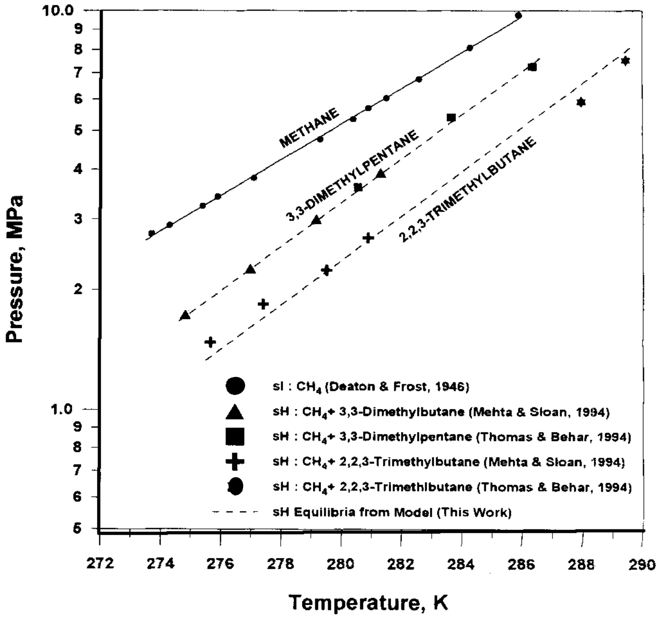

Figure 3. *s*H hydrate equilibrium data vs. model for methyl-substituted butane and pentanes.

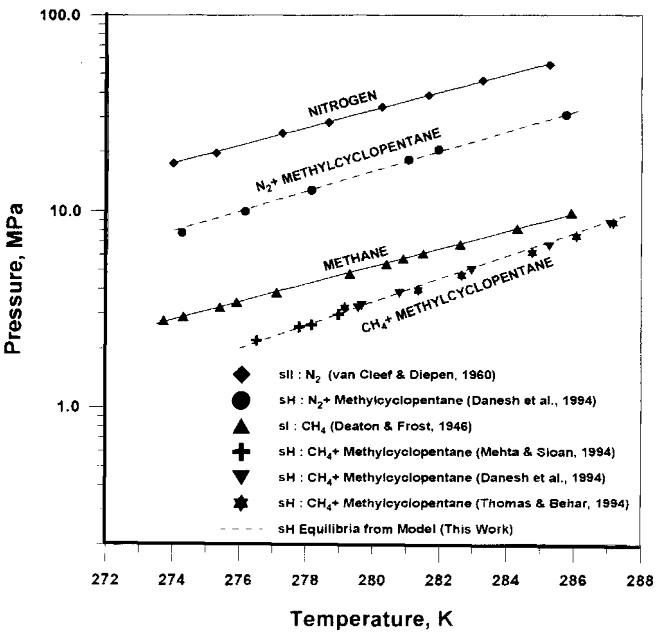

Figure 4. sH hydrate equilibrium data vs. model for methylcyclopentane with nitrogen and methane as help guests.

sodium chloride. *s*H equilibria was measured for methane + isopentane with 10 wt. % NaCl, and for methane + neohexane and methane + *tert* butyl methyl ether, with 12 wt. % NaCl. We used our model to make *a priori* predictions of the *s*H equilibria of methane with isopentane and neohexane in the presence of salt. We needed to calculate the activity of water (the last term in Eq. 6) in the liquid phase, to account for the influence of NaCl. The activity coefficient model of Pitzer and Mayorga (1973) as simplified by Englezos and Bishnoi (1988) for hydrates was used to calculate the activity of water.

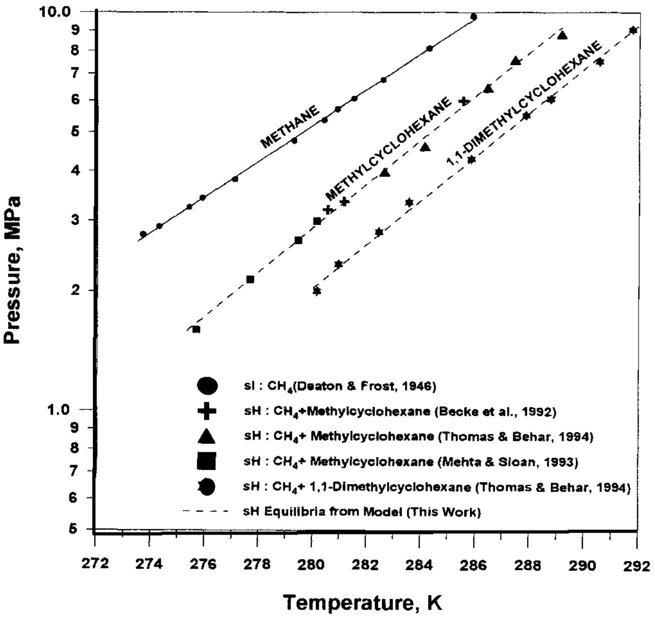

Figure 5. sH hydrate equilibrium data vs. model for cycloalkanes.

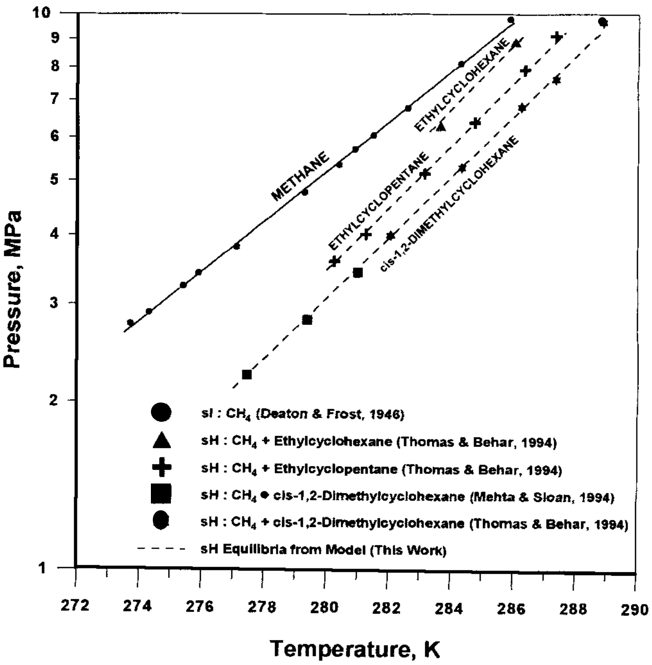

Figure 6. sH hydrate equilibrium data vs. model for cycloalkanes.

The predicted *s*H equilibria was compared against the *s*H equilibrium data of Hutz and Englezos (1995), and as shown in Figure 11, our model could predict the data within an accuracy of ±2%.

The excellent fit between data and results from the model as illustrated by all the above figures validates the use of these improved reference properties and Kihara parameters. These parameters can be easily incorporated into a generalized hy-

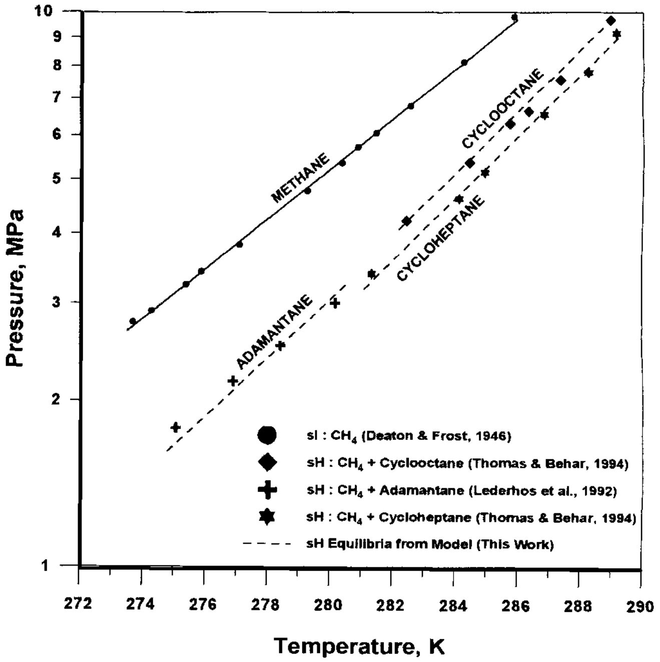

Figure 7. sH hydrate equilibrium data vs. model for cycloalkanes.

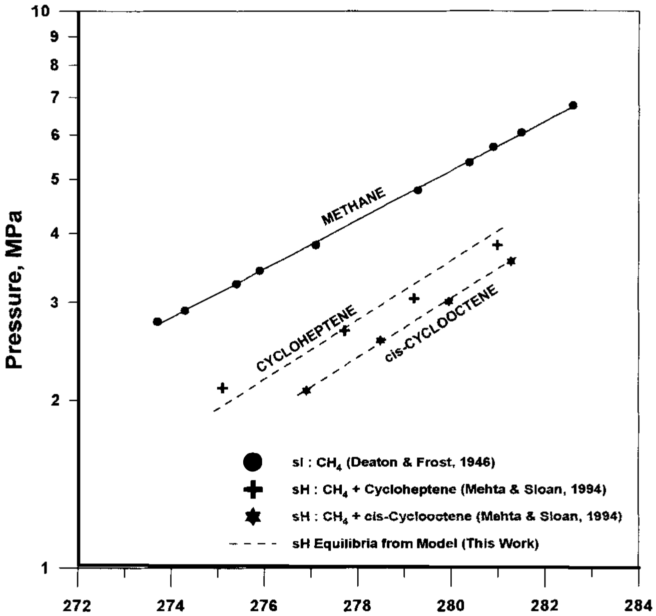

Figure 8. sH hydrate equilibrium data vs. model for cycloalkenes.

drate prediction routine which will enable the prediction of all known hydrate structures for any given single or multicomponent system.

Effect of Cage Occupancy

Recently, Avlonitis (1994) has suggested a new approach for determining accurate Kihara parameters for hydrates

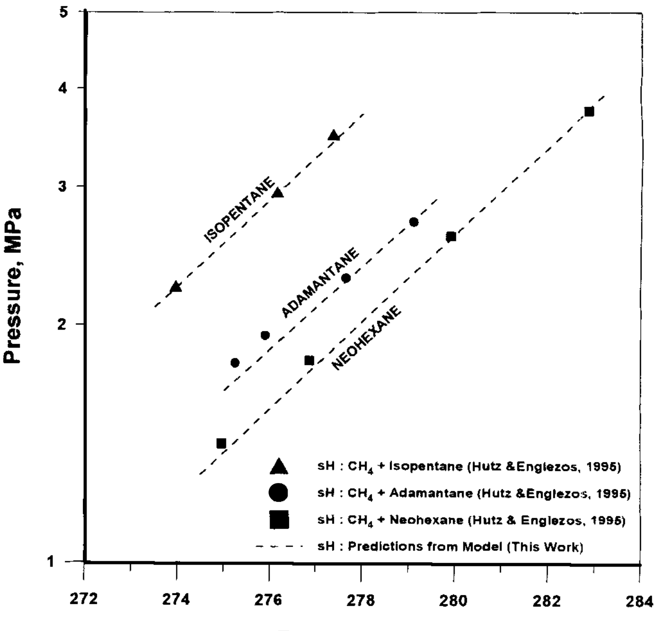

Figure 10. Predictions of sH hydrate equilibrium.

based upon hydrate cage occupancies which have been experimentally determined using NMR spectroscopy. In this work, we investigated the feasibility of using Avlonitis' approach by deriving the Kihara parameters of xenon based upon cage occupancies. Using these parameters of xenon and the previously determined Kihara parameters of neohexane, our objective was to make *a-priori* predictions for the *s*H equilibria of xenon + neohexane and compare them against the recently reported *s*H equilibrium data of xenon + neohexane by Makogon et al. (1995).

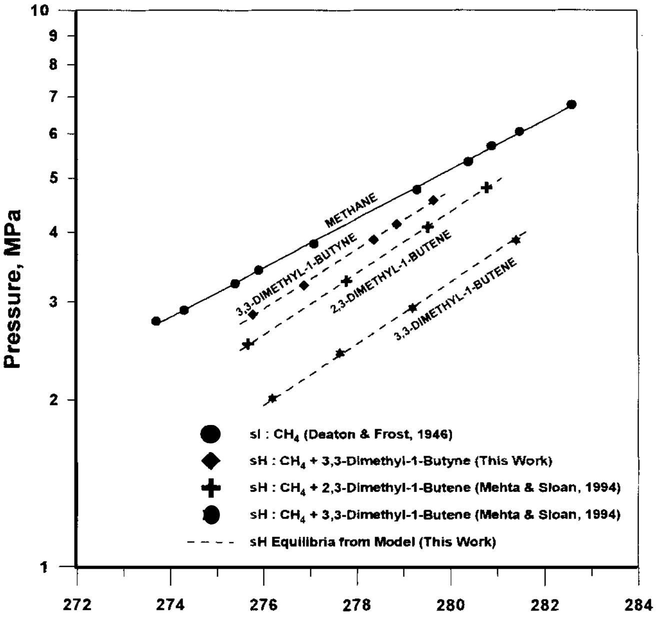

Figure 9. sH hydrate equilibrium data vs. model for methyl-substituted alkenes and alkynes.

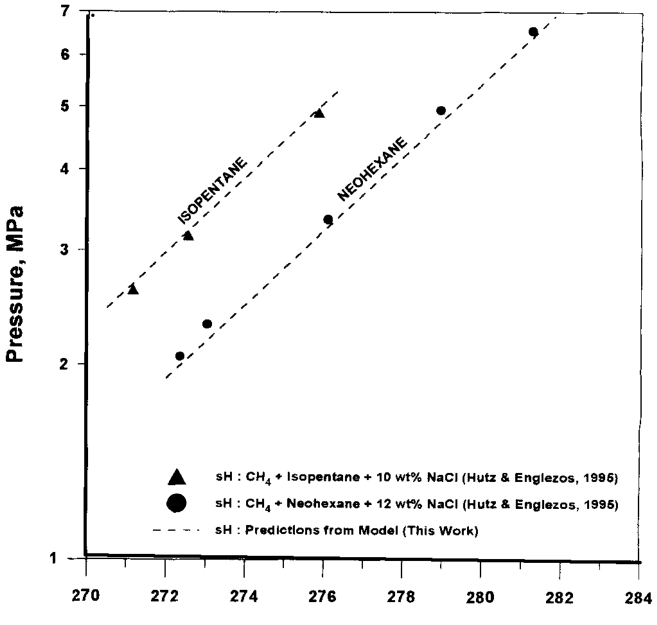

Figure 11. Prediction of sH hydrate equilibrium in the presence of salt.

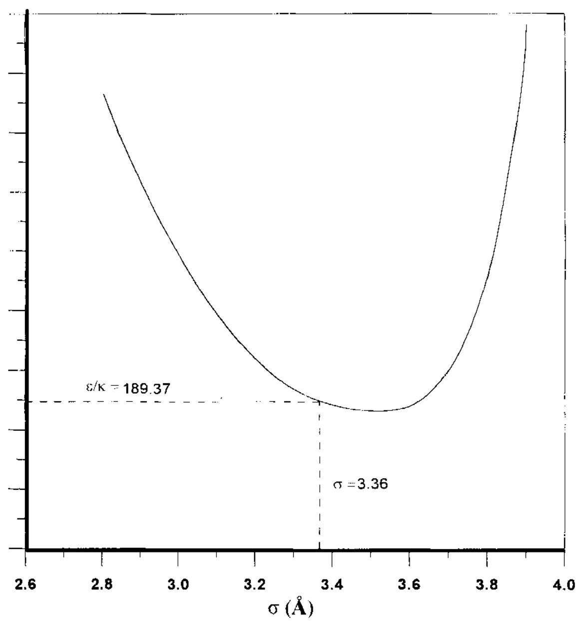

Figure 12. Infinite set of Kihara parameters which accurately predict the *s*I xenon hydrate dissociation pressure at 273.15 K.

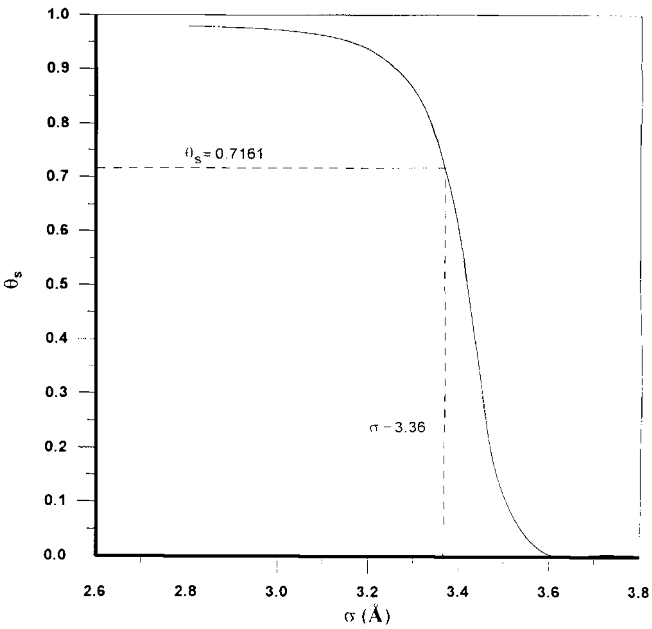

Figure 13. Fractional occupancy θ_s of the small *s*I hydrate cage by xenon as a function of the Kihara parameter σ.

Instead of optimizing the Kihara parameters of xenon using the entire range of *s*I xenon equilibrium data reported by Aaldijk (1971), the parameters were derived from a single temperature (273.15 K) and corresponding equilibrium pressure (152.4 kPa). A single data point was chosen as the basis of the optimization since xenon hydrate cage occupancy was measured via NMR only at the ice point by Davidson et al. (1986). The core radius of xenon was calculated from the virial and viscosity correlations of Tee et al. (1966), and for various fixed values of σ; the corresponding value of ϵ/k was optimized by fitting Eqs. 1 and 6 as discussed in the previous section.

Figure 12 shows that there is an infinite set of the Kihara parameters σ and ϵ/k, which can accurately fit the xenon experimental data at the ice point. It is apparent that all these pairs of Kihara parameters cannot be correct despite the fact that each would yield the same dissociation pressure. This plot also clearly demonstrates the observation of John et al. (1985) that the wrong Kihara parameters, wrong cell potentials, and wrong Langmuir constants could still lead to the right dissociation pressures.

In order to determine a unique set of Kihara parameters for xenon, the data shown in Figure 12 were recast in terms of the small cage occupancy θ_s (Eq. 2), as a function of the Kihara parameter σ shown in Figure 13. Using the xenon occupancy θ_s (0.7161 ± 0.0161) at the ice point reported by Davidson et al. (1986), a unique value of σ (3.36 Å) was determined from Figure 13, and the for ϵ/k (189.37 K) from Figure 12. It was interesting to note that this unique set of parameters corresponding to the correct experimentally measured occupancy did not occur at the minima of the σ vs. ϵ/k plot in Figure 12.

The *s*I xenon dissociation pressures were predicted using these values of σ and ϵ/k, and as shown in Figure 14, they could fit the experimental data not only at 273. 15 K, but also over a fairly wide range of temperature (255–285 K) within an accuracy of ±5%. This result validated Avlonitis' approach at least for single-guest systems. Next, using these optimized parameters of xenon and the previously optimized parameters of neohexane (derived from the *s*H data of methane + neohexane as discussed in the previous section), an *a priori* prediction was made for the *s*H hydrate system of

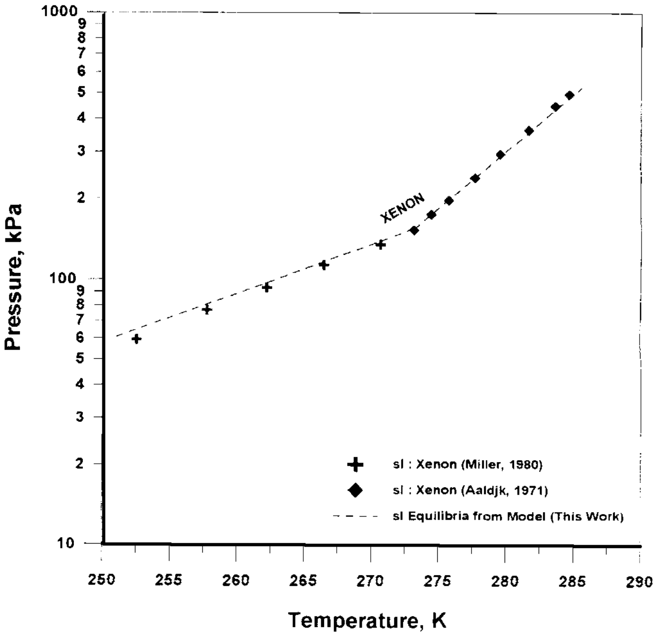

Figure 14. *s*I hydrate fit for pure xenon *s*I hydrates with Kihara parameters reduced from pure xenon data which also accurately predicts fractional occupancies at 273.15 K.

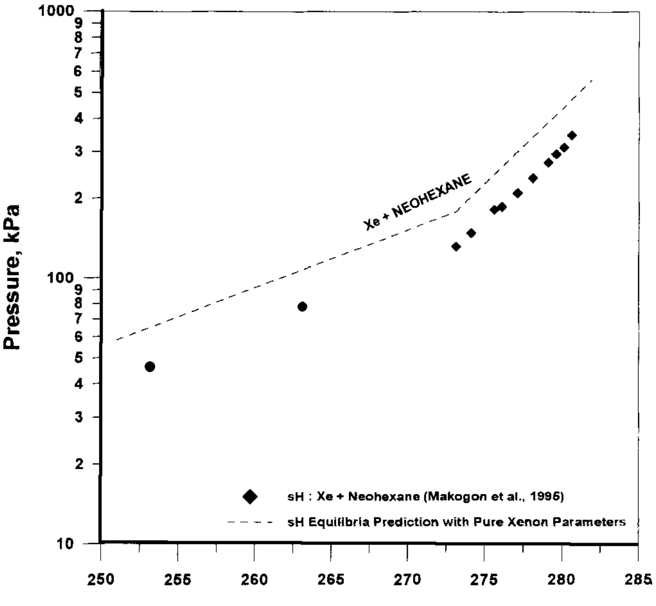

Figure 15. sH hydrate prediction for xenon+neohexane using xenon parameters which give accurate occupancies of sI hydrate at 273.15 K.

The *s*H hydrate equilibria is overpredicted by more than 30%.

xenon + neohexane. As seen from Figure 15, the direct prediction of the *s*H equilibria using the unmodified parameters lead to very unsatisfactory results with errors exceeding 30%.

An alternative approach was adopted to determine a unique set of xenon parameters which could accurately fit both the *s*I and *s*H equilibrium data. Pairs of ϵ/k and σ were determined by using Aaldjk's (1971) pure xenon *s*I hydrate data over a wide range of temperatures instead of just one data point. Pairs of ϵ/k and σ were also determined for xenon by fitting the xenon + neohexane *s*H equilibrium data of Makogon et al. (1995), while keeping the parameters of neohexane the same as determined previously (Table 3). The resulting curves of ϵ/k vs. σ are shown in Figure 16, and their point of intersection yielded a unique pair of ϵ/k (190.55 K) and σ (3.339 Å). This set of parameters could accurately predict the *s*H equilibria of xenon + neohexane as shown in Figure 17 as well as the *s*I equilibria of pure xenon. Using this set of parameters, the predicted xenon occupancy θ_s (0.8081) in the small *s*I cage was found to be about 10% higher than the experimentally determined occupancy θ_s (0.7161) of Davidson et al. (1986).

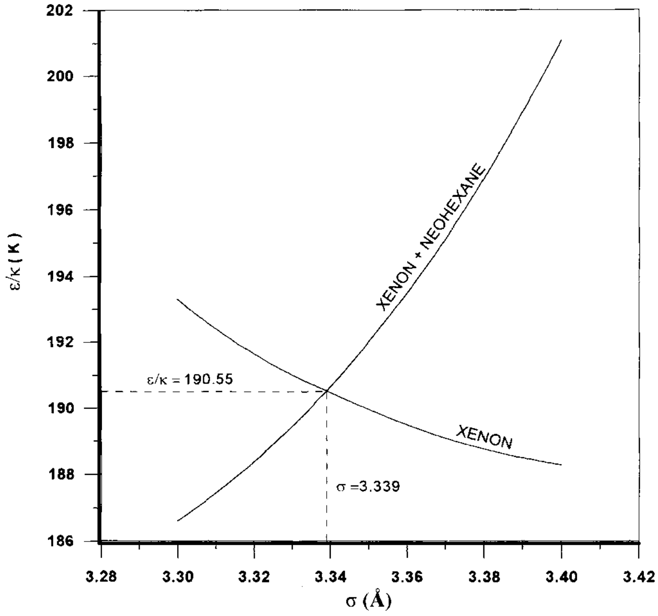

Figure 16. Unique pair of xenon Kihara parameters which satisfy both sI and sH equilibria.

The above investigation illustrates the problems involved in determining unique parameters which are experimentally justifiable, and it represents the limit of the statistical model. While the approach suggested by Avlonitis (1994) is innovative, the paucity of experimental data on hydrate cage occupancies severely limits the use of the method. Moreover, cage occupancies are as yet undetermined for most industrially important molecules such as the natural gas formers. Measurements of cage occupancies using such methods as NMR and Raman spectroscopy are likely to profoundly affect the existing models for hydrate equilibria.

sH Hydrates at Cryogenic Temperatures

During the measurement of vapor-liquid equilibria (VLE) at cryogenic temperatures, isomers of pentanes and hexanes were routinely used as bath fluids in the past due to their low freezing points. According to Kobayashi (1975), bath fluids used in these thermodynamic studies at Rice University were typically C_5^+ compounds. The bath fluids were exposed to the atmosphere, often continuously for several months. During cleanup operations of the bath, Kobayashi noticed small solid

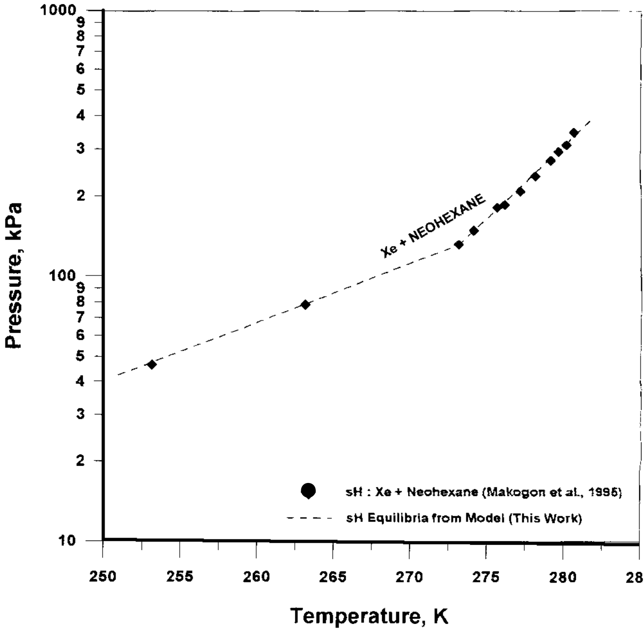

Figure 17. Accurate prediction of xenon+neohexane sH equilibria using revised xenon Kihara parameters.

crystals on the top and along the edges of the bath. Upon withdrawing these crystals and melting them in an unattended open container, two distinct liquid phases (water and hydrocarbon) were recovered. Gas may have evolved, but was not observed.

Kobayashi speculated that these solid crystals were probably hydrates. However at the time of these observations in the late 60s and early 70s, *s*H hydrates were not known to exist. Molecules larger than *n*-butane (a *s*II former) with a diameter greater than approximately 7.1 Å were considered to be nonhydrate formers. Several molecules such as isopentane and methylcyclopentane which are now known to be *s*H formers were in fact explicitly cited as examples of nonhydrate formers (Katz et al., 1959). Consequently, Kobayashi's observation of the solid crystals from the bath fluids went largely unnoticed.

Recently, we revisited Kobayashi's observation made over 20 years ago with the objective of determining whether the solid crystals recovered by Kobayashi were in fact *s*H hydrates with the bath fluid comprising the large guest, the constituents of air comprising the small guest, and water being furnished by the moisture content in the atmosphere. To explore this possibility, we initially noted the most common bath fluids in Kobayashi's laboratory for the measurement of VLE data at cryogenic temperatures. The bath fluids included high purity (99^{+}%) isopentane (Hoover, 1965; Carruth, 1970; Styrjek, 1972), a mixture of *n*-pentane and isopentane (Price, 1957), and isohexane (Wichterle, 1970). These experiments were conducted at temperatures as low as 125 K, up to 250 K. Isopentane stood out in this list due to its ability to form *s*H hydrate, and consequently we investigated the possible formation of *s*H hydrates from air + isopentane at very low temperatures.

Initially, we derived the optimum Kihara parameters for the constituents of air, which are chiefly oxygen and nitrogen (Table 3). Kihara parameters for nitrogen were used unchanged from Sloan (1990), but for oxygen they were derived by fitting the experimental data of van Cleef and Diepen (1962) using the methods outlined in the earlier sections. Figure 18 shows that the experimental data of both nitrogen and oxygen hydrates (*s*II) could be fit within an error of ±2%. Based upon these parameters, the *s*II hydrate equilibria of air (assuming 79% N_2 + 21% O_2) was predicted, as shown in Figure 18.

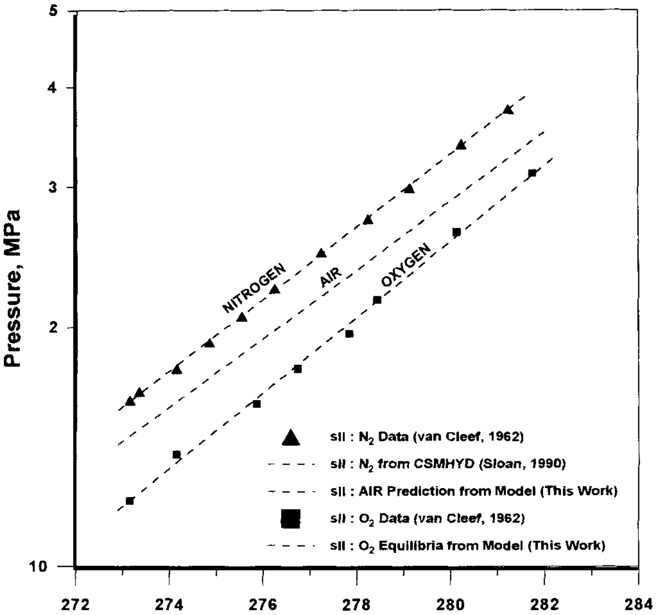

Figure 18. Experimental data vs. model fit for *s*II hydrates of nitrogen and oxygen, and prediction of *s*II hydrates of air.

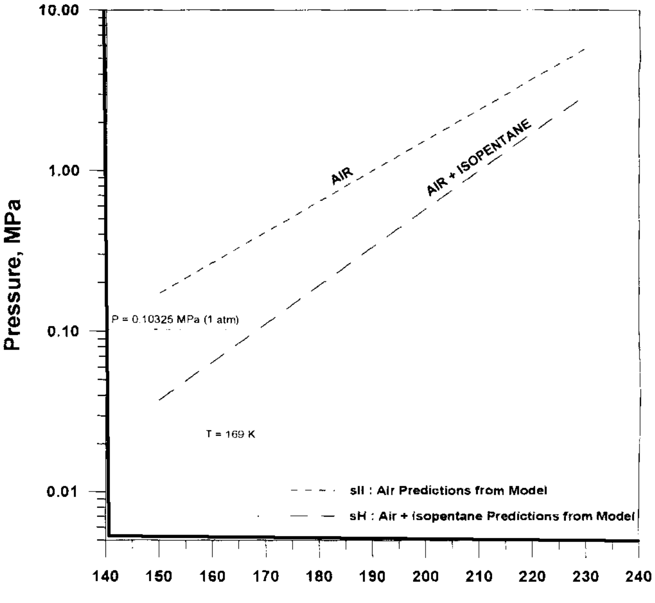

Figure 19. Prediction of *s*H hydrates of air+isopentane.

Next, the *s*H equilibria of air + isopentane was predicted using these optimized Kihara parameters for oxygen and nitrogen, and the parameters of isopentane as derived earlier from the *s*H equilibrium data of methane + isopentane. The fugacity of isopentane at the low temperatures of interest was assumed to be equal to its vapor pressure. The predicted *s*H equilibria of air + isopentane, and the *s*II equilibria of air hydrates, is shown in Figure 19. It can be seen from the figure that at atmospheric pressure and a temperature of about 169 K, *s*H hydrates could indeed exist as stable entities. These predictions validate the possibility that the solid crystals observed by Kobayashi were actually *s*H hydrates—a full 20 years before their formal discovery.

We also predicted the *s*H equilibria of a few mixtures like *n*-pentane + isopentane. The predicted *s*H equilibria for a system of air + 95% *n*-pentane + 5% isopentane is shown in Figure 20. Since *n*-pentane is a nonhydrate former, it acts a diluent and consequently the *s*H equilibria for this system lies above that of air + isopentane. However, even with only 5% isopentane present in this mixture, *s*H hydrates could still crystallize at a temperature of about 150 K at atmospheric pressure. Finally, assuming an equimolar mixture of isopentane + neohexane, the predicted *s*H equilibrium line shown in Figure 20 lies below that of air + isopentane, since neohexane is also a *s*H hydrate former. At atmospheric pressure, *s*H hydrates could crystallize at temperatures up to 190 K.

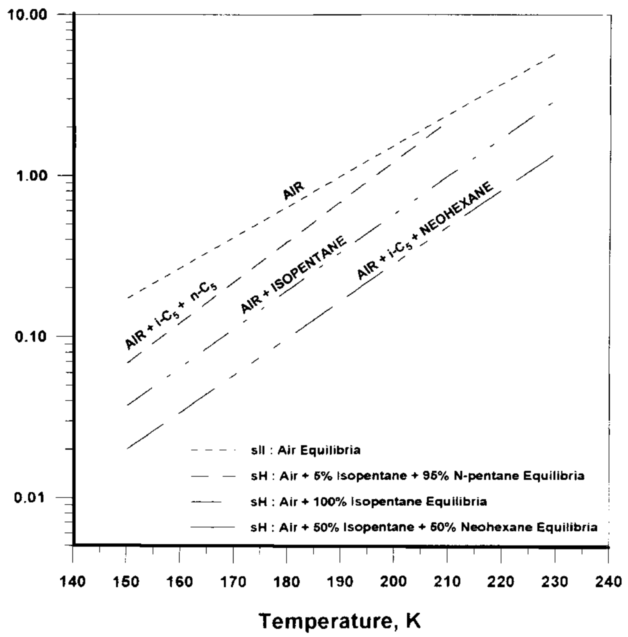

Figure 20. Prediction of *s*H hydrates for air with mixtures of isopentane, *n*-pentane, and neohexane.

These predictions clearly demonstrate the possible impact of *s*H hydrates at cryogenic temperatures. They also indicate that *s*H hydrate may play a critical role in the hydrocarbon processing industry, where the presence of even trace amounts of a heavy liquid hydrocarbon could lead to the formation of *s*H hydrate.

Conclusions

Refined thermodynamic and molecular parameters for the accurate prediction of *s*H hydrates were presented. Using these parameters in conjunction with the statistical thermodynamics model could fit all extant *s*H experimental data within an accuracy of ±6%. The model could also make *a-priori* predictions of *s*H equilibria in the presence of salt and accurately fit experimental data. These parameters could easily be incorporated into existing hydrate equilibrium models, and facilitate prediction of the equilibria of any hydrate structure for single or multicomponents systems.

The feasibility of using hydrate cage occupancies to derive refined Kihara parameters was explored. It was concluded from our study that more experimental data on hydrate cage occupancies is required to justify this method of determining unique Kihara parameters. Techniques such as NMR and Raman spectroscopy could yield highly accurate values of hydrate cage occupancies, which could significantly improve current hydrate prediction models. Finally, the probable existence of stable *s*H hydrates at atmospheric pressure and cryogenic temperatures was substantiated on the basis of the model predictions.

Acknowledgments

The authors would like to acknowledge Professor R. Kobayashi, Rice University, for relating his experiences with hydrates at cryogenic temperatures. The assistance of graduate student Eric Maase for hydrate predictions with salt is also appreciated. We also gratefully acknowledge the support of the National Science Foundation under grant CTS 9309595.

Notation

a = Kihara spherical core radius, Å
C_{ki} = Langmuir constant of type k molecule in type i cage, MPa
i = cavity type
k = molecule type or Boltzmann's constant, J/K
P = pressure, MPa
r = radial distance from the center of the molecule, A
R = gas constant, J/mol/K, or cavity radius, A
T_o = reference temperature, 273.15 K
Δv_w^0 = volume difference between empty hydrate lattice and ice, cm^3/mol

Greek letters

β = empty hydrate lattice
ϵ = depth of intermolecular potential well, J/mol
μ = chemical potential, J/mol
$\Delta \mu_w$ = chemical potential difference between empty hydrate lattice and ice, J/mol
$\Delta \mu_w^0$ = reference chemical potential difference between empty hydrate lattice (β phase) and ice (α phase) at 273.15 K and zero absolute pressure, J/mol
σ = distance between molecular core surfaces at zero potential energy, Å

Literature Cited

Aaldijk, L., "Monovariante Gashydraatevenwichtehn in Het Steelsel Xenon-Water," PhD Thesis, Technical Univ., Delft, The Netherlands (1971).

Avlonitis, D., "The Determination of Kihara Potential Parameters from Gas Hydrate Data," *Chem. Eng. Sci.*, **49**(8), 1161 (1994).

Becke, P., D. Kessel, and I. Rahiman, "Influence of Liquid Hydrocarbons on Gas Hydrate Equilibrium," SPE 25032, 159, Euro. Petrol. Conf., Soc. of Petrol. Engrs., Cannes, France (1992).

Carruth, G. F., "Determination of the Vapor Pressures of N-Parafins and Extension of a Corresponding States Correlation to Low Reduced Temperatures," PhD Thesis, Rice Univ., Houston (1970).

Danesh, A., B. Tohidi, R. W. Burgass, and A. C. Todd, "Hydrate Equilibrium Data of Methylcyclopentane with Methane or Nitrogen," *Chem. Eng. Res. Des.*, **72**(A2), 197 (1994).

Davidson, D. W., J. A. Ripmeester, and Y. P. Handa, "Xenon-129 NMR and Thermodynamic Parameters of Xenon Hydrate," *J. Phys. Chem.*, **90**, 6549 (1986).

Deaton, W. M., and E. M. Frost, "Gas Hydrates and Their Relation to the Operation of Natural Gas Pipelines," *U.S. Bur. of Mines Monog.*, 8 (1946).

Dharmawardhana, P. B., W. R. Parrish, and E. D. Sloan, "Experimental Thermodynamic Parameters for the Prediction of Natural Gas Hydrate Dissociation Conditions," *Ind. Eng. Chem. Fund.*, **19**(4), 410 (1980).

Engelzos, P., and P. R. Bishnoi, "Prediction of Gas Hydrate Formation Conditions in Aqueous Electrolyte Solutions," *AIChE J.*, **34**(10), 1718 (1988).

Handa, Y. P., and J. S. Tse, "Thermodynamic Properties of Empty Lattices of Structure I and Structure II Clathrate Hydrates," *J. Phys. Chem.*, **90**(22), 5917 (1986).

Holder, G. D., G. Corbin, and K. D. Papadopoulos, "Thermodynamic and Molecular Properties of Gas Hydrates from Mixtures Containing Methane, Argon and Krypton," *Ind. Eng. Chem. Fund.* **19**(3), 282 (1980).

Holder, G. D., S. P. Zetts, and N. Pradhan, "Phase Behavior in Systems Containing Clathrate Hydrates," *Rev. in Chem. Eng.*, *5*, 1 (1988).

Holder, G. D., S. Zele, R. Enick, and C. LeBlond, "Modeling Thermodynamics and Kinetics of Hydrate Formation," *Annals New York Acad. Sci.*, **715**, 344 (1994).

Hoover, A. E., "Virial Coefficients of Methane and Ethane," PhD Thesis, Rice Univ., Houston (1965).

Hutz, U., and P. Englezos, "Measurement of Structure H Hydrate

Phase Equilibrium and the Effect of Electrolytes," *Int. Conf. on Fluid Properties and Phase Equilibr. for Chem. Process Des.*, Snowmass, CO (1995).

John, V. T., K. D. Papadopoulos, and G. D. Holder, "A Generalized Model for Predicting Equilibrium Conditions for Gas Hydrates," *AIChE J.*, **31**(2), 252 (1985).

Katz, D. L., D. Cornell, R. Kobayashi, F. H. Poettmann, J. A. Vary, J. R. Elenbaas, and C. F. Weinaugh, *Handbook of Natural Gas Engineering*, Chap. 5, McGraw-Hill, New York (1959).

Kobayashi, R., personal communication with E. D. Sloan (Feb., 1975).

Lederhos, J. P., A. P. Mehta, G. B. Nyberg, K. J. Warn, and E. D. Sloan, "Structure H Clathrate Hydrate Equilibria of Methane and Adamantane," *AIChE J.*, **38**(7), 1045 (1992).

Makogon, T. Y., A. P. Mehta, and E. D. Sloan, "Structure H Hydrate Equilibria of 2,2-dimethylbutane with Methane and Xenon," *J. Chem. Eng. Data.*, **41**(2), 315 (1996).

Marshall, D. R., S. Saito, and R. Kobayashi, "Hydrates at High Pressure: Part I, Methane-Water, Argon-Water and Nitrogen-Water Systems," *AIChE J.*, **10**(2), 202 (1964).

McKoy, V., and O. Sinangolu, "Theory of Dissociation Pressures of Some Gas Hydrates," *J. Chem. Phys.*, **38**(12), 2946 (1963).

Mehta, A. P., and E. D. Sloan, "Structure H Hydrate Phase Equilibria of Methane + Liquid Hydrocarbon Mixtures," *J. Chem. Eng. Data*, **38**(4), 580 (1993).

Methta, A. P., and E. D. Sloan, "A Thermodynamic Model for Structure-H Hydrates," *AIChE J.*, **40**(2), 312 (1994b).

Menten, P. D., W. R. Parrish, and E. D. Sloan, "Effect of Inhibitors on Hydrate Formation," *Ind. Eng. Chem. Process. Dev.*, **20**, 399 (1981).

Parrish, W. R., and J. M. Prausnitz, "Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures," *Ind. Eng. Chem. Proc. Des. Dev.*, **11**, 26 (1972).

Pitzer, K. S., and G. Mayorga, "Thermodynamics of Electrolytes: II. Activity and Osmotic Coefficients for Strong Electrolytes with One of Both Ions Univalent," *J. Phys. Chem.*, **77**(19), 2300 (1973).

Price, A. R., "Low Temperature Vapor-Liquid Equilibrium in Light Hydrocarbon Mixtures Methane-Ethane-Propane System," PhD Thesis, Rice Univ., Houston (1957).

Reid, R. C., J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, New York (1987).

Ripmeester, J. A., J. S. Tse, C. I. Ratcliffe, and B. M. Powell, "A New Clathrate Hydrate Structure," *Nature*, **325**(6100), 135 (1987).

Ripmeester, J. A., C. I. Ratcliffe, and J. S. Tse, "The Nuclear Magnetic Resonance of ^{129}Xe Trapped in Clathrates and Some Other Solids," *J. Chem. Soc. Farad. Trans.*, **1**, 84(11), 3731 (1988).

Ripmeester, J. A., and C. I. Ratcliffe, "^{129}Xe NMR Studies of Clathrate Hydrates: New Guests for Structure II and Structure H," *J. Phys. Chem.*, **94**(25), 8773 (1990).

Sassen, R., and I. R. MacDonald, "Evidence of Structure H Hydrate, Gulf of Mexico, Continental Slope," *Org. Geochem.*, **22**(6), 1029 (1994).

Sloan, E. D., *Clathrate Hydrates of Natural Gases*, Marcel Dekker, New York (1990).

Stackelberg, M. von, and H. R. Muller, "Feste Gas Hydrate II, Struktur und Raumchemie," *Z. Elekt.*, **58**, 25 (1954).

Stryjek, R., "Low Temperature Vapor-Liquid Equilibria of the Nitrogen-Methane, Nitrogen-Ethane, and Nitrogen-Methane-Ethane Systems," PhD Thesis, Rice Univ., Houston (1972).

Tee, L. S., S. Gotoh, and W. E. Stewart, "Molecular Parameters for Natural Fluids: The Kihara Potential with Spherical Core," *Ind. Eng. Chem. Fund.*, **5**(3), 363 (1966).

Thomas, M., and E. Behar, "Structure H Hydrate Equilibria of Methane and Intermediate Hydrocarbon Molecules," GPA Convention, New Orleans (Mar. 7-9, 1994).

van Cleef, A., and G. A. M. Diepen, "Gas Hydrates of Nitrogen and Oxygen: I and II," *Rec. Trav. Chim.*, **84**, 1085 (1962).

van der Waals, J. H., and J. C. Platteeuw, "Clathrate Solutions," *Adv. Chem. Phys.*, **2**(1), 1 (1959).

Wichterle, I., "Low Temperature Vapor-Liquid Equilibria in the Methane-Ethane-Propane Ternary and Associated Binary Methane Systems with Special Consideration of the Equilibria in the Vicinity of the Critical Temperature of Methane," Postdoctoral Monog., Rice Univ., Houston (1970).

Manuscript received July 13, 1995, and revision received Oct. 2, 1995.