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Ethane and Carbon Dioxide Gas Hydrate Incipient Conditions in Reverse Micelles

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Abstract

A reversed-micellar solution is defined as a system of water, oil and an amphiphile (surfactant). It has been shown that gas hydrate formation in reverse-micelle systems provides a means for in-situ control of the droplet size, which in turn can be used to manipulate the properties of any material that has been formed in the water droplet. In this study, the incipient conditions for ethane and carbon dioxide gas hydrate formation in the presence of AOT-water-isooctane were carried out. Subsequently, the results were modelled using the model of van der Waals and Platteeuw in conjunction with a model for the activity of water in reverse micelles and the Peng Robinson equation of state. The predictions were seen to fit the experimental data well.

Keywords: Reverse micelles, gas hydrates, model, carbon dioxide, ethane.

1. Introduction

Tremendous scientific interest has been generated regarding nanoscale materials with a size of 1 - 100 nm because of the advantages resulting from the size reduction to the nanoscale. A reversed-micellar solution is defined as a system of water, oil and an amphiphile (surfactant). The nano-sized water droplets are confined in a continuous hydrocarbon phase and present a kind of microreactor in which to carry out chemical reactions and precipitations. Due to their special and unique properties, reverse micelles have begun to receive attention from both basic research and industry. Some important technological applications of nanomaterials are catalysis, pharmaceuticals, recording media and semiconductors. Because of the wide range of applications, the research for efficient methods to recover large quantities of nanoparticles with well-defined physiochemical properties is an important task.

At appropriate conditions of low temperature and elevated pressure, clathrate hydrates, which are crystalline inclusion compounds formed from water and low molecular weight gases, can be induced to form within the reversed micellar solution and subsequently precipitate out. This phenomenon can be utilised to provide in-situ control of the micelle size and it

can eventually bring about pressure-induced phase transitions to release the particles from solution (Rao et al., 1990; John et al., 1991; Phillips et al., 1991).

In order to assess the feasibility of using clathrate hydrate formation for precipitating nanomaterials from reverse micelles, it is necessary to have relevant thermodynamic data. Unfortunately, the necessary thermodynamic information that is required is extremely sparse. The intention of this work is the obtainment of ethane and carbon dioxide hydrate equilibrium points of a microemulsion system.

2. Experimental Apparatus and Procedure

The formation of hydrates takes place inside the high-pressure cell described by Dholabhai et al. (1996). In order to be able to detect hydrates visually during the experiment, the cell is made of sapphire. The volume of the cell can be modified by moving a piston up and down through a gear mechanism. Several inlets for measurements of temperature, pressure and sample lines are in the top of the piston and in the bottom flange (four in the top for injecting/discharging gas + measuring pressure + vapour phase temperature, two in the bottom for injecting solution + measuring liquid temperature). Pressure inside the cell is measured with the differential pressure transducer. The

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thermocouples are type T with a span from -60 to 90°C and an accuracy of 0.5% of current temperature. The cell is placed in a constant-temperature bath filled with an ethylene glycol-water mixture (50% of each weight) and temperature is controlled by a vapour compression cycle.

The reversed micellar solution is prepared on a weight basis out of bis (2-ethylhexyl) sodium sulfosuccinate (AOT; Aldrich 98%), isooctane (2,2,4-Trimethylpentan, EMD 99.95% purity) and water purified by a double reversed osmosis. Gas components in this work are methane (PRAXAIR, ME 3.7UH, 99.97%), ethane (PRAXAIR, ET2.0, 99.0%) and carbon dioxide (PRAXAIR, CD4.0, 99.99%ANA).

Before injecting the solution into the inside of the experimental cell, it had to be cleaned and dried in order to avoid contamination through dilution or inhibition. For this purpose, the cell was flushed repeatedly with pure isooctane at room temperature and subsequently it was dried with pressurized helium. Finally, helium was removed from the system by several injections of the experimental gas and the cell was purged one additional time with the experimental solution. Around 15ml of solution were injected using a syringe. It is important to ensure that no air is injected during this process. Thus, the gas phase is pure experimental gas.

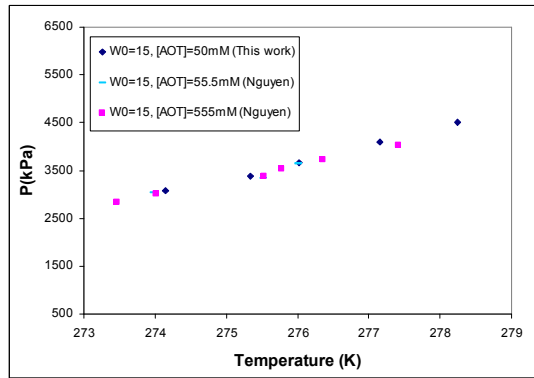


Figure 1. Methane Hydrate Equilibrium in $w_0 = 15$.

Gas was then injected first to a pressure of 10-20% higher than the expected equilibrium value. The hydrate equilibrium point was found by alternately decreasing and increasing the system pressure to decompose and reform the hydrates. Progressively smaller adjustments in pressure were made with every single step until the difference between the point at which hydrates appeared (hydrates appearance point) and disappeared (hydrate disappearance point) was less than 50 kPa at a constant temperature. The hydrate equilibrium line consists of the closest hydrate disappearance points in every single temperature. The experimental apparatus and

procedure was validated by duplicating the results of Nguyen et al. (1989) that were obtained for methane hydrates in reverse micelles ($w_0=15$). Figure 1 shows a comparison of methane hydrate incipient conditions measured in this study with data reported in the literature. The close match observed supports the reliability of experimental methods used in this work.

3. Thermodynamic Model

A general phase equilibrium model, based on the equality of component fugacities in all phases, has been implemented in Microsoft® Excel-VBA in order to model clathrate hydrate equilibria in reverse micelles. In summary, the statistical thermodynamic based model of van der Waals and Platteeuw (1959) in conjunction with the Peng Robinson equation of state, which was modified using a new alpha function developed especially for natural gas components and water (Coquelet et al., 2004) was used to estimate the equilibrium pressure required to form ethane and carbon dioxide gas hydrates.

At equilibrium conditions, the chemical potential of each component in every single phase must be equal

$$\begin{aligned}\mu_i^L &= \mu_i^V \quad (i=1,N) \\ \mu_j^H &= \mu_j^V \quad (j=1,NH)\end{aligned}$$

where N is the total number of components (including water), NH number of hydrate forming components, L is liquid phase, V is vapour phase and H is the hydrate phase.

From van der Waals and Platteeuw (1959) and Holder et al. (1980), the chemical potential of water in the hydrate and the liquid phase can be obtained. The fundamental equations are

$$\begin{aligned}\Delta\mu_w^{MT-H} &= RT \sum_i \nu_i \ln(1 + \sum_j C_{ij} f_j) \quad (1) \\ \frac{\Delta\mu_w^{MT-L}}{RT} &= \frac{\Delta\mu_w^{L0}}{RT_0} - \int_{T_0}^T \frac{\Delta h_w}{RT} dT + \int_0^P \frac{\Delta v_w}{RT} dP - \ln a_w \quad (2)\end{aligned}$$

The previous equations can be numerically solved for pressure if the Langmuir constant C_{ij} is known:

$$C_{ij} = \frac{4\pi}{kT} \int_0^{R_j - a_i} (e^{-W_{ij}(r)/kT}) r^2 dr \quad (3)$$

where, $W(r)$ is the smoothed-cell potential function in the cavity

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

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

where:

$N = 4, 5, 10$ or 11

Z = the coordination number of the cavity

R = the free cavity radius

r = distance of the guest molecule from the cavity center

σ = core distance at zero potential

a = radius of the spherical core

ε = maximum attractive potential

The fugacity f , is calculated using the Peng-Robinson equation of state

On Equation (2), the first term on the right is the reference chemical potential. The second term gives the temperature dependence at constant (zero) pressure. The third corrects the pressure to the final equilibrium pressure. The temperature dependence of the enthalpy difference, Δh_w , is given by:

$$\Delta h_w = \Delta h_w^0(T_0) + \int_{T_0}^T \Delta C p_w dT \quad (6)$$

where $\Delta C p_w$ is heat capacity difference between the empty hydrate and pure water phases. It also depends on the temperature

$$\Delta C p_w = \Delta C p_w^0(T_0) + b(T - T_0) \quad (7)$$

The fourth term represents the activity of water in the liquid phase and it can be calculated as:

$$a_w = \frac{\hat{f}_w}{f_w^0} \quad (8)$$

where $\hat{f}_w$ is the fugacity of water in the liquid phase at the predetermined conditions (T,P) and f_w^0 is the fugacity of pure water at reference state.

The thermodynamic reference properties for hydrates which are taken from Dharmawardhana et al. (1980), Barkan et al. (1997) and Parrish et al. (1972), used in the model are presented in TABLE I:

TABLE I. PARAMETERS FOR HYDRATE FORMATION.

Parameter	Structure I
$\Delta \mu_w^0$ (J/mol)	1297
Δh_w^0 (J/mol) (a)	1395
$\Delta C p_w^0$ (J/mol K)	-38.13+0.141*(T-273.15)
Δv_w (cm ³ /mol) (b)	3.0

(a) In the liquid water region subtract 6011 J/mol

(b) In the liquid water region add 1.6 cm³/mol

In order to extend this well established thermodynamic model from pure water to situations involving reverse-micelles, Nguyen et al. (1993) used the expressions derived by Kubik et al. (1982) and Jonsson et al. (1986) to describe the activity of water in the reverse micelles:

$$\ln a_w^{RM} = \frac{3N_A \bar{v}_w}{R_0} \left[\frac{\Delta E^{el}}{A} + \frac{\sigma RT}{F} + \frac{kT}{2\pi R_0^2} \ln \left(1 + \frac{c_{solv}}{c_{am}} n_{am} \right) \right] + RT \ln x_w - RT \frac{K_1}{K_2} \exp \left(-\frac{w_0}{K_2} \right) \quad (9)$$

where, R_0 and σ are the mean charge surface radius and the surface charge density respectively and they were calculated by Kubik et al. (1982);

$$R_0 = \frac{3w_0 \bar{v}_w}{f_{AOT}} \quad (10)$$

and

$$\sigma = \frac{z_{am} e}{f_{AOT}} \quad (11)$$

f_{AOT} represents the area of the interface covered by one surfactant molecule (AOT). Initially, this property was measured as a function of R_0 by Eicke (1976), however, later on, these values were presented in a much more convenient way by Eicke et al. (1984) and Kinugasa et al. (2002) as a function of w_0 . Based on this, it seems suitable for the purpose of computational calculations to approximate the curve with a polynomial function:

$$f_{AOT} (nm^2) = 1.2376E - 5w_0^3 - 9.7382E - 4w_0^2 + 2.6026E - 2w_0 + 0.28889 \quad 5 \leq w_0 \leq 30 \quad (12)$$

n_{am} is calculated using the correlation derived by Matzke et al. (1992) considering AOT as a surfactant:

$$n_{am} = 32.1 - 1.25w_0 + 0.873w_0^2 \quad (13)$$

and ΔE^{el} is calculated by minimising the Gibbs free energy (Kubik et al., 1982)

$$\left(\frac{\partial G}{\partial A} \right)_{T,P} = - \left[\frac{2\Delta E^{el}}{A} - \gamma \right] = 0 \quad (14)$$

The last term in Equation (9) represents the hydration energies at low water contents and contains two constants K_1 and K_2 , which are adjustable parameters in order to match the experimental data. It can be seen that Equation (9) approaches $RT \ln x_w$ as $w_0 \rightarrow \infty$, which is the case for pure water.

4. Results and Discussion

Incipient three phase H-L-V equilibrium data were measured for ethane and carbon dioxide clathrate hydrates in reversed micellar solutions. Experiments for ethane were carried out with initial water to surfactant ratios (w_0) of 20, 15 and 10. Experiments were also attempted in reverse micelle solutions with w_0 of 5 and 8. However, at these concentrations it was not possible to stabilise the hydrates in the existing apparatus. At this point the reason for this is not clear. Similarly, experiments for carbon dioxide were carried out with initial water to surfactant ratios (w_0) of 20, 15, 10 and 8; however, at high values of w_0 (20 & 15) and when subjected to the experimental conditions, these micellar solutions were unstable.

Figures 2 to 4 and 5 to 6 show the experimental results and predictions for ethane and carbon dioxide respectively. As mentioned in the previous section, the “hydrate disappearance point” point is taken to be the incipient point for hydrate formation. In all cases, it can be seen that forming hydrates in reverse-micelle solutions has an inhibiting effect on the pressure required to form gas hydrates; this pressure was directly correlated to the molar ratio water to surfactant (w_0). This phenomenon was qualitatively explained by Nguyen et al. (1989) considering the differences between bulk water and the water forming from the microaqueous pool in the reverse micelles where the latter contains some bound water near the interface oil water, which makes more difficult the hydrate formation. Figures 2 through 6 also show the results obtained using the thermodynamic model of van der Waals and Platteeuw (1959) with the model of Nguyen et al. (1993) for calculating the activity of water in reverse micelles; showing that the predictions are in good agreement with the experimental data. The parameters K_1 and K_2 in Equation (9) were optimised using least squares to match the experimental hydrate formation conditions. The values of K_1 and K_2 are presented in TABLE II. Jonsson et al. (1987) cites typical values of K_2 for phospholipids ranging from 2 to 6.

TABLE II. LOW WATER HYDRATATION ENERGY PARAMETERS.

Hydrate Former	K_1	K_2	Range of Validity
CO ₂	0.6942	2.9797	$8 \leq w_0 < \infty$
C ₂ H ₆	1.9861	2	$10 \leq w_0 < \infty$

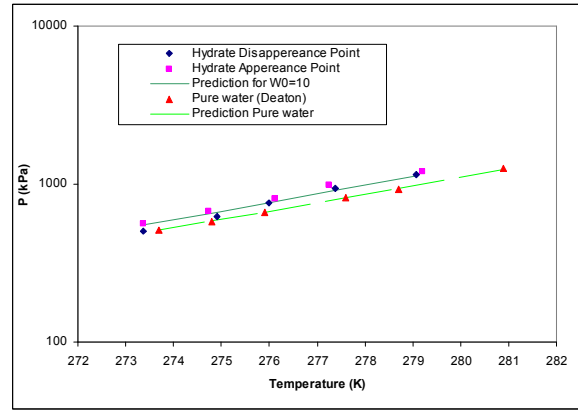


Figure 2. Ethane Hydrate Equilibrium in $w_0 = 10$.

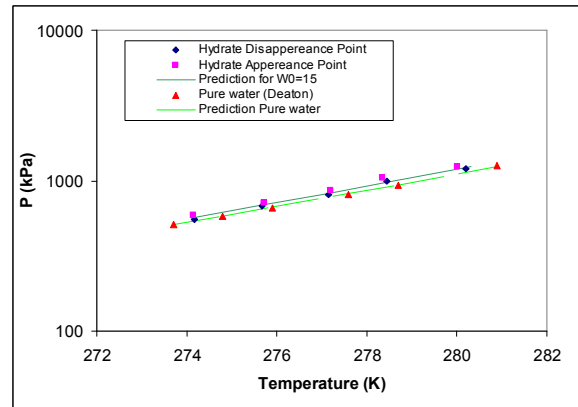


Figure 3. Ethane Hydrate Equilibrium in $w_0 = 15$.

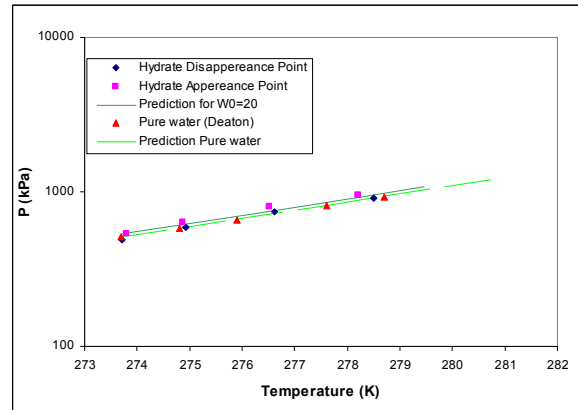


Figure 4. Ethane Hydrate Equilibrium in $w_0 = 20$.

From Figures 1 to 6, it is also possible to estimate the heat of dissociation (ΔH_d), which is defined as the enthalpy change to dissociate the hydrate phase to a vapour and aqueous liquid. This value can be approximated using the well-known Clausius-Clapeyron relation:

$$\Delta H_d = -zR \frac{d(\ln P)}{dT} \quad (15)$$

As seen in *Figures 1 through 6* the slopes of the curves are approximately constant for each forming gas, implying that the heat of dissociation is independent of the water to surfactant molar ratio (w_0). Table 3 reports the heats of dissociation of each gas hydrate in the range of temperature studied:

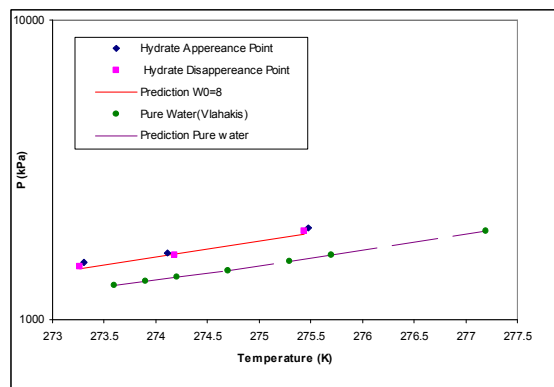


Figure 5. CO_2 Hydrate Equilibrium in $w_0 = 8$.

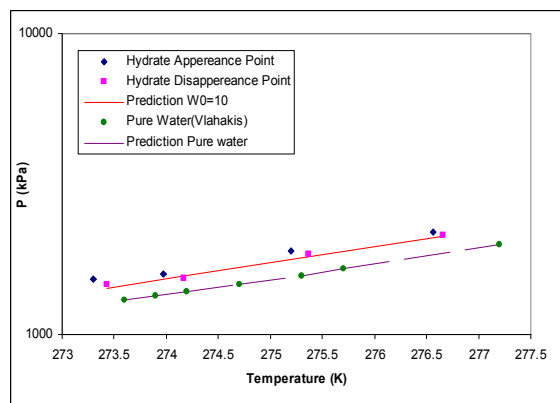


Figure 6. CO_2 Hydrate Equilibrium in $w_0 = 10$.

TABLE III: HEAT OF DISSOCIATION OF GAS HYDRATES.

Hydrate Former	(ΔH_d) calc, (kJ/mol)	(ΔH_d) meas, (kJ/mol)	Reference
CO_2	66.0	-	
C_2H_6	71.6	71.8	Handa (1986)

5. Conclusions

Experiments were carried out to determine the equilibrium conditions for ethane and carbon dioxide gas hydrates in reversed micellar solutions consisting of water droplets in isooctane, stabilised with AOT. It was observed that forming gas hydrates in reverse micelles had an inhibiting effect on the pressure required for hydrate formation and that the inhibiting effect increased as the initial water to surfactant ratio was decreased. Likewise, the heat of dissociation

was calculated and shown to be independent of the initial Waals and Platteeuw w_0 . Additionally, the results were modelled using statistical thermodynamics coupled with the model of Nguyen et al. (1993) to calculate the activity of water in reverse micelles, and it was seen that it was possible to correlate the results with reasonable accuracy.

Nomenclature

A	interfacial area (m^2)
a	activity
c	concentration (M)
e	electronic charge (1.602×10^{-19} Coul)
Δe_{el}	electrostatic interaction energy (J)
F	Faraday's constant (96485 Coul/mol)
G	Gibbs free energy (J)
k	Boltzmann's constant (1.38×10^{-23} J/K)
N_A	Avogadro's number (6.023×10^{23} molec/mol)
n	aggregation number
T	temperature (K)
$\bar{v}_w$	partial molecular volume of water (29.9×10^{-3} nm ³ /molec)
w_0	initial water to surfactant molar ratio
x	liquid phase mole fraction
z	charge number

Greek Letters

γ	interfacial free energy (J/m^2)
σ	surface charge density (Coul/ m^2)

Subscripts / superscripts

am	amphiphile
RM	reverse micelle
$solv$	solvent
w	water

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References

- Barkan, E. S. A., Shienin, D. A., 1993, "A General Technique for the Calculation of Formation Conditions of Natural Gas Hydrates", *Fluid Phase Equilibria*, Vol. 86, pp. 111-136.
- Coquelet, C., Chapoy A., Richon D., 2004, "Development of a New Alpha Function for the Peng-Robinson Equation of State: Comparative Study of Alpha Function Models for Pure Gases (Natural Gas Components) and Water-Gas Systems", *International Journal of Thermophysics*, Vol. 25 (No. 1), pp. 133-58.

- Deaton, W. M., Frost, E. M., 1946, "Gas Hydrates and Their Relation to the Operation of Natural Gas Pipelines", *US Bur Mines Monograph* 8, pp. 101-108.
- Dharmawardhana, P. B., Parrish, W. R., Sloan, E. D., 1980, "Experimental Thermodynamic Parameters for the Prediction of Natural Gas Hydrate Dissociation Conditions", *Ind. Eng. Chem. Fundam.*, Vol. 19 (No. 4), pp. 410-414.
- Dholabhai, P. D., Parent, J. S., Bishnoi, P. R., 1996, "Carbon Dioxide Hydrate Equilibrium in Aqueous Conditions Containing Electrolytes and Methanol Using a New Apparatus", *Ind. Eng. Chem. Res.*, Vol. 35, pp. 819-826.
- Eicke, H. F., Rehak, J., 1976, "On the Formation of Water/Oil-Microemulsions", *Helvetica Chimica Acta*, Vol. 59, pp. 2883-2891
- Eicke, H. F., Kvita P., 1984, *Reverse Micelles-Biological and Technological Relevance of Amphiphilic Structures in Apolar Media*, Pileni P. L. and Straub B. E (eds.), Plenum Press, New York.
- Handa, Y. P., 1986, "Compositions, Enthalpies of Dissociation and Heat Capacities in the Range 85 to 270K for Clathrate Hydrates of CH₄, C₂H₆, C₃H₈ and Enthalpy of Dissociation of Isobutane Hydrate as Determined by a Heat Flow Calorimeter", *J. Chem. Therm.*, Vol. 18, pp. 915-921.
- Holder, G. D., Corbin, G., Papadopoulos D., 1980, "Thermodynamic and Molecular Properties of Gas Hydrates from Mixtures Containing Methane, Argon and Krypton", *Ind. Eng. Chem. Fundam.*, Vol. 19, pp. 282-286.
- John, V. T., Rao, A., Nguyen H., Phillips, J., 1991, "Pressurized Gases in Contact with Liquid Reversed Micellar Solutions-Effects on Micellar Size and Stability, and Biological Applications", *Journal of Supercritical Fluids*, Vol. 4, pp. 238-243.
- Jonsson, B., Wennerstrom, H., 1987, "Phase Equilibria in a Three-Component Water-Soap-Alcohol System. A Thermodynamic Model", *J. Phys. Chem.*, Vol. 91, pp. 338-352.
- Kinugasa, T., Kondo, A., Nishimura, S., Miyauchi, Y., Nishii, Y., Watanabe, K., Takeuchi H., 2002, "Estimation for Size of Reverse Micelles Formed by AOT and SDEHP Based on Viscosity Measurement", *Colloids and Surfaces A*, Vol. 204, pp. 193-199.
- Kubik, R., Eicke, H., Jonsson, B., 1982, "On the Activity of Water and the Concept of the Interfacial Free Energy in W/O Microemulsions", *Helvetica Chimica Acta*, Vol. 65 (No. 14), pp. 170-177.
- Matzke, S. F., Creagh, A. L., Haynes, C. A., Praunitz, J. M., Blanch, H. W., 1992, "Mechanism of Protein Solubilization in Reversed Micelles", *Biotechnol. Bioeng.*, Vol. 40 (No. 1), pp. 91-102.
- Nguyen, H. T., Kommareddy, N., John, V. T., 1993, "A Thermodynamic Model to Predict Clathrate Hydrate Formation in Water-in-Oil Microemulsion Systems; *Journal of colloid and interface Science*, Vol. 155, pp. 482-487.
- Nguyen, H. T., Phillips, J. B., John, V. T., 1989, "Clathrate Hydrate Formation in Reversed Micellar Solutions", *The Journal of Physical Chemistry*, Vol. 93 (No. 25), pp. 8123-8126.
- Parrish, W. R., Prausnitz, J. M., 1972, "Dissociation Pressures of Gas Hydrates Formed by Gas Mixtures", *Ind. Eng. Chem. Process. Des. Dev.*, Vol. 11, pp. 26-35.
- Phillips, J., Nguyen, H., John, V. T., 1991, "Protein Recovery from Reversed Micellar Solutions Through Contact with a Pressurized Gas Phase", *Biotech Prog.*, Vol. 7, pp. 43-48.
- Rao, M., Nguyen H., John, V. T., 1990, "Enzyme Activity in Reversed Micelles as Modified by Hydrate Formation", *Biotech. Prog.*, Vol. 6 (No. 6), pp. 465-471.
- Van der Waals, J. H., Platteeuw, J. C., 1959, "Clathrate Solutions", *Adv. Chem. Phys.*, Vol. 2 (No. 1), pp. 1-57
- Vlahakis, J. G., Chen, H., Suwandi, M. S., Barduhn, A. J., 1972 "The Growth Rate of Ice Crystals: Properties of Carbon Dioxide Hydrates, a Review of Properties of 51 Gas Hydrates", Syracuse U Research and Development Report 830, prepared by US Department of the Interior