

Thermal Analysis of Polymer–Water Interactions and Their Relation to Gas Hydrate Inhibition

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ABSTRACT: Gas hydrates formed in oil production pipelines are crystalline solids where hydrocarbon gas molecules such as methane, propane, and their mixtures are trapped in a cagelike structure by hydrogen-bonded water molecules to form undesirable plugs. Methanol and glycol are currently used to prevent these plugs via thermodynamic inhibition. Small amounts of water-soluble polymers may provide an alternate approach for preventing gas hydrates. In this study, we expand the fundamental understanding of water–polymer systems with differential scanning calorimetry. Non-freezable bound water was used to quantify polymer–water interactions and relate them to the chemical structure for a series of polymers, including acrylamides, cyclic lactams, and *n*-vinyl amides. For good interactions, the water structure

needs to be stabilized through hydrophobic interactions. An increased hydrophobicity of the pendant group also appears to favor polymer performance as a gas hydrate inhibitor. Good inhibitors, such as poly(diethyl acrylamide) and poly(*N*-vinyl caprolactam), also show higher heat capacities, which indicate higher hydrophobicity, than poor performers such as polyzwitterions, in which hydrophilicity dominated. The phase behavior and thermodynamic properties of dilute polymer solutions were also evaluated through measurements of the heat of demixing and lower critical solution temperature. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2642–2653, 2007

Key words: crystallization; heat capacity; phase behavior

INTRODUCTION

Water is the major component in offshore pipelines where gas hydrates are formed. Gas hydrates are crystalline solids where hydrocarbon gas molecules such as methane, propane, and their mixtures are trapped in a cagelike structure by hydrogen-bonded water molecules.¹ Gas hydrates cause flow problems in the pipelines and often plug the pipelines to cause slow oil production. Gas hydrate control in oil production flow lines is typically carried out with methanol and/or glycol as thermodynamic inhibitors. These inhibitors change the activity for water² and, thus, depress the temperature at which hydrates form on cooling. Thermodynamic models have been reported in the literature¹ that predict performance of these inhibitors by measurement of changes in the activity of water. A small amount of polymers, when added to water, also interfere with hydrate formation. They are believed to function by interfering with the kinetics of hydrate formation rather than by thermodynamics. An understanding of the nature of polymer interactions with water will help in the design of novel polymers with improved performance.

Thermal analysis [differential scanning calorimetry (DSC)] is used to quantify polymer–water interactions and provide insights into the mechanism of gas hydrate inhibition. The literature contains many reports on the use of DSC to study water–polymer interactions^{3–17} and indicates that these interactions are strongly dependent on the chemical structure of the polymer. There are several systems where interactions can be quite strong so that water can fail to crystallize on cooling and, shows only a glass transition.¹³ In this study, we aimed to quantify the interactions of several polymer systems of interest to us as possible hydrate inhibitors. Analysis of the phase behavior and thermodynamic properties of dilute solutions are reported in this paper. Polymer–water interactions for a large number of water-soluble polymers were evaluated through measurements of bound water, heat of demixing (ΔH_{demix}), and heat capacity (C_p). Thermodynamic studies of polymer solutions were used to develop relationships between polymer solubility and the inhibition activity of polymers. Structure–property relationships developed were also used to predict the performance of these polymers as inhibitors for gas hydrate formation and to provide insights into the mechanism of hydrate inhibition in the production pipeline.

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EXPERIMENTAL

All measurements were carried out on a TA Instruments DSC 2910 instrument equipped with a liquid

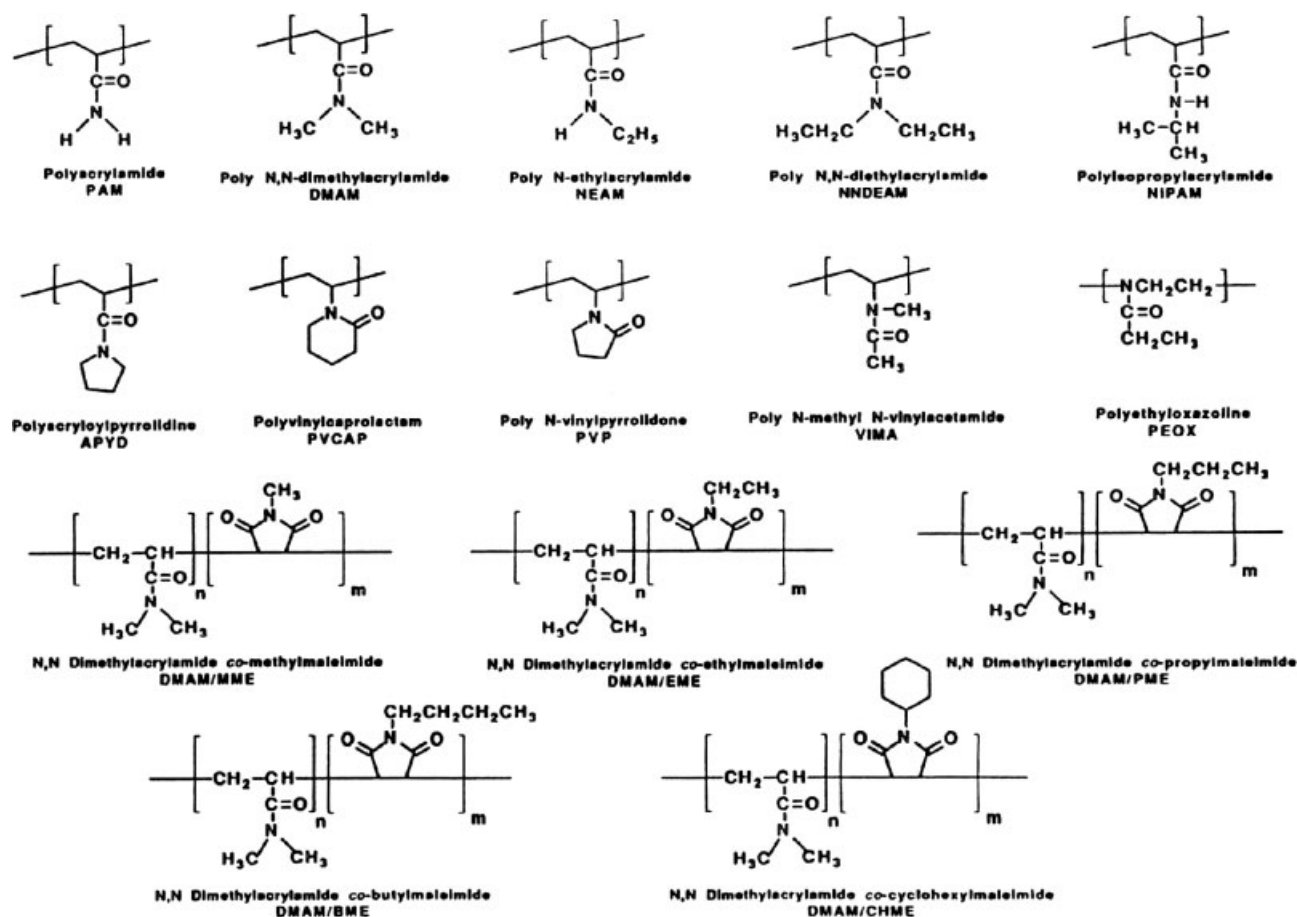


Figure 1 Chemical structures of various polymers.

nitrogen cooling accessory. Hermetic pans of aluminum were used, and the typical sample mass was less than 10 mg. Both temperature and heat of fusion were well calibrated with suitable standards.

Bound water evaluation

A large number of polymers and copolymers synthesized at ExxonMobil were evaluated with calorimetry. Figure 1 lists the details and chemical structures of these polymers. In a typical experiment, a known weight of polymer (dried in a vacuum oven for 24 h at 60°C) was placed in the hermetic pan, and water was added with a microsyringe. The mixture was hermetically sealed and allowed to equilibrate for a minimum of 12–14 h before it was analyzed for crystallization and melting behavior of water. All samples were loaded at room temperature, equilibrated at 15°C to build enough coolant around the DSC cell, cooled to -70°C at 5°C/min, held for 25 min, and heated at a heating rate of 5°C/min to 50°C. Data was stored for both cooling and heating experiments. Filtered synthetic sea water was used in addition to the distilled water, and this was prepared by the addition of a measured amount of sea salt mix-

ture to distilled water. R is defined as the ratio of grams of water to dry polymer weight. All heats of transition were recorded with respect to dry polymer weight.

C_p measurements

All measurements were carried out with modulated differential scanning calorimetry (MDSC). An isothermal method of obtaining C_p was used, as this has been shown to improve the precision of measurements compared to conventional DSC.¹⁸ In all cases, a period of 80 s and an amplitude of 1°C were used to produce the sinusoidal modulation needed to give a direct measure of C_p . The data was corrected with a sapphire standard, and the reproducibility of our measurements was within 1–2%. Two different kinds of experiments were carried out. In one, measurements of C_p were carried out for dried poly(*N*-vinyl pyrrolidone) (PVP) with a molecular weight of 1,000,000 and containing incremental amounts of filtered brine. R , the ratio of the weight of brine to grams of dried polymer, was varied between 0 and 5. All samples were equilibrated overnight. C_p was isothermally measured for several compositions at 283 and 273 K. In another experiment,

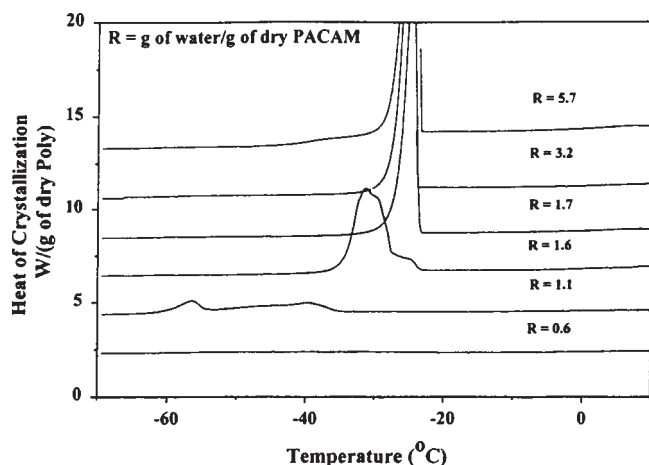


Figure 2 Crystallization of synthetic sea water in PACAM.

dilute solutions of poly(*N*-vinyl caprolactam) (PVCap), poly(diethyl acrylamide) (PDEAM), and poly[*N*-3-sulfo-propyl]-*N*-methacryloyl-oxyethyl-*N,N*-dimethyl ammonium betaine] (PSPE) with various concentrations (0.01–0.5 mol/L of water) were used to isothermally determine C_p at 273 K.

Flory–Huggins interaction parameter (χ) for dialyzed PVP in brine

χ was determined for dialyzed PVP (molecular weight = 10,000) in brine using Flory–Huggins equation.¹⁹ Solutions with various concentrations were cooled from room temperature to -25°C and heated at a slow heating rate of $1^\circ\text{C}/\text{min}$. From the onset temperature for the melting transition of ice grown from brine, the interaction of polymer with brine was calculated.

Lower critical solution temperature (LCST) and ΔH_{demix} measurements

LCST and ΔH_{demix} were measured for dilute inhibitor solutions with concentrations of 0.5 and 1.0 mol/L. The solutions were equilibrated overnight and sampled after they were cooled in an ice bath for few minutes until the solution became clear. These were encapsulated in aluminum pans sealed hermetically, cooled to -10°C , and followed by heating to 80°C at a heating rate of $10^\circ\text{C}/\text{min}$.

Measurements of the heat of mixing and ΔH_{demix} are usually carried out with a microcalorimeter that uses about 1 g of sample to increase the sensitivity of the event. A few samples were, therefore, analyzed with a solution calorimeter from Setaram (model: BT 2.15 D), and the data were compared with that measured with MDSC. ΔH_{demix} values obtained from the microcalorimeter were almost double those obtained from MDSC, which indicated that the sensitivity of the microcalorimeter was twice as good as that of MDSC. Because in this investigation comparative values were

more desired than the absolute values, demixing measurements carried out with MDSC are discussed.

Flow measurements for gas hydrate formation and inhibition

The miniloop consisting of a flow pipeline was used to test gas hydrate formation under production pipeline conditions of high pressure (up to 1000 psi) and low temperature (e.g., subambient low temperature conditions that exist under subsea conditions and in permafrost regions).¹ Gas hydrates of hydrocarbon gases, such as mixtures of methane and propane, form under these flow conditions. This small-scale flow pipeline allowed us to investigate both thermodynamic and kinetic polymeric inhibitors for their effect on either the slowing or prevention of gas hydrate formation. A small ball was added to the flow, and its mobility was tracked in terms of time taken for it to flow from one point to another. So long as the hydrates were small and did not increase the viscosity of the flow, the ball kept moving, and the time taken did not change. As hydrates began to grow in size, they impeded the flow, and the movement of the ball slowed down to ultimately stop when the line was plugged. The time taken for the ball to completely stop moving was called ball stop time (BST) and gave a measure of the kinetic inhibition efficacy of the polymeric inhibitor.

RESULTS AND DISCUSSION

Evaluation of nonfreezable bound water (NFBW) from hydration experiments

The crystallization and melting traces from -70 to 50°C for hydration experiments of polyacrylamide (PACAM) in synthetic sea water are plotted in Figures 2 and 3. Incremental amounts of water in the system resulted in the crystallization of water ($R \geq 1.1$). Below an R

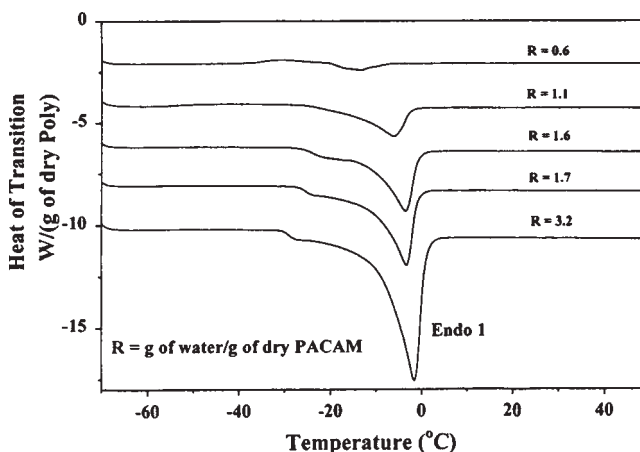


Figure 3 Melting of synthetic sea water in PACAM.

value of 1.1, water failed to crystallize. The endotherm corresponding to melting for this R value, was, in fact, preceded by an exotherm corresponding to cold crystallization with an almost equal heat of crystallization and melting, which indicated that crystallization occurred only during heating (cold crystallization) and no crystals formed when this mixture cooled. The cooling trace for $R = 1.1$ showed evidence of the formation of two types of crystals (two exotherms were observed, one corresponding to a fast-grown form and another to a slow-grown form). On heating, the second type of crystals (formed later on cooling) reorganized, and only a single melting corresponding to freezable water (FBW) was observed. All higher values (between R values of 1.1 and 3.2) showed a single sharp crystallization exotherm at a crystallization on set temperature of -23°C that corresponded to only the fast-grown crystals. In all these systems, a cold crystallization exotherm just before the melting endotherm was observed on heating and was associated with the crystallization of the supercooled water. For higher water content, the crystallization exotherm on cooling became more important and shifted to higher temperatures (approaching that of pure water), whereas no more crystallization on heating was detected. In all cases above $R = 1.1$, a single melting endotherm corresponding to crystals of FBW was observed.

A typical analysis of the total heat of fusion of the FBW measured as a function of water content for PACAM is plotted in Figure 4. This linear variation of the heat of endothermic transition versus R was used to derive the number of moles of NFBW that were associated with 1 mol of polymer repeat units [intercept at zero heat of fusion divided by the slope of the plot (average apparent melting enthalpy of the freezable bound water)]. An analogous analysis was also performed for the total heat of crystallization exotherms; this is also plotted in Figure 4. The

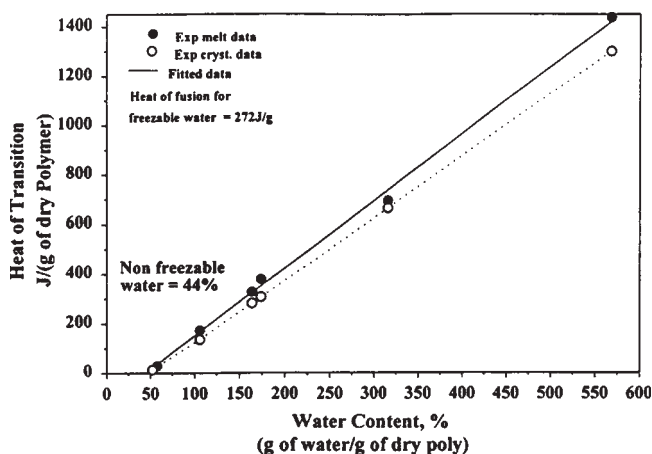


Figure 4 Bound water analysis for PACAM (a poor inhibitor) from heat-of-transition data.

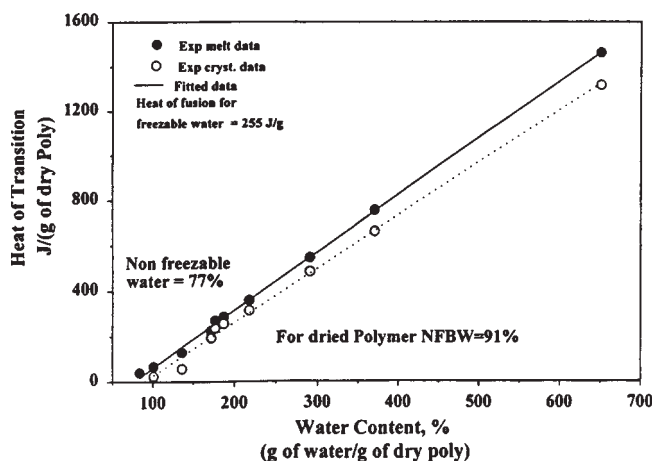


Figure 5 Bound water analysis for VC713 (a good inhibitor) from heat-of-transition data.

values obtained from these two plots were quite close (the slightly higher value from the heating data was due to the annealing of crystals of water below the temperature where they formed). A value of 2.0 mol of NFBW/mol of dry polymer for PACAM was obtained. A typical analysis for a polymer with much higher bound water is shown in Figure 5 for VC713 (a terpolymer of PVP, PVCap, and amino-propyl methacrylate). This terpolymer had 6.7 mol of NFBW/mol of polymer repeat units (average weight of the trimers). In addition to VC713, polymers such as PVP and PVCap, which were shown to be good hydrate inhibitors by the Colorado School of Mines,²⁰ also had high NFBW (5.2 and 6.5 mol, respectively). PACAM, described in Figure 4 with only 2.0 mol of NFBW, was shown by the Colorado School of Mines to be a poor inhibitor. These results indicate that a higher amount of NFBW appeared to favor inhibition, and the bound water data for these four polymers showed the same order of performance of these polymers as gas hydrate inhibitors.

The effect of molecular weight on NFBW was also evaluated for a series of PVPs with different molecular weights (10,000, 40,000, 360,000, and 1,000,000). Bound water was independent of molecular weight, as it represents the number of water molecules corresponding to each repeat unit of the polymer. The parameter NFBW measured only the strongest interactions between the polymer and water, which were probably limited to the innermost hydration shells (discussed later in this section). Interactions in dilute solutions were not limited to only the presence of NFBW. In the hydration shells around the polymer, interactions weakened in going from the interior to the outside of the sphere. The effect of the weak interactions was reflected on the melting of water from dilute polymer solutions. As the concentration of the polymer increased, the activity of water decreased. This resulted in a decrease of the transi-

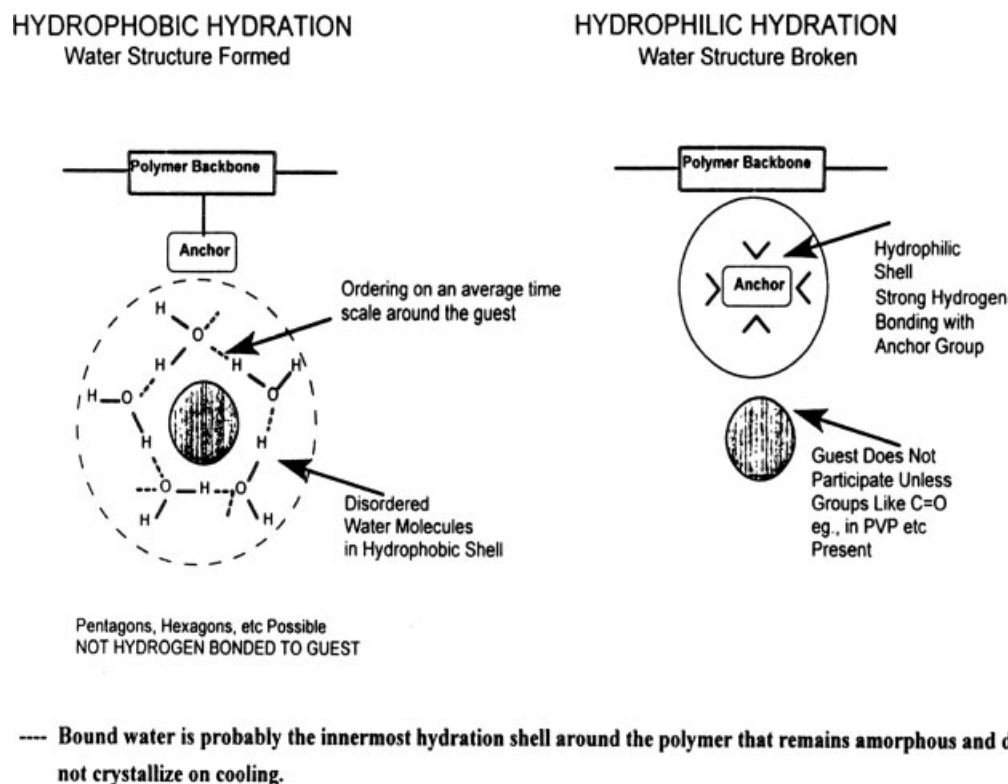


Figure 6 Scheme of hydrophobic and hydrophilic hydration shells around the pendant group of the polymeric inhibitor.

tion temperatures for the phase transitions of ice to water. The decrease in heat of fusion of ice grown in the presence of polymers most likely is due to the formation of defect ice crystals. For example, the melting of ice from the dilute solutions of PVP (molecular weight = 10,000) in distilled water showed a reduction in the heat of fusion from a value of 325.3 J/g for pure distilled water to 217 J/g for 2 mol/L of PVP solution. The onset of the melting transition changed from a value of -0.7°C for distilled water to -2.5°C for the same solution. From the decrease in heat of fusion, the total amount of water that was measurably affected by the polymer was about 67%.



Concept of NFBW

Water in polymers behaves abnormally and is different from pure water. The sharp, first-order phase transitions characteristic of bulk water shift in temperature, and the heat of transition changes for water that interacts with the polymer. Bulk water melts in the vicinity of 0°C . The melting and crystallization behavior of water changes in the presence of polymers. For example, a 1.0 mol/L solution of PVP depressed the freezing point of water by 1.2°C . These interactions arise from hydrogen bonding (hydrophilic interactions) between water and the polar groups (e.g., carbonyl moieties in PVP) and also from hydrophobic interactions between the nonpolar groups (e.g., pyrrolidone rings in PVP) and water.

These interactions affect the kinetics and thermodynamics of the crystallization and melting of water. For some water-polymer systems, some of the water fails to crystallize on cooling. This type of water is referred to as NFBW to distinguish it from the water that crystallizes on cooling (FBW).³⁻¹³ NFBW has been determined in the literature through an analysis of the crystallization and melting of bulk water for a large number of polymers, such as PVP,^{3,5} PVCap,³ poly(*N*-vinyl-*N*-methylformamide),³ poly(ethylene oxide),⁵ poly(methacrylic acid),⁵ poly(hydroxyethyl methacrylate),⁶⁻⁸ and polyzwitterions.⁸ Some of these polymers, for example, PVCap and PVP, that bind a large amount of water have shown good performance as hydrate inhibitors, whereas others that bind poorly to water have low amounts of bound water [ca. 2 for poly(ethylene oxide)] and are also observed to be poor inhibitors. The amount of NFBW depends on the chemical structure, and in addition, polymer mobility and conformational changes have also been shown to affect the structural organization of water. The extent of these interactions depends on the nature of binding sites (polar and nonpolar) that are present in the polymer. The order of decreasing bond strength, for example, is Ion-ion > Water-ion > Water-polar = Polar-polar = Water-water > Water-hydrophobic.

The literature definition of NFBW is rather ambiguous. Experiments based on calorimetry and NMR have been carried out extensively to probe the physi-

TABLE I
Effect of the Chemical Structure on Bound Water in the PACAMs

Polymer	R1	R2	Bound water (mol/mol of repeat units)	Miniloop subcooling (°F)
Acrylamide	—H	—H	2.0	6.0
NMAM	—H	—CH ₃	3.3	NA
DMAM	—CH ₃	—CH ₃	4.3	11.4
NEAM	—H	—CH ₂ CH ₃	4.7	12.5
NIPAM	—H	—CH—CH ₃ CH ₃	5.2	19.0
NNDEAM	—CH ₂ CH ₃	—CH ₂ CH ₃	5.7	21.5
	NA	NA	5.3	25.2
	NA	NA	5.9	19.0

The structure of PACAM is $\left[\text{CH}_2 - \underset{\begin{array}{c} | \\ \text{C}=\text{O} \\ | \\ \text{N} \\ / \quad \backslash \\ \text{R}_2 \quad \text{R}_1 \end{array}}{\text{CH}} \right]_n$. NA = not applicable; NEAM = poly(*N*-ethylacrylamide); NIPAM = polyisopropylacrylamide; NNDEAM = poly(*N,N*-diethylacrylamide).

cal significance of bound water. Some reports suggest that the inability of water to freeze is not a thermodynamic phenomenon but is caused by kinetic factors, whereas some are of the opinion that water, in fact, binds to the polymer and, hence, fails to freeze. There is no conclusive evidence that shows that NFBW is the amorphous phase of water (amorphous water is reported to have a glass transition at 135 K with a corresponding change in C_p of 35 J K⁻¹ mol⁻¹).¹⁴

Water is a highly hydrogen-bonded liquid in which pentamers and hexamers are known as the major structures and are well reported in the literature. In terms of the hydration phenomenon, polymer-water interactions extend into the bulk phase through hydrophilic and hydrophobic hydration spheres, and the interaction is strongest at the center of the sphere (Fig. 6). Frank and Evans¹⁵ were the first to elucidate the effect of dissolved molecules on the structure of water where the presence of nonpolar gases was shown to form microscopic icebergs around the gas molecules. This idea was later developed in the concept of hydrophobic hydration, which exists along with hydrophilic hydration. In view of the existence of hydration spheres, bound water is a quantity that measures the strongest interaction of the polymer with water, and these interactions are most likely limited to the innermost hydration shells. It was shown through our experimental studies, described later, that bound water most likely measured contributions from both hydrophobicity and hydrophilicity.

A large number of water-soluble polymers and copolymers synthesized were evaluated to quantify their interactions with water in terms of NFBW. Measurements were carried out for undried and oven-dried polymers with both distilled and synthetic sea water (brine). The typical errors in these measurements of NFBW were within $\pm 3\%$. The results of these analysis are discussed in the following sections.

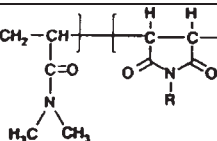
Effect of chemical substitution on bound water PACAMs

The relationship between bound water and chemical substitution is given in Table I for the PACAM family. Also listed are the flow loop performance data and BST results. BST is not a desirable performance test for hydrate inhibition as the test uses tetrahydrofuran (a hydrate former), which changes the solvent quality of water and effects reliability. Within the family of PACAMs, bound water increased with increasing hydrophobicity of the guest group [pendant $-\text{N}(\text{R})_2$ group]. On the basis of bound water alone, we could predict that polyacryloylpyrrolidone (PAYPD; structure shown in Fig. 1) and another PACAM with a cyclic structure in the pendant groups [polyacryloylmorpholine (PAMPHL)] would show good hydrate inhibition. The measured flow loop data for these two were indeed rather high (25.2 and 19.0, respectively). Hence, it appeared that increasing guest-group hydrophobicity was beneficial to inhibitor performance, and larger groups had a higher hydrophobicity associated with them (see the next paragraph on bound water

TABLE II
Effect of the Chemical Structure on Bound Water in the Copolymers of DMAM/
Maleimides

Polymer	R	Bound water (mol/mol of repeat units)	Miniloop subcooling (°F)
DMAM/ME	H	2.9	NA
DMAM/MME	CH ₃	3.8	NA
DMAM/EME	CH ₂ CH ₃	5.3	18.0
DMAM/PME	(CH ₂) ₂ CH ₃	3.9	17.5
DMAM/BME	(CH ₂) ₃ CH ₃	4.4	16.8
DMAM/NBME	(CH ₂) ₃ CH ₃	5.2	NA
DMAM/CHME	C ₆ H ₅	5.9	NA

The structure of the copolymer is $\left[\text{CH}_2 - \underset{\text{C}=\text{O}}{\underset{\text{N}(\text{H}_3\text{C})_2}{\text{CH}}} \right] \left[\text{C}(\text{H}) = \underset{\text{O}}{\text{C}} - \underset{\text{O}}{\text{C}} - \text{N}(\text{R}) - \underset{\text{O}}{\text{C}} = \text{C}(\text{H}) \right]$. NA = not applicable;



MME = methylmaleimide; BME = butylmaleimide; NBME = N-butylmaleimide. ME, MME, EME, and so on were the maleimide comonomer units, and R in column 2 represents the change in R on the maleimide part.

and guest volume). On the basis of the good performance of polyisopropylacrylamide (PIPAM), PDEAM, PAPYD, and PAMPHL, it appeared that there were a critical number of moles of NFBW that controlled the inhibition activity. For the PACAMs, the critical value was probably between 4.0 and 5.0 mol of bound water/mol of polymer repeat units. It is well known that pentamers and hexamers are the major structures in hydrogen-bonded liquid. Thus, the innermost shell was most likely to have a few pentamers and hexamers of water molecules to give a labile structure with a coordination number of about 20–24.

Bound water in poly(*N,N*-dimethylacrylamide) (DMAM)/maleimide copolymers

Table II lists the bound water measured for a series of copolymers of DMAM with maleimides. As seen for the PACAMs, bound water increased with the hydrophobicity of the pendant group. It was 2.8 for methacrylamide (ME) and 5.2 for N-butylmaleimide (NBME). Among ethylmaleimide (EME), propylmaleimide (PME), and NBME, bound water was higher for the EME-based copolymer. For copolymers containing PME and NBME, a large amount of reorganization occurred on heating the poorly crystallized FBW. These poorer crystals of ice were probably associated with the compositional inhomogeneity in the copolymers, and their reorganization on heating caused difficulty in the analysis of the melting transition. This gave rise to lower values of NFBW for PME and NBME. The copolymer with 11% cyclohexylmaleimide (CHME) showed the highest value of about 6.0 mol of bound water. Thus, on the basis of bound water alone, its performance in the miniloop could be predicted to be better than that of the copolymer with NBME groups.

Correlation of bound water with flow loop performance for various inhibitors

NFBW for a large number of polymers and copolymers was correlated with flow loop performance. The data are plotted in Figure 7. On this basis, it looked like it was possible to correlate bound water and inhibitor testing. Thus, bound water that measured both hydrophobicity and hydrophilicity appeared to be a necessary condition for a good inhibitor performance.

Polyzwitterions

As shown previously, a larger amount of bound water appeared to lead to better inhibitor performance. According to a report in the literature,⁹ zwitterionic polymers bind a large amount of NFBW. We, therefore, also measured two polyzwitterions {poly(ammonium sulfopropyl betaines) with slightly different side

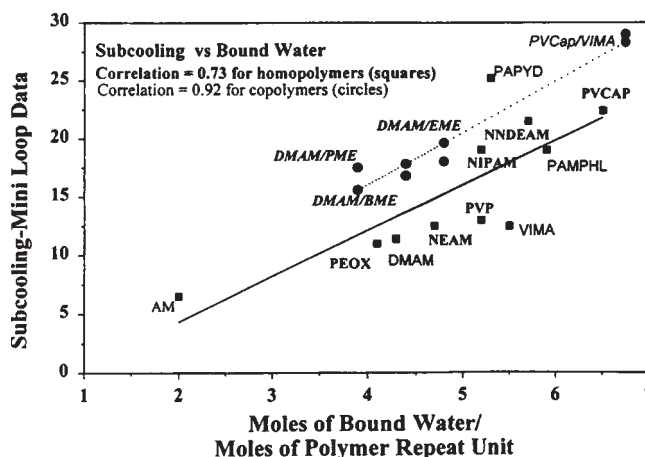


Figure 7 Correlation of bound water to inhibitor performance in the miniloop.

groups, PSPE and poly[(*N*-3-sulfopropyl)-*N*-methacryloyl amido propyl-*N,N*-dimethyl ammonium betaine] (PSPP).⁹ These had very high values for bound water (between 7 and 8 mol/mol of polymer repeat units). If indeed bound water was a sufficient condition to the predict performance of polymers, these polyzwitterions should have performed the best as hydrate inhibitors because these had the highest bound water. Both zwitterions had very poor BSTs (14 and 10 min for PSPE and PSPP, respectively), and on the basis of these screening results, they were poor hydrate inhibitors. Indeed, the performance of PSPE in the miniloop subcooling was poor (6°F compared to some good inhibitors that had subcoolings greater than 20°F). As mentioned earlier, bound water is a combined measure of both hydrophobicity and hydrophilicity. It was clear from the analysis of acrylamides, lactam-ring-containing polymers, and also, to some extent, copolymers of DMAM/maleimides that an increase in hydrophobicity could be probed with bound water analysis and higher hydrophobicity was beneficial to performance. The poor performance of the zwitterions as hydrate inhibitors was most likely due to the dominance of hydrophilicity. Thus both hydrophobicity and hydrophilicity can lead to high values of bound water. Hydrophilicity and hydrophobicity can be distinguished through measurements of C_p . Hence, C_p 's were obtained for polymer-water systems to establish the fact that the poor performance of PSPE and PSPP was indeed due to the dominance of hydrophilicity.

Thermodynamics of polymer hydration and phase behavior of dilute solutions

Heat capacities C_p

Hydrophilic and hydrophobic hydration could be distinguished through thermodynamic measurements of C_p .^{13,16} The value of C_p for bulk pure water is $4.18 \text{ J K}^{-1} \text{ g}^{-1}$. Vibrations, librations, and configurational contributions (molecules can adopt different positions and orientations) contribute to the C_p of water. The C_p of ice is $2.1 \text{ J K}^{-1} \text{ g}^{-1}$ and can be explained on the basis of three vibrations and three librations of water molecules fixed in a crystal lattice. Classically, each mode should contribute a value of R to the C_p , and thus, the total C_p for ice should be $2.8 \text{ J K}^{-1} \text{ g}^{-1}$. The low measured value of ice of only $2.1 \text{ J K}^{-1} \text{ g}^{-1}$ was mainly the result of a relatively high Debye temperature (1000 K) of the librations, and these were, therefore, not fully excited. Liquid water has, in addition, configurational contributions to C_p . Brine is expected to have a C_p lower than that of pure water because the dipole interactions with salt restrict the mobility of water molecules. Similarly, hydrophilic interactions between polar groups in a polymer and water would

be expected to lower the C_p of water; the extent of this would depend on the strength of the interactions. A low value for the C_p of water was indeed reported, for example, in collagen, methylcellulose, and several crystalline salt hydrates.¹¹ An increase in the C_p of dilute polymer solutions of PVCap¹⁶ and poly(*N*-vinyl propylacetamide)¹⁷ in water has been reported to arise due to the dominance of hydrophobic interactions. Thus, on the basis of C_p alone, one can distinguish both hydrophilic and hydrophobic interactions by comparing the measured C_p of water. In addition, strongly immobilized water molecules and those that are in liquidlike structures can also be distinguished through these measurements.

C_p of brine in the presence of PVP (molecular weight = 1,000,000). C_p measurements were carried out to probe the mobility of NFBW that was considered to interact strongly with the inhibitors. Figure 8 shows the total measured C_p for the brine-PVP (1,000,000) system calculated with respect to the dry polymer weight. The measured data extended to $R = 6$ (at all values of R , the polymer was the continuous phase, and the water was the dispersed phase) but were omitted from the plot to clearly show the events at lower compositions. Important conclusions that can be drawn from this plot are

1. There was a linear response of change in C_p with composition above a value of R of about 1.0, which indicated that the C_p of brine in the system beyond $R = 1$ was independent of the concentration. With the additivity rule, one could obtain the partial specific heat capacity of brine (C_{p1}) from the measured total C_p of the polymer-brine system as follows:

$$C_p/W_2 = C_{p1}R + C_{p2}$$

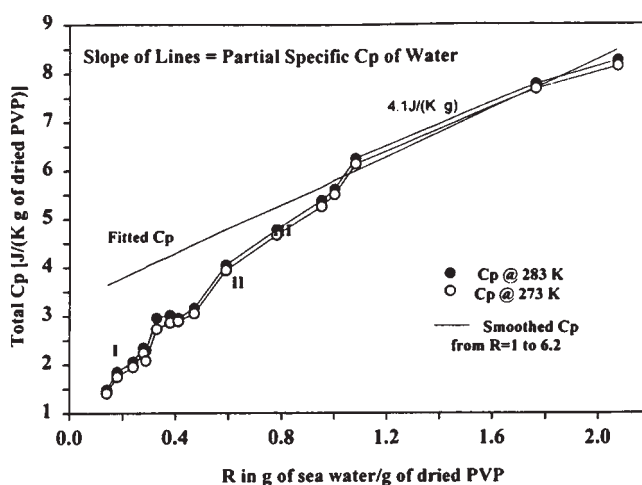


Figure 8 Hydration in PVP (molecular weight = 1,000,000) probed through C_p measurements.

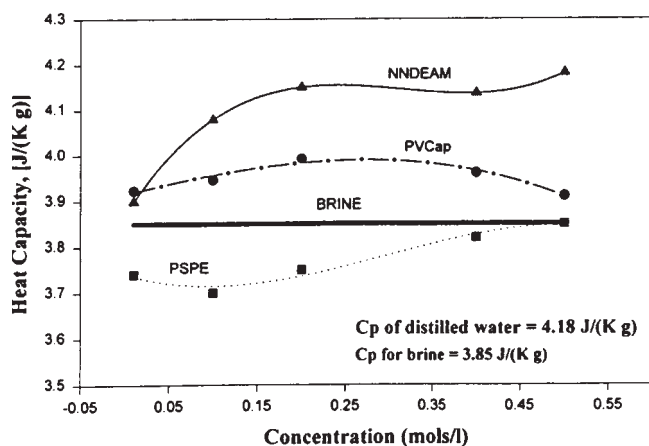


Figure 9 C_p 's of dilute polymer solutions measured as a function of concentration.

where R is the ratio of brine with respect to dry polymer weight and W_2 is the weight of the polymer. The partial specific heat capacity (C_{p1}) thus calculated for brine for this region was about $4.1 \text{ J K}^{-1} \text{ g}^{-1}$. This could be compared to the C_p of pure brine, which was $3.85 \text{ J K}^{-1} \text{ g}^{-1}$ at the same temperature, and was obtained by the same isothermal modulation technique. The higher C_p of brine in the presence of PVP indicated that in the liquid state, some additional configurational contributions to C_p were present in the system. It is known that presence of hydrophobicity in polymers results in an increase in C_p , as configurational contributions increase beyond those present in water.^{16,17} A five-member ring in the pendant group of PVP has both hydrophilic ($-\text{C}=\text{O}$ group) and hydrophobic characteristics. Hydrophilicity would result in a decrease in the C_p of brine, whereas hydrophobicity would increase it. Because the C_p of brine was indeed increased in the presence of PVP, we concluded that the hydrophobic effect of PVP dominated in this system and was given by the excess C_p over that of brine.

- The stepwise changes in C_p between R values of 0 and 1 indicated that with increasing content of brine, hydration probably occurred in steps. Such a step hydration process has been shown to exist in the case of biological polymers.¹¹
- The break at about $R = 1$ from a nonlinear to a linear response corresponded to a value of about 5 mol of brine/mol of polymer repeat units. This was the same as that calculated from the bound water analysis method described previously. Hence, up to $R = 1$, the mobility of water was greatly affected by the polymer. A detailed evaluation of the structure and mobility of absorbed brine (NFBW) in these systems could be obtained if the C_p of polymer is known. We expect that if NFBW is truly immo-

bilized, its contribution to the total C_p would be close to that of ice. This analysis was not attempted in this study as the purpose of these measurements was to probe only the effect of polymer on the freezable bound water. A brief description of the state of the system at various values of R will help understand the results further, and this will be the subject of a separate publication.

C_p of dilute solutions of PDEAM, PVCap, and PSPE in brine

C_p measurements for dilute polymer solutions with different concentrations (0.01–0.5 mol/L of water) were also carried out at 283 K. This system was different than the system described previously, where the polymer was the continuous phase. The experimental data for the dilute solution C_p 's are plotted in Figure 9. These measurements were more realistic of the dilute solution form, in which these polymers find applications as hydrate inhibitors. The total measured C_p of the solution for PDEAM and PVCap was always higher than that of pure brine regardless of the concentration. A higher C_p is an indication of hydrophobicity.^{16,17} [For very dilute solutions (0.01 mol/L and possibly 0.1 mol/L), the measured C_p 's were considered to be representative of C_p of brine, but for higher concentrations, the partial molar C_p of brine needed to be considered as was done for the system described previously.] These two polymers had very good flow loop performance (see Fig. 7). For the poor performer, PSPE, the C_p 's were consistently lower than that of brine and, thus, indicated that hydrophilicity dominated in this system. Thus, hydrophobicity could be distinguished from hydrophilicity with C_p 's as has been done for many other polymers. For a polymer to be a good performer as a hydrate inhibitor, the presence of hydrophobicity appears to be a necessary condition.

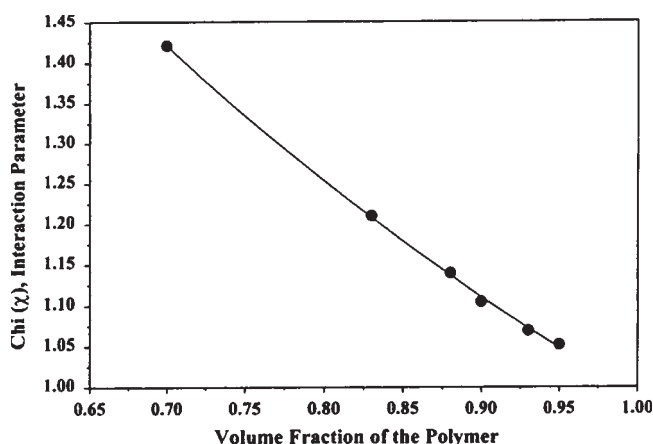


Figure 10 Thermodynamic χ for PVP (molecular weight = 10,000) and sea water as a function of concentration.

TABLE III
Thermodynamic Data and Inhibitor Performance

Polymer	ΔH_{demix} (J K ⁻¹ mol ⁻¹)	LCST [DSC/visual (°C)]	Miniloop subcooling (°F)
Acrylamides			
PACAM	16.3	21.6/NA	6.0
NEAM	34.2	23.6/48.0	12.5
NNDEAM	179.0	21.0/23.0	21.5
NIPAM	467.3	21.5/21.0	19.0
Cyclic lactams			
PVP	16.0	48.0/>100	12.7
PVCap	154.0	26.0/33.0	21.0
N-vinyl amides			
VIMA	17.0	12, 20, 41/>100	12.5
VIMA/VCap	40.0	34.5/100	29.0
VIMA/IPMA	230.7	42.5/44	31.0

NA = not applicable; NEAM = poly(*N*-ethylacrylamide); NNDEAM = poly(*N,N*-diethylacrylamide); NIPAM = polyisopropylacrylamide.

χ for dialyzed PVP in brine

χ for dilute solutions of dialyzed PVP in brine was obtained with a Flory–Huggins analysis of the depression in melting point of ice grown from dilute polymer solutions.¹⁹ The endotherms corresponding to the phase transition of ice to water were obtained at slow heating rate of 1°C/min. The data for χ as a function of volume fraction are plotted in Figure 10. χ is a measure of interactions between a polymer and the solvent (brine) and is a probe for the determination of solvent quality. A positive χ that decreased with concentration was obtained for PVP. χ was expected to be positive as long as there were no specific bonds being formed between the two components and was usually found to be close to 1. Specific interactions, such as hydrogen bonds or donor–acceptor links between polymer and brine, would lead to a negative χ . On the basis of a positive value for χ obtained for PVP, it was clear that no such hydrophilic interactions were predominant in the PVP solutions. For PSPE, χ was shown to be negative.⁹ Thus, the measurement of χ was another way for us to distinguish between hydrophobic and hydrophilic interactions, but this was limited to polymers with narrow molecular weight distributions. In addition, χ also varied with temperature and changes in phase composition during melting, and this also contributed to the uncertainty in its evaluation. This study was limited to dialyzed PVP solutions as almost all of the other polymers and copolymers synthesized had molecular heterogeneity.

ΔH_{demix} and LCST

The polymers used as inhibitors were unique as they all exhibited a LCST. This is the temperature at which the polymer phase separates on heating from a single-phase solution. The thermodynamics and phase behavior of dilute solutions have been well documented in the literature.^{19,21,22} LCST for polymers results from

a balance between hydrogen bonding and hydrophobic effects in aqueous solutions of water and polymers.²² When the temperature of a dilute polymer solution is raised, increasingly unfavorable entropic contributions to the free energy of mixing arise. Eventually, these overcome the favorable enthalpy changes associated with hydrogen bonds between the polymer and water, and the polymer phase separates. This phenomenon of phase separation is accompanied by absorption of heat. With a DSC, both LCST and ΔH_{demix} can, thus, be conveniently and accurately measured. Through the changes in LCST and ΔH_{demix} , one can, thus, probe the hydrophobic–hydrophilic effects of a polymer. In addition, it was reported in the literature that calorimetry²² can also quantify the effects of cosolvents on these phase transitions. In this study, we analyzed the effects of methanol and salinity on both LCST and ΔH_{demix} and these results are also discussed.

LCST and ΔH_{demix} measurements for dilute polymer solutions

The thermodynamics of phase behavior of the dilute polymer solutions in sea water were measured on

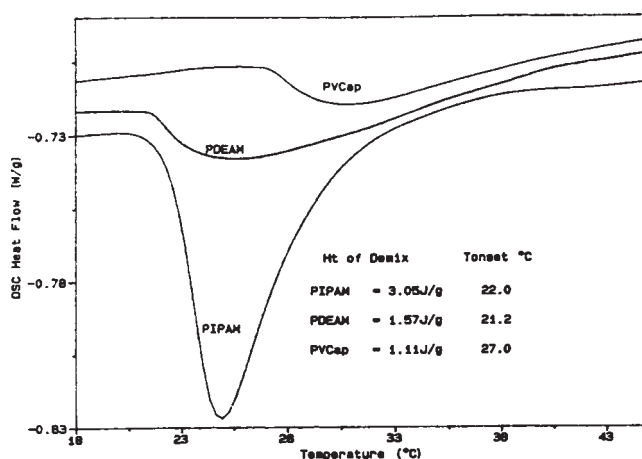


Figure 11 ΔH_{demix} and LCST for inhibitors at a concentration of 0.5 mol/L. (Tonset = onset of demixity.)

heating for a large number of polymers and copolymers. The thermodynamic data and inhibitor performance are given in Table III for selected families of polymers. The calorimetric LCST data were much more precise than the cloud-point temperatures obtained visually. Figure 11 shows the change in ΔH_{demix} for polymers that performed well as hydrate inhibitors. For the lactam-containing polymers and copolymers, an increase in the ring size resulted in an increase in ΔH_{demix} . Similar to the cyclic lactams, high values of ΔH_{demix} for PACAMs and *N*-vinyl amides were associated with higher hydrophobicity and indicated better performance (Table III). There were, however, many other copolymers (e.g., DMAM/maleimide series) and polymers [e.g., NMAM, poly(ethylene oxalate) (PEOx)] that showed small, multiple endothermic peaks. A possible explanation for these multiple peaks was the compositional inhomogeneity in the copolymers and polydispersity in case of homopolymers. The sensitivity of the measurements was half as good as a micro-DSC as the heat of fusion obtained with DSC were about half than that from a micro-DSC.

The endothermic change during demixing was attributed to the breaking of the polymer–water hydrogen bonds only.²³ It was, therefore, surprising to see an increase in ΔH_{demix} due to an increase in the hydrophobicity in PACAMs and the lactam polymers. It was possible that an increase in hydrophobicity increased the charge on the carbonyl oxygen present in the pendant group. It appeared that, like bound water, ΔH_{demix} also contained contributions from both hydrophilicity and hydrophobicity and could be defined as follows:

$$\Delta H_{\text{demix}} \propto \text{Hydrogen bond strength} + \text{Hydrophobicity}$$

Because polymers with large ΔH_{demix} adsorbed easily on the growing hydrate surface, they performed better as hydrate inhibitors.

Effect of salinity on LCST and ΔH_{demix}

ΔH_{demix} was also measured for polymers such as PDEAM, PVCap, PIPAM, and poly(*N*-methyl-*N*-vinylacetamide) (VIMA)–IPMA in distilled water to explore the nature of bonding between water and the polymers. Higher ΔH_{demix} and LCST were obtained in distilled water when compared to brine. The data for ΔH_{demix} and LCST were as follows: PDEAM = 364.4 J/g and 29.1°C, PIPAM = 350.2 J/g and 31.7°C, PVCap = 219.4 J/g and 32.6°C, and VIMA–IPMA = 256 J/g and 42.5°C. All the polymers were, thus, more soluble in distilled water and had a much higher interaction energy compared to their solutions in brine. An enhanced solubility of PIPAM was reported in the presence of charged surfactants,²⁴ and this was attributed to the surfactant creating a charged electrostatic barrier that opposed polymer collapse and aggrega-

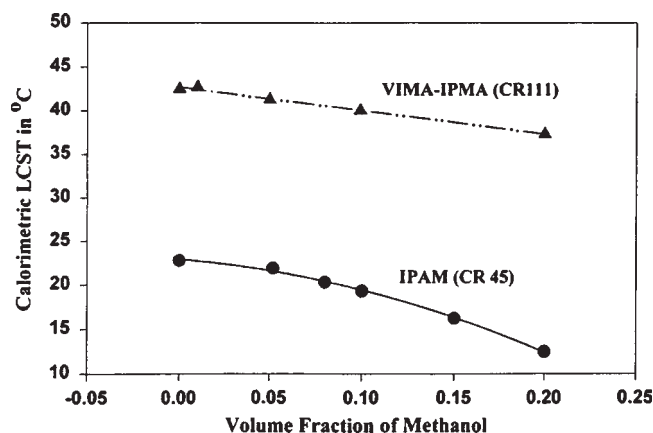


Figure 12 Effect of methanol on the LCST of IPAM and VIMA–IPMA copolymers as a function of concentration.

tion. We observed just the reverse of this phenomenon (the addition of salt decreased ΔH_{demix} and LCST). It was, therefore, possible that addition of salt only caused a decrease in the number of polymer–water contacts. Because fewer water molecules were available in a brine solution to hydrogen bond with polymer, ΔH_{demix} was lower, and the polymer precipitated earlier. As salinity increased, the solvent became poorer for the polymer, and polymer adsorption to the hydrate surface was, thus, favored.

Effect of methanol on LCST and ΔH_{demix} . Figure 12 shows the effect of methanol on the LCST of VIMA–IPMA copolymer. This copolymer was one of the best hydrate inhibitors with a subcooling close to 30°F. In the field trials of this candidate, it is important to know the effect of methanol on the phase behavior. This is because methanol used as a thermodynamic inhibitor will be gradually replaced with a polymer solution to determine the efficacy of kinetic inhibition. The addition of incremental amounts of methanol reduced the LCST and ΔH_{demix} . Water–methanol interactions reduced water–polymer interactions.²² As polymer–water hydrogen bonds were reduced, the polymer precipitated at a lower temperature.

CONCLUSIONS

Thermal analysis provided insights into polymer–water interactions. Relationships were established between the chemical structure and thermodynamic properties for series of polymers, acrylamides, cyclic lactams, *n*-vinyl amides, and so on. Thermodynamic studies of the polymer solutions were also used to evaluate the relationships between polymer solubility and inhibition activity of the polymers. The phenomenon of hydrophobic hydration and the role of hydrophobicity appeared to be critical factors in the control of the polymer activity in water. Water–polymer interactions were quantified through bound water,

C_p , and ΔH_{demix} measurements. NFBW depended on the chemical structure. Within a family of polymers, bound water increased with increasing hydrophobicity of the polymer, and a balance of hydrophobicity and hydrophilicity was also critical for optimum interactions. This parameter appeared to correlate reasonably well with the flow measurement data for gas hydrate inhibition regardless of the family of polymers. For a polymer to perform well as an inhibitor for gas hydrate formation, it needed to possess at least 5 mol of NFBW/mol of polymer repeat units. It was also shown through C_p measurements that although a balance of hydrophobicity and hydrophilicity is a must, the driving force for good performance was hydrophobicity. The phase behavior of dilute solutions explored the phenomenon of LCST and the corresponding heat absorbed to cause precipitation of the polymers from the solution. A large ΔH_{demix} was observed for polymers that showed better performance as inhibitors. The solubility of the polymers was changed with the salinity of the solution, and an increase in salinity lowered both LCST and ΔH_{demix} .

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