



Phase equilibria for petroleum reservoir fluids containing water and aqueous methanol solutions: Experimental measurements and modelling using the CPA equation of state

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ABSTRACT

Thermodynamic inhibitors, such as methanol, are widely used to reduce the risks associated with gas hydrate formation. The work presented in this communication is the result of a study on the phase equilibria of petroleum reservoir fluids in the presence of aqueous methanol solutions. Experimental hydrate dissociation data, for systems composed of methane/water/methanol and natural gas/water/methanol, in addition to experimental freezing point depression data for aqueous methanol solutions, are reported. A statistical thermodynamic approach, with the cubic-plus-association equation of state (CPA-EoS), is employed to model the phase equilibria. The hydrate-forming conditions are modelled by the solid solution theory of van der Waals and Platteeuw. The thermodynamic model was used to predict the hydrate dissociation conditions of methane and natural gases in the presence of distilled water or methanol aqueous solutions. Predictions of the developed model are validated against independent experimental data and the data generated in this work. A good agreement between predictions and experimental data is observed, supporting the reliability of the developed model.

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1. Introduction

Formation of gas hydrates can lead to serious operational, economic and safety problems in the petroleum industry due to potential blockage of oil and gas equipment [1]. Current industry practice for hydrate prevention is injecting hydrate inhibitors at the upstream end of pipelines based on the calculated/measured hydrate phase boundary, water cut, worst pressure and temperature conditions, and the amount of inhibitor lost to non-aqueous phases. Amongst alcohols, methanol has historically been the most popular inhibitor, due to its cost and its effectiveness (weight basis) for the prevention of hydrate formation [1]. Methanol is probably one of the most versatile solvents in the chemical and petroleum industry, used in many areas such as, gas sweetening units, gas hydrate inhibition in offshore/arctic drilling operations and in oil/gas pipelines. The most significant drawback of methanol is its high losses in hydrocarbon phases. Depending on operating conditions, solubility loss of methanol into the sales gas can be very high and loss to the liquid hydrocarbon phase can also be important. Therefore, it is of practical significance to study the thermodynamic equilibria of

hydrocarbon systems in the presence of methanol over a wide range of temperatures and pressures.

In this communication, new experimental measurement of the locus of incipient hydrate–liquid water–vapour (H–L_W–V) curve for systems containing methane or natural gases in the presence of aqueous solution of methanol over a wide range of concentrations, pressures and temperatures are presented. Furthermore, new experimental data on the freezing point depressions of water in the presence of various concentrations of methanol are presented.

A thermodynamic model using the well-proven cubic-plus-association equation of state (CPA-EoS) [2] has been employed to model the phase equilibria. The thermodynamic model is based on uniformity of fugacity of each component throughout all the phases. The hydrate phase is modelled by the solid solution theory of van der Waals and Platteeuw [3] using the previously reported Kihara potential parameters [4]. Good agreement between experimental data and predictions is observed supporting the reliability of the developed model.

2. Experimental

2.1. Materials

Methanol used in experiments was 99.5%+ pure, supplied by Sigma–Aldrich. Ultra high purity grade methane gas (99.995% pure)

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Table 1
Composition of natural gases (NG1 and NG2) used in the tests reported in this work.

Component	NG1 (mol%)	NG2 (mol%)
C ₁	88.3	89.35
C ₂	5.40	5.15
C ₃	1.50	1.38
iC ₄	0.20	0.17
nC ₄	0.30	0.23
iC ₅	0.10	0.07
nC ₅	0.09	0.06
N ₂	2.39	1.14
CO ₂	1.72	2.45
Total	100.00	100.00

supplied by BOC was used. Two natural gases (compositions given in Table 1) as supplied by BOC, were used. All solutions were prepared using deionized water. Aqueous solutions of methanol used in this work were prepared gravimetrically in this laboratory.

2.2. Atmospheric experimental apparatus and procedures

Freezing point measurements at atmospheric pressure were made using an apparatus and method developed at Heriot-Watt University [5]. A detailed description of the apparatus and test procedure can be found elsewhere [6]. For each system, the freezing points were measured at least three times to check the repeatability and consistency. The final freezing point of the aqueous solution is taken as the average of all the runs.

2.3. High pressure experimental apparatus and procedures

Dissociation point measurements were conducted using the isochoric step-heating method developed in this laboratory, which has been previously demonstrated as being considerably more reliable and repeatable than conventional continuous heating and/or visual techniques [7]. A detailed description of the apparatus and test procedure can be found elsewhere [8]. In this work, new experimental hydrate dissociation data for various systems consisting of methane/water/methanol and natural gas/water/methanol were measured over a wide range of aqueous methanol concentration (forms 10–60 mass%) concentration and pressure up to 40 MPa.

3. Thermodynamic modelling

For a system at equilibrium, from a thermodynamic view-point, the criterion for phase equilibrium is the equality of chemical potentials of each component in all coexisting phases. For an isothermal system this will reduce to the equality of fugacity of each component in different phases. The fugacity of each compo-

Table 3
Vapour liquid data for the methane–methanol binary system.

Reference	Year of publication	Type of data	T (K)	P (MPa)	No. of points
Methane–methanol					
Krichevsky and Koroleva [21]	1941	PTy	273.15–348.15	2.5–70	38
Shenderei et al. [22]	1961	PTx	213.15–248.15	0.1 (atm)	4
Hemmaphardh and King [23]	1972	PTy	288.15–333.15	3.61–6.46	27
Yaacobi and Ben-Naim [24]	1974	PTx	283.15–303.15	0.1 (atm)	5
Schneider [25]	1978	PTx	273.15–323.15	0.0004–10.3	17
Lazalde-Crabtree et al. [26]	1980	PTy	227.55–273.15	4.14–5.681	5
Francesconi et al. [27]	1981	PTy and PTx	282.45–566.65	24–208	115
Yarym-Agaev et al. [28]	1985	PTxy	298.15–338.15	2.5–12.5	15
Brunner et al. [29]	1987	PTx and PTy	298.15–373.15	3–105.1	78
Hong et al. [30]	1987	PTxy	220–330	1.38–41.37	83
Schlichting et al. [31]	1993	PTy	242.15–283.15	2.0–10.0	17
Ukai et al. [32]	2002	PTx	280.15	2.112–6.027	9
Wang et al. [33]	2003	PTx	283.15–303.15	5–40	24

Table 2
CPA parameters for the associating compounds considered in this work [10].

	a_0 (bar L ² mol ⁻²)	b (L/mol)	c_1	ε (bar L mol ⁻¹)	β ($\times 10^3$)
Water	1.228	0.01452	0.6736	166.55	69.2
Methanol	4.053	0.03098	0.4310	245.91	16.1

nent has been calculated by the well-proven cubic-plus-association equation of state [2]. The CPA-EoS combines the well-known Soave-Redlich-Kwong (SRK) EoS for describing the physical interactions with the Wertheim's first-order perturbation theory, which can be applied to different types of hydrogen-bonding compounds. CPA-EoS has been shown in the past to be a successful model for phase equilibria calculations for systems containing water, hydrocarbons glycols and alcohols [2,8,9]. A detailed description of the thermodynamic model used in this work can be found elsewhere [8,9]. In summary, the statistical thermodynamics model uses the CPA-EoS and classical mixing rules for fugacity calculations in all fluid phases. The CPA-EoS in terms of pressure P is given by Kontogeorgis et al. [10]:

$$P = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b)} - \frac{1}{2} \frac{RT}{V_m} \left(1 + \rho \frac{\partial \ln(g)}{\partial \rho} \right) \sum_i x_i \sum_{A_i} (1 - X^{A_i}) \quad (1)$$

where the physical term is that of the SRK-EoS and the association term is taken from the SAFT-EoS [11]. $a(T)$ is the energy parameter, b the co-volume parameter (assumed to be temperature independent, in agreement with most published equations of state), ρ is the molar density of the fluid, g the simplified expression of the radial distribution function as suggested by Kontogeorgis et al. [10], X^{A_i} the mole fraction of pure component i not bonded at site A , and x_i is the mole fraction of component i .

Based on the fact that the association term depends on the number and type of association sites for the associating compound, for a highly hydrogen-bonded substances like water a four-site (4C) association scheme was adopted since it is considered that hydrogen bonding occurs between the two hydrogen atoms and the two lone pairs of electrons in the oxygen atom of water molecules. For alcohols, the two-site (2B) or the three-site (3B) association schemes may be applied. The results from Huang et al. [11] and from Kontogeorgis et al. [12] suggest the use of the two-site association scheme for methanol, which proposes that hydrogen bonding occurs between the hydroxyl hydrogen and one of the lone pairs of electrons from the oxygen atom in another alcohol molecule. The CPA-EoS pure compound parameters for associating compounds, used for fugacity calculations in this paper, have been obtained by Kontogeorgis et al. [10], and are listed in Table 2.

Table 4
Vapour liquid data for the ethane–methanol binary system.

Reference	Year of publication	Type of data	T (K)	P (MPa)	No. of points
Ethane–methanol					
McDaniel [34]	1911	PTx	295.65–318.35	0.1 (atm)	4
Ma and Kohn [35]	1964	PTxy	248.15–373.15	1.013–6.08	30
Hemmaplardh and King [23]	1972	PTy	288.15–333.15	1.196–3.506	22
Yaacobi and Ben-Naim [24]	1974	PTx	283.15–303.15	0.1 (atm)	5
Ohgaki et al. [36]	1976	PTxy	298.15	1.094–4.125	5
Lazalde-Crabtree et al. [26]	1980	PTy	267.15–278.15	1.911–2.204	4
Brunner [37]	1985	Critical curves	250.85–512.64	3.7–17.9	25
Zeck and Knapp [38]	1985	PTx	240–298.15	0.41–4.195	38
Lam and Luks [39]	1991	PTx	263.15–303.15	1.825–4.488	18
Ishihara et al. [40]	1998	PTxy	298.15	0.97–6.77	11
Wang et al. [33]	2003	PTx	283.2–303.2	0.5–3	20
Ruffine et al. [41]	2005	PTx	273.15	0.174–2.323	10

Table 5
Vapour liquid data for the propane–methanol binary system.

Reference	Year of publication	Type of data	T (K)	P (MPa)	No. of points
Propane–methanol					
Nagahama et al. [42]	1971	PTx	293.15	0.2705–0.8045	11
Brunner [37]	1985	Critical curves	370–512.6	4.2–8.7	25
Galivel-Solastiouk et al. [43]	1986	PTxy	313.1–373.1	0.35–4.28	32
Leu et al. [44]	1992	PTxy	310.07–352.2	0.032–3.173	24
Ma and Xu [45]	1993	PTx	273.15–298.15	0.1 (atm)	6
Yonker et al. [46]	1998	PTxy	394.15	1.2–6	20

Table 6
Vapour liquid data for the *n*-butane–methanol binary system, and the *i*-butane–methanol binary system.

Reference	Year of publication	Type of data	T (K)	P (MPa)	No. of points
<i>n</i> -Butane–methanol					
Kretschmer and Wiebe [47]	1952	PTx	298.15–323.15	0.05–0.102	12
Petty and Smith [48]	1955	PTy	322.04–410.93	0.103–3.544	29
Miyano and Hayduk [49]	1986	PTx	283.15–313.15	0.1 (atm)	4
Leu et al. [44]	1992	PTxy	469.9	3.787–6.917	7
Ma and Xu [45]	1993	PTx	298.15–323.15	0.1 (atm)	8
<i>i</i> -Butane–methanol					
Kretschmer and Wiebe [47]	1952	PTx	298.15–323.15	0.04–0.102	12
Leu and Robinson [44]	1992	PTx	273.15–373.15	0.004–2.0	49
Ma and Xu [45]	1993	PTx	298.15–323.15	0.1 (atm)	8

The pure component energy parameter of CPA is given by a Soave-type temperature dependency:

$$a(T) = a_0 \left[1 + C_1 \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (2)$$

where T_c is the experimental critical temperature.

The extension of the CPA-EoS to mixtures containing multi-associating compounds requires mixing rules only for parameters of the SRK-EoS part. When the CPA-EoS is used for mixtures, the SRK part requires the conventional van der Waals one-fluid mixing rules for b and $a(T)$, while the association part requires only combining rules for association energy and volume parameters.

The arithmetic mean for the cross-association energy and the geometric mean for the cross-association volume have been applied to calculate the association energy and volume parameters between different associating molecules [13]. More details of the model have been previously presented [9].

For modelling the ice phase, the fugacity of a pure solid (as for a supersaturated pure liquid) has been calculated using the Poynting correction [14,15]. More details about ice phase modelling in this work can be found elsewhere [6]. The hydrate phase is modelled using the solid solution theory of van der Waals and Platteeuw [3], as developed by Parrish and Prausnitz [16]. The equation recommended by Holder et al. [17] is used to calculate the heat capacity difference between the empty hydrate lattice and pure liquid water.

Table 7
Vapour liquid data for the nitrogen–methanol binary system.

Reference	Year of publication	Type of data	T (K)	P (MPa)	No. of points
Nitrogen–methanol					
Krichevskii and Ilinskaya [50]	1945	PTy	273.15–348.15	0.004–70.928	41
Kretschmer et al. [51]	1946	PTx	248.15–323.15	0.007–0.05	4
Krichevskii and Lebedewa [52]	1947	PTx	273.15–348.15	4.904–29.485	21
Hemmaplardh and King [23]	1972	PTy	288.15–333.15	2.938–6.363	28
Lazalde-Cabtree et al. [26]	1980	PTy	227.55–283.15	3.84–6.12	7
Weber et al. [53]	1984	PTxy	223.15–300	2.1–17.93	29
Brunner et al. [29]	1987	PTy and PTx	298.15–373.15	2.635–100	55
Schlichting et al. [31]	1993	PTy	241.15–282.15	1.0–11.5	34
Laursen and Andersen [54]	2002	PTy and PTx	298.15–318.15	4.6–10.1	24

Table 8
Vapour liquid data for the carbon dioxide–methanol binary system.

Reference	Year of publication	Type of data	T (K)	P (MPa)	No. of points
Carbon dioxide–methanol					
Kunerth [55]	1922	PTx	291.15–309.15	0.1 (atm)	10
Krichevsky and Koroleva [21]	1941	PTy	298.15–348.15	0.004–70.928	19
Krichevskii and Lebedeva [52]	1947	PTx	273.15–348.15	6.9–697	27
Bezdel and Teodorovich [56]	1958	PTx	223.15–348.15	0.1–3.04	50
Shenderei et al. [22]	1958	PTx	194.45–273.15	0.01–0.1	28
Shenderei et al. [57]	1959	PTx	213.15–247.15	0.1–1.62	31
Usyukin and Shleinikov [58]	1963	PTx	203.15–273.15	0.1 (atm)	10
Yorizane et al. [59]	1969	PTx	243.15–273.15	0.4–3.3	21
Katayama et al. [60]	1975	PTxy	298.15	0.219–6.128	13
Ohgaki and Katayama [61]	1976	PTx	298.15–313.15	0.6–8.06	17
Semenova et al. [62]	1979	PTxy	323.15–398.15	0.5–18.5	70
Weber et al. [53]	1984	PTx	233.15–298.15	0.3–5.1	59
Brunner et al. [29]	1987	PTxy	241.8–282.9	0.4–3.5	16
Hong and Kobayashi [63]	1988	PTxy	230–330	0.69–10.65	64
Schroedter et al. [64]	1991	PTx	260–298.2	0.2–5.5	38
Leu et al. [65]	1991	PTxy	323.2–477.6	0.0558–12.75	40
Yoon et al. [66]	1993	PTxy	313.2	0.7–8.21	13
Schlichting et al. [31]	1993	PTy	241.15–283.15	0.4–3.6	16
Page et al. [67]	1991	PTxy	333.15–393.15	9.3–15.3	67
Reighard et al. [68]	1996	PTx	298.25–373.05	1.54–15.55	70
Chang et al. [69]	1997	PTxy	291.15–313.14	0.56–8.03	75
Chiehming et al. [70]	1998	PTxy	291.15–313.15	5.6–7.22	77
Elbaccouch et al. [71]	2000	PTxy	312.95–313.05	1.139–7.534	11
Joung et al. [72]	2001	PTxy	313.15–342.8	0.67–7.37	60
Bezanehtak et al. [73]	2002	PTxy	278.15–308.15	1.5–7.43	34
Zhu et al. [74]	2002	PTxy	323.15–473.15	6–16.2	25
Laursen et al. [75]	2002	PTxy	298.15–313.15	1.24–6.34	16
Xia et al. [76]	2004	PTx	313.75–395	0.3–9.7	29

The Kihara model for spherical molecules is applied to calculate the potential function for compounds forming hydrate phases [4]. Kihara potential parameters for hydrate formers are taken from Tohidi-Kalorazi [18]. More details about hydrate modelling used in this work can be found elsewhere [8].

4. Results and discussions

4.1. Application of the CPA-EoS to self-associating systems

For a binary mixture that contains a self-associating (water or methanol) and a non-associating compound (methane, ethane, propane, ...), the binary interaction parameter k_{ij} is the only adjustable parameter and no combining rules are required for the association energy and volume. For estimating the k_{ij} parameters the following objective function was employed:

$$OF = \sum_i^{NP} \left(\frac{x_i^{\text{calc}} - x_i^{\text{exp}}}{x_i^{\text{exp}}} \right)^2 \quad (3)$$

Experimental data related to water/methanol content in gases are rare and often associated with errors, as a review of data sets measured at same temperature and pressure conditions indicated [8]. This is partly due to the fact that water/methanol content in vapour phase is difficult to measure. However, measuring gas solubility in water/methanol is easier than measuring the water/methanol content of gases. Due to this fact, the gas solubility in water/methanol was employed for tuning the binary interaction parameters (BIPs) between natural gas components and water, and natural gas components and methanol.

In a previous work, for each binary system of water, a temperature-dependent binary interaction parameter was introduced and tuned to provide a good description of experimental data. The available data from the literature used for tuning the binary interaction parameters between each of non-associating compounds and water were gathered and presented previously

[19]. Tables 3–8 show the references of the reported measurements for each of non-associating compounds solubility in methanol available in the open literature. By minimizing the average absolute deviations in the solubility, the following simple expression has been established for binary system of methanol:

$$k_{ij} = A + B \times T \quad (4)$$

where A and B are two constants and T is the temperature in Kelvin. The optimized interaction parameters are presented in Table 9 (BIPs between hydrocarbons heavier than butane and methanol have been set to zero). The validation of the model for binaries with water has been presented elsewhere by the inclusion of a suitable binary interaction parameter [8]. Figs. 1 and 2 present the results of the CPA modelling for predicting the solubility of methane/propane/nitrogen/carbon dioxide in methanol and the methanol content in the gas phase, respectively. As methane is the major component of natural gas (about 87% by mole), a methane system is chosen as a key system for predicting the concentrations of methanol in vapour phase in natural gas systems, where the loss of methanol could be an issue of economical importance. The model predictions (Fig. 2) are in an excellent agreement with the experimental data, demonstrating the reliability of the developed model.

Table 9
The optimized values for interaction parameters between each of the non-associating compounds and methanol (used in Eq. (4)).

	A	B
Methane	0.04869	0
Ethane	−0.02398	0.00018
Propane	−0.04571	0.00031
iso-Butane	−0.22227	0.00073
n-Butane	0.29791	−0.00092
Carbon dioxide	0.08676	−0.00028
Nitrogen	0.17438	−0.00073

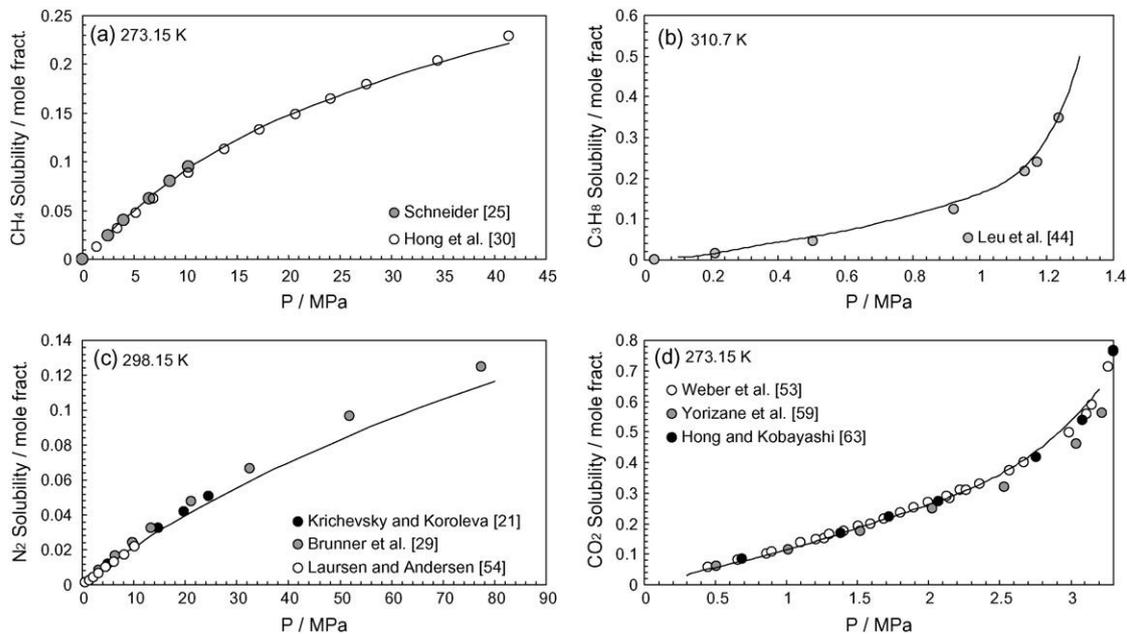


Fig. 1. Experimental and calculated solubility of methane (a), propane (b), nitrogen (c) and carbon dioxide (d) in methanol.

4.2. Application of the CPA-EoS to cross-associating systems

Following the tuning of BIPs between each non-associating compound and water or methanol the capability of the CPA-EoS to describe VLE of methanol–water mixtures over an extended temperature and pressure range using a temperature-dependent interaction parameter has been studied.

As tested by other researchers [20] and examined in our previous work on modelling of MEG and water [9], the use of vapour liquid equilibrium data and ice point data in the presence of inhibitor aqueous solutions for tuning the model can lead to successful predictions of hydrate phase boundaries [9]. The experimental VLE binary data of water and methanol reported in Table 10, (with the exception of the data of Dalager et al. [82], Kato et al. [83,84], Maripuri and Ratcliff [85] and Kuyhara et al. [90], which were kept as independent data for validation of the model), and the ice-liquid equilibrium conditions (using the melting point data reported in the CRC Handbook) were used for tuning the binary interaction param-

eters between water and methanol in the range of 190 K to 373 K using the following objective function.

$$OF = \begin{cases} \sum_i^{NP} \left(\frac{p_i^{\text{calc}} - p_i^{\text{exp}}}{p_i^{\text{exp}}} \right)^2, & \text{for VLE data} \\ \sum_i^{NP} \left(\frac{T_i^{\text{calc}} - T_i^{\text{exp}}}{T_i^{\text{exp}}} \right)^2, & \text{for SLE data} \end{cases} \quad (5)$$

The following expression is proposed for methanol and water:

$$k_{ij} = 3.4463 \times 10^{-6} T^2 - 9.5986 \times 10^{-4} T - 0.1197 \quad (6)$$

The new experimental freezing point depressions of water in the presence of various concentrations of methanol measured in the present study, as well as the average deviation between runs are tabulated in Table 11 and kept as independent data for validation of the model. Both VLE and SLE phase equilibria calculations for

Table 10

Vapour Liquid equilibrium data for the water–methanol binary system (BP: bubble point, DP: dew point and FP: freezing point).

Reference	Year of publication	Type of data	T (K)	P (MPa)	N.pts
Water–methanol					
Washburn [77]	1930	FP	217–266	0.1 (atm)	7
Feldman and Dahlstrom [78]	1936	FP	233–266	0.1 (atm)	6
Frank et al. [79]	1940	FP	217–263	0.1 (atm)	7
Gristvold and Buford [80]	1949	BP	340.95–364.25	0.1 (atm)	8
Ross [81]	1954	FP	188–266	0.1 (atm)	8
Dalager [82]	1969	BP and DP	337.85–373.15	0.1 (atm)	26
Kato et al. [83]	1970	BP and DP	337.15–373.15	0.1 (atm)	24
Kato et al. [84]	1970	BP	339.15–368.15	0.1 (atm)	10
Maripuri and Ratcliff [85]	1972	BP and DP	338.8–370.0	0.1 (atm)	16
McGlashan and Williamson [86]	1976	BP	308.15–338.15	0.006–0.1	39
Ott et al. [87]	1979	FP	157–273	0.1 (atm)	30
Ochi and Kojima [88]	1987	BP	371.15–373.15	0.1 (atm)	20
Pushin and Glagoleva [89]	1992	FP	177–260	0.1 (atm)	15
Kurihara et al. [90]	1995	BP and DP	323.15–333.15	0.03–0.07	50
Green and Venek [91]	1995	BP	291.15	0.1 (atm)	11
Khilfaoui et al. [92]	1997	BP and DP	337.15–373.15	0.1 (atm)	12
Christensen [93]	1998	BP and DP	333.15–373.15	0.02–0.1	5
Yao et al. [94]	1999	BP and DP	318.15	0.01–0.04	11
Lide [95]	2004	FP	176–272	0.1 (atm)	57

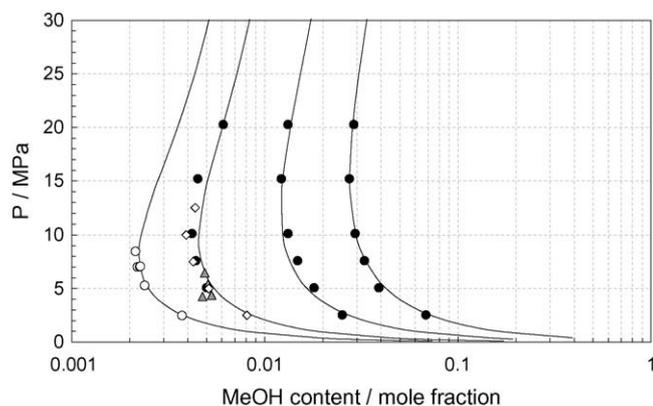


Fig. 2. Experimental and predicted methanol content in the gas phase of the methane–methanol system. Experimental data at 348.15 K and 323.15 K from Krichevsky and Koroleva (●) [21]. Experimental data at 298.15 K from Krichevsky and Koroleva (●) [21], Hemmaplardh and King (▲) [23] and Yarym-Agaev et al. (◇) [28]. Experimental data at 283.15 K from Schlichting et al. (○) [31].

Table 11

Experimental (this work) freezing point depressions of water in the presence of methanol aqueous solutions (σ_{exp} : average deviation between runs).

mass% of MeOH in aqueous solution	ΔT_{exp} (± 0.1 K)	σ_{exp}
5	−3.13	0.11
10	−6.56	0.10
15	−10.43	0.06
20	−14.84	0.19
25	−19.56	0.12
30	−25.13	0.21
40	−37.95	0.05

the binary cross-associating mixture of methanol and water have been performed and presented in Figs. 3 and 5. As Fig. 3 shows the model accurately calculates freezing points of water–methanol system for different concentrations of methanol. Also as demonstrated in Figs. 4 and 5, the developed model can predict accurately methanol–water vapour liquid equilibrium.

4.3. Application of the model to hydrate modelling

The model is further tested for predicting the hydrate phase boundary in systems containing methane or natural gas and methanol as hydrate inhibitor. Methane and natural gas hydrate dissociation data measured in the present study are tabulated in Tables 12 and 13, respectively.

Figs. 6 and 7 show the comparison between new methane or natural gas hydrate dissociation conditions for different concentrations of methanol as hydrate inhibitor measured in this work in addition

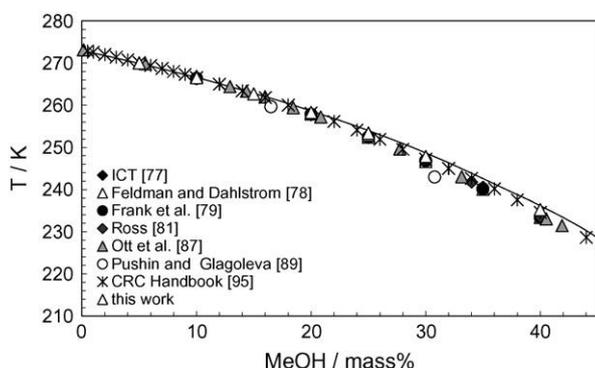


Fig. 3. Experimental and calculated water freezing point temperatures in the presence of various concentrations of methanol.

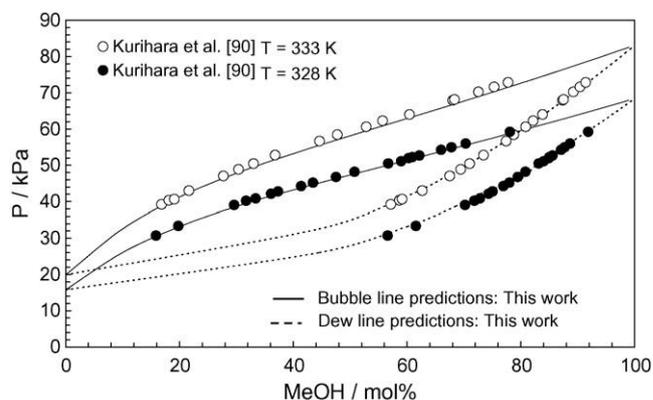


Fig. 4. Experimental and predicted methanol concentrations in vapour and liquid phases for methanol–water systems at 328.15 K and 333.15 K.

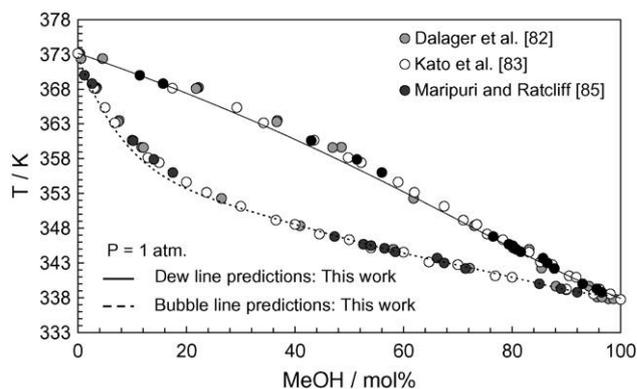


Fig. 5. Experimental and predicted methanol concentrations in vapour and liquid phases for methanol–water systems at 1 atm.

Table 12

Experimental (this work) methane hydrate dissociation conditions in the presence of methanol aqueous solutions.

Methanol		T (K) (± 0.1)	P (MPa) (± 0.008)
mass%	mol%		
10	5.878	274.21	4.378
		278.75	7.019
		282.72	10.963
		284.25	13.079
		287.05	19.305
20	12.321	266.32	3.516
		273.65	6.915
		278.45	13.190
		281.75	19.650
		261.15	3.985
30	19.413	267.35	7.584
		273.04	14.479
		274.7	18.705
		249.45	2.654
		263.85	11.411
40	27.258	267.85	19.712
		271.15	33.819
		251.45	6.819
		241.85	2.592
		239.45	4.716
60	45.744	244.35	8.577
		248.45	15.734
		253.15	33.922

Table 13

Experimental (this work) natural gas hydrate dissociation conditions in the presence of methanol aqueous solutions.

Methanol		T (K) (± 0.1)	P (MPa) (± 0.008)
mass%	mol%		
NG 1		280.75	3.806
10	5.878	285.95	7.033
		287.65	10.342
		290.2	16.651
		260.05	2.517
40	27.258	264.75	3.868
		269.45	8.363
		272.95	20.229
NG 2		275.55	36.066
60	45.744	242.55	2.021
		249.15	4.142
		253.45	8.051
		254.75	14.63
		256.55	21.031
		257.55	28.052
		258.95	36.343

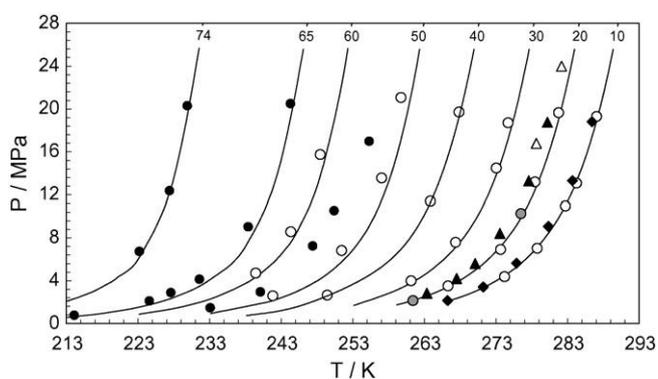


Fig. 6. Experimental and predicted methane hydrate dissociation (structure I) conditions in the presence of methanol aqueous solutions. Experimental data from Ng et al. (●) [96], Ng and Robinson (◆) [97], Blanc and Tournier-Lasserve (Δ) [98], Svartas and Fadnes (⊙) [99], and this work (○) (model predictions are independent from experimental data).

to the data from the literature up to 40 MPa and the model results using the BIPs obtained based on Eq. (6). The model predictions are seen to agree well with the experimental data (the maximum deviation between experimental data and the model is in order of ± 1 K). However, the published experimental data by Ng et al. [96] for 50 mass% of methanol in aqueous solution are consistently dis-

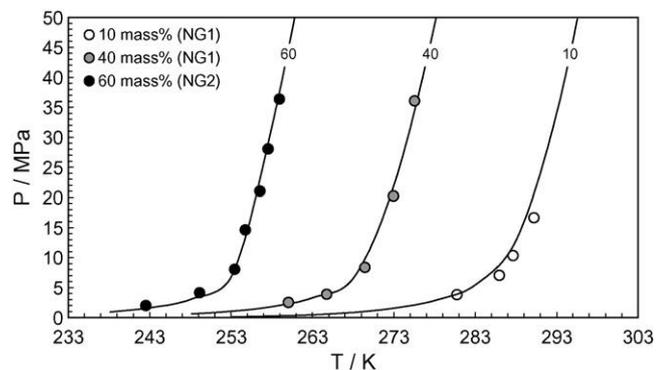


Fig. 7. Experimental (this work) and predicted hydrate dissociation conditions (structure II) for two natural gases (composition listed in Table 1) in with the presence of methanol aqueous solutions.

placed to higher pressures as compared to the experimental data from this work and predictions of the model (see Fig. 6). It should be noted that these data could be regarded as independent as hydrate dissociation data were not used in the development and optimisation of the thermodynamic model.

5. Conclusions

In this work, a thermodynamic model using the well-proven CPA-EoS has been employed and extended to model the phase equilibria of hydrocarbon systems in the presence of aqueous methanol solutions. In this work, novel experimental three-phase H-L_W-V equilibrium data for both methane and natural gas in the presence of aqueous methanol solutions for pressures between 2 and 40 MPa are presented. Furthermore, new experimental freezing point depressions of water in the presence of various concentrations of methanol are reported.

The cubic-plus-association equation of state has been applied to model multi-phase equilibria in mixtures containing water and methanol. The predictions of the developed model are compared against independent experimental data and the data generated in this work over a wide range of temperature, pressure and inhibitor concentration. A good agreement between predictions and experimental data is observed, demonstrating the reliability of the developed model. The CPA-EoS has proven to be a very successful model for multi-phase multi-component mixtures containing hydrocarbons, methanol and water.

List of symbols

a	energy parameter of the equation of state
A	molecular species
b	co-volume parameter
B	molecular species
BIP	binary interaction parameter
BP	bubble point
CPA	cubic-plus-association
DP	dew point
EoS	equation of state
FP	freezing point
g	radial distribution function
k	binary interaction parameter
MEG	ethylene glycol
MeOH	methanol
NG	natural gas
OF	objective function
P	pressure
R	universal gas constant
sI	structure I
sII	structure II
T	temperature
V	molar volume
x	mole fraction of the component
X	mole fraction of the specific molecule not bonded to the specific site

Subscripts

0	reference property
c	critical property
exp	experimental property
H	hydrate
i, j	molecular species
L	liquid state
m	mixture
V	vapour state
W	water

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References

- [1] E.D. Sloan Jr., *Clathrate Hydrates of Natural Gases*, Marcel Dekker, Inc., New York, 1998.
- [2] G.M. Kontogeorgis, M.L. Michelsen, G.K. Folas, S. Derawi, N. Von Solms, E.H. Stenby, *Ind. Eng. Chem. Res.* 45 (2006) 4855–4868.
- [3] J.H. van der Waals, J.C. Platteeuw, *Adv. Chem. Phys.* 2 (1959) 1–57.
- [4] T. Kihara, *Rev. Mod. Phys.* 25 (1953) 831–843.
- [5] R. Anderson, M. Llamedo, B. Tohidi, R.W. Burgass, *J. Phys. Chem. B* 107 (2003) 3507–3514.
- [6] H. Haghghi, A. Chapoy, B. Tohidi, *Ind. Eng. Chem. Res.* 47 (2008) 3983–3989.
- [7] B. Tohidi, R.W. Burgass, A. Danesh, A.C. Todd, K.K. Østergaard, *Ann. N. Y. Acad. Sci.* 912 (2000) 924–931.
- [8] H. Haghghi, A. Chapoy, B. Tohidi, *Oil Gas Sci. Technol.*, doi:10.2516/ogst:2008043.
- [9] H. Haghghi, A. Chapoy, B. Tohidi, *Fluid Phase Equilib.* 276 (2009) 24–30.
- [10] G.M. Kontogeorgis, I.V. Yakoumis, H. Meijer, E.M. Hendriks, T. Moorwood, *Fluid Phase Equilib.* 158 (1999) 201–209.
- [11] S.H. Huang, M. Radosz, *Ind. Eng. Chem. Res.* 29 (1990) 2284–2294.
- [12] G.M. Kontogeorgis, M.L. Michelsen, G.K. Folas, S. Derawi, N. von Solms, E.H. Stenby, *Ind. Eng. Chem. Res.* 45 (2006) 4869–4878.
- [13] S.O. Derawi, G.M. Kontogeorgis, M.L. Michelsen, E.H. Stenby, *Ind. Eng. Chem. Res.* 42 (2003) 1470–1477.
- [14] J.M. Smith, H.C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, McGraw-Hill Inc., New York, 1987.
- [15] F.E. Anderson, J.M. Prausnitz, *AIChE J.* 32 (1986) 1321–1333.
- [16] W.R. Parrish, J.M. Prausnitz, *Ind. Eng. Chem. Process Des. Dev.* 11 (1972) 26–35.
- [17] G.D. Holder, G. Corbin, K.D. Papadopoulos, *Ind. Eng. Chem. Fundam.* 19 (1980) 282–286.
- [18] B. Tohidi-Kalorazi, Ph.D. Thesis, Heriot-Watt University, 1995.
- [19] A. Chapoy, H. Haghghi, B. Tohidi, *J. Chem. Thermodyn.* 40 (2008) 1030–1037.
- [20] D. Avlonatis, A. Danesh, A.C. Todd, *Fluid Phase Equilib.* 94 (1994) 181–216.
- [21] I. Krichevsky, M. Koroleva, *Acta Physicochim. URSS* 15 (1945) 327–348.
- [22] E.R. Shenderi, Y.D. Zelvenskii, F.P. Ivanovskii, *Gazov. Prom-st* 6 (1961) 42–45.
- [23] B. Hemmaplardh, A.D. King, *J. Phys. Chem.* 76 (1972) 2170–2175.
- [24] M. Yaacobi, A. Ben-Naim, *J. Phys. Chem.* 78 (1974) 175–178.
- [25] R. Schneider, *Doktor-Ingenieur Dissertation*, TUB, Berlin, 1978.
- [26] H. Lazalde-Crabtree, G.J.F. Breedveld, J.M. Prausnitz, *AIChE J.* 26 (1980) 462–470.
- [27] A.Z. Francesconi, H. Lentz, E.U. Franck, *J. Phys. Chem.* 85 (1981) 3303–3307.
- [28] N.L. Yarym-Agaev, R.P. Sinyavskaya, I.I. Koliushko, L.Y. Levinton, *Zh. Prikl. Khim.* 58 (1985) 165–168.
- [29] E. Brunner, W. Huelten Schmidt, G. Schlichthaerle, *J. Chem. Thermodyn.* 19 (1987) 273–291.
- [30] J.H. Hong, P.V. Malone, M.D. Jett, R. Kobayashi, *Fluid Phase Equilib.* 38 (1987) 83–96.
- [31] H. Schlichting, R. Langhorst, H. Knapp, *Fluid Phase Equilib.* 84 (1993) 143–163.
- [32] T. Ukai, D. Kodama, J. Miyazaki, M. Kato, *J. Chem. Eng. Data* 47 (2002) 1320–1323.
- [33] L.K. Wang, G.J. Chen, G.H. Han, X.Q. Guo, T.M. Guo, *Fluid Phase Equilib.* 207 (2003) 143–154.
- [34] A.S. McDaniel, *J. Phys. Chem.* 15 (1911) 587–610.
- [35] Y.H. Ma, J.P. Kohn, *J. Chem. Eng. Data* 9 (1964) 3–5.
- [36] K. Ohgaki, F. Sano, T. Katayama, *J. Chem. Eng. Data* 21 (1976) 55–58.
- [37] E. Brunner, *J. Chem. Thermodyn.* 17 (1985) 671–679.
- [38] S. Zeck, H. Knapp, *Int. J. Thermophys.* 6 (1985) 643–656.
- [39] D.H. Lam, K.D. Luks, *J. Chem. Eng. Data* 36 (1991) 307–311.
- [40] K. Ishihara, H. Tanaka, M. Kato, *Fluid Phase Equilib.* 144 (1998) 131–144.
- [41] L. Ruffine, A. Barreau, I. Brunella, P. Mougins, J. Jose, *Ind. Eng. Chem. Res.* 44 (2005) 8387–8392.
- [42] K. Nagahama, S. Suda, T. Hakuta, M. Hirata, *Sekiyu Gakkaishi* 14 (1971) 252–258.
- [43] F. Galivel-Solastiouk, S. Laugier, D. Richon, *Fluid Phase Equilib.* 28 (1986) 73–85.
- [44] A.D. Leu, D.B. Robinson, S.Y. Chung, C.J. Chen, *Can. J. Chem. Eng.* 70 (1992) 330–334.
- [45] P. Ma, M. Xu, *Tianranqi Huagong* 18 (1993) 54–56.
- [46] C.R. Yonker, J.C. Linehan, J.L. Fulton, *J. Supercrit. Fluid* 14 (1998) 9–16.
- [47] C.B. Kretschmer, R. Wiebe, *J. Am. Chem. Soc.* 74 (1952) 1276–1277.
- [48] L.B. Petty, J.M. Smith, *Ind. Eng. Chem.* 47 (1955) 1258–1265.
- [49] Y. Miyano, W. Hayduk, *J. Chem. Eng. Data* 31 (1986) 77–80.
- [50] I.R. Krichevskii, A.A. Ilinskaya, *Zh. Fiz. Khim.* 19 (1945) 621.
- [51] C.B. Kretschmer, J. Nowakowska, R. Wiebe, *Ind. Eng. Chem.* 38 (1946) 506–509.
- [52] R. Krichevskii, E.S. Lebedewa, *Zh. Fiz. Khim.* 21 (1947) 715–718.
- [53] W. Weber, S. Zeck, H. Knapp, *Fluid Phase Equilib.* 18 (1984) 253–278.
- [54] T. Laursen, S.I. Andersen, *J. Chem. Eng. Data* 47 (2002) 1173–1174.
- [55] W. Kunerth, *Phys. Rev.* 19 (1922) 512–524.
- [56] L.S. Bezdell, V.P. Teodorovich, *Gazov. Prom-st* 3 (1958) 38–43.
- [57] E.R. Shenderi, Y.D. Zelvenskii, F.P. Ivanovskii, *Khim. Prom-st Moscow (USSR)* 4 (1959) 328.
- [58] I.P. Usyukin, V.M. Shleinikov, *Neftepererab. Neftekhim. (Moscow)* 1 (1963) 33–39.
- [59] M. Yorizane, S. Sadamoto, H. Masuoka, Y. Eto, *Kogyo Kagaku Zasshi* 72 (1969) 2174–2177.
- [60] T. Katayama, K. Ohgaki, G. Maekawa, M. Goto, Nagano, T., *J. Chem. Eng. Jpn.* 8 (1975) 89–92.
- [61] K. Ohgaki, T. Katayama, *J. Chem. Eng. Data* 21 (1976) 53–55.
- [62] A.I. Semenova, E.A. Emelyanova, S.S. Tsimmerman, D.S. Tsiklis, *Russ. J. Phys. Chem.* 53 (1979) 1428–1430.
- [63] J.H. Hong, R. Kobayashi, *Fluid Phase Equilib.* 41 (1988) 269–276.
- [64] F. Schroedter, W.M. Melzer, H. Knapp, *Gas Sep. Purif.* 5 (1991) 161–172.
- [65] A.D. Leu, S.Y.K. Chung, D.B. Robinson, *J. Chem. Thermodyn.* 23 (1991) 979–985.
- [66] J.H. Yoon, H.S. Lee, H. Lee, *J. Chem. Eng. Data* 38 (1993) 53–55.
- [67] S.H. Page, S.R. Goates, M.L. Lee, *J. Supercrit. Fluid* 6 (1993) 95–101.
- [68] T.S. Reighard, S.T. Lee, S.V. Olesik, *Fluid Phase Equilib.* 123 (1996) 215–230.
- [69] C.J. Chang, C.Y. Day, C.M. Ko, K.L. Chiu, *Fluid Phase Equilib.* 131 (1997) 243–258.
- [70] C.J. Chiehming, C. Kou-Lung, D. Chang-Yih, *J. Supercrit. Fluid* 12 (1998) 223–237.
- [71] M.M. Elbaccouch, M.B. Raymond, J.R. Elliott, *J. Chem. Eng. Data* 45 (2000) 280–287.
- [72] S.N. Joung, C.W. Yoo, H.Y. Shin, S.Y. Kim, K.P. Yoo, C.S. Lee, W.S. Huh, *Fluid Phase Equilib.* 185 (2001) 219–230.
- [73] K. Bezanetk, G.B. Combes, F. Dehghani, N.R. Foster, D.L. Tomasko, *J. Chem. Eng. Data* 47 (2002) 161–168.
- [74] H.G. Zhu, Y.L. Tian, L. Chen, J.J. Feng, H.F. Fu, *Gaodeng Xuexiao Huaxue Xuebao* 23 (2002) 1588–1591.
- [75] T. Laursen, P. Rasmussen, S.I. Andersen, *J. Chem. Eng. Data* 47 (2002) 198–202.
- [76] J. Xia, M. Jodecke, A. Perez-Salado Kamps, G. Maurer, *J. Chem. Eng. Data* 49 (2004) 1756–1759.
- [77] E.W. Washburn, *International Critical Tables (ICT) of Numerical Data, Physics, Chemistry and Technology*, National Research Council, 1926–1930.
- [78] H.B. Feldman, W.G. Dahlstrom, *Ind. Eng. Chem.* 28 (1936) 1316–1317.
- [79] H. Frank, F.H. Conrad, E.F. Hill, E.A. Ballman, *Ind. Eng. Chem.* 32 (1940) 542–543.
- [80] J. Gristvold, C.B. Buford, *Ind. Eng. Chem.* 41 (1949) 2347.
- [81] H.K. Ross, *Ind. Eng. Chem.* 46 (1954) 601–610.
- [82] P. Dalager, *J. Chem. Eng. Data* 14 (1969) 298–301.
- [83] M. Kato, H. Konishi, M. Hirata, *J. Chem. Eng. Data* 15 (1970) 435–439.
- [84] M. Kato, H. Konishi, M. Hirata, *J. Chem. Eng. Data* 15 (1970) 501–505.
- [85] V.O. Maripuri, G.A. Ratcliff, *J. Chem. Eng. Data* 17 (1972) 366–369.
- [86] M.L. McGlashan, A.G. Williamson, *J. Chem. Eng. Data* 21 (1976) 196–199.
- [87] J.B. Ott, J.R. Goates, B.A. Waite, *J. Chem. Thermodyn.* 11 (1979) 739–746.
- [88] K. Ochi, K. Kojima, *J. Chem. Eng. Jpn.* 20 (1987) 6–10.
- [89] N.A. Pushin, A.A. Glagoleva, *J. Chem. Soc. Trans.* 121 (1922) 2813–2834.
- [90] K. Kurihara, T. Minoura, K. Takeda, K. Kojima, *J. Chem. Eng. Data* 40 (1995) 679–684.
- [91] S.J. Green, I.E. Venek, *Ind. Eng. Chem.* 47 (1995) 103–109.
- [92] B. Khlfouai, A.H. Meniai, R. Borja, *Fluid Phase Equilib.* 127 (1997) 181–280.
- [93] S.P. Christensen, *Fluid Phase Equilib.* 150–151 (1998) 763–773.
- [94] J. Yao, H. Li, S. Han, *Fluid Phase Equilib.* 162 (1999) 253–260.
- [95] D.R. Lide, *Hand Book of Chemistry and Physics*, 85th ed., CRC Press, Boca Raton, FL, 2004.
- [96] H.J. Ng, C.J. Chen, T. Saeterstad, *Fluid Phase Equilib.* 36 (1987) 99–106.
- [97] H.J. Ng, D.B. Robinson, *Fluid Phase Equilib.* 21 (1985) 144–155.
- [98] C. Blanc, J. Tournier-Lasserre, *World Oil* 211 (1990) 63–68.
- [99] T.M. Svartas, F.H. Fadnes, *The 2nd International Offshore and Polar Engineering Conference*, vol. 1, 1992, pp. 614–619.