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Phase Behavior of High Pressure and Temperature Gas Reservoirs: Water Solubility and Density Measurement and Modeling from (3.7 to 132) MPa and Temperatures from (422 to 478) K

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ABSTRACT: New water content and gas phase density data were measured for two synthetic light and intermediate gas mixtures from (3.7 to 132) MPa at temperatures of (422 and 478) K. The Cubic-Plus-Association equation of state (CPA EoS) was implemented in this study to reproduce the measured data. Accurate predictions were generated for the compositions of the equilibrium liquid and vapor phases by the CPA equation once the cross-association between molecules of water and light saturated hydrocarbons was considered in the phase equilibrium calculations. The performance of the CPA equation with zero binary interaction coefficients between water and hydrocarbons in reproducing the water content data was satisfactory; however the predicted hydrocarbons solubility data were poor. By coupling the CPA equation with the concept of cross-association no improvement was observed in the gas phase density predictions compared to the predicted results of the CPA equation with zero or tuned binary interaction coefficients.

INTRODUCTION

Technology advancements have enabled the oil and gas industry to explore and exploit ultradeep energy resources, e.g., gas reservoirs in North Sea, Gulf of Mexico, and north of Africa, which are mostly characterized as high pressure and temperature hydrocarbon reservoirs. The water solubility in hydrocarbon gas mixtures increases with temperature and becomes more considerable at low pressure conditions. This situation generally occurs around the wellbore in high temperature gas reservoirs, and therefore, the flow and production of hydrocarbon fluids can be affected by the soluble water. In addition, the solubility of hydrocarbon compounds in water increases with pressure and temperature and becomes significant at extreme conditions which in turn can affect the gas in place calculations. Also, the soluble water in hydrocarbon gas reservoirs forms a fraction of the produced water which must be considered in the design of surface facilities. The produced water can form hydrates in the pipelines under favorable conditions or cause corrosion damage in the surface facilities. Therefore an accurate knowledge of the water content of hydrocarbon reservoirs is a key factor in the phase behavior studies and design of surface facilities.

In order to obtain an accurate estimate of the water and hydrocarbons solubilities at reservoir conditions, a thermodynamic model is required to precisely reproduce the phase behavior of hydrocarbon mixtures over a wide range of conditions. However, most of the thermodynamic models are not capable of representing the phase behavior of water−hydrocarbon mixtures due to the polar and associating nature of water. Over the last two decades, new thermodynamic models have been developed which incorporate the association concept in the phase behavior studies of complex mixtures containing polar compounds such as water.[1,2] The Cubic-Plus-Association equation of state[2] (CPA EoS) is proven as a powerful tool in the phase behavior studies of the binary systems of water−hydrocarbon and nonhydrocarbon compounds over a wide range of pressure and temperature conditions.[3−5] The CPA equation is also implemented in the phase behavior modeling of the water−hydrocarbon mixtures.[4,5] It must be mentioned that there are only a few accurate experimental solubility data available in the literature for hydrocarbon mixtures which are mostly measured at low pressure and temperature conditions for ternary and quaternary systems.[6−11] Therefore, the accuracy of the CPA equation to reproduce the solubility data of complex mixtures of water and hydrocarbon compounds at higher pressure and temperature conditions is not quite known.

The current study is devoted to the phase behavior investigation of dry gas reservoirs in terms of water solubility and density at elevated conditions. A series of experiments were conducted for pressures up to 132 MPa at two temperatures of (422 and 478) K and new water content and gas phase density data were generated for two light and intermediate dry gas mixtures. The light gas mixture was considered to particularly examine effects of light hydrocarbons as dominant components of dry gas mixtures on the solubility of water in the vapor phase. The synthetic intermediate gas mixture as a representative of real dry gas mixtures was formed by addition of heavier hydrocarbons to

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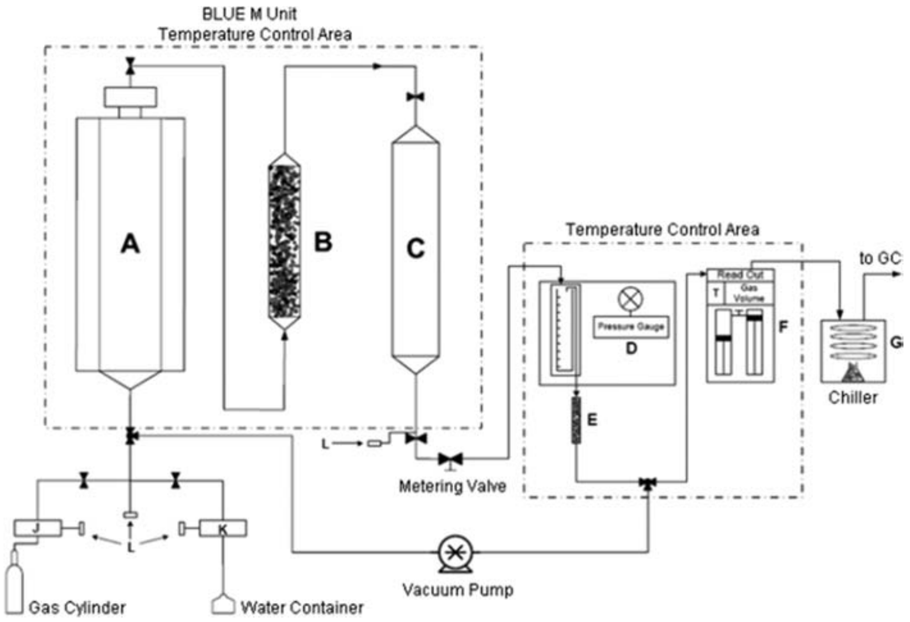

Figure 1. Schematic of experimental apparatus: A, gas mixing vessel; B, demister vessel; C, pycnometer; D, equilibrium flash separator; E, desiccant; F, gasometer; G, chiller; J, gas booster; K, Quizix pump; L, pressure transducer.

the light gas mixture. The newly formed mixture was considered to study effects of heavier hydrocarbons on the water content and density of gas mixtures. In addition, the new generated data were used for reliability evaluation of the CPA equation of state in correlating the phase behavior of high pressure and temperature hydrocarbon gas mixtures.

In the subsequent sections, first a brief description of the experimental procedure is explained. Next, the CPA equation combined with the concept of cross-association is described. Furthermore, new measured water content and density data of the water-saturated gas mixtures are presented. Finally, the adjusted CPA equation of state, using physical properties of pure water and solubility data of binary mixtures of water and pure hydrocarbons provided in the literature, is applied to predict the new measured water content and density data of the examined synthetic gas mixtures. Moreover, the solubility predictions of CPA are evaluated against the solubility data of a real gas mixture[6] measured at lower pressures and temperatures compared to the conditions of the current study.

EXPERIMENTAL SECTION

Materials. Pure hydrocarbons with the least certified purity of 0.9995 mol fraction and the light gas mixture with reported analytical uncertainties of (0.0006 and 0.0002) mol fraction for ethane and propane, respectively, were purchased from Praxair Canada Inc. Anhydrous calcium sulfate crystals (0.97 mol fraction $CaSO_4$ and 0.03 mol fraction $CoCl_2$), which are used as the desiccant, were purchased from W. A. Hammond Drierite Company Ltd. A Barnstead Mega-Pure Water Still MP-1 distillation unit is used to produce distilled water.

Experimental Procedure. Figure 1 shows a schematic diagram of the experimental setup. Intermediate gas mixtures were made in the laboratory based on the mass distribution of each component in the mixture. On the basis of 600 g of gas mixture, the desired mole fraction of each component in the mixture was converted to mass or volume and the mixture was prepared by transferring hydrocarbons separately into a previously evacuated tank positioned on a weight scale. Transferring order was from heavier hydrocarbons to lighter hydrocarbons. The heaviest hydrocarbons, i.e., hexane, pentane, and 2-methylbutane, which are in the liquid state at room temperature were transferred to the tank using a buret based on their volumes. Each gaseous hydrocarbon was directly transferred into the tank from a high pressure source tank on the basis of mass. Table 1 shows the composition of two light and intermediate gas mixtures (BG I and BG II, respectively) used in the current study. The equipment and experimental procedure are explained in details elsewhere.[3] In order to generate new water content and water-saturated gas density data, experiments were performed at two constant temperatures of (422 and 478) K over a wide range of pressure from 3.7 to 132 MPa. A brief description of the experimental procedure applied in this study is explained below:

In order to measure the water content of each gas mixture, a liquid—vapor equilibrium system of water and gas mixture was

Table 1. Composition of Gas Mixtures Examined in This Work

gas mixture	BG I	BG II
component	($x \pm 2\sigma^a$)	($x \pm 2\sigma^c$)
methane	0.96^b	0.70 ± 0.04
ethane	0.030 ± 0.001	0.110 ± 0.008
propane	0.0100 ± 0.0004	0.060 ± 0.004
2-methylpropane	0	0.040 ± 0.004
butane	0	0.040 ± 0.004
2-methylbutane	0	0.020 ± 0.002
pentane	0	0.020 ± 0.004
hexane	0	0.0100 ± 0.0002
gas specific gravity	0.578	0.883

[a] Analytical uncertainties reported by Praxair Canada Inc. [b] No uncertainty is reported for methane. [c] Standard deviations (σ) are based on 9 chromatographic analyses.

Table 2. Measured and Predicted Water Content Data of Gas Mixtures (BG I and BG II)[a]

gas mixture	T/K	p/MPa	y_{H_2O}	$U_c(y_{H_2O})$	nCPA-PR, $K_{ij} = 0$	AD %	nCPA-PR, $K_{ij}(T)$	AD %	sCPA-PR	AD %
BG I	424.41	3.69	0.15	0.01	0.149	0.0	0.144	4.0	0.146	2.7
BG I	424.41	7.32	0.077	0.004	0.080	3.9	0.075	2.6	0.077	0.0
BG I	424.41	14.20	0.044	0.002	0.047	6.8	0.041	6.8	0.044	0.0
BG I	424.41	21.76	0.033	0.002	0.0345	4.5	0.0282	14.5	0.0318	3.6
BG I	424.41	27.61	0.028	0.001	0.0297	6.1	0.0231	17.5	0.0271	3.2
BG I	424.41	34.60	0.025	0.001	0.0261	4.4	0.0193	22.8	0.0237	5.2
BG I	424.41	41.62	0.022	0.001	0.0237	7.7	0.0167	24.1	0.0216	1.8
BG I	424.41	69.14	0.0179	0.0006	0.0185	3.4	0.0115	35.8	0.0174	2.8
BG I	424.41	103.41	0.0150	0.0006	0.0154	2.7	0.0088	41.3	0.0153	2.0
BG I	478.20	3.71	0.491	0.008	0.511	4.1	0.506	3.1	0.508	3.5
BG I	478.20	7.44	0.270	0.004	0.277	2.6	0.266	1.5	0.271	0.4
BG I	478.20	14.01	0.164	0.002	0.164	0.0	0.149	9.1	0.156	4.9
BG I	478.20	21.38	0.118	0.002	0.1200	1.7	0.1016	13.9	0.1112	5.8
BG I	478.20	28.14	0.097	0.001	0.0998	2.9	0.0798	17.7	0.0911	6.1
BG I	478.20	35.03	0.084	0.001	0.0871	3.7	0.0661	21.3	0.0788	6.2
BG I	478.20	41.84	0.076	0.001	0.0786	3.4	0.0570	25.0	0.0709	6.7
BG I	478.20	69.43	0.0574	0.0006	0.0601	4.7	0.0378	34.1	0.0553	3.7
BG I	478.20	104.30	0.0480	0.0006	0.0492	2.5	0.0275	42.7	0.0476	0.8
BG I	478.20	132.57	0.0434	0.0006	0.0437	0.7	0.0230	47.0	0.0443	2.1
BG II	422.60	3.74	0.134	0.008	0.138	3.0	0.134	0.0	0.135	0.7
BG II	422.60	7.09	0.074	0.004	0.078	5.4	0.073	1.4	0.075	1.4
BG II	422.60	14.95	0.041	0.002	0.045	9.8	0.039	4.9	0.042	2.4
BG II	422.60	20.79	0.029	0.001	0.0350	20.7	0.0283	2.4	0.0318	9.7
BG II	422.60	28.06	0.025	0.001	0.0295	18.0	0.0225	10.0	0.0266	6.4
BG II	422.60	34.61	0.023	0.001	0.0266	15.7	0.0194	15.7	0.0239	3.9
BG II	422.60	41.43	0.0208	0.0008	0.0244	17.3	0.0173	16.8	0.0221	6.3
BG II	422.60	69.41	0.0166	0.0006	0.0187	12.7	0.0120	27.7	0.0175	5.4
BG II	422.60	102.18	0.0147	0.0006	0.0161	9.5	0.0099	32.7	0.0156	6.1
BG II	422.60	132.65	0.0130	0.0006	0.0140	7.7	0.0084	35.4	0.0141	8.5
BG II	478.50	3.76	0.475	0.008	0.508	6.9	0.504	6.1	0.505	6.3
BG II	478.50	7.21	0.282	0.004	0.288	2.1	0.277	1.8	0.281	0.4
BG II	478.50	14.13	0.163	0.002	0.167	2.5	0.151	7.4	0.158	3.1
BG II	478.50	21.38	0.117	0.002	0.1250	6.8	0.1052	10.1	0.1147	2.0
BG II	478.50	28.18	0.096	0.001	0.1053	9.7	0.0838	12.7	0.0952	0.8
BG II	478.50	35.04	0.082	0.001	0.0930	13.4	0.0704	14.1	0.0835	1.8
BG II	478.50	41.81	0.074	0.001	0.0845	14.2	0.0615	16.9	0.0758	2.4
BG II	478.50	70.21	0.0568	0.0008	0.0644	13.4	0.0419	26.2	0.0593	4.4
BG II	478.50	103.37	0.0489	0.0006	0.0523	7.0	0.0318	35.0	0.0505	3.3
BG II	478.50	130.08	0.0430	0.0006	0.0461	7.2	0.0271	37.0	0.0462	7.4

[a] Combined expanded uncertainties $U_c(y_{H_2O})$ in the measured water content data are calculated using the propagation of error analysis (level of confidence = 0.95). The uncertainty value in measured temperatures $u(T)$ is ± 0.06 K and for each measured pressure $u(p)$ is 0.0025 of its value.

established in a mixing vessel and the water-saturated vapor phase was transferred to the pycnometer through the demister at the equilibrium pressure and temperature of the system. Next, the contents of the pycnometer were transferred to the gasometer through a desiccant that captures the water volume existing in the gas stream. The volume of the gas mixture was measured at the gasometer conditions. Afterward, the dehydrated gas mixture was sent into a chiller to ensure that the total amount of dissolved water in the gas mixture was captured. However, no water was observed in the chiller in all experiments. The outlet gas stream from the chiller was passed through a gas chromatography device for composition analysis. The dehydrated gas mixture composition was compared with the dry gas mixture composition to ensure that there was no material balance error in each experiment. The total volume of gas mixture measured in the gasometer was converted to moles of gas by assuming the ideal behavior of gases at the standard condition. The total amount of water absorbed by the desiccant, the difference between desiccant weights before and after each experiment measured by a weigh scale, was converted to moles of water and reported as water mole fraction in the vapor phase. The density of the vapor phase was calculated as a ratio of total mass of water and hydrocarbons to the volume of pycnometer. The same procedure was repeated at a constant temperature for other pressure steps over a wide range from (3.7 to 132) MPa to measure the water solubility in two different gas

Table 3. Measured and Predicted Density Data of Water-Saturated Gas Mixtures (BG I and BG II)[a]

gas mixture	T/K	p/MPa	ρ/kg·m^{-3}	U_c (ρ)/kg·m^{-3}	nCPA-PR, K_{ij} = 0	AD %	nCPA-PR, $K_{ij}(T)$	AD %	sCPA-PR	AD %
BG I	424.41	3.69	17	1	18	5.9	18.2	7.1	18.2	7.1
BG I	424.41	7.32	33	2	36	9.1	36	9.1	36	9.1
BG I	424.41	14.20	64	4	71	10.9	70	9.4	71	10.9
BG I	424.41	21.76	97	6	107	10.3	106	9.3	107	10.3
BG I	424.41	27.61	117	8	133	13.7	132	12.8	133	13.7
BG I	424.41	34.60	143	8	161	12.6	160	11.9	161	12.6
BG I	424.41	41.62	165	10	186	12.7	184	11.5	185	12.1
BG I	424.41	69.14	223	12	259	16.1	258	15.7	259	16.1
BG I	424.41	103.41	267	14	319	19.5	317	18.7	319	19.5
BG I	478.20	3.71	19.2	0.4	17.6	8.3	17.4	9.4	17.5	8.9
BG I	478.20	7.44	34.9	0.8	34	2.6	33.4	4.3	33.7	3.4
BG I	478.20	14.01	64	1	63	1.6	61.4	4.1	62	3.1
BG I	478.20	21.38	94	2	94	0.0	91.4	2.8	92.6	1.5
BG I	478.20	28.14	118	2	120	1.7	117	0.8	119	0.8
BG I	478.20	35.03	140	2	144	2.9	141	0.7	143	2.1
BG I	478.20	41.84	160	2	166	3.8	163	1.9	166	3.8
BG I	478.20	69.43	224	4	237	5.8	233	4.0	237	5.8
BG I	478.20	104.30	266	4	298	12.0	293	10.2	298	12.0
BG I	478.20	132.57	292	4	333	14.0	328	12.3	334	14.4
BG II	422.60	3.74	25	2	28	12.0	28	12.0	28	12.0
BG II	422.60	7.09	50	4	57	14.0	56	12.0	57	14.0
BG II	422.60	14.95	106	8	120	13.2	118	11.3	119	12.3
BG II	422.60	20.79	156	10	176	12.8	172	10.3	173	10.9
BG II	422.60	28.06	198	12	226	14.1	222	12.1	222	12.1
BG II	422.60	34.61	229	14	261	14.0	257	12.2	258	12.7
BG II	422.60	41.43	259	16	291	12.4	286	10.4	287	10.8
BG II	422.60	69.41	338	20	382	13.0	377	11.5	378	11.8
BG II	422.60	102.18	374	22	429	14.7	424	13.4	425	13.6
BG II	422.60	132.65	406	24	467	15.0	463	14.0	464	14.3
BG II	478.50	3.76	24.9	0.6	22.7	8.8	22.4	10.0	22.5	9.6
BG II	478.50	7.21	49	1	47	4.1	46.1	5.9	46.3	5.5
BG II	478.50	14.13	99	2	97	2.0	94.4	4.6	95.2	3.8
BG II	478.50	21.38	147	2	147	0.0	142	3.4	144	2.0
BG II	478.50	28.18	188	4	188	0.0	182	3.2	184	2.1
BG II	478.50	35.04	221	4	223	0.9	217	1.8	219	0.9
BG II	478.50	41.81	248	4	254	2.4	246	0.8	249	0.4
BG II	478.50	70.21	322	6	342	6.2	334	3.7	338	5.0
BG II	478.50	103.37	373	6	405	8.6	397	6.4	401	7.5
BG II	478.50	130.08	401	8	439	9.5	432	7.7	435	8.5

[a] Combined extended uncertainties $U_c(\rho)$ in the measured density data are calculated using the propagation of error analysis (level of confidence = 0.95). The uncertainty value in measured temperature $u(T)$ is ± 0.06 K and for each measured pressure $u(p)$ is 0.0025 of its value.

mixtures.

$$n_{\mathrm{gas}} = \frac{P_{\mathrm{lab}} V_{\mathrm{gas}}^{\mathrm{sep}}}{R T_{\mathrm{gas}}^{\mathrm{sep}}} \tag{1}$$

$$n_{\mathrm{w}} = \frac{m_{\mathrm{w}}}{\mathrm{MW}_{\mathrm{w}}} \tag{2}$$

$$y_{\mathrm{w}} = \frac{n_{\mathrm{w}}}{n_{\mathrm{gas}} + n_{\mathrm{w}}} = \frac{n_{\mathrm{w}}}{n_{\mathrm{vapor}}} \tag{3}$$

$$\rho_{\mathrm{vapor}} = \frac{n_{\mathrm{vapor}} \mathrm{MW}_{\mathrm{vapor}}}{V_{\mathrm{pyc}}} \tag{4}$$

where subscripts lab, w, and pyc denote the laboratory condition, water phase, and pycnometer and superscripts sep and sc denote separator and standard conditions, respectively.

THEORETICAL SECTION

The CPA equation of state is implemented in this study to predict the water content and density of hydrocarbon gas mixtures. In the original CPA formulation,[2] the physical part of the equation is represented by the SRK equation of state.[12]

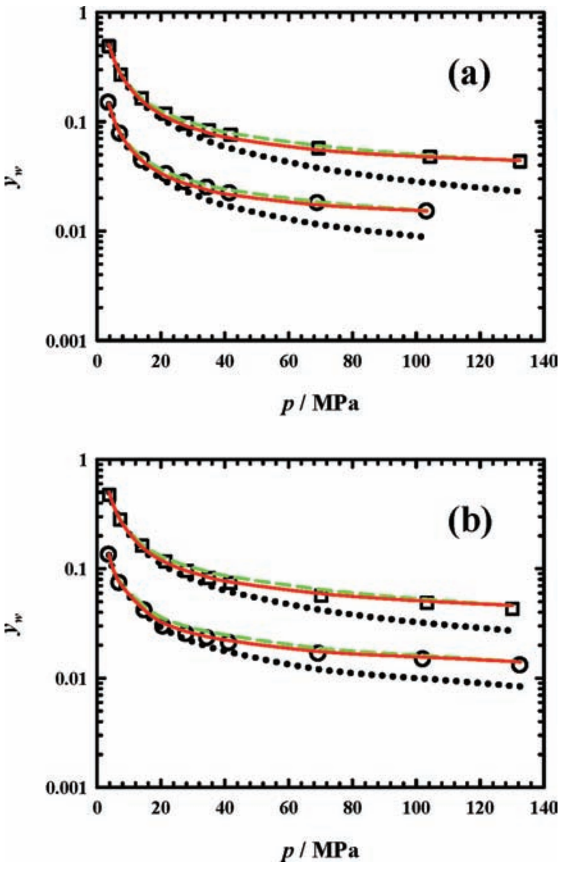

Figure 2. Water content of synthetic gas mixtures. (a) BG I, experimental data at 424.41 K (○) and 478.20 K (□). (b) BG II, experimental data at 422.60 K (○) and 478.50 K (□). Black dotted lines: nCPA-PR with temperature-dependent K_{ij}, green dash lines: nCPA-PR with $K_{ij} = 0$, and red solid lines: sCPA-PR.

However, in the current study, the physical term is represented by the modified Peng−Robinson equation of state,[13] and the nCPA-PR acronym is used in this work to distinguish between the CPA-SRK and CPA-PR formulations. A detailed description of the nCPA-PR equation is described elsewhere.[3]

The densities of the saturated phases are predicted by using the corrected molar volume term

$$\rho = \frac{\mathrm{MW}}{v^{\mathrm{cor}}} \tag{5}$$

$$v^{\mathrm{cor}} = v^{\mathrm{EoS}} + c \tag{6}$$

$$c = \sum_i x_i c_i \tag{7}$$

where v^{cor} is the corrected molar volume and c is the molar volume correction term.

In general, association is considered between molecules of one associating compound (self-association) or between molecules of different associating compounds (cross-association). In a recent study Li and Firoozabadi[5] improved the performance of the nCPA-PR equation in the phase equilibrium calculations of water−hydrocarbon binary systems by incorporating the concept of cross-association between molecules of water and light hydrocarbons (methane and ethane). They also investigated the binary systems of water and other heavier alkanes and concluded that the cross-association should not be considered in these systems.

In order to simplify the phase equilibrium calculations, Li and Firoozabadi[5] treated methane and ethane as pseudoassociating components which have similar association sites as water. They considered four association sites belonging to two different types α and β for water and four association sites belonging to two different types α_i' and β_i' for methane and ethane. They also assumed that no self-association occurs between molecules of methane or ethane ($\Delta^{\alpha_i'\alpha_i'} = \Delta^{\alpha_i'\beta_i'} = 0$), and the cross-associations are symmetrical ($\Delta^{\alpha\beta_i'} = \Delta^{\beta\alpha_i'}$). Moreover, they related the cross-association strength to the self-association strength of water molecules by a temperature dependent cross-association parameter s_{ij}

$$\Delta^{\alpha\beta_i'} = s_{ij}\Delta^{\alpha\beta} \tag{8}$$

Most recently, Tabasinejad et al.[3] successfully applied the above approach (sCPA-PR) in correlating the high pressure and high temperature phase behavior of water−methane system. Details of this approach can be found elsewhere.[3,5]

In the following sections, the sCPA-PR model represents the nCPA-PR equation coupled with the concept of cross-association where the nCPA-PR model only considers the self-association between molecules of water.

■ RESUTLS AND DISCUSSION

New measured water content and density data are reported in Tables 2 and 3, respectively, for two different light and intermediate dry gas mixtures called BG I and BG II, respectively. The solubility data of water in both gas mixtures are plotted in Figure 2. It is noted that the increase of water solubility in hydrocarbon mixtures with temperature becomes substantial at higher temperature conditions which is illustrated in Figure 2. A comparison between water content data of BG I and BG II shows that light hydrocarbons, which are the dominant fractions in gas reservoirs, have the most significant influence on the solubility of water in hydrocarbons, while the effect of heavier hydrocarbons with low concentrations in gas mixtures on water solubility is negligible.

The density data of both water-saturated gas mixtures at two reported temperatures are plotted in Figure 3. In addition, the density predictions of Dranchuk and Abou-Kassem method (DAK)[14] for water-free BG I and BG II at corresponding temperatures are presented in Figure 3. A comparison between measured data shows that, for each water-saturated gas mixture at a constant pressure, the temperature has a marginal effect on density. However, DAK predictions show that the density of a free-water gas mixture decreases with temperature at a constant pressure. Comparing the total number of moles and molecular weight of each water-saturated gas mixture at different experimental temperatures, it was noticed that at a constant pressure the number of moles and molecular weights were similar. This implies equality of densities. In fact, the changes in the number of moles and molecular weight of each gas mixture, due to the mass transfer of hydrocarbons into the aqueous phase, are minimized by distribution of water molecules into the gas mixture.

The nCPA-PR equation is applied in this study to predict the measured solubility and density data of BG I and BG II. The association scheme 4C described by Huang and Radosz[1] is considered for water in the current study. The parameters of the nCPA-PR equation of state required to accurately represent the physical properties of water are taken from literature.[3]

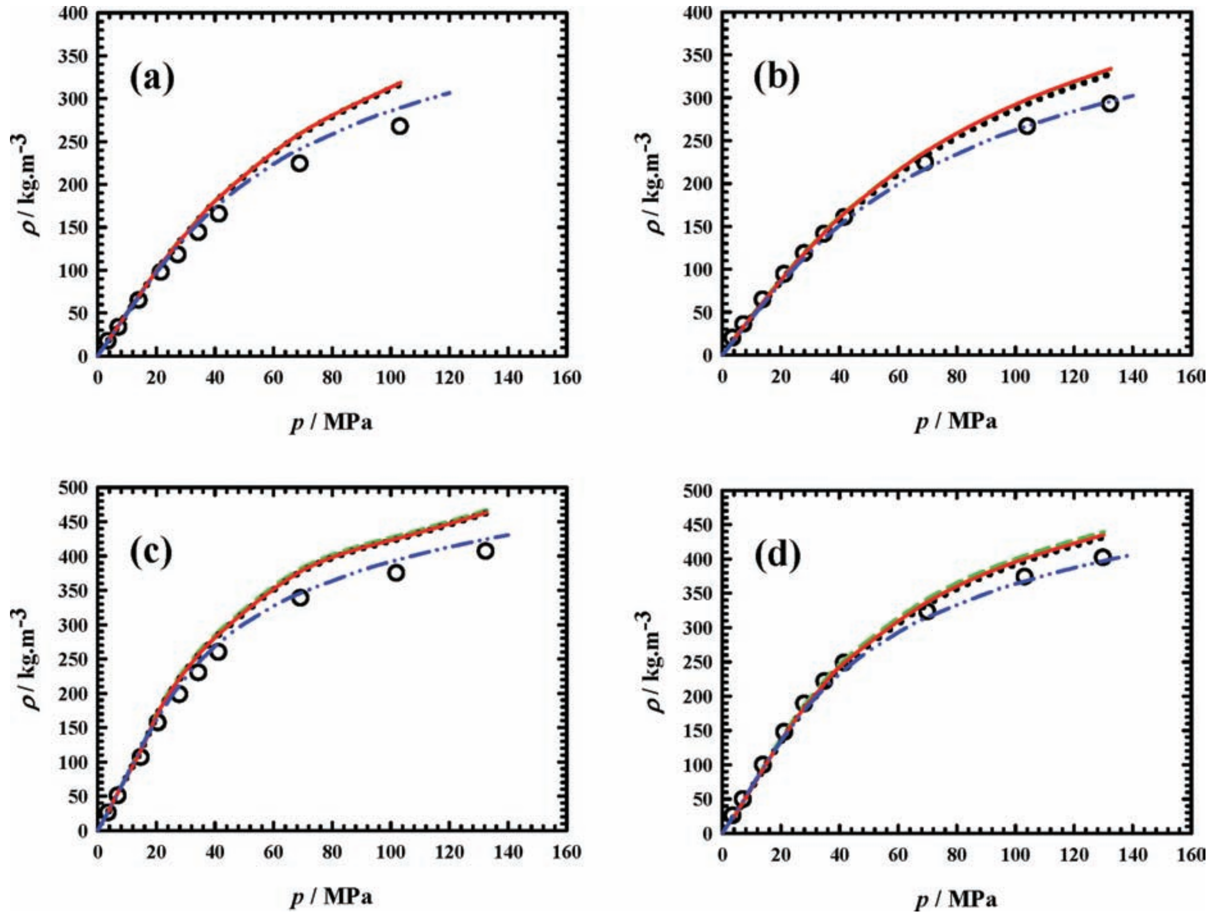

Figure 3. Density of gas mixtures. (a) water-saturated BG I, experimental data at 424.41 K; (b) water-saturated BG I, experimental data at 478.20 K; (c) water-saturated BG II, experimental data at 422.60 K; (d) water-saturated BG II, experimental data at 478.50 K. Black dotted lines, nCPA-PR with temperature-dependent K_{ij}; green dash lines, nCPA-PR with $K_{ij} = 0$; and red solid lines, sCPA-PR. Blue dash-dot-dot lines represent predictions of DAK[14] method for water-free gas mixtures at corresponding temperatures.

Using these parameters, nCPA-PR reproduces the vapor pressure and saturated liquid density data of water with average absolute deviations (AAD) of 0.459 % and 1.437 %, respectively, in a temperature range from 274 K to 0.98 T_C. To further improve the predicted saturated liquid density data of water, a temperature-dependent correction term (c_{water}) is developed in the current study which reduces the AAD to 0.158 % in the same temperature range. The volume correction term is generated using a sixth order polynomial which accurately reproduces the deviations between experimental saturated liquid density data of water and predictions of nCPA-PR in a temperature range from (274 to 595) K.

$$v_{\text{water}}^{\text{corr}} = v_{\text{water}}^{\text{nCPA-PR}} + c_{\text{water}} \qquad (9)$$

$$c_{\text{water}} = c_6 T_{r_w}{}^6 + c_5 T_{r_w}{}^5 + c_4 T_{r_w}{}^4 + c_3 T_{r_w}{}^3 + c_2 T_{r_w}{}^2 + c_1 T_{r_w} + c_0 \qquad (10)$$

where $c_0 = 0.092\,11$, $c_1 = -0.827\,15$, $c_2 = 3.155\,52$, $c_3 = -6.479\,94$, $c_4 = 7.501\,66$, $c_5 = -4.626\,67$, and $c_6 = 1.185\,56$. The new generated volume correction term for water (c_{water}) has been used in density calculations in the subsequent sections. For pure hydrocarbon components, the physical properties reported by Danesh[15] are implemented in equilibrium calculations. A zero volume correction term has been assumed for all hydrocarbons in the current study.

In order to highlight the effect of cross-association between molecules of water and light hydrocarbons (methane and ethane on water solubility data, the predicted results of the CPA equation with and without cross-association (sCPA-PR and nCPA-PR models, respectively) are compared with the measured data. Literature experimental solubility data of water-hydrocarbon binary systems[7,16−23] have been used to generate the binary interaction coefficients (K_{ij}) and cross-association factors (s_{ij}). These parameters are produced in a way to minimize the average absolute deviation between experimental and generated data of the investigated models.

$$\text{AAD} = \frac{1}{n}\left[\sum_n \left(\frac{|y_{\text{exp}} - y_{\text{calc}}|}{y_{\text{exp}}}\right) + \sum_n \left(\frac{|x_{\text{exp}} - x_{\text{calc}}|}{x_{\text{exp}}}\right)\right] \qquad (11)$$

Table 4 summarizes the new generated binary interaction coefficients and cross-association factors which are correlated with reduced temperature of hydrocarbons. The K_{ij} values between water and iso-alkanes are assumed to be the same as water and n-alkanes values. The binary interaction coefficients between nonassociating compounds are calculated using a group

Table 4. Physical and Association Binary Interaction Coefficients and Association Factors Used in the nCPA-PR and sCPA-PR Models

model	methane (1)—water (2) system [(310.93—510.93) K][a]	refs	AAD % in y_2[b]	AAD % in x_1[b]
nCPA-PR	$K_{ij} = -0.2080T_{r_{c1}}^{\ 4} + 1.8241T_{r_{c1}}^{\ 3} - 6.1843T_{r_{c1}}^{\ 2} + 9.9388T_{r_{c1}} - 6.1378$	16 and 19	11.49	3.26
sCPA-PR	$K_{ij} = -0.1028T_{r_{c1}}^{\ 2} + 1.1609T_{r_{c1}} - 1.5488$ $s_{ij} = 0.0628T_{r_{c1}}^{\ 2} - 0.1826T_{r_{c1}} + 0.1315$		2.12	2.37
	ethane (1)—water (2) system [(310.93—510.93) K][a]	refs	AAD % in y_2[b]	AAD % in x_1[b]
nCPA-PR	$K_{ij} = 0.3853T_{r_{c2}}^{\ 3} - 2.0707T_{r_{c2}}^{\ 2} + 3.8028T_{r_{c2}} - 2.0502$	17 and 18	17.02	3.74
sCPA-PR	$K_{ij} = 1.0260T_{r_{c2}}^{\ 3} - 4.1425T_{r_{c2}}^{\ 2} + 6.1672T_{r_{c2}} - 2.9747$ $s_{ij} = 0.1539T_{r_{c2}}^{\ 3} - 0.4223T_{r_{c2}}^{\ 2} + 0.4191T_{r_{c2}} - 0.1491$		4.31	3.37
	propane (1)—water (2) system [(310.90—427.60) K][a]	ref	AAD % in y_2[b]	AAD % in x_1[b]
nCPA-PR	$K_{ij} = 0.7267T_{r_{c3}}^{\ 3} - 2.9083T_{r_{c3}}^{\ 2} + 4.0846T_{r_{c3}} - 1.7663$	21	8.55[c]	1.95
	butane (1)—water (2) system [(310.93—510.93) K][a]	ref	AAD % in y_2[b]	AAD % in x_1[b]
nCPA-PR	$K_{ij} = -0.3455T_{r_{c4}}^{\ 3} + 0.6209T_{r_{c4}}^{\ 2} + 0.1378T_{r_{c4}} - 0.2924$	20	20.22[c]	4.93
	pentane (1)—water (2) system [(310.93—533.15) K][a]	ref	AAD % in y_2[b]	AAD % in x_1[b]
nCPA-PR	$K_{ij} = 0.5031T_{r_{c5}} - 0.3508\ [T_{r_{c5}} < 0.9]$ $K_{ij} = -0.2263T_{r_{c5}}^{\ 2} + 0.3449T_{r_{c5}} - 0.026\ [0.9 \leq T_{r_{c5}} < 1.14]$	7	14.85[c]	2.93
	hexane (1)—water (2) system [(303.95—443.15) K][a]	refs	AAD % in y_2[b]	AAD % in x_1[b]
nCPA-PR	$K_{ij} = -1.3335T_{r_{c6}}^{\ 2} + 2.3736T_{r_{c6}} - 0.9851$	22 and 23	9.34[d]	2.95

[a] The temperature range that correlations are valid. [b] LVE or/and LLE. [c] Significant deviations between measured and predicted solubility data at low temperature conditions. [d] correlated data were used for optimization.

contribution-based model developed for the PR equation of state.[24]

The predicted results of the nCPA-PR and sCPA-PR models for the water content of BG I and BG II are shown in Table 2 and Figure 2. Predictions show that nCPA-PR underestimates the high pressure water solubility data of both gas mixtures, whereas the generated solubility data by the sCPA-PR model indicate that the incorporation of the concept of cross-association drastically improves the performance of the CPA equation and it has to be considered in the phase behavior calculations of gas mixtures particularly at high pressure conditions.

It has been previously shown[3,5] that by assuming cross-association between molecules of water and methane and also water and ethane, the CPA equation can correctly represent the equilibrium compositions of the vapor phases of the binary systems of water—methane and water—ethane over an extensive range of pressures and temperatures. The origin of cross-association between molecules of water and light hydrocarbons can be attributed to the temporary separation of the centers of positive and negative charges of methane and ethane. This assumption can be caused by high pressure conditions plus the strong permanent polar moments of water molecules.[5] Therefore, more accurate high pressure solubility data are expected to be estimated by sCPA-PR compared to nCPA-PR for gas mixtures with high concentrations of methane and ethane, e.g., BG I and BG II in the current study. It is worth mentioning that both nCPA-PR and sCPA-PR have almost identical accuracy in reproducing the liquid phase compositions of water—methane and water—ethane systems.[3,5]

The water solubility data were also predicted by the nCPA-PR model with zero binary interaction coefficients between all compounds. The generated results are shown in Table 2 and Figure 2. More accurate water solubility data are predicted by this model compared to the nCPA-PR model with the tuned K_{ij} values. This accurate performance has been previously observed for predictions of water content of individual light hydrocarbons using nCPA-PR[3] or nCPA-SRK[4] where better predictions were obtained for the vapor phase composition over a wide range of pressures using zero K_{ij} values compared to predictions generated with tuned K_{ij} values. It must be emphasized here that in spite of successful performance of the CPA equation with zero K_{ij} values in reproducing water content of single light hydrocarbons, the model severely fails to estimate hydrocarbon solubility in the aqueous phase.[3,4] The same conclusion has been reached in the current study for hydrocarbons solubilities in water for a real gas mixture at temperatures and pressures lower than the current work. This system will be discussed later in this article.

The measured density data of the water-saturated BG I and BG II are compared with predictions of nCPA-PR with tuned and zero K_{ij} values and also sCPA-PR in Table 3 and Figure 3. Density calculations have been carried out by integrating the volume correction term for water (eq 9) in each model while a zero volume correction term was assumed for all hydrocarbons of the examined mixtures. All of the models have approximately the same accuracy in reproducing the saturated density data with better performance at 478 K compared to 422 K (or 424 K).

To further evaluate the accuracy of the CPA model in predicting VLE compositions of water-saturated natural gas mixtures, reported water and hydrocarbon solubilities of a natural gas mixture at pressures and temperatures lower than the current work were compared with the predictions of nCPA-PR with zero K_{ij} values, nCPA-PR with tuned K_{ij} values, and sCPA-PR with tuned K_{ij} and s_{ij} values. The reported equilibrium solubility data were measured by Dodson and Standing[6] for a natural gas

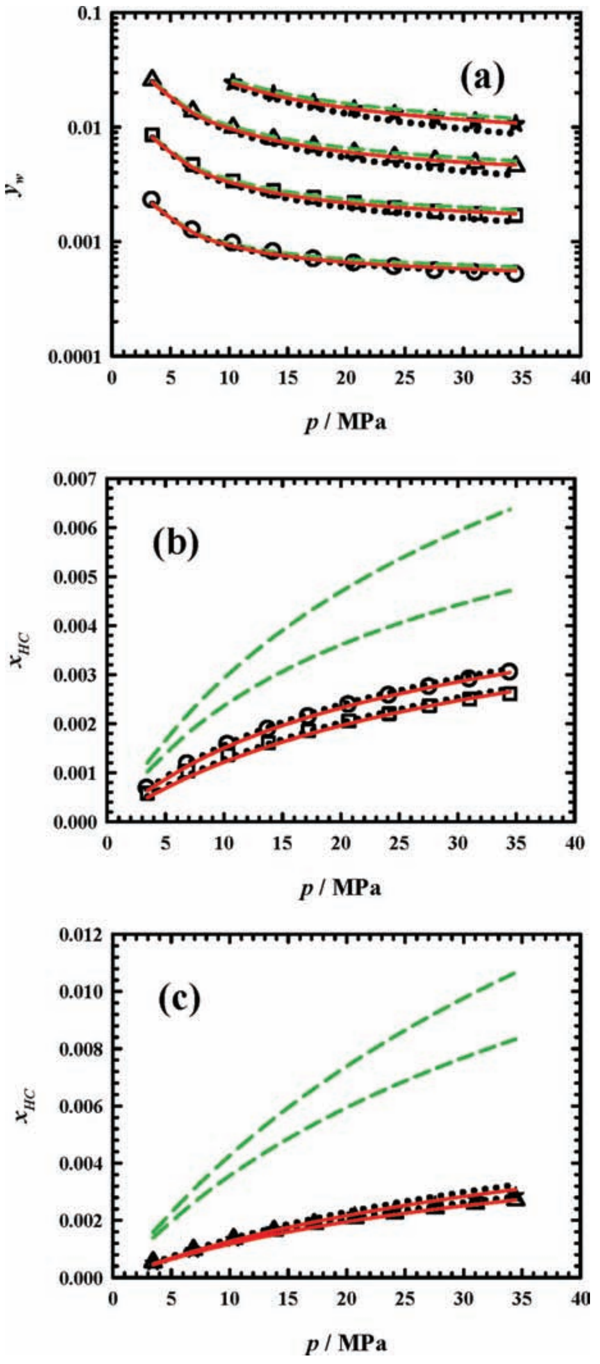

Figure 4. (a) Water solubility in natural gas mixture from bottom to top at 310.93 K (○), 338.71 K (□), 366.48 K (Δ), and 394.26 K (b) Hydrocarbons solubility in water at 310.93 K (○) and at 338.71 K (□). (c) Hydrocarbons solubility in water at 366.48 K (Δ) and at 394.26 K (★). Green dash, black dotted, and red solid lines represent the predicted results of the nCPA-PR with zero K_{ij}, nCPA-PR with tuned K_{ij}, and sCPA-PR models, respectively, at corresponding temperatures.

mixture with a specific gravity of 0.655 in a temperature range from (310.93 to 394.26) K and pressures up to 35 MPa. No experimental uncertainty in the measurements was reported by Dodson and Standing.[6] The natural gas mixture mainly consisted of methane and small fractions of heavier hydrocarbons (C_1: 88.51 mol %, C_2: 6.02 mol %, C_3: 3.18 mol %, iC_4: 0.46 mol %, nC_4: 0.85 mol %, and iC_5+: 0.98 mol %).

The reported and predicted solubility data are shown in Figure 4. The best predictions are generated by sCPA-PR for both gas solubility in water and water solubility in natural gas. The nCPA-PR model with tuned K_{ij} values reproduces gas solubility in water with the same accuracy as the sCPA-PR model while it underestimates water solubility in the gas mixture as pressure increases. As can be seen from Figure 4, deviations between predicted water solubilities by nCPA-PR with tuned K_{ij} values and reported data are more evident at higher temperatures, i.e., (366.48 and 394.26) K, for the entire range of experimental pressures. Despite the satisfactory performance of the nCPA-PR with zero K_{ij} in reproducing the quantity of water in the vapor phase, predictions using this model for hydrocarbons solubility in water are approximately 2 to 5 times higher than the predictions of the sCPA-PR model and the reported solubility data.

CONCLUSION

New measured water content and density data were generated for two light and intermediate gas mixtures at high temperature conditions over a wide range of pressures. The measured data showed that at high temperature conditions, water solubility in hydrocarbon gas mixtures substantially increases with temperature particularly at low pressure conditions. By comparing the measured density data of each gas mixture at two different experimental temperatures, it was concluded that temperature had a marginal effect on the density of both studied water-saturated gas mixtures.

The CPA equation of state with and without incorporation of the cross-association concept was applied to reproduce the new measured and literature solubility data of gas mixtures. Consideration of cross-association between molecules of water and light hydrocarbons originated from the assumption of the temporary water-induced polar moments of light saturated hydrocarbons.[5] By comparing measured and predicted solubility data, it was verified that the concept of cross-association, implemented in the sCPA-PR model, considerably improves the predicted water solubility data of hydrocarbon gas mixtures particularly at high pressure conditions. In addition, accurate predictions were generated for hydrocarbon solubilities in the aqueous phase by sCPA-PR.

Results showed that nCPA-PR with tuned K_{ij} values is only reliable in predicting the aqueous phase composition. Good estimates were obtained for water content of hydrocarbon gas mixtures using nCPA-PR with zero K_{ij} values; however, predictions of hydrocarbons solubility in water were entirely erroneous.

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