Interfacial Tension of (Methane + Nitrogen) + Water and (Carbon Dioxide + Nitrogen) + Water Systems

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Interfacial tension data of (CH_4 + N_2) + H_2O and (CO_2 + N_2) + H_2O systems were measured using a pendant-drop method. The temperature and pressure ranges were 298−373 K and 1−30 MPa, respectively. The effects of gas composition, temperature, and pressure on the interfacial tension of the systems studied have been investigated. The linear gradient theory (LGT) was used to calculate the interfacial tensions of these two systems. The results show good agreement between the calculated and experimental interfacial tension data for the (CH_4 + N_2) + H_2O system. However, it was found that the LGT model with one adjustable parameter is inadequate to give accurate predictions for the CO_2 + H_2O system and thus is not suitable for the description of the (CO_2 + N_2) + H_2O system.

Introduction

The interfacial tension of (gas + water) systems plays an important role in many processes; for example, in oil/gas production and processing, the variation of interfacial tension with temperature, pressure, and gas composition strongly influences the fluid flow in reservoir porous media/process equipment. However, interfacial tension data are relatively scarce in the literature, especially for the gas mixture + water systems at elevated pressures. For developing a generalized interfacial tension model suitable for application to a reservoir and for use in process simulation, sufficient basic data are required.

In this work, the pendant-drop method was used to measure the high-pressure interfacial tensions for the (CH_4 + N_2) + H_2O system and the (CO_2 + N_2) + H_2O system at a series of gas compositions, temperatures, and pressures. The linear gradient theory (LGT) model developed by Zuo and Stenby[1−3] was used to calculate the interfacial tensions of these two systems. Good agreement with the experimental data of the (CH_4 + N_2) + H_2O system was observed. However, the single adjustable parameter LGT model was found to be unable to give accurate results for the CO_2 + H_2O system and the (CO_2 + N_2) + H_2O system.

Experimental Section

Materials. Methane, nitrogen, and carbon dioxide were supplied by the Beijing Analytical Instrument Corp. with a purity of 99.99 vol %. (Methane + nitrogen) and (carbon dioxide + nitrogen) mixtures were prepared (by moles) using the pure gases, and the compositions were analyzed by gas chromatograph HP6890. Laboratory-distilled water was redistilled and degassed prior to experimentation.

Apparatus and Experimental Procedure. A D. B. Robinson pendant-drop high-pressure interfacial tension apparatus equipped with an improved data acquisition system was used. As the apparatus and the experimental procedure have been described in detail in previous papers
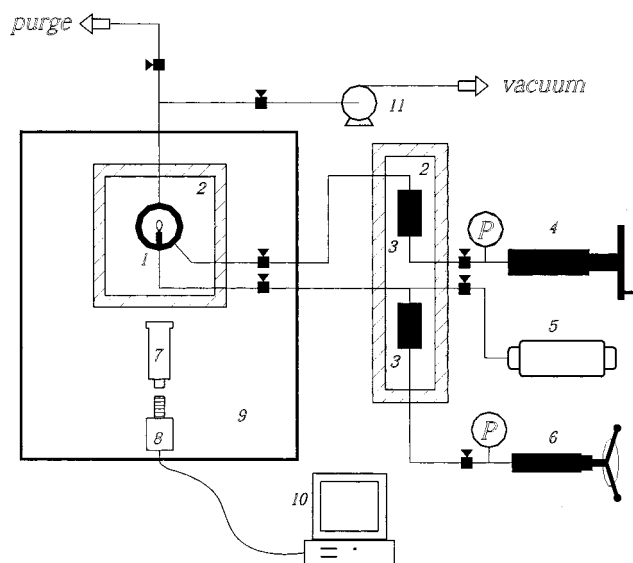
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Figure 1. Schematic diagram of the experimental apparatus: 1, pedant-drop cell; 2, thermostat; 3, sample cylinder; 4, JEFRI 100-1-10 HB pump; 5, gas tank; 6, JEFRI 10-1-12-NA pump; 7, microscope; 8, video camera; 9, vibration isolation bench; 10, computer; 11, vacuum pump.

published by this laboratory,[4,5] only a brief description is given below.

The schematic diagram of the experimental system is shown in Figure 1. The gas bubble is formed inside the pedant-drop cell. Its profile is magnified by the microscope and recorded by computer through the video camera. The dimensions of the bubble profile can be measured automatically using software developed in our laboratory.

The maximum working pressure of the experimental system is 34.5 MPa, and the operating temperature range is from room temperature to 473 K. The uncertainties of pressure and temperature measurements are ±0.01 MPa and ±0.1 K, respectively.

Calculation of Interfacial Tension. The interfacial tension data reported were calculated through the equation

Table 1. Measured Interfacial Tension (γ) Data and Corresponding Density Difference ($\Delta\rho$) between Gas and Liquid Phases

	298.15 K		313.15 K		333.15 K		353.15 K		373.15 K	
P/MPa	$\Delta\rho$/kg·m^{-3}	γ/mN·m^{-1}	$\Delta\rho$/kg·m^{-3}	γ/mN·m^{-1}	$\Delta\rho$/kg·m^{-3}	γ/mN·m^{-1}	$\Delta\rho$/kg·m^{-3}	γ/mN·m^{-1}	$\Delta\rho$/kg·m^{-3}	γ/mN·m^{-1}
System 1: Pure N_2 + H_2O										
1.00	986.13	71.43	981.84	69.36	973.48	65.68	962.67	62.17	951.26	58.03
3.00	975.68	70.45	961.19	68.26	954.21	64.94	944.62	61.43	934.29	57.00
5.00	942.51	69.23	940.62	67.25	935.09	64.28	926.77	60.43	917.56	56.10
10.00	888.88	67.21	890.22	65.05	888.42	62.74	883.32	58.66	876.92	54.25
15.00	837.91	65.54	842.38	63.32	844.17	60.85	842.15	57.30	838.40	53.16
20.00	790.99	63.94	798.12	61.65	803.04	59.44	803.75	55.77	802.37	52.37
25.00	748.75	63.15	757.94	60.55	765.37	57.80	768.35	54.67	768.98	51.68
30.00	711.18	62.66	721.86	59.82	731.20	56.41	735.99	53.66	738.28	51.11
System 2: (23.64 mol % CH_4 + 76.36 mol % N_2) + H_2O										
1.00	987.24	71.28	982.90	68.78	974.48	65.62	963.61	62.01	952.15	58.33
3.00	967.47	69.71	964.21	68.02	957.07	64.68	947.34	60.81	936.87	57.01
5.00	947.50	68.80	945.42	67.20	939.66	63.71	931.13	60.29	921.72	56.18
10.00	897.62	66.33	898.79	64.76	896.72	61.30	891.34	58.13	884.63	54.41
15.00	849.73	64.41	854.10	62.93	855.66	59.40	853.34	56.21	849.24	53.18
20.00	805.77	62.95	812.83	60.77	817.51	58.39	817.89	55.05	816.13	51.99
30.00	732.62	60.29	742.86	58.46	751.64	55.54	755.88	52.92	757.63	50.49
System 3: (50.09 mol % CH_4 + 49.01 mol % N_2) + H_2O										
1.00	988.48	71.12	984.09	68.80	975.60	65.78	964.67	61.90	953.15	58.06
3.00	971.04	69.80	967.62	67.82	960.30	64.58	950.41	60.89	939.79	56.90
5.00	953.12	68.76	950.85	66.79	944.83	63.49	936.06	60.04	926.42	56.02
10.00	907.31	65.91	908.36	64.20	906.03	61.75	900.34	57.68	893.31	53.94
15.00	862.48	63.12	866.95	61.54	868.39	59.05	865.80	55.58	861.38	52.46
20.00	821.50	61.00	828.72	59.04	833.33	57.28	833.49	54.34	831.39	51.19
30.00	755.49	57.96	765.42	56.45	773.81	54.02	777.58	51.64	778.83	49.17
System 4: (74.93 mol % CH_4 + 25.07 mol % N_2) + H_2O										
1.00	989.67	71.30	985.22	68.72	976.66	65.32	965.68	62.01	954.11	58.03
3.00	974.44	69.70	970.88	67.39	963.38	64.10	953.32	60.84	942.56	57.02
5.00	958.48	68.05	956.02	65.84	949.76	63.08	940.76	59.54	930.90	55.98
10.00	916.37	64.77	917.39	62.55	914.86	60.10	908.90	57.24	901.58	54.00
15.00	874.02	61.42	878.79	60.13	880.30	57.71	877.55	55.23	872.86	52.18
20.00	835.57	58.97	843.18	57.58	847.99	55.63	848.07	53.41	845.74	50.78
30.00	776.57	54.98	786.20	53.66	794.26	52.50	797.71	50.62	798.57	48.54
System 5: (24.97 mol % CO_2 + 75.03 mol % N_2) + H_2O										
1.00	985.58	69.33	980.95	67.95	972.32	64.90	961.39	61.74	948.47	58.32
5.00	936.22	60.47	933.52	59.72	927.46	58.71	918.97	56.34	908.38	54.21
10.00	868.88	53.44	870.68	53.25	869.58	52.78	865.20	51.23	858.17	50.01
15.00	799.82	49.78	807.16	49.37	811.90	49.22	812.16	47.87	808.97	47.49
20.00	734.40	47.71	746.62	47.64	756.77	47.02	761.41	46.09	761.86	45.47
30.00	626.33	45.30	643.46	45.05	660.26	44.31	671.07	43.21	677.01	41.64
System 6: (50.72 mol % CO_2 + 49.28 mol % N_2) + H_2O										
1.00	985.23	67.96	980.29	66.29	971.45	63.96	960.42	60.50	947.48	57.15
5.00	927.16	56.10	925.12	55.60	919.73	54.83	911.80	53.30	901.76	51.46
10.00	832.05	46.65	840.87	47.24	845.71	47.68	845.17	46.79	840.87	45.35
15.00	721.81	41.58	746.10	42.33	765.32	42.83	774.77	41.86	777.78	40.92
20.00	620.30	40.07	654.61	40.12	685.94	40.24	704.96	38.87	715.30	37.87
30.00	484.55	37.66	517.50	36.86	554.58	36.18	582.86	34.77	602.56	33.61
System 7: (75.85 mol % CO_2 + 24.15 mol % N_2) + H_2O										
1.00	984.69	65.85	979.52	64.74	980.57	62.92	959.42	59.33	946.48	55.97
5.00	912.05	49.63	912.70	51.20	921.60	52.02	903.06	51.47	894.07	49.09
10.00	741.46	37.24	782.66	40.96	819.25	43.09	816.25	42.75	817.81	41.84
15.00	514.31	33.08	604.37	35.74	688.64	38.47	713.36	37.74	731.61	36.97
20.00	400.13	31.88	468.74	33.69	562.21	35.18	607.60	34.10	642.32	33.72
30.00	297.77	32.72	337.68	32.83	403.86	33.51	445.51	30.33	489.11	29.23

developed by Andreas et al.[6]

$$\gamma = \frac{\Delta\rho g d_e^2}{H} \qquad (1)$$

where γ denotes the interfacial tension, $\Delta\rho$ is the density difference between the two phases, g is the gravitational constant, and d_e is the maximum diameter of the drop. Andreas et al.[6] have prepared a detailed table of $1/H$ as a function of (d_s/d_e), where d_s is the diameter of the drop at a selected horizontal plane at heights equal to d_e.

Calculation of Coexisting Phase Density. The multiparameter MOU/GRI equation of state developed by Li and Guo[7] was used to determine the gas-phase densities; the uncertainty of the calculated densities is 0.24%. The solubility of methane and nitrogen in water is negligible at the experimental conditions, so their influence on the density of aqueous phase is ignored.[8,9] Therefore, the density of pure water at the same temperature and pressure was used for the aqueous phase. However, the solubility of carbon dioxide in water is appreciable. The solubility of carbon dioxide and the density of the saturated aqueous phase were evaluated according to the method proposed by Chang et al.[10] Comparison of the calculated CO_2 solubility with experimental data reported by Weibe[11] indicates an absolute average deviation of 2.9%. The estimated uncertainty of the calculated density of aqueous phase is ~0.55%.

Results and Discussion

The interfacial tension data for the $(CH_4 + N_2)$ + H_2O and $(CO_2 + N_2)$ + H_2O systems are presented in Table 1 along with the corresponding density difference ($\Delta\rho$) between the coexisting gas and liquid phases. An overall
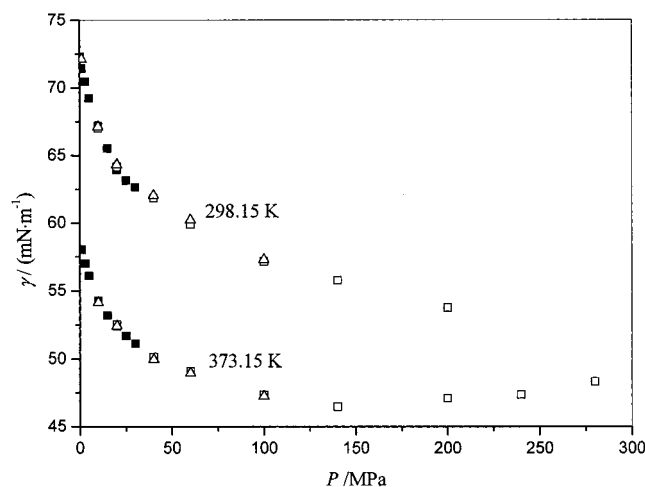
Figure 2. Comparison of interfacial tension data measured for $N_2 + H_2O$ systems at 298.15 K and 373.15 K: ■, this work; □, Weigand and Franck;[12] △, Tian et al.[14]

analysis of the whole experimental and calculation procedure indicates the maximum error in the reported interfacial tension data is ± 0.06 mN·m^{-1}.

For checking the apparatus and experimental procedure used in this study, the interfacial tension data of the $N_2 + H_2O$ system were measured and compared with the literature data reported by Weigand and Franck[12] and Tian et al.[13] Good agreement with the literature data was observed (See Figure 2).

On the basis of the measured interfacial tension, we have tried to analyze the effects of pressure, temperature, and gas composition on the interfacial tension of the $(CH_4 + N_2) + H_2O$ and $(CO_2 + N_2) + H_2O$ systems within the range of experimental temperature and pressure.

For the $(CH_4 + N_2) + H_2O$ system, the dependence of interfacial tension (γ) on pressure, temperature, and gas composition is relatively simple. When gas composition and temperature are fixed, γ decreases as the pressure increases, with a slightly steeper slope in the lower pressure range. When gas composition and pressure are fixed, γ always decreases with increasing temperature. Under fixed temperature and pressure conditions, γ decreases as methane content increases.

For the $(CO_2 + N_2) + H_2O$ system, the dependence of γ on pressure is nearly the same as that for the $(CH_4 + N_2) + H_2O$ system but with one exception. For the gas mixture with high carbon dioxide concentration (75.0 mol %), the $\gamma-P$ isotherm measured at 298.15 K showed a minimum at ~ 20 MPa. A similar phenomenon was observed by Wesch et al.[14] for the $CO_2 + H_2O$ system at 313.15 K. In fact, if the pressure is high enough, the minimum on the $\gamma-P$ curve can be observed also for the $N_2 + H_2O$ system.[12]

The temperature dependence of γ for the $(CO_2 + N_2) + H_2O$ system is rather complex. At low pressures, the increase of temperature always results in the lowering of γ at the composition range studied, but because the slopes of $\gamma-P$ isotherms are different, these curves could intersect each other at high pressures and make the temperature dependence of γ more complex. This complicated temperature dependence can also be observed from the interfacial tension data of $CO_2 + H_2O$ reported by Wesch et al.[14]

The composition dependence of γ for the $(CO_2 + N_2) + H_2O$ system is similar to that of the $(CH_4 + N_2) + H_2O$ system. When temperature and pressure are fixed, the increase of the mole fraction of CO_2, the component with a lower interfacial tension than N_2, will always decrease γ.

Interfacial Tension Calculation Using the LGT Model

Linear Gradient Theory. Traditionally, the Parachor method developed by Weinaug and Katz[15] was used for interfacial tension calculations. Although this method and its extensions had been successfully applied to many hydrocarbon systems remote from the critical point, it is not suitable even for the interfacial tension calculation of $CH_4 + H_2O$ systems.[16] Recently, Zuo and Stenby[1-3] developed a Linear Gradient Theory (LGT) based on the rigorous gradient theory.[17-23] In the LGT theory, it is assumed that the number densities of each component are linearly distributed across the interface. Therefore, it is unnecessary to solve a set of complicated differential or algebraic density-profile equations as required in the rigorous gradient theory. Zuo and Stenby have applied this model to a variety of mixtures including hydrocarbon + water mixtures. However, the LGT theory has not been widely tested for the interfacial tension between gas mixtures and water because the available interfacial tension data for such systems are scarce in the open literature. In this work, the LGT model was further tested on the interfacial tension data of gas mixtures + water systems measured in this laboratory.

According to the LGT model, the interfacial tension (σ) for an N-component equilibrium system at temperature T and pressure P is evaluated by

$$\sigma = \int_{n_{1V}}^{n_{1L}} \sqrt{2c[\Phi(\bar{n}) - \Phi_B]}\, dn_1 \tag{2}$$

$$\Phi(\bar{n}) = f^0(\bar{n}) - \sum_{i=1}^{N} n_i \mu_i \tag{3}$$

where $\Phi_B = -P$, c denotes the influence parameter of the mixture, $\Phi(\bar{n})$ is a grand thermodynamic potential energy density, n_{iV} and n_{iL} denote the number density of component i in the bulk vapor phase and liquid phase, respectively, μ_i is the chemical potential of component i in the bulk vapor or liquid phase, f^0 stands for the Helmholtz free-energy density, n_i is the number density of component i, and N denotes the number of components (component 1 refers to water). It is assumed that $n_i(z) - n_i$ at position z on the interface with width h is linearly distributed across the interface:

$$\frac{dn_i(z)}{dz} = \frac{\Delta n_i}{h} = \frac{n_{iL} - n_{iV}}{h} \quad i = 1, 2, ..., N \tag{4}$$

The properties of the homogeneous fluid (μ_i and f^0) are estimated by the SRK equation of state.[24] Classical mixing rules for energy parameter a and co-volume parameter b were used:

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j \sqrt{a_i a_j}(1 - k_{ij}) \tag{5}$$

$$b = \sum_{i=1}^{N} x_i b_i \tag{6}$$

The mixing rule of influence parameter c in eq 2 is

$$c = \sum_{i=1}^{N} \sum_{j=1}^{N} \sqrt{c_{ii} c_{jj}}(1 - l_{ij})\left(\frac{\Delta n_i}{\Delta n_1}\right)\left(\frac{\Delta n_j}{\Delta n_1}\right) \tag{7}$$

where l_{ij} is a binary interaction coefficient. The pure-

Table 2. Average Absolute Deviation (AAD[a]) of the Calculated Interfacial Tensions (mN·m⁻¹) for (CH₄ + N₂) + H₂O Systems Using the LGT Model[b]

	CH₄ mol % in the (CH₄ + N₂) gas mixture			
T/K	0.00	23.64	50.09	74.93
298.15	0.37	0.39	0.33	0.35
313.15	0.36	0.34	0.37	0.48
333.15	0.35	0.67	0.61	0.70
353.15	0.65	0.86	0.84	0.88
373.15	1.29	1.13	1.13	1.11
overall average	0.60	0.68	0.66	0.70

[a] $AAD = (1/N_P)\sum_j |\gamma_{calcd} - \gamma_{exptl}|_j$. [b] Experimental data measured in this work.

component influence parameter c_{ii} is calculated from the dimensionless ratio $c/ab^{2/3}$. Zuo and Stenby[3] suggested that $c/ab^{2/3}$ is a substance-dependent constant for pure hydrocarbons and inorganic gases but is temperature dependent for water. The temperature effect was correlated as

$$\frac{c}{ab^{2/3}} = 2.2192 \times 10^{-2} + 4.7263 \times 10^{-5}(T/K) + 1.5780 \times 10^{-6}(T/K)^2 \quad (8)$$

Calculation Results. To calculate the interfacial tension between gas mixtures and water, it is necessary to determine the appropriate binary interaction parameters k_{ij} in eq 5 and l_{ij} in eq 7. According to Zuo and Stenby's suggestion, all k_{ij} values were set to zero and only l_{ij} values between gases and water were considered.

l_{1,N_2} and l_{1,CH_4} were determined by fitting the experimental interfacial tension data of pure gas + water systems. The interfacial tension data of the N₂ + H₂O system measured in this work and the interfacial tension data for the CH₄ + H₂O system reported by Sachs and Meyn[8] were used in regression. The following temperature-dependent correlations have been established for l_{ij}:

$$l_{1,N_2} = 5.04776 - 0.0174\,T/K \quad (9)$$

$$l_{1,CH_4} = 0.88977 - 0.0027\,T/K \quad (10)$$

The above empirical correlations are different from the temperature-dependent l_{ij} correlations proposed by Zuo and Stenby,[3] which were obtained by fitting other interfacial tension data.

The calculated interfacial tension data for the (CH₄ + N₂) + H₂O systems are shown in Table 2 and Figure 3, respectively. Table 2 indicates that the AAD is <1 mN·m⁻¹ for all of the gas mixtures studied. From Figure 3, it can be seen that the prediction results are in excellent agreement with experimental data at low temperatures, but slightly larger deviations were observed at high temperatures.

To examine the applicability of the LGT model to the (CO₂ + N₂) + H₂O system, it was tested first on the pure CO₂ + H₂O system based on the interfacial tension data reported by Wesch et al.[14] The regression result for the data measured at 313 K is shown in Figure 4. It can be seen from Figure 4 that the LGT model overestimates the interfacial tension at low and moderate pressures but underestimates it at high pressures. This indicates that the current LGT model is not adequate for gas mixtures containing high concentrations of carbon dioxide. Hence, further tests on the interfacial tension calculation for the (CO₂ + N₂) + H₂O system have not been performed.
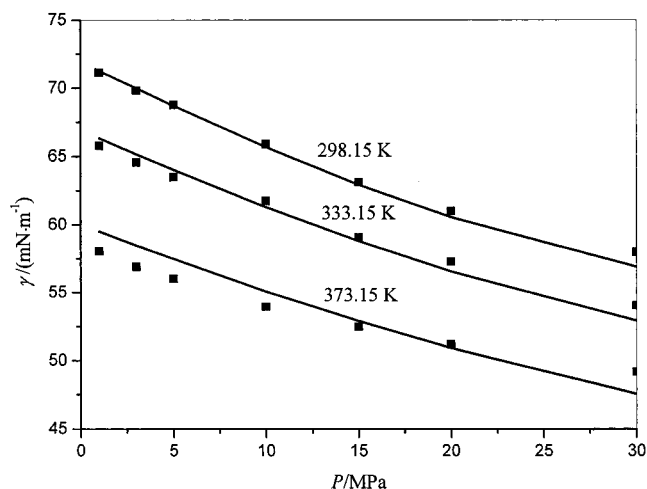

Figure 3. Comparison of experimental and calculated $\gamma - P$ isotherms for the (50.09 mol % CH₄ + 49.01 mol % N₂) + H₂O system: ■, experimental; —, calculated.
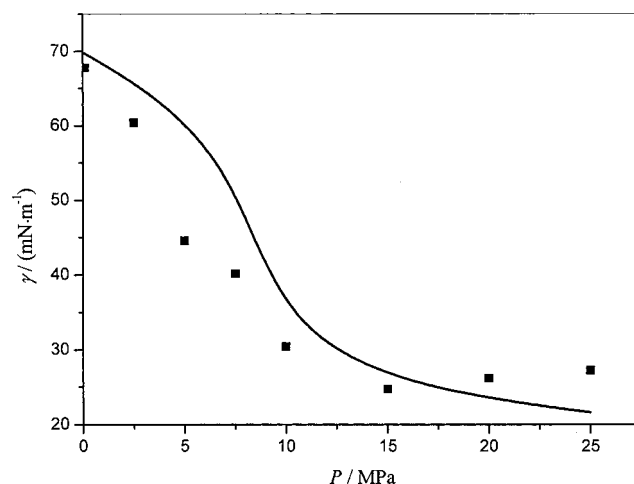

Figure 4. Comparison of experimental and calculated $\gamma - P$ isotherms for the CO₂ + H₂O system at 313.15 K: ■, Wesch et al.;[14] —, calculated.

Conclusions

Interfacial tensions of the (CH₄ + N₂) + H₂O and (CO₂ + N₂) + H₂O systems were measured using a pendant-drop apparatus. The effects of gas composition, temperature, and pressure on the interfacial tension of the systems studied have been analyzed. The linear gradient theory (LGT) developed by Zuo and Stenby[1−3] was used to describe the interfacial tension between gas mixtures and water. Good agreements were obtained for the (CH₄ + N₂) + H₂O system; however, it was found that the LGT model in its present form cannot be applied to interfacial tension calculation between water and gas mixtures containing high concentrations of carbon dioxide.

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