J. Chem. Eng. Data **1997,** *42,* 69−73 **69**

Solubilities of Methane, Nitrogen, Carbon Dioxide, and a Natural Gas Mixture in Aqueous Sodium Bicarbonate Solutions under High Pressure and Elevated Temperature

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An apparatus for measuring the solubility of gases in aqueous electrolyte solutions under high pressure and elevated temperature conditions is described. The solubility of methane, carbon dioxide, nitrogen, and a natural gas mixture in aqueous sodium bicarbonate solutions were measured up to 58 MPa and 403 K. The modified Patel−Teja equation of state proposed by Zuo and Guo (1991) for aqueous electrolyte systems was applied to correlate the measured solubility data, and satisfactory results were obtained.

Introduction

The solubility of natural gas mixtures in formation water (brine) plays an important role in estimating the natural gas reserve, the formation/dissociation conditions of methane hydrates in situ, and the interfacial tension of the hydrocarbon−formation water system. However, solubility data at high pressure and elevated temperature conditions for aqueous electrolyte systems are rare.

Recently, in the reservoirs found at the South China Sea area, the main salt species in the formation water is sodium bicarbonate, and the solubility data of gases in aqueous sodium bicarbonate solutions under reservoir conditions have not previously been reported.

The objective of this work is to measure the solubility of methane, nitrogen, carbon dioxide (major components of the natural gas exploited in the South China Sea area), and a typical natural gas mixture in aqueous sodium bicarbonate solutions of various concentrations. Such results are useful for testing/developing thermodynamic models. The modified Patel−Teja equation of state proposed by Zuo and Guo (1991) for high-pressure electrolyte systems was selected in this work.

Since the salt species contained and the composition of formation water vary considerably from the reservoir location and geological conditions, it is time consuming and costly to measure the natural gas solubility in formation water directly; hence, it will be of great value to establish a reliable prediction method.

Experimental Section

Apparatus. The schematic flow diagram of the experimental apparatus used for measuring the solubility of gas in aqueous electrolyte solutions is shown in Figure 1. The equilibrium cell is a 600 cm^3 stainless steel cell, which is immersed in an oil bath. The agitation is achieved by a mechanical rocking system. The maximum working pressure and temperature are 68 MPa and 423 K, respectively. The temperature in the oil bath can be controlled to within ±0.1 K, and the precision of pressure measurements (using Heise pressure gage) is ±0.01 MPa. A pressure balance cell is connected to the main system for keeping the system pressure undisturbed during the liquid sampling process.

Table 1. Composition of the Natural Gas Mixture Studied

component	mol %	component	mol %
nitrogen	1.34	isobutane	0.45
carbon dioxide	0.45	pentane	0.07
methane	92.04	isopentane	0.14
ethane	3.46	C_6^+	0.24
propane	1.47	Σ	100.00
butane	0.34		

Table 2. Mole Fraction Solubility *x* of Methane in Pure Water

A. measured in this work			B. data of O'Sullivan and Smith (1970)		
temp/K	pressure/MPa	10^4x	temp/K	pressure/MPa	10^4x
324.15	10.24	15.13	324.65	10.13	14.27
	20.26	21.82		20.26	22.79
	30.40	28.10		30.39	28.70
	40.52	32.37		40.52	33.40
	50.65	37.04		50.65	37.30
	54.40	38.80		61.78	40.90
	58.00	40.11			
375.15	5.60	8.87	375.65	10.23	13.55
	10.60	14.00		20.37	22.05
	20.60	23.03		30.59	28.70
	30.60	28.84		40.84	33.30
	40.00	33.81		50.77	38.50
	50.00	38.02		61.21	41.90
	58.00	41.10			

Materials. Methane, carbon dioxide, and nitrogen were supplied by Beijing Analytical Instrument Corp. The purity of individual gases checked by HP 5890A gas chromatography are methane 99.99 mass %, carbon dioxide 99.99 mass %, and nitrogen 99.95 mass %. Analytical grade sodium bicarbonate was purchased from the Beijing Chemical Reagents Corp.

The synthetic natural gas mixture studied was prepared by combining the separator gas and separator liquid (collected from a gas condensate field) at a selected gas/oil ratio. The composition of the prepared gas mixture analyzed by HP 5890A gas chromatography is given in Table 1, in which, C_6^+ stands for the small amount of C_6 and heavier hydrocarbons.

Experimental Procedure. Prior to performing the experiment, the whole system was evacuated by a vacuum pump. Approximately 450 cm^3 of degassed liquid solvent

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S0021-9568(96)00275-0 CCC: $14.00

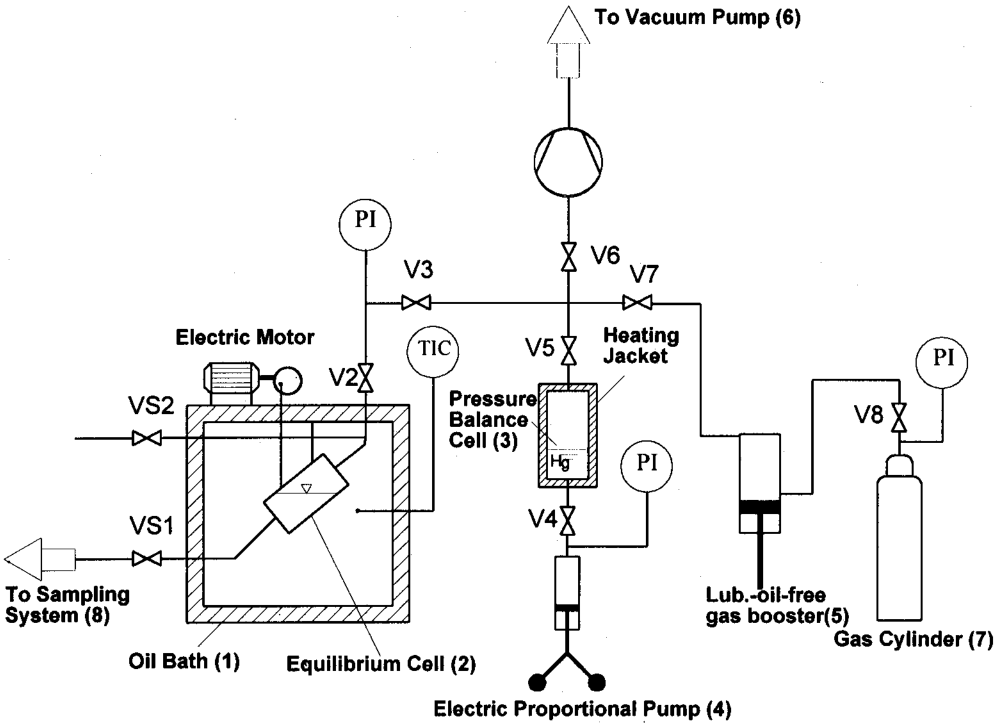

Figure 1. Schematic flow diagram of the apparatus for measuring gas solubility under high pressure and high temperature.

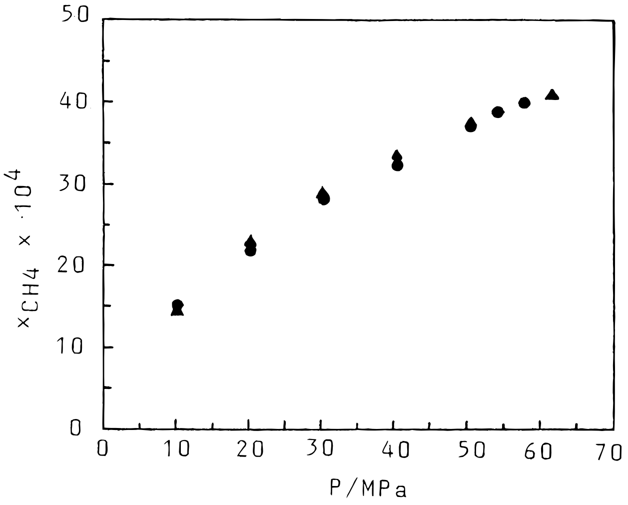

Figure 2. Comparison of the solubility of methane in pure water measured in this work and literature reported data: (●) this work, T = 324.15 K; (▲) O'Sullivan and Smith (1970), T = 324.65 K.

was transferred into the equilibrium cell through valve VS2. When the operating pressure was lower than the gas cylinder pressure, the pure gas sample (methane, nitrogen, or carbon dioxide) was introduced directly from the gas cylinder. In cases, where the system pressure exceeded the gas cylinder pressure, a lubricating-oil-free gas booster was used to raise the gas pressure. After charging the liquid and gas, the equilibrium cell was kept under agitation conditions for 8 h and then left for another 1 h.

Once the equilibrium condition was established, a liquid phase sample was withdrawn from the cell through valve VS1. During the sampling process, the system pressure was maintained nearly constant. This was achieved by opening valves V2, V3, and V4 and using an electric displacement pump to adjust the system pressure. The liquid sample collected under pressure was allowed to flash to atmospheric pressure. The volume of flashed gas was measured by a RUSKA gas meter (accuracy ±1 cm^3), and the amount of residue liquid was weighed by an electronic balance (accuracy ±0.0001 g).

Table 3. Mole Fraction Solubility x of Methane in the Aqueous $NaHCO_3$ Solutions

T = 324.15 K		T = 374.15 K		T = 403.15 K	
P/MPa	10^4x	P/MPa	10^4x	P/MPa	10^4x
		2 mass % $NaHCO_3$			
5.35	8.29	5.20	8.13	5.40	8.57
10.20	11.87	10.40	12.14	10.60	12.74
20.40	20.35	20.20	19.20	20.30	19.62
30.73	26.76	30.40	26.21	30.20	26.75
40.60	31.42	40.50	30.77	40.30	32.27
50.50	36.10	50.60	35.82	50.20	36.44
57.40	39.85	56.30	38.57	57.25	40.36
		5 mass % $NaHCO_3$			
5.70	5.72	5.20	5.04	5.30	5.42
10.70	9.68	10.20	9.25	10.10	9.18
21.00	16.30	20.60	15.67	20.40	15.60
30.60	21.26	30.40	21.15	30.40	21.43
41.60	26.87	40.10	25.72	40.40	26.53
50.70	30.72	50.60	30.46	50.40	31.10
56.60	33.43	56.60	32.85	58.00	34.27
		7 mass % $NaHCO_3$			
5.60	3.01	5.10	2.76	5.20	2.97
10.42	7.14	10.30	6.31	10.20	6.50
20.40	12.73	20.20	12.48	20.50	12.47
30.50	17.81	30.20	17.52	30.30	18.05
40.80	22.62	40.46	21.17	40.70	22.81
50.40	25.56	50.30	25.20	50.60	26.35
57.60	28.44	56.50	27.52	57.50	29.26

Test Run. For checking the reliability of the apparatus and experimental procedure used in this work, the solubility data of methane in pure water were measured. The measured data were compared with literature data reported by O'Sullivan and Smith (1970) and are shown in Table 2 and Figure 2, respectively. The agreement between the two data sources is satisfactory.

Experimental Results. The mole fraction solubilities measured for methane, nitrogen, carbon dioxide, and a natural gas mixture in aqueous sodium bicarbonate solutions under high pressures and elevated temperatures are tabulated in Tables 3−5. The salt concentrations (2, 5, and 7 mass %) are in the range of the sodium bicarbonate content in the formation water at the South China Sea area. The accuracy of the measured solubility data is

Table 4. Mole Fraction Solubility x of Nitrogen in the Aqueous $NaHCO_3$ Solutions

T = 323.15 K		T = 373.15 K		T = 403.15 K	
P/MPa	10^4x	P/MPa	10^4x	P/MPa	10^4x
		2 mass % $NaHCO_3$			
5.70	4.16	5.20	4.03	5.30	4.18
10.60	7.34	10.20	7.21	10.70	7.37
20.70	12.96	20.60	12.82	20.20	13.16
30.30	18.07	30.50	18.37	30.55	18.58
40.42	22.46	40.80	22.53	40.70	23.10
50.20	26.40	50.43	26.06	50.20	26.56
55.30	28.21	56.30	28.13	56.40	28.88
		5 mass % $NaHCO_3$			
5.22	2.84	5.30	2.86	5.50	2.87
10.50	5.24	10.40	5.15	10.20	5.34
20.40	9.73	20.50	9.61	20.30	9.81
30.50	13.61	30.20	13.59	30.40	13.84
40.20	17.03	40.50	17.34	40.60	17.65
50.65	20.44	50.20	20.71	50.30	20.82
56.70	21.56	57.60	22.06	57.20	23.04
		7 mass % $NaHCO_3$			
10.30	4.52	10.40	4.50	10.50	4.64
20.44	8.36	20.30	8.32	20.20	8.58
30.40	12.11	30.30	12.08	30.50	12.25
40.50	14.43	40.60	14.53	40.70	15.12
50.70	17.41	50.40	17.55	50.85	17.83
56.50	18.78	57.50	18.60	57.40	19.40

Table 5. Mole Fraction Solubility x of Carbon Dioxide in the Aqueous $NaHCO_3$ Solutions

T = 323.15 K		T = 373.15 K		T = 403.15 K	
P/MPa	x	P/MPa	x	P/MPa	x
		2 mass % $NaHCO_3$			
5.20	0.00672	5.20	0.00518	5.40	0.00424
10.60	0.01064	10.40	0.00892	10.20	0.00735
20.20	0.01717	20.40	0.01502	20.50	0.01381
30.80	0.02291	30.75	0.02016	30.70	0.01870
40.24	0.02648	40.20	0.02415	40.60	0.02274
50.60	0.02976	50.50	0.02682	50.20	0.02542
56.80	0.03117	57.60	0.02867	57.40	0.02636
		5 mass % $NaHCO_3$			
5.00	0.00546	5.80	0.00424	5.60	0.00325
10.30	0.00904	10.25	0.00742	10.30	0.00572
20.00	0.01452	20.80	0.01321	20.60	0.01204
28.70	0.01940	30.90	0.01834	32.10	0.01713
40.50	0.02376	40.20	0.02152	40.30	0.01983
50.40	0.02643	50.70	0.02475	50.20	0.02265
57.60	0.02783	57.40	0.02604	56.40	0.02377
		7 mass % $NaHCO_3$			
5.20	0.00464	5.40	0.00323	5.40	0.00226
10.40	0.00782	10.50	0.00613	10.60	0.00484
20.80	0.01364	20.20	0.01124	20.54	0.00973
30.50	0.01772	30.65	0.01523	31.60	0.01405
40.60	0.02068	40.40	0.01823	41.20	0.01686
50.80	0.02315	50.20	0.02059	50.70	0.01892
57.20	0.02401	56.80	0.02176	57.30	0.01973

estimated as 5% for CH_4 and 10% for N_2 and CO_2 (chemical reactions involved).

The solubility data of the natural gas mixture (for composition see Table 1) in 5 mass % $NaHCO_3$ solution are listed in Table 6 and plotted in Figure 3. The compositions (on salt-free basis) of the equilibrium liquid phase under three temperatures are tabulated in Table 7.

Application of the MPT EOS

The modified Patel–Teja equation of state (MPT EOS) proposed by Zuo and Guo (1991) for high-pressure aqueous electrolyte systems was applied to correlate the measured gas solubility data. In a recent article, Tse and Bishnoi (1994) compared the performance of three thermodynamic models for describing the phase equilibria of aqueous electrolyte systems and concluded that the MPT EOS gives the best results. For the ease of reference, the MPT EOS is briefly described as follows:

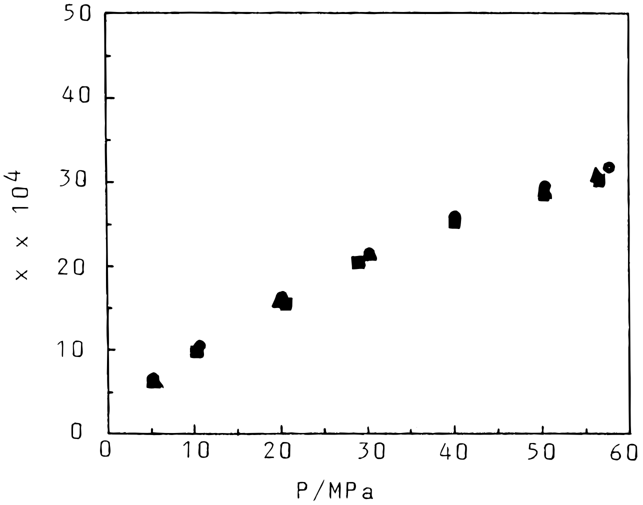

Figure 3. Solubility of the natural gas mixture in 5 mass % $NaHCO_3$ solution: (▲) T = 323.15 K; (■) T = 373.15 K; (●) T = 403.15 K.

Table 6. Mole Fraction Solubility x of the Natural Gas Mixture in the 5 Mass % $NaHCO_3$ Solution

T = 323.15 K		T = 373.15 K		T = 403.15 K	
P/MPa	10^4x	P/MPa	10^4x	P/MPa	10^4x
5.54	6.33	5.20	6.21	5.40	6.65
10.35	10.32	10.35	9.74	10.54	10.41
19.70	15.65	20.60	15.44	20.30	16.18
30.44	21.28	29.00	20.47	30.40	21.47
40.20	25.41	40.20	25.20	40.20	25.74
50.40	28.78	50.30	28.52	50.45	29.36
56.30	30.62	56.50	30.12	57.70	31.62

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+c(v-b)} \tag{1}$$

Expressions for calculating the EOS parameters (a, b, and c) for ionic species have been developed, and the calculation of the fugacity coefficient of component/ion i in an electrolyte system (ϕ_i) was separated into two parts:

$$\ln \phi_i = \ln \phi_i^{\text{EOS}} + \ln \phi_i^{\text{DH}} \tag{2}$$

The original PT EOS proposed by Patel and Teja (1982) was used to evaluate the term $\ln \phi_i^{\text{EOS}}$, and the $\ln \phi_i^{\text{DH}}$ term was calculated by using the following modified Debye–Huckel model proposed by Li and Pitzer (1986):

$$\ln \phi_i^{\text{DH}} = -A\left[\frac{2z_i^{\,2}}{B}\ln\left(\frac{1+BI^{1/2}}{1+\text{B}/\sqrt{2}}\right) + \left(\frac{I^{1/2}Z_i^{\,2} - 2I^{2/3}}{I+BI^{1/2}}\right)\right] \tag{3}$$

$$I = 0.5\sum_i x_i z_i^{\,2} \tag{4}$$

$$A = \frac{1}{3}\left(\frac{2\pi N_{\text{a}} d_0}{M_{\text{s}}}\right)^{1/2}\left(\frac{e^2}{DkT}\right)^{3/2} \tag{5}$$

$$B = 2150(d_0/DT)^{1/2} \tag{6}$$

where D, e, Z, M_s, and d_0 denote dielectric constant, electronic charge, number of charges, molecular weight of solvent, and solvent density, respectively. *It should be noted that the Debye–Huckel term is neglected for nonelectrolyte systems and for the gas phase* (assuming no ionic species are present in the gas phase).

Table 7. Mole Fraction Composition of the Equilibrium Liquid Phase for the Natural Gas + 5 Mass % $NaHCO_3$ Solution System

T/K	P/MPa	$x(N_2)$	$x(CO_2)$	$x(C_1)$	$x(C_2)$	$x(C_3)$	$x(C_4^+)$	$x(H_2O)$
323.15	5.54	0.3760×10^{-5}	0.9925×10^{-5}	0.5990×10^{-3}	0.1177×10^{-4}	0.3146×10^{-5}	0.5381×10^{-5}	0.9994
	10.35	0.6089×10^{-5}	0.1202×10^{-4}	0.9773×10^{-3}	0.2599×10^{-4}	0.5552×10^{-5}	0.5016×10^{-5}	0.9990
	19.70	0.1377×10^{-4}	0.2366×10^{-4}	0.1497×10^{-2}	0.2574×10^{-4}	0.2160×10^{-5}	0.2629×10^{-5}	0.9984
	30.44	0.1709×10^{-4}	0.3413×10^{-4}	0.2027×10^{-2}	0.3209×10^{-4}	0.5660×10^{-5}	0.1164×10^{-4}	0.9979
	40.20	0.2800×10^{-4}	0.4927×10^{-4}	0.2407×10^{-2}	0.3623×10^{-4}	0.3913×10^{-5}	0.1629×10^{-4}	0.9975
	50.40	0.2913×10^{-4}	0.5736×10^{-4}	0.2730×10^{-2}	0.3989×10^{-4}	0.4432×10^{-5}	0.1721×10^{-4}	0.9971
	56.30	0.2462×10^{-4}	0.5873×10^{-4}	0.2901×10^{-2}	0.4155×10^{-4}	0.5022×10^{-5}	0.3135×10^{-4}	0.9969
373.15	5.20	0.7570×10^{-5}	0.1096×10^{-4}	0.5878×10^{-3}	0.9712×10^{-5}	0.1211×10^{-5}	0.3782×10^{-5}	0.9994
	10.35	0.1169×10^{-4}	0.1636×10^{-4}	0.9267×10^{-3}	0.1426×10^{-4}	0.1802×10^{-5}	0.3146×10^{-5}	0.9990
	20.60	0.5512×10^{-5}	0.2714×10^{-4}	0.1476×10^{-2}	0.2657×10^{-4}	0.4292×10^{-5}	0.4215×10^{-5}	0.9985
	29.00	0.1247×10^{-4}	0.3730×10^{-4}	0.1953×10^{-2}	0.3382×10^{-4}	0.5609×10^{-5}	0.4831×10^{-5}	0.9980
	40.20	0.1814×10^{-4}	0.4266×10^{-4}	0.2404×10^{-2}	0.3760×10^{-4}	0.9500×10^{-5}	0.8089×10^{-5}	0.9975
	50.30	0.2387×10^{-4}	0.4520×10^{-4}	0.2728×10^{-2}	0.4700×10^{-4}	0.4050×10^{-5}	0.3765×10^{-5}	0.9971
	56.50	0.1904×10^{-4}	0.5500×10^{-4}	0.2863×10^{-2}	0.4882×10^{-4}	0.9638×10^{-5}	0.1690×10^{-4}	0.9970
403.15	5.40	0.4708×10^{-5}	0.1282×10^{-4}	0.6298×10^{-3}	0.9589×10^{-5}	0.1297×10^{-5}	0.6810×10^{-5}	0.9993
	10.64	0.4424×10^{-5}	0.1484×10^{-4}	0.1001×10^{-2}	0.1417×10^{-4}	0.1676×10^{-5}	0.5080×10^{-5}	0.9990
	20.30	0.6601×10^{-5}	0.2131×10^{-4}	0.1554×10^{-2}	0.2825×10^{-4}	0.3721×10^{-5}	0.4288×10^{-5}	0.9984
	30.40	0.1129×10^{-4}	0.3626×10^{-4}	0.2058×10^{-2}	0.3386×10^{-4}	0.5325×10^{-5}	0.1975×10^{-5}	0.9979
	40.20	0.2085×10^{-4}	0.5112×10^{-4}	0.2447×10^{-2}	0.3933×10^{-4}	0.6538×10^{-5}	0.8958×10^{-5}	0.9974
	50.45	0.9395×10^{-5}	0.4149×10^{-4}	0.2816×10^{-2}	0.4480×10^{-4}	0.7428×10^{-5}	0.1718×10^{-4}	0.9971
	57.70	0.1372×10^{-4}	0.4882×10^{-4}	0.3047×10^{-2}	0.4313×10^{-4}	0.7589×10^{-5}	0.1708×10^{-5}	0.9968

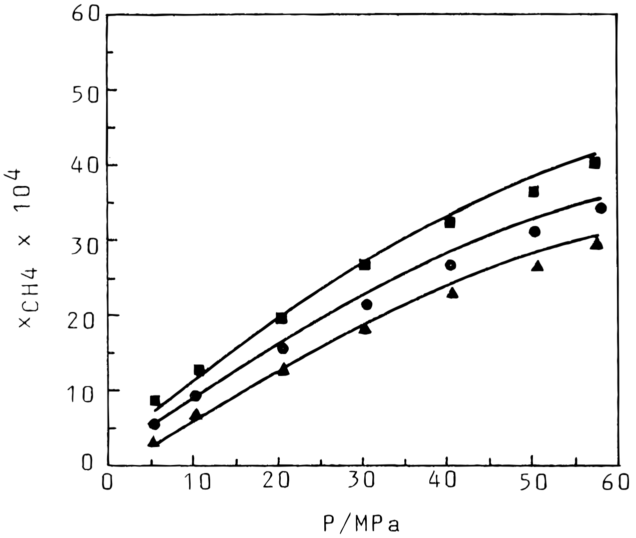

Figure 4. Solubility of methane in aqueous $NaHCO_3$ solutions at T = 403.15 K: (■) 2 mass % $NaHCO_3$; (●) 5 mass % $NaHCO_3$; (▲) 7 mass % $NaHCO_3$; (—), calculated.

Table 8. Gas−Salt Binary Parameters (A_{ij}) Determined from Solubility Data of Gas + H_2O + $NaHCO_3$ Systems[a]

gas	N_p	T range/ K	P range/ MPa	salt conc range/ mass %	binary parameter, A_{ij}	AAD-P/ %[b]
CH_4	63	324−403	50−58	2−7	−12.32	11.22
N_2	60	323−403	50−58	2−7	−6.90	8.28
CO_2	63	323−403	50−58	2−7	−8.39	7.78
overall						9.11

[a] Binary parameter for water−salt pair: $A_{w-s} = -5.20$. [b] AAD-P (%) = $(1/N_P)\sum_{j=1}^{N_P}|(P_{cal} - P_{exp})/P_{exp}|_j \times 100$.

The mixing rules used for parameters a, b, and c are

$$b = \sum_i x_i b_i \tag{7}$$

$$c = \sum_i x_i c_i \tag{8}$$

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2}(1 - k_{ij}) - \frac{2dg_\infty^E}{\ln \frac{Q + d}{Q - d}} \tag{9}$$

where

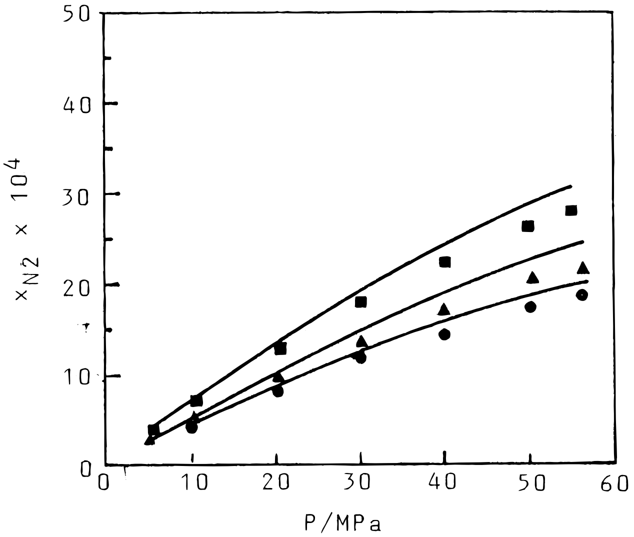

Figure 5. Solubility of nitrogen in aqueous $NaHCO_3$ solutions at T = 323.15 K: (■) 2 mass % $NaHCO_3$; (▲) 5 mass % $NaHCO_3$; (●) 7 mass % $NaHCO_3$; (—) calculated.

$$d = \sqrt{bc + \frac{(b + c)^2}{4}} \tag{10}$$

$$Q = (3b + c)/2 \tag{11}$$

$$g_\infty^E = RT\sum_i \sum_j x_i x_j A_{ij} \tag{12}$$

A_{ij} in eq 12 is a binary interaction parameter. The detailed description of the MPT EOS and the nomenclature of symbols are referred to in the original article by Zuo and Guo (1991).

The optimum A_{ij} values determined for the systems studied in this work and the average deviations of data correlation are listed in Table 8. Figures 4−6 show the comparisons of calculated and experimental gas solubility data for the CH_4 + H_2O + $NaHCO_3$ system at 403.15 K, the N_2 + H_2O + $NaHCO_3$ system at 323.15 K, and the CO_2 + H_2O + $NaHCO_3$ system at 373.15 K, respectively.

Conclusions

An apparatus was built to measure the gas solubility under high-pressure and elevated temperature conditions. The solubility data of methane, nitrogen, carbon dioxide,

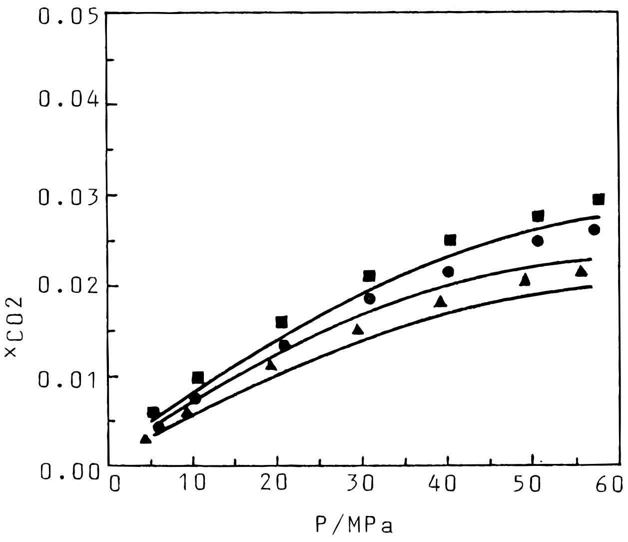

Figure 6. Solubility of carbon dioxide in aqueous $NaHCO_3$ solutions at T = 403.15 K: (■) 2 mass % $NaHCO_3$; (●) 5 mass % $NaHCO_3$; (▲) 7 mass % $NaHCO_3$; (—) calculated.

and a natural gas mixture in aqueous sodium bicarbonate solutions have been measured up to 58 MPa and 403 K. The MPT equation of state proposed by Zuo and Guo (1991) was used to correlate the experimental data, and satisfactory results were observed.

Acknowledgment

The authors wish to thank Mr. W.-D. Ma for his help in carrying out the experimental work.

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Received for review August 12, 1996. Accepted October 8, 1996.[⊗] The financial support provided by the China National Petroleum & Natural Gas Corp. is gratefully acknowledged.

JE960275N

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.