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## Density of Carbon Dioxide + Brine Solution from Tianjin Reservoir under Sequestration Conditions

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**ABSTRACT:** Density data of carbon dioxide (CO<sub>2</sub>) + brine solution from Tianjin reservoir were determined using magnetic suspension balance (MSB). Measurements were performed in the pressure range (10 to 18) MPa and at the temperatures (313 to 353) K. CO<sub>2</sub> mass fraction in solution was selected up to 0.040. The experimental results revealed that the density of CO<sub>2</sub> + brine solution decreases with increasing temperature and increase with increasing pressure. The density of CO<sub>2</sub> + brine solution increases almost linearly with increasing mass fraction of CO<sub>2</sub> in solution. The slope of the density vs CO<sub>2</sub> mass fraction curves decreased from 0.222 to 0.185 as temperature increased from 313 to 353 K and is independent of pressure. Two regression functions were developed to describe the density data of CO<sub>2</sub>-free brine and CO<sub>2</sub> + brine solution from Tianjin reservoir under sequestration conditions, and the errors between experimental results and prediction were within 0.004% and 0.03%, respectively.

## INSTRUCTION

The sequestration of CO<sub>2</sub> into geological formations (e.g., deep saline formations, depleted oil and gas fields, and unmineable coal seams), as one of carbon capture and storage (CCS) technologies, has been considered as a promising option for reducing CO<sub>2</sub> emissions and mitigating climate change.<sup>1</sup> Among all the geological formations, deep saline formations provide the largest capacity for CO<sub>2</sub> geological sequestration as a result of their size and wide distribution throughout the globe in all sedimentary basins. It is already known that a density difference of 0.1 kg·m<sup>-3</sup> is sufficient to drive a natural CO<sub>2</sub>-bearing solution to either sink or buoy,<sup>2</sup> which is one of the main factors affecting the safety and efficacy of CO<sub>2</sub> sequestration. The density value of CO<sub>2</sub> + brine solution is also necessary for the storage capacity estimates of the target sequestration formation. Therefore, density change of the brine due to dissolution of CO<sub>2</sub> under sequestration conditions is indispensable for accurate simulation of CO<sub>2</sub> sequestration process and CO<sub>2</sub> migration in formation brine.

During the last several decades, many investigators have studied the densities of aqueous CO<sub>2</sub> solution under deep ocean conditions such as the CO<sub>2</sub> seawater solution at 276.15 K and 35 MPa by Ohsumi et al.,<sup>3</sup> the CO<sub>2</sub> aqueous solution from (278.15 to 293.15) K and (6.44 to 29.49) MPa by Teng and Yamasaki,<sup>4</sup> Parkinson and Nevers<sup>5</sup> have reported the densities of CO<sub>2</sub> + water solution in a temperature range from (278.10 to 313.70) K and pressures up to 3.4 MPa. Yaginuma et al.<sup>6</sup> have measured the densities of CO<sub>2</sub> + distilled water solution at 304.15 K and pressures up to 10 MPa. However, these results are not suitable for CO<sub>2</sub> deep saline formation sequestration because of the low temperature or the low pressure. Li et al.<sup>7</sup> have reported the densities of CO<sub>2</sub> + brine solution from the Weyburn reservoir at a temperature of 332.15 K and pressures up to 29 MPa. But they have not clarified the relationship between densities of CO<sub>2</sub> formation brine solution and temperature. Besides, according to the analysis of Duan et al.<sup>8</sup> and Hu

Table 1. Analysis of Brine Sample from Tianjin Reservoir

calcium/(mol·kg <sup>-1</sup> )	0.000045
sodium/(mol·kg <sup>-1</sup> )	0.020025
magnesium/(mol·kg <sup>-1</sup> )	0.000143
potassium/(mol·kg <sup>-1</sup> )	0.000410
iron/(mol·kg <sup>-1</sup> )	0.000004
chloride/(mol·kg <sup>-1</sup> )	0.012667
sulfate/(mol·kg <sup>-1</sup> )	0.002094
bicarbonate/(mol·kg <sup>-1</sup> )	0.001967
pH at 290.55 K	8.44

et al.,<sup>9</sup> most of the density data are inconsistent with each other and the accuracy is not sufficient for assessing CO<sub>2</sub> sequestration. In conclusion, for the density of CO<sub>2</sub> + brine solution under practical sequestration conditions (high pressure, elevated temperature, and various CO<sub>2</sub> mass fractions), more experimental measurements are required.

In recent years, the Chinese government has planned to launch a CO<sub>2</sub> sequestration pilot project in Tianjin city, located in the northeast of the North China Plain. Therefore, the present paper reports the experimental densities of CO<sub>2</sub> + brine solution from Tianjin reservoir. The experiments have been conducted in the pressure range (10 to 18) MPa and at temperatures (313 to 353) K. These pressure and temperature conditions were chosen on the basis of the common *p*–*T* ranges (*p* > 10 MPa, *T* > 313 K) of CO<sub>2</sub> storage sites. In view of the solubility of CO<sub>2</sub> in water,<sup>10–12</sup> the CO<sub>2</sub> mass fraction in solution was selected up to 0.040. Two new equations for quantitative estimation of the densities of CO<sub>2</sub>-free brine and CO<sub>2</sub> + brine solution from Tianjin reservoir under sequestration conditions have been proposed.

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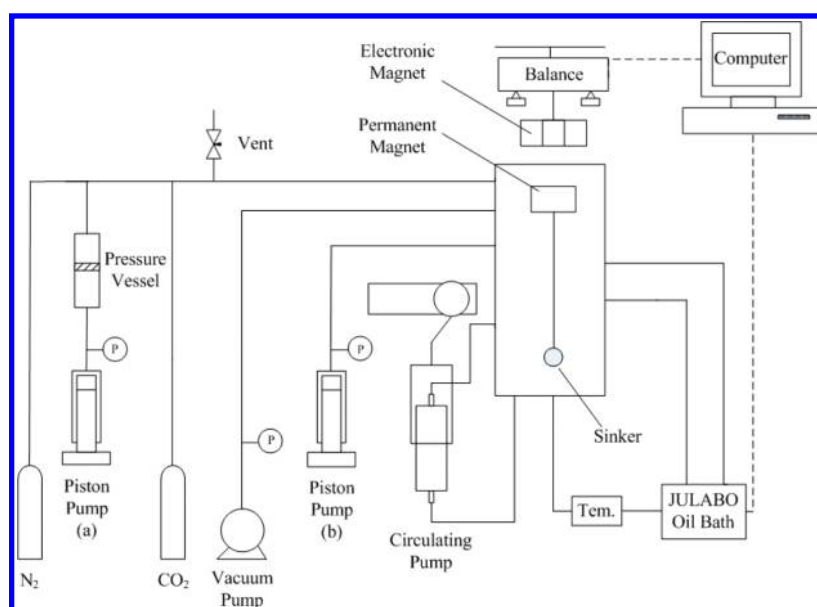


Figure 1. Schematic diagram of experimental apparatus.

Table 2. Experimental Densities  $\rho$  of CO<sub>2</sub>-Free Brine from Tianjin Reservoir and Deviations from the Values  $\rho_{\text{EOS}}$  Calculated from EOS of Zhenhao Duan et al.<sup>8</sup>

$T/\text{K}$	st dev( $T$ )/mK	$p/\text{MPa}$	st dev( $p$ )/kPa	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\rho_{\text{EOS}}/\text{g}\cdot\text{cm}^{-3}$	$100\cdot(\rho - \rho_{\text{EOS}})/\rho$
313.21	6.241	10.00	0.955	0.99815	0.99776	0.039
313.24	7.790	12.01	1.018	0.99900	0.99861	0.039
313.21	7.614	14.00	0.900	0.99988	0.99947	0.041
313.17	12.151	16.01	1.227	1.00073	1.00033	0.040
313.08	4.484	18.01	0.974	1.00162	1.00121	0.041
323.20	6.370	10.01	0.932	0.99398	0.99354	0.044
323.20	11.421	12.00	0.833	0.99483	0.99438	0.045
323.22	9.546	14.01	0.509	0.99568	0.99522	0.046
323.23	13.015	16.00	0.717	0.99652	0.99606	0.046
323.21	13.160	18.01	0.659	0.99737	0.99691	0.046
332.95	9.315	10.02	1.060	0.98933	0.98883	0.051
332.97	7.940	12.01	1.129	0.99018	0.98966	0.053
332.99	8.297	14.00	0.900	0.99102	0.99050	0.052
333.00	5.931	16.00	0.422	0.99186	0.99134	0.052
333.00	5.647	18.01	0.509	0.99270	0.99218	0.052
343.00	16.918	10.00	0.830	0.98391	0.98341	0.051
343.11	21.042	12.01	0.978	0.98471	0.98421	0.051
343.20	16.918	14.01	0.999	0.98550	0.98501	0.050
343.23	15.511	16.00	0.978	0.98635	0.98584	0.052
343.22	15.036	18.01	0.797	0.98721	0.98669	0.053
353.22	16.806	10.00	0.897	0.97784	0.97737	0.048
353.11	14.540	12.01	0.999	0.97881	0.97831	0.051
353.10	11.293	14.01	1.285	0.97967	0.97918	0.050
353.12	10.826	16.00	1.139	0.98052	0.98003	0.050
353.16	9.771	18.01	0.702	0.98136	0.98087	0.050

## EXPERIMENTAL SECTION

**Materials.** The CO<sub>2</sub> and N<sub>2</sub> were supplied by Dalian Da-te Gas Ltd. According to the gas chromatographic analysis and the dew point analysis, the purity of CO<sub>2</sub> and N<sub>2</sub> are 0.9999 and 0.99999, respectively. Both of them were used for density

measurement without further purification. The brine sample belongs to the bottomhole sample. It was collected at the wellhead of the well, through which the formation brine was extracted. The Tianjin Formation is a 23–69 m thick massive sandstone formation located at a depth of 1480–1653 m beneath the ground surface. The composition of the formation brine

**Table 3.** Experimental Densities  $\rho$  of CO<sub>2</sub> + Brine Solution from Tianjin Reservoir and Deviations from the Values  $\rho_{\text{EOS}}$  Calculated from EOS of Zhenhao Duan et al.<sup>8</sup>

$T/\text{K}$	st dev( $T$ )/mK	$p/\text{MPa}$	st dev( $p$ )/kPa	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\rho_{\text{EOS}}/\text{g}\cdot\text{cm}^{-3}$	$100\cdot(\rho - \rho_{\text{EOS}})/\rho$
$w = 0.010$						
313.24	9.546	10.00	1.062	1.00062	1.00000	0.062
313.25	14.405	12.01	1.125	1.00148	1.00086	0.062
313.25	14.836	14.00	1.367	1.00233	1.00172	0.061
313.24	9.743	16.00	1.408	1.00317	1.00258	0.059
313.24	9.546	18.00	6.038	1.00402	1.00343	0.059
323.22	6.079	10.01	0.532	0.99645	0.99557	0.088
323.24	11.726	12.00	1.021	0.99729	0.99642	0.087
323.21	10.180	14.00	0.881	0.99815	0.99729	0.086
323.21	5.647	16.01	0.637	0.99900	0.99815	0.085
323.23	5.149	18.00	0.798	0.99983	0.99898	0.085
333.22	7.638	10.19	0.539	0.99167	0.99061	0.107
333.24	5.686	12.00	0.700	0.99244	0.99138	0.107
333.24	7.020	14.00	0.780	0.99329	0.99224	0.106
333.22	10.376	16.00	0.408	0.99414	0.99310	0.105
333.19	6.000	18.00	0.957	0.99501	0.99397	0.105
343.23	9.634	10.01	2.955	0.98620	0.98495	0.127
343.21	5.836	12.01	1.180	0.98706	0.98583	0.125
343.18	4.702	14.00	0.999	0.98794	0.98671	0.125
343.18	6.757	16.00	0.717	0.98879	0.98758	0.122
343.17	5.898	18.01	0.884	0.98965	0.98844	0.122
353.25	15.718	10.00	7.743	0.98017	0.97887	0.133
353.23	14.127	12.00	7.013	0.98105	0.97976	0.131
353.22	14.136	14.00	4.180	0.98193	0.98065	0.130
353.20	10.360	16.01	0.926	0.98283	0.98154	0.131
353.18	6.761	18.00	1.239	0.98370	0.98242	0.130
$w = 0.021$						
313.13	5.936	10.01	0.884	1.00311	1.00252	0.059
313.16	4.523	12.01	1.267	1.00396	1.00338	0.058
313.14	6.216	14.01	1.168	1.00482	1.00426	0.056
313.14	9.962	16.00	1.311	1.00566	1.00512	0.054
313.15	10.553	18.00	1.165	1.00650	1.00598	0.052
323.13	18.173	10.01	1.032	0.99881	0.99786	0.095
323.09	2.887	12.01	0.669	0.99968	0.99875	0.093
323.12	4.924	14.01	0.793	1.00053	0.99961	0.092
323.12	9.002	16.00	0.902	1.00135	1.00047	0.088
323.14	8.065	18.01	1.215	1.00217	1.00132	0.085
333.15	13.126	10.01	0.859	0.99387	0.99259	0.129
333.14	11.389	12.01	1.007	0.99472	0.99347	0.126
333.14	12.496	14.02	0.834	0.99558	0.99435	0.124
333.13	8.732	16.01	1.493	0.99643	0.99522	0.121
333.13	7.267	18.00	0.959	0.99727	0.99608	0.119
343.15	5.774	10.01	0.645	0.98833	0.98682	0.153
343.14	6.903	12.01	1.007	0.98920	0.98771	0.151
343.14	8.681	14.02	0.884	0.99006	0.98860	0.147
343.13	8.242	16.01	0.881	0.99091	0.98947	0.145
343.13	13.290	18.00	1.251	0.99176	0.99034	0.143
353.15	14.528	10.01	1.308	0.98217	0.98059	0.161
353.16	7.614	12.01	1.532	0.98302	0.98148	0.157
353.17	14.689	14.02	0.676	0.98391	0.98237	0.157
353.13	16.129	16.02	0.722	0.98479	0.98329	0.152
353.10	8.836	18.02	0.999	0.98567	0.98419	0.150

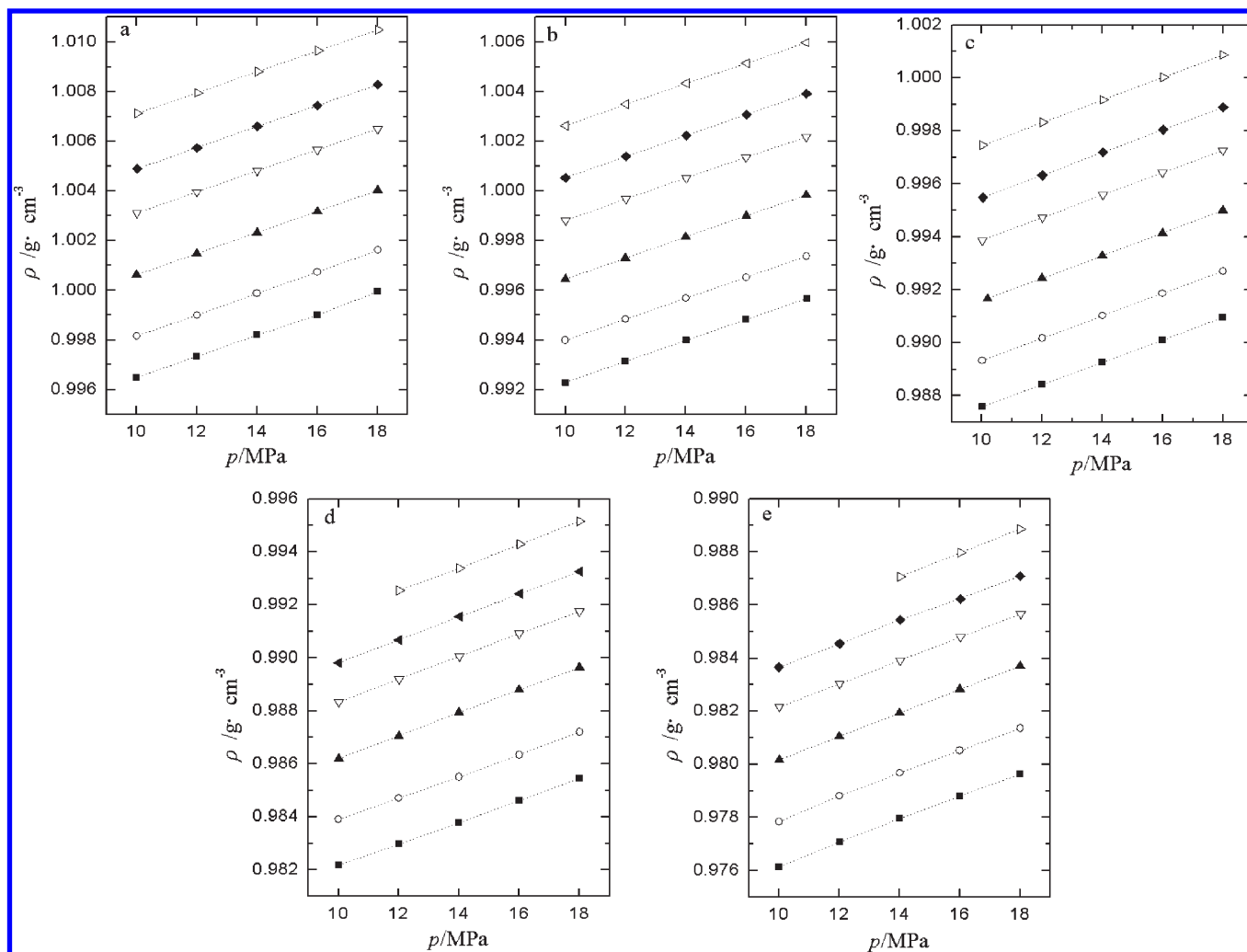
Table 3. Continued

T/K	st dev(T)/mK	p/MPa	st dev(p)/kPa	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\rho_{\text{EOS}}/\text{g}\cdot\text{cm}^{-3}$	$100\cdot(\rho - \rho_{\text{EOS}})/\rho$
<i>w</i> = 0.030						
313.09	5.964	10.02	1.718	1.00489	1.00458	0.031
313.08	9.931	12.01	0.402	1.00574	1.00547	0.027
313.05	9.409	14.01	1.032	1.00660	1.00636	0.024
313.06	6.806	16.01	0.745	1.00744	1.00723	0.021
313.07	9.079	18.00	0.690	1.00828	1.00809	0.019
323.07	11.055	10.00	1.376	1.00053	0.99975	0.078
323.07	14.225	12.01	0.501	1.00138	1.00063	0.075
323.07	10.646	14.01	0.403	1.00223	1.00151	0.072
323.07	13.585	16.01	1.200	1.00308	1.00238	0.070
323.05	10.029	18.01	0.745	1.00392	1.00325	0.067
333.06	5.936	10.04	4.096	0.99548	0.99433	0.116
333.07	9.759	12.01	0.816	0.99632	0.99520	0.112
333.06	5.964	14.02	1.020	0.99719	0.99609	0.110
333.04	11.293	16.01	0.999	0.99804	0.99698	0.106
333.02	8.847	18.01	0.475	0.99889	0.99787	0.102
343.08	13.667	10.01	0.917	0.98981	0.98838	0.144
343.07	13.825	12.01	0.875	0.99068	0.98928	0.141
343.02	8.837	14.01	0.915	0.99155	0.99021	0.135
343.03	10.072	16.01	0.824	0.99241	0.99109	0.133
343.08	5.936	18.01	1.187	0.99325	0.99194	0.132
353.07	12.459	10.00	0.516	0.98366	0.98202	0.167
353.09	15.607	12.01	1.291	0.98455	0.98292	0.166
353.06	10.744	14.01	0.556	0.98544	0.98384	0.162
353.07	16.918	16.01	0.721	0.98624	0.98473	0.153
353.07	12.836	18.00	0.632	0.98709	0.98562	0.149
<i>w</i> = 0.040						
313.04	12.158	10.01	0.717	1.00711	1.00690	0.021
313.07	14.346	12.01	0.929	1.00795	1.00777	0.018
313.07	13.933	14.02	1.160	1.00880	1.00866	0.014
313.06	7.838	16.01	0.680	1.00964	1.00955	0.009
313.05	11.100	18.01	0.832	1.01048	1.01043	0.005
323.03	15.299	10.01	1.083	1.00262	1.00185	0.077
322.99	8.729	12.01	1.670	1.00349	1.00276	0.073
323.05	13.529	14.01	1.049	1.00432	1.00361	0.071
323.11	5.145	16.01	1.200	1.00513	1.00447	0.066
323.10	3.755	18.00	1.235	1.00597	1.00535	0.062
333.06	7.614	10.02	1.579	0.99746	0.99619	0.127
333.07	6.594	12.01	0.900	0.99832	0.99708	0.124
333.06	5.500	14.02	1.141	0.99917	0.99799	0.118
333.06	5.036	16.01	0.977	1.00002	0.99888	0.114
333.06	5.090	18.00	0.992	1.00087	0.99976	0.111
343.06	13.229	12.01	1.938	0.99255	0.99099	0.157
343.13	14.039	14.02	0.565	0.99338	0.99186	0.153
343.07	15.581	16.02	0.917	0.99429	0.99279	0.151
343.03	12.623	18.00	0.759	0.99516	0.99371	0.146
353.07	5.898	14.01	1.276	0.98707	0.98540	0.169
353.05	14.346	16.02	1.248	0.98797	0.98632	0.167
353.02	5.903	18.00	1.102	0.98887	0.98724	0.165

sample was determined and the results were presented in Table 1. The cations in the sample were determined using atomic absorption spectrophotometer with flame atomization (Unicam model 969). The anions in the sample were determined by ion-chromatography

(Shimadzu SCL-10A<sub>SP</sub>) with nonsuppressor conductivity detector.

**Apparatus.** The experimental apparatus is shown schematically in Figure 1. The main apparatus was the MSB, including a



**Figure 2.** Density of  $\text{CO}_2$ -free brine and  $\text{CO}_2$  + brine solution from Tianjin reservoir versus pressure  $p/\text{MPa}$  at different temperatures and  $\text{CO}_2$  concentrations: a, 313 K; b, 323 K; c, 333 K; d, 343 K; e, 353 K; ■, pure water; ○,  $\text{CO}_2$ -free brine; ▲,  $w = 0.010$ ; ▴,  $w = 0.021$ ; ◆,  $w = 0.030$ ; △,  $w = 0.040$ ; dots: experimental; Line: predicted.

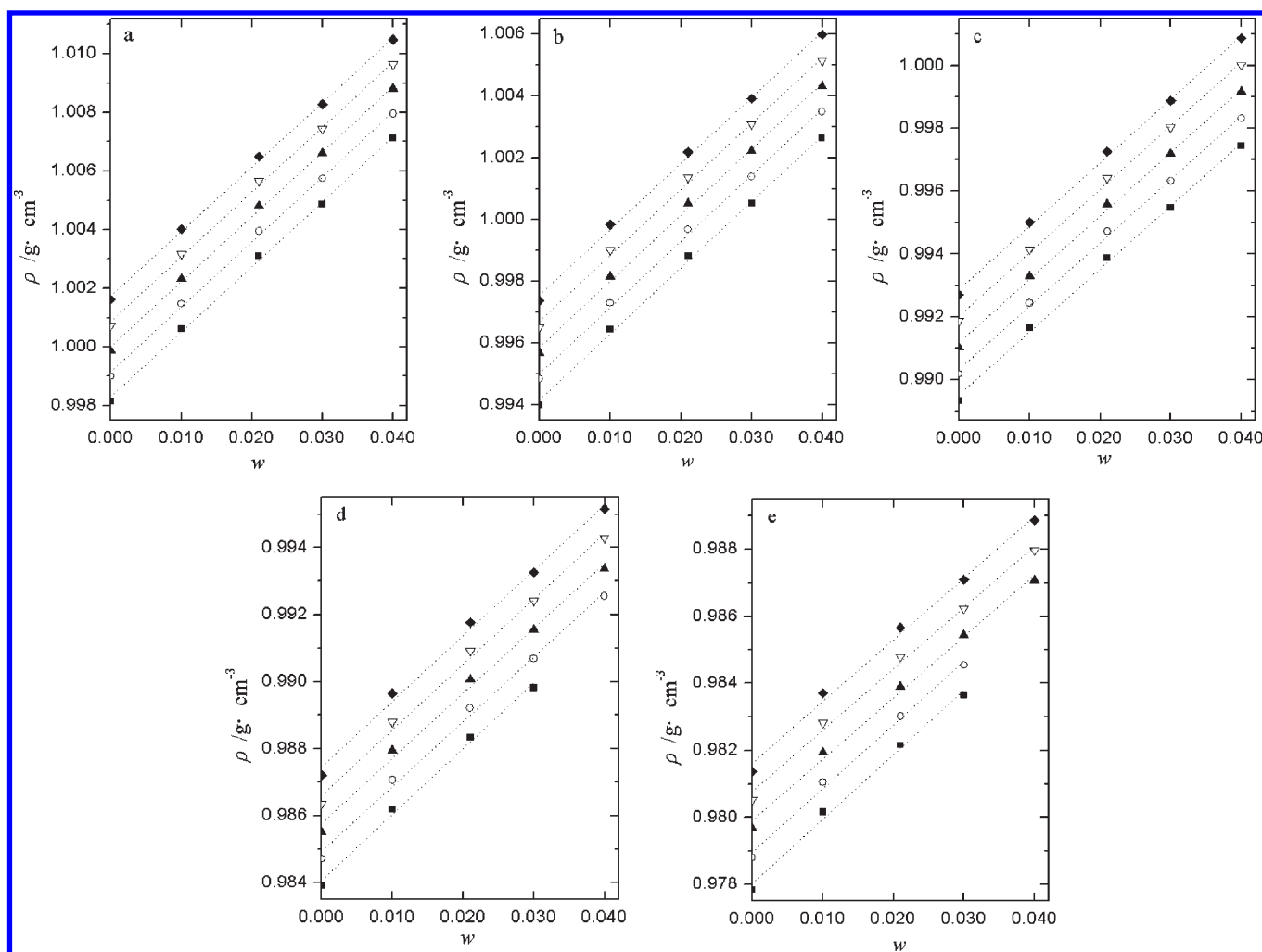
microbalance, a measuring cell, a sinker, a magnetic suspension coupling, and a control system, manufactured by Rubotherm Präzisionsmesstechnik GmbH. The MSB installed in our laboratory was suitable for operation in the temperature range (253 to 423) K and at pressures up to 20 MPa. The temperature in density measurement was controlled with a double-walled thermostatic jacket, which fits exactly around the measuring cell. The jacket was filled with circulating oil, whose temperature was controlled with a JULABO FP 50-ME Refrigerated/Heating Circulator. The sample temperature was measured with a Pt100 temperature probe located in the measuring cell just below the sinker. The controlling accuracy of temperature was  $\pm 0.01$  K. The pressure was measured with a pressure sensor (20 MPa, reproducibility 0.08%) located in a measuring gas connection tube by means of a T-piece. To enhance the dissolution of  $\text{CO}_2$  and maintain  $\text{CO}_2$  solution inside the measuring cell in a uniform state, a circulating pump (AKICO, Japan) was installed. The piston pump (a) and the pressure vessel were used to pressurize the nitrogen to the exact pressure in leakage detection of the experimental system. The piston pump (b) was used to pressurize and transfer the brine sample.

Before the experiment, the densities of nitrogen and deionized water were measured to test the accuracy and

reliability of the experimental system. Nitrogen and deionized water were chosen to be test fluids mainly because their densities have been studied extensively. Comparison of experimental results and the standard values taken from National Institute of Standards and Technology (NIST) shows that our experiment values are in good accordance with the standard values with a maximum deviation of 0.05% for  $\text{N}_2$  and 0.03% for water within the temperature and pressure range studied.

**Principle of Operation.** The working principle of the MSB has been described extensively elsewhere.<sup>13,14</sup> Nevertheless, several important points should be noted here. The main advantage of MSB compared with other densimeters is that the magnetic suspension coupling allows the measuring force to be transmitted contactlessly from the measuring cell to a microbalance at ambient atmosphere. This means that mass changes of a sample can be recorded even under extreme conditions with the utmost accuracy.

For a MSB, the buoyancy method using Archimedes' principle is used to obtain high precision density measurements by a sinker, whose volume is known, weighed in a measuring fluid. The buoyancy that the sinker experiences indicates the density of



**Figure 3.** Density of CO<sub>2</sub> + brine solution from Tianjin reservoir versus CO<sub>2</sub> mass fraction under selected pressures at different temperatures: a, 313 K; b, 323 K; c, 333 K; d, 343 K; e, 353 K; ■, 10 MPa, ○, 12 MPa, ▲, 14 MPa, ▽, 16 MPa, ◆, 18 MPa; dots, experimental; line, predicted.

the fluid. According to Archimedes' principle, the density of the measured fluid can be calculated from

$$\rho = \frac{m - W}{V} \quad (1)$$

where  $m$  is the true (vacuum) mass of the sinker;  $W$  is its apparent mass (weighed in fluid-filled measuring cell); and  $V$  is the volume of the sinker at absolute temperature  $T$  and pressure  $p$ , which can be obtained accurately from its known volume,  $V_0$ , at specified reference conditions ( $T_0, p_0$ ) from the expression:

$$V = V_0 \left[ 1 + \alpha_T(T - T_0) - \frac{1}{K_T}(p - p_0) \right] \quad (2)$$

where  $\alpha_T$  is the isobaric thermal expansion coefficient and  $K_T$  is the isothermal compressibility module. Both of  $\alpha_T$  and  $K_T$  are functions of temperature for the sinker material and were informed by the manufacturer of the MSB.

## RESULTS AND DISCUSSION

**Experimental Densities.** The measured densities of CO<sub>2</sub>-free brine and CO<sub>2</sub> + brine solution from Tianjin reservoir are

presented in Tables 2 and 3, respectively. Each data point represents the average result from ten measurements or more. The uncertainty of CO<sub>2</sub>-free brine density caused by pressure and temperature measurement is assessed to be 0.01% and that of CO<sub>2</sub> + brine solution density results from pressure and temperature measurement, as well as CO<sub>2</sub> mass fraction analysis, is estimated to be 0.025%. The uncertainty caused by sinker volume determination, force transmission error, and balance weightings are included in the total uncertainty of the MSB. The total uncertainty of the MSB is 0.1% as stated in the technical specification.

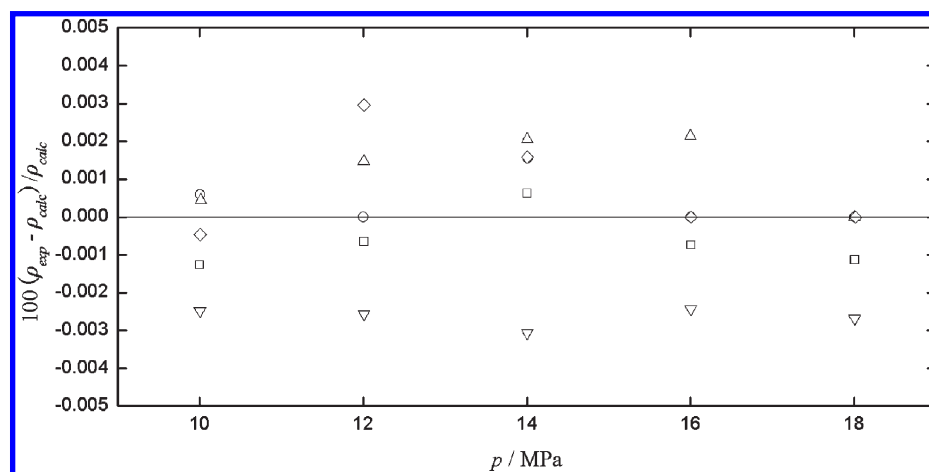
The experimental values are compared to the values calculated for the EOS proposed by Zhenhao Duan et al.<sup>8</sup> As shown in Table 2, the experimental densities of CO<sub>2</sub>-free brine agree with the calculated values within 0.053%. Table 3 shows that the experimental densities of the CO<sub>2</sub> + brine solution and the calculated values are also consistent with each other within 0.17%, with an average relative deviation of about 0.1%.

These experimental results are also plotted as a function of pressure for different CO<sub>2</sub> concentrations at different temperatures in Figure 2. The solid rectangles and the open circles represent the density of pure water taken from NIST and the experimental density of CO<sub>2</sub>-free brine, respectively. The rest of the plots represent the densities of CO<sub>2</sub> + brine solution at



Table 4. Coefficients in eqs 3 and 4

$i$	$a_i$	$b_i$	$c_i$	$d_i$	$e_i$
0	$8.11951 \times 10^{-1}$	$1.83484 \times 10^{-3}$	$8.255116 \times 10^{-1}$	$6.453167 \times 10^{-4}$	$3.300099 \times 10^{-3}$
1	$1.54810 \times 10^{-3}$	$-8.65129 \times 10^{-6}$	$1.463710 \times 10^{-3}$	$-1.401649 \times 10^{-6}$	$1.380885 \times 10^{-6}$
2	$-3.08794 \times 10^{-6}$	$1.32615 \times 10^{-8}$	$-2.954866 \times 10^{-6}$	$2.218350 \times 10^{-9}$	$-1.567212 \times 10^{-8}$



**Figure 4.** Deviations of experimental densities  $\rho_{\text{exp}}$  of  $\text{CO}_2$ -free brine from the correlation of eq 3  $\rho_{\text{calc}}$  versus pressure  $p/\text{MPa}$  at different temperatures:  $\square$ , 313 K;  $\circ$ , 323 K;  $\triangle$ , 333 K;  $\nabla$ , 343 K;  $\diamond$ , 353 K.

different  $\text{CO}_2$  concentrations,  $w$ . As shown in Figure 2, the density of Tianjin brine is larger than that of pure water at the same experimental conditions. For a given  $\text{CO}_2$  mass fraction, the density of  $\text{CO}_2$  + brine solution increases with increasing pressure almost linearly. The slopes of the solution density curves appeared to be the same as that of the  $\text{CO}_2$ -free brine and pure water within experimental error.

The measured results are also plotted as a function of  $\text{CO}_2$  mass fraction for different pressures at different temperatures in Figure 3. In Figure 3, the intercept of each curve represents the density of the  $\text{CO}_2$ -free brine. As shown in Figure 3, for a constant pressure, the density of  $\text{CO}_2$  brine solution increased with increasing  $\text{CO}_2$  mass fraction almost linearly. Haugen et al.<sup>2</sup> and Song et al.<sup>15</sup> explained this phenomenon before. They claimed that the slopes of the  $\text{CO}_2$  seawater solution density vs  $\text{CO}_2$  mass fraction curves were 0.182 and 0.275  $\text{g}\cdot\text{cm}^{-3}$ , respectively, and were independent of temperature. However, according to our research, the slope of the  $\text{CO}_2$  brine solution density vs  $\text{CO}_2$  mass fraction curves is closely related to temperature; it decreases from 0.222 to 0.185  $\text{g}\cdot\text{cm}^{-3}$  as the temperature increases from 313 to 353 K. This trend is conceivable because according to Lu et al.,<sup>16</sup> the density of  $\text{CO}_2$  brine solution can be less than that of the surrounding  $\text{CO}_2$ -free formation brine when the temperature is higher than the equal density temperature (varying with pressure and salinity of the formation brine). **In this case, the plume of dissolved  $\text{CO}_2$  will mitigate upward due to buoyancy force and leak to groundwater aquifers or to the surface. In other words, formations with higher temperatures are less suitable for  $\text{CO}_2$  storage than cooler formations, if all other conditions remain unchanged.**

And it also can be found from the Figure 3 that the slope of the  $\text{CO}_2$  + brine solution density vs  $\text{CO}_2$  mass fraction curves is independent of pressure, which is in accordance with the existing results.<sup>3,7</sup>

**Fitting of the Experimental Density Data.** The density of  $\text{CO}_2$ -free brine is a function of both temperature and pressure. As Figure 2 shows, it is proportional to pressure at a constant temperature. On the basis of this relationship, the experimental density data of  $\text{CO}_2$ -free brine have been fitted to an equation:

$$\rho_0/(\text{g}\cdot\text{cm}^{-3}) = \sum_{i=0}^2 (a_i + b_i p/\text{MPa})(T/\text{K})^i \quad (3)$$

where  $T$  is temperature,  $p$  is pressure;  $a_i$  and  $b_i$  are coefficients and are presented in Table 4.

The density of  $\text{CO}_2$  + brine solution is a function of temperature, pressure and  $\text{CO}_2$  mass fraction. As shown in Figures 2 and 3, it is proportional to pressure and  $\text{CO}_2$  mass fraction. The experimental data of  $\text{CO}_2$  brine solution have also been fitted to an equation:

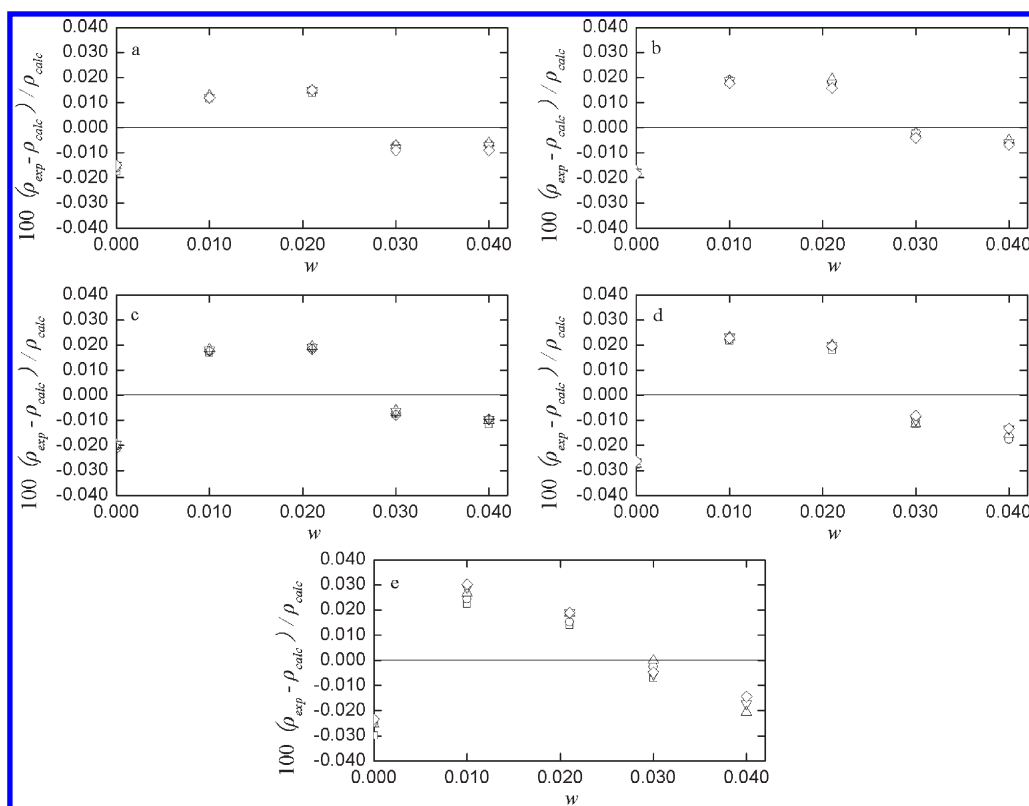
$$\rho/(\text{g}\cdot\text{cm}^{-3}) = \sum_{i=0}^2 (c_i + d_i p/\text{MPa} + e_i w')(T/\text{K})^i \quad (4)$$

where  $T$  is temperature;  $p$  is pressure;  $w$  is the mass fraction of  $\text{CO}_2$  in the solution;  $w'$  is the  $\text{CO}_2$  mass percentage,  $w' = w \times 100$ ;  $c_i$ ,  $d_i$ ,  $e_i$  are coefficients that can be estimated by minimizing the residual sum of squares. The results are presented in Table 4.

The functional form of eqs 3 and 4 was chosen on the basis of giving the smallest residuals for interpolation over the experimental conditions. Moreover, these equations enable the data to be cast into isothermal or isobaric forms to facilitate comparison with other experimental data.

For the five isotherms and the pressure range we have explored, Figure 4 shows the relative deviation of each experimental density value of  $\text{CO}_2$ -free brine from the value calculated from eq 3 as a function of pressure. As can be seen, eq 3 can accurately reproduce the experimental data, where the average deviation is 0.002% and the maximum deviation is 0.004%.





**Figure 5.** Deviations of experimental densities  $\rho_{\text{exp}}$  of  $\text{CO}_2$  + brine solutions from the correlation of eq 4  $\rho_{\text{calc}}$  versus  $\text{CO}_2$  mass fraction under selected pressures at different temperatures: a, 313 K; b, 323 K; c, 333 K; d, 343 K; e, 353 K;  $\square$ , 10 MPa,  $\circ$ , 12 MPa,  $\triangle$ , 14 MPa,  $\nabla$ , 16 MPa,  $\diamond$ , 18 MPa.

Figure 5 shows the relative deviation of experimental density value of  $\text{CO}_2$  + brine solution from the value calculated from eq 4 as a function of  $\text{CO}_2$  mass fraction at different temperatures. Comparing the experimental values and the calculated values, the  $(p, \rho, T, w)$  surfaces defined by eq 4 with the parameters listed in Table 4 describe the whole set of the present experimental results with maximum deviation of 0.03%, across the temperature range from (313 to 353) K and at pressures up to 18 MPa, which indicates that eq 4 can correlate the density data of  $\text{CO}_2$  + brine solution from Tianjin reservoir well.

## CONCLUSIONS

In this work, we studied the influence of the pressure [(10, 12, 14, 16, 18) MPa], the temperature [(313, 323, 333, 343, 353) K], and the concentration of  $\text{CO}_2$  [(0.010, 0.021, 0.030, 0.040) mass fraction] on the density of Tianjin formation brine. The following conclusions were obtained: (1) Dissolution of  $\text{CO}_2$  increases the densities of  $\text{CO}_2$  Tianjin formation brine. (2) For a constant  $\text{CO}_2$  mass fraction, the density of  $\text{CO}_2$  brine solution increases linearly with increasing pressure. (3) For a constant pressure, the density of  $\text{CO}_2$  brine solution increases linearly with increasing  $\text{CO}_2$  mass fraction in solution. The slope of the density vs  $\text{CO}_2$  mass fraction decreases from 0.222 to 0.185 as the temperature increased from 313 to 353 K and is independent of pressure. (4) The prediction gave a good fit to the experimental density data of  $\text{CO}_2$ -free brine and  $\text{CO}_2$  + brine solution.

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