

Effect of compressed CO₂ on the properties of AOT reverse micelles studied by spectroscopy and phase behavior

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Combination of reverse micellar solutions and supercritical or compressed carbon dioxide (CO₂) is a new and interesting topic. This work conducted the first study on the effect of compressed CO₂ on the micro-properties (e.g., micropolarity, ionic strength, *pH*) of the sodium bis(2-ethylhexyl) sulfosuccinate reverse micelles in isooctane by phase behavior measurement, Fourier transform infrared and UV-vis spectroscopic techniques. The results show that CO₂ can dissolve in both the organic-continuous phase and the water cores of the reverse micelles. The properties of the reverse micelles can be tuned continuously by changing the pressure of CO₂ because the solubility of CO₂ in the solution and in the water cores depends on the pressure. CO₂ in the water cores can be ionized to produce HCO₃⁻¹ and H⁺. The micropolarity and ionic strength of the water cores increase with the pressure of CO₂. Accordingly, the *pH* is reduced as the pressure and water-to-surfactant molar ratio (*w*₀) are increased. © 2003 American Institute of Physics.
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I. INTRODUCTION

Supercritical fluids have received much attention due to their various valuable applications.¹⁻⁴ Supercritical (SC) or compressed CO₂, in particular, is most attractive because it is readily available, inexpensive, nontoxic, nonflammable, and has environmentally benign characteristics.⁵⁻⁷ One of the important applications of SC or compressed CO₂ is to precipitate the solutes from solutions, which is known as a gas antisolvent (GAS) process.⁸⁻¹¹ Many applications of the GAS processes, such as the particle formation and material processing,¹²⁻¹⁴ fractionation and separation,^{15,16} and controlling the polymerization reaction in organic solvents^{17,18} have been reported.

Reverse micelles have been used in many areas ranging from dissolution and extraction of hydrophiles and proteins,¹⁹⁻²² chemical reactions,²³⁻²⁷ preparation of nanoparticles²⁸⁻³² to other applications in the pharmaceutical and cosmetic industry.³³⁻³⁶ Sodium bis(2-ethylhexyl)sulfosuccinate (AOT), an anionic surfactant to form reverse micelles in nonpolar solvent with many good qualities,³⁷⁻³⁹ is widely used. Water is readily solubilized in the polar core of the reverse micelles to form a "water pool" characterized by the water-to-surfactant molar ratio *w*₀, which serves as a novel microreactor for carrying out many kinds of reactions.⁴⁰⁻⁴⁴ In addition, the reaction rates within "water pools" inside the reverse micelles can be easily controlled by water loading and *pH* of the "water pools."⁴⁵⁻⁴⁷

The combination of reverse micellar solutions and compressed CO₂ is an interesting topic and may find more applications with some unique advantages. Recently, we have pro-

posed a novel route to recover the biomolecules (lysozyme and bovine serum albumin) and different nanoparticles stabilized in the reverse micelles using compressed CO₂ as antisolvent.⁴⁸⁻⁵¹ It was found that by controlling the CO₂ pressures, pure product could be recovered from the reverse micelles while the surfactants remained in the organic-continuous phase. This process can easily be applied to a range of inorganic or organic nanoparticles with many potential advantages such as its simplicity, time-saving, characteristics, and that the solutions can be easily recycled. Furthermore, it is expected that the properties of the reverse micelles should be tuned by the control of CO₂ pressure, which shows potential application not only in material production but also in the chemical reactions in micellar cores. Therefore, the related fundamental investigation on this kind of system, i.e., the CO₂-expanded reverse micelles, is of great importance to both pure and applied sciences. In previous work, we have studied the effect of compressed CO₂ on the stability and microstructure of the AOT reverse micelles at different conditions using synchrotron radiation small-angle x-ray scattering.⁵² In this work, we furthered our fundamental research on the CO₂-expanded reverse micelles. The influence of the compressed CO₂ on the microproperties of the reverse micelles was conducted by the combination of visual inspection, Fourier transform infrared, (FTIR) and UV-vis spectroscopy. It was found that the microproperties of the micellar cores such as micropolarity, ionic strength, and *pH* could be changed by the pressure of CO₂.

II. EXPERIMENT

A. Materials

CO₂ (>99.995% purity) was provided by Beijing Analytical Instrument Factory. The surfactant AOT (with 99%

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purity) was purchased from Sigma. Bromophenol blue (BPB) (90% purity, Beijing Organic Chemical Plant) was used as the pH indicator. Citric acid (>99.0% purity, Chengdu Chemical Plant) and sodium hydroxide (>96.0% purity, Beijing Yili Fine Chemical Plant) were used to prepare the buffer solutions. The isooctane (A.R. grade) was supplied by Beijing Chemical Plant. Double distilled water was used.

B. Preparation of the reverse micellar solutions

The AOT/water/isooctane reverse micellar solution was prepared by dissolving AOT in isooctane, then the desired amount of water was injected into the AOT–isooctane solution. The mixture was shaken by hand until the solution was completely clear. The reverse micelles containing the probe (BPB) were prepared by adding a suitable quantity of aqueous solution of probe into the AOT/isooctane solution. In all spectroscopic measurements, the concentration of BPB after the sample cells were full of CO_2 -expanded solution was 4×10^{-6} M.

C. Phase behavior of reverse micellar solution with compressed CO_2

The apparatus used to study the expansion curves and the cloud point pressure of the solution was the same as that used previously.⁴⁸ It consisted mainly of a view cell of 50.0 ml, a high-pressure pump, a constant temperature water bath, and a pressure gauge. The high-pressure pump was model DB-80, which was used to charge CO_2 into the system. The accuracy of the pressure gauge, which was composed of a transducer (FOXBORO/ICT) and an indicator, was ± 0.025 MPa in the pressure range of 0–20 MPa. The temperature of the water bath was controlled by a HAAKE D3 digital controller, and the accuracy of the temperature measurement was ± 0.1 °C.

In a typical experiment, the air in the sample cell was first replaced by CO_2 . A suitable amount of reverse micellar solution was loaded into the view cell. CO_2 was then charged into the cell to a suitable pressure after the thermal equilibrium had been reached. A magnetic stirrer was used to enhance the mixing of CO_2 and reverse micellar solution. The volume of the liquid phase did not change with time after equilibrium was reached. The pressure and the volume at equilibrium condition were recorded. More CO_2 was added and the volume of the liquid phase at another pressure was determined. The volume expansion coefficients were calculated on the basis of the liquid volumes before and after dissolution of CO_2 . Water and probes were precipitated from the reverse micelles as the pressure of CO_2 was high enough, which could be observed at the bottom of the optical cell. Increasing the pressure further the micellar solution became cloudy. The pressure at which the surfactant begins to precipitate is called a cloud point pressure.

D. FTIR spectra

The FTIR spectroscopic apparatus consisted mainly of a gas cylinder, a high-pressure pump, an IR spectrometer (SENSOR 27), and a high-pressure IR sample cell. The

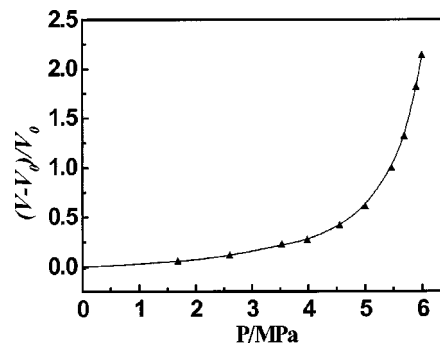


FIG. 1. Effect of temperature and pressure on volume expansion coefficient of the reverse micellar solution at 303.2 K ($[AOT]=0.1$ M, $w_0=8$).

sample cell was composed mainly of a stainless steel body and two zinc sulfide (ZnS) windows (2.25 cm in diameter and 0.60 cm thick), which was thermostated to ± 0.1 °C of the desired temperature by an electric heater and temperature controller. The internal volume and the path length of the cell were 1.48 ml and 1.56 cm, respectively. The pressure gauge used was the same as that discussed earlier. In the experiment, a suitable amount of the micellar solution was charged into the cell. The temperature of the cell was stabilized at 303.2 K, and CO_2 was compressed into the cell to the desired pressure. The IR spectrum was recorded using a computer after equilibrium had been reached. Each sample was recorded with 32 scans at an effective resolution of 2 cm^{-1} .

E. UV–vis spectra

A TU-1201 UV spectrophotometer was used to measure the pH of the reverse micelles at different CO_2 pressures. The high-pressure UV sample cell and the experimental procedures were similar to those used for the IR spectrum measurement described earlier. The main difference was that two quartz windows were used, and the volume and the optical path length of the sample cell were 1.44 ml and 1.12 cm, respectively. The pH of citric acid buffers was calibrated against a pH meter (pHS-3B, Shanghai REX Instrumental Plant).

III. RESULTS AND DISCUSSION

A. Phase behavior

In this work, volume expansion coefficient (ΔV) of the solution is defined by

$$\Delta V = (V - V_0) / V_0, \quad (1)$$

where V is the volume of the solution expanded by CO_2 , and V_0 is the volume of the CO_2 -free solution. Figure 1 shows the volume expansion ratio of the micellar solution ($[AOT]=0.1$ M, $w_0=8$) versus the pressure at 303.2 K obtained in this work. As expected, the volume expansion coefficient increases with increasing pressure. We have also studied the effects of AOT concentration (0.05 and 0.1 M) and w_0 (2, 5, 8, 10, and 15) on the volume expansion in this work, which reveals that the effects are not considerable. The determined volume expansion coefficient allows us to deter-

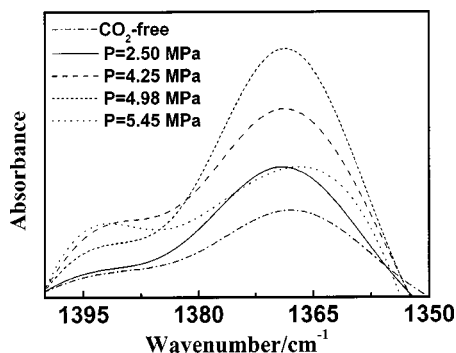


FIG. 2. IR spectra of the CO₂-expanded reverse micelles (AOT = 0.1 M, $w_0=8$) at 303.2 K and different pressures in the absorption region of 1400–1350 cm⁻¹.

mine how much CO₂-free reverse micellar solution should be loaded into sample cell for the IR and UV investigations.

In this work, we determined the pressures at which the water begins to precipitate at 303.2 K (P_w). For the reverse micellar solutions with $w_0=2, 5, 8, 10, 15,$ and 25 ([AOT] = 0.1 M), the P_w values are 5.76, 5.58, 5.41, 5.38, 5.23, and 5.07 MPa, respectively. It is evident that P_w decreases with the increasing w_0 . This behavior results mainly from the fact that most water molecules in the reverse micelles are strongly hydrogen-bonded with the polar head of the surfactant at lower w_0 .^{53,54} We also determined the cloud point pressures (P_c) of the reverse micellar solution at 303.2 K with AOT concentrations of 0.05 and 0.1 M. P_c values at these two concentrations are 6.07 and 5.91 MPa, respectively. It can be concluded that the water precipitates before the precipitation of the surfactant.

B. FTIR study

The FTIR is a commonly used technique to study the microstructure of reverse micelles.^{55–58} Many studies about the water/AOT/oil reverse micelles using the FTIR spectroscopy have been reported in the absence of CO₂.^{55–58} In these studies, the broad band of hydroxyl stretching [ν (O–H)], centered at 3600 cm⁻¹, is usually used in detailed investigations of water/AOT/oil microemulsion.^{55–58} Unfortunately, in this work, the absorption band cannot be utilized to study the properties of water in the reverse micelles because it is over-

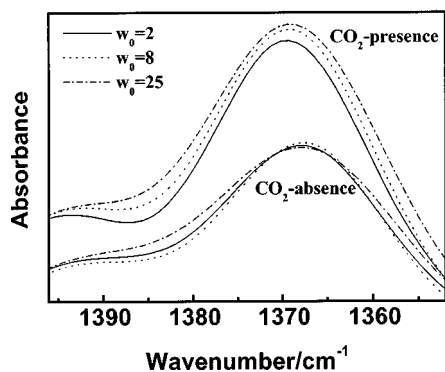


FIG. 3. IR spectra of the reverse micelles (AOT = 0.1 M) in the absorption region of 1396–1352 cm⁻¹ at 303.2 K with $w_0=2, 8,$ and 25 .

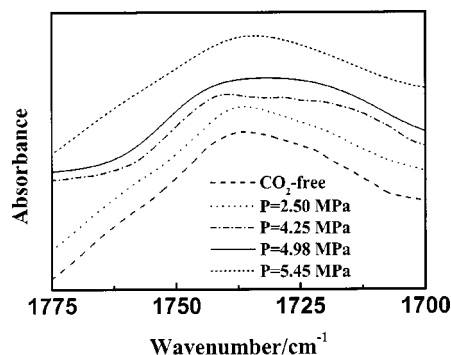


FIG. 4. IR spectra of the carbonyl stretching vibration of AOT reverse micelles (AOT = 0.1 M, $w_0=8$) at 303.2 K and different pressures.

lapped with the intense absorption of CO₂ in the region of 3840–3470 cm⁻¹. However, we can get some useful information about the microstructure of the reverse micelles by analyzing the two bands in the wavelength ranges of 1400–1350 and 1775–1700 cm⁻¹, as shown in Figs. 2–6.

As examples, Fig. 2 shows the IR absorption bands of the reverse micellar solutions ($w_0=8$) at different pressures in the wavelength range of 1400–1350 cm⁻¹. The lowest peak in Fig. 2 is the absorption of the CO₂-free reverse micelles, where the broad band is attributed to the symmetrical bending vibration of methyl group around 1375 cm⁻¹ [$\delta_s(\text{CH}_3)$], the wagging vibration of methylene group around 1366 cm⁻¹, 1385 cm⁻¹ [$\omega(\text{CH}_2)$], and the symmetrical bending vibration of methylene group around 1393 cm⁻¹ [$\delta_s(\text{CH}_2)$] of isooctane and AOT, respectively.⁵⁸ Other spectra are the bands of the reverse micelles in the presence of CO₂ at different pressures. It is evident that by increasing the pressure from 2.50 to 4.98 MPa, the intensity of the band increases progressively. It suggests that CO₂ dissolved in the water cores can be ionized and HCO₃⁻¹ is formed, and there is more HCO₃⁻¹ at the higher pressures. This is similar to earlier investigations about the interaction between CO₂ and bulk water or in the reverse micelles formed in SC CO₂. CO₂ dissolves in the “water pool” of reverse micelles formed in SC CO₂ and can be ionized ($\text{H}_2\text{O} + \text{CO}_2 = \text{H}^+ + \text{HCO}_3^-$), which makes the “water pool” acidic.^{59–62} Clarke *et al.*⁶² indicated that a broad but strong absorption peak around 1360 cm⁻¹ in water/

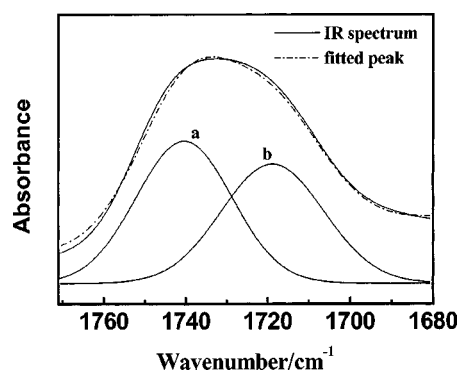


FIG. 5. Deconvoluted carbonyl stretch peak of the reverse micelles (AOT = 0.1 M, $w_0=8$) at 303.2 K and $P_{\text{CO}_2}=4.98$ MPa.

$\text{CF}_3\text{O}(\text{CF}_2\text{CF}(\text{CF}_3)\text{O})_3\text{CF}_2\text{COO}^-\text{NH}_4^+/\text{CO}_2$ reverse micelles was due to the formation of HCO_3^- . Figure 2 also demonstrates that the intensity of this band decreases when the pressure reaches 5.45 MPa, indicating the reduced quantity of HCO_3^- within the micellar cores. This is easily understood because most water is precipitated from the micellar cores at this pressure. The IR spectra of the CO_2 -free and CO_2 -expanded reverse micellar solutions at 2.50 MPa with w_0 values of 2, 8, and 25 are given in Fig. 3. Obviously, the band of the CO_2 -free reverse micelles is nearly independent of the w_0 , while the intensity of the band of the CO_2 -expanded reverse micelles increases with w_0 . This can be attributed to the formation of HCO_3^- in the water cores. The amount of the free water in reverse micelles increases with increasing w_0 . Thus, more HCO_3^- is formed in the reverse micelles with the larger w_0 , and the absorption peak becomes higher.

The changes of carbonyl stretching vibration [$\nu(\text{C}=\text{O})$] situated around 1730 cm^{-1} with the pressure also give microstructure information on the CO_2 -expanded reverse micelles.^{55,58,63,64} The broad peak with an asymmetric shape shown in Fig. 4 suggests that the band is a fusion of peaks corresponding to carbonyl groups in different microenvironments.^{55,63,64} A Gaussian curve fitting program is used to treat these peaks. As an example, Fig. 5 shows the peak in one spectrum (solid line) of Fig. 4 before and after the treatment, and the two peaks centered at 1740 ± 2 and $1721 \pm 2\text{ cm}^{-1}$ are obtained, which correspond to different carbonyls in *gauche* and *trans* configurations of the rotational isomerism of AOT, respectively.^{55,63,64} The variations of peak intensity ratio ($I_r = I_{1740}/I_{1721}$) are related to the polarity of the environment. In a more polar region, the ratio (I_r) decreases because more conformations change from *gauche* to *trans*.⁶³

The intensity ratio (I_r) as a function of CO_2 pressure is given in Fig. 6. The ratio decreases slightly with the increase in CO_2 pressure at pressures lower than 5.41 MPa. This demonstrates that the micropolarity and ionic strength of the water cores are enhanced by the dissolved CO_2 . This effect is more significant at higher pressures because the solubility of CO_2 in the water cores should increase with increasing pressure. The enhanced micropolarity and ionic strength result in more polar groups directing toward the polar side of the interface, i.e., the configurations transfer from *gauche* to *trans*. Therefore, the ratio decreases with the increase of CO_2 pressure. The I_r at 5.45 MPa is much higher because most of the water in the reverse micelles is precipitated as discussed earlier ($P_w = 5.41\text{ MPa}$). It can be concluded from the above-given analysis that CO_2 in the solution cannot only tune the properties of the solvent, but also can change the ionic strength and the polarity of the water cores.

C. UV-vis study

To explore the *pH* value inside the reverse micelles is also very interesting. In this work, the *pH* of the water cores inside the reverse micelles was measured using UV-vis spectra, and an acid sensitive indicator (BPB) was used as the probe.⁶⁵⁻⁶⁷

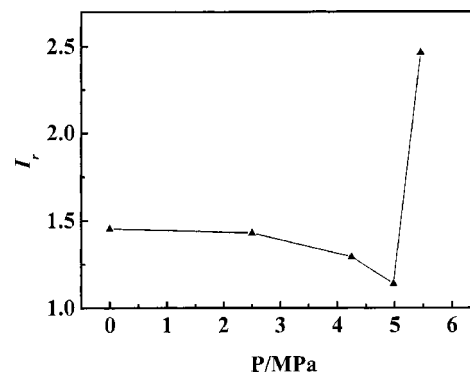


FIG. 6. Variation of intensity ratio ($I_r = I_{1740}/I_{1721}$) as a function of CO_2 pressures for the AOT reverse micelles (AOT = 0.1 M, $w_0 = 8$) at 303.2 K.

In order to obtain the working curve, we first determined the UV spectra of BPB in citric acid buffers with different *pH* values. Some typical spectra are shown in Fig. 7. In Fig. 7, two absorption peaks appear at 430 and 590 nm. This spectral feature corresponds to the proton dissociation of BPB.⁶⁵⁻⁶⁷ At lower *pH*, the BPB would be expected to exist as a neutral molecule, which has an electronic transition at 430 nm. While at higher *pH*, it exists as ionized species and an electronic transition occurs at 590 nm. With the decreasing *pH*, the absorbance at 430 nm increases, while the absorbance at 590 nm decreases. The absorbance intensity ratios centered at 430 nm I_{430} and 590 nm I_{590} are usually used to indicate *pH* in the buffer solutions.⁶⁷ The I_{430}/I_{590} values decrease linearly with increased *pH* values in the citric buffers, as shown in Fig. 8. The results in Fig. 8 are used as a working curve to study the *pH* of water cores in the reverse micelles.

Equilibrium *pH* measurements of water cores inside the reverse micelles were carried out at 303.2 K and different pressures, and the w_0 values were 5, 10, and 15, respectively. As examples, Fig. 9 demonstrates some spectra of the BPB in the water core of the reverse micelles ($[\text{AOT}] = 0.1\text{ M}, w_0 = 5$) in the presence of CO_2 . It can be seen that the absorbance around 430 nm increases with the increasing CO_2 pressure, while the absorbance around 590 nm is decreased. The *pH* values inside the AOT reverse micelles under different CO_2 pressures were obtained from the working line shown in Fig. 8, and the results are plotted in Fig. 10 as

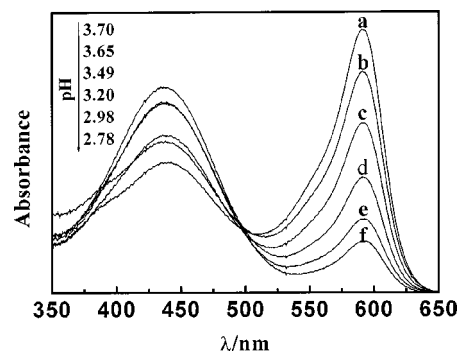


FIG. 7. Absorption spectra of BPB ($4 \times 10^{-6}\text{ M}$) in citric acid buffers over the wavelength range 350–650 nm.

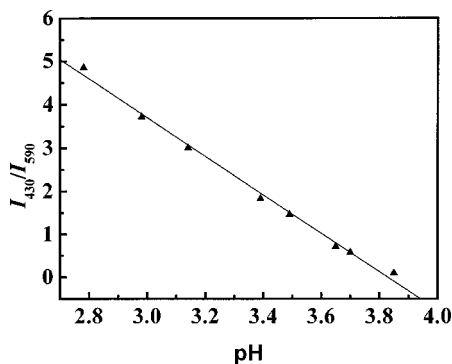


FIG. 8. Dependence of the ratio I_{430}/I_{590} on the pH of citric acid buffers at 303.2 K.

a function of CO₂ pressure. As can be observed, for all the reverse micelles with the different w_0 values, the pH of the water cores decreases with the increasing CO₂ pressure. These changes result mainly from the CO₂ dissolved and ionized in the water cores. According to Henry's law, an increase in pressure should enhance the solubility of CO₂ in the water cores. Therefore, more CO₂ is ionized and the acidity of the solution increases. These results are consistent with those of the IR studies, i.e., the ionic strength of the water cores increases with the increasing CO₂ pressures. In addition, Fig. 10 shows clearly that at a given CO₂ pressure, the pH inside the reverse micelles decreases gradually as w_0 changes from 5 to 15. This results mainly from the fact that polarity of the water domains inside the reverse micelles increases as w_0 is increased,^{63,64,68,69} and thus more CO₂ can be ionized. The pH of bulk water is smaller than those of the water cores in the reverse micelles at the same pressure, indicating that the polarity of the bulk water is stronger. As an alternative, a coherent explanation also could be that the AOT micelle offers a slight barrier to CO₂ partitioning into the micelle water pool, as observed in the case of water-in-supercritical CO₂ reverse micelles formed in the presence of the perfluorocarboxylate surfactant PFPE.⁶⁰ For that system, the measured water core pH differs from the pH calculated assuming complete saturation of the water pool by 0.5 pH units, a value in good agreement with those obtained from data in Fig. 10 of the present work.

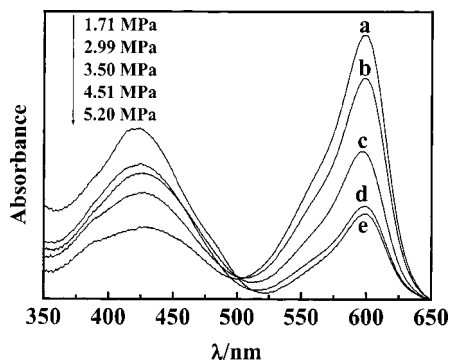


FIG. 9. Absorption spectra of BPB (4×10^{-6} M) in water/AOT/isooctane ($w_0 = 15$) at 303.2 K and different CO₂ pressures.

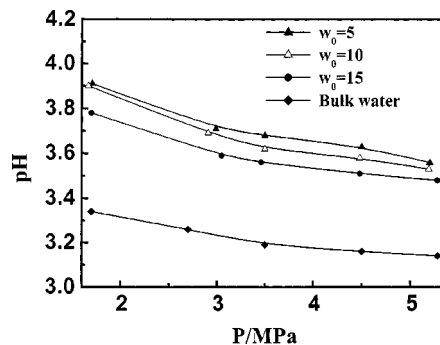


FIG. 10. The pH of bulk water and water cores inside the water/AOT/isooctane reverse micelles in equilibrium with different compressed CO₂ ($T = 303.2$ K, $[AOT] = 0.1$ M).

IV. CONCLUSION

The effect of compressed CO₂ on the properties of the water/AOT/isooctane reverse micellar solution has been studied with FTIR and UV-vis spectroscopic measurements, along with the phase behavior observation. The results show that the compressed CO₂ can dissolve in both organic-continuous phase and the water cores of the reverse micelles. The compressed CO₂ in the isooctane expands the organic-continuous phase. The CO₂ in the water cores changes the pH , ionic strength, and micropolarity of the water cores inside the reverse micelles. These properties of the reverse micelles can be tuned continuously by changing the pressures of CO₂ because the solubility of CO₂ in the solution and in the water cores depends on the pressure.

ACKNOWLEDGMENTS

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