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Characterization of pH in Liquid Mixtures of Methanol/H_2O/CO_2

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The presence of H_2O and CO_2 in enhanced-fluidity liquids changes the pH in these mixtures due to the formation of carbonic acid. The acid−base equilibria in enhanced-fluidity liquids will also be affected by the reduction in the dielectric constant with the addition of CO_2. The pH of enhanced-fluidity liquid mixtures at room temperature was determined from the UV/visible absorption spectra of several pH indicators. pH values of methanol/H_2O/CO_2 mixtures with CO_2 proportions as high as 19.2 mol % are reported. The effect of adding buffer to methanol/H_2O/CO_2 mixtures on pH was also studied. It was also shown that pressure variation did not significantly influence the pH of enhanced-fluidity liquids.

Enhanced-fluidity liquid mixtures include high-polarity solvents such as alcohols and water combined with liquefied gases, such as CO_2.[1,2] These mixtures provide the advantages of high solvent strength and fast mass transfer inherited from liquids and liquefied gases, respectively. Enhanced-fluidity liquid mixtures can be used to advantage for a range of separation problems.[1−3] For example, when methanol/CO_2 and methanol/H_2O/CO_2 liquid mixtures were used as mobile phases for chromatographic separations, advantages such as improved separation efficiency, increased optimum linear velocity, lower pressure drop, and decreased analysis time were observed.[1,2] Methanol/H_2O/CO_2 mixtures were also used effectively as extraction solvents for polar solutes. Substantially improved extraction recoveries and increased extraction rates were previously reported for phenolic pollutants and phenyoxyacid herbicides on house dust,[3,4] as well as atrazine and its metabolites in sediments.[5]

Enhanced-fluidity liquid mixtures of high polarity often include H_2O as one of the components. If combined with CO_2, the pH of the mixtures will change due to the formation of carbonic acid. In reversed-phase high-performance liquid chromatography (HPLC), the pH of the mobile phase is varied to control the charge of ionizable analytes. A recent reversed-phase HPLC separation of triazine herbicides with high pK_a values was profoundly affected by the presence of CO_2 and H_2O in an enhanced-fluidity liquid mobile phase.[6] With the proportion of CO_2 in the mobile phase up to 20 mol %, diminished resolution was observed between ammeline (pK_a 4.2) and hydroxyatrazine (pK_a 4.9). Buffered mixtures of methanol/H_2O/CO_2 mobile phases were also used to improve the chiral resolution of 1,1′-binaphthyl-2,2′diyl-hydrogen phosphate.[7] When up to 20 mol % CO_2 was added to a methanol/ammonium nitrate mixture, the resolution increased from 0.45 to 0.78. Higher efficiency and longer retention time were observed as well. Obviously, it is imperative to investigate pH variation of enhanced-fluidity liquid mixtures in which both H_2O and CO_2 are present.

Potentiometric methods are capable of pH measurements under high-pressure conditions.[8−13] However, the standardization under such conditions is not always stable.[12] Difficulties in probing a tightly sealed system under elevated pressure still exist, especially when gaseous components are involved.

Besides traditional potentiometric pH measurements, spectrophotometric experiments can also be used to measure the acidity of the system of interest.[14−18] Xiang et al.[17] determined pH values for aqueous sulfuric acid and sulfuric acid/ammonia mixtures under sub- to supercritical conditions (pressure up to 400 atm, temperature up to 400 °C) using the changes in the UV/visible spectrum of acridine. Toews et al.[16] used the changes in the spectrum of bromophenol blue to measure pH in aqueous solutions that were heated to 70 °C and pressurized with CO_2 up to 200 atm. pH values ranging from 2.80 to 2.95 were reported for water in contact with supercritical CO_2.

This study describes spectrophotometric determinations of pH in methanol/H_2O/CO_2 mixtures. pH values of these mixtures with CO_2 content up to 19.2 mol % are reported. The effect of the addition of aqueous buffer on pH control in the methanol/H_2O/CO_2 mixtures was studied.

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THEORY

The dissociation of a pH indicator, a weak acid, can be observed through its UV/visible absorbance spectra. If the acidic form (HIn) and the basic form (In^-) of the indicator absorb ultraviolet or visible light, their absorbance ratio is proportional to the [H^+] of the solvation medium.

$$A_{\mathrm{HIn}}/A_{\mathrm{In-}} \propto [\mathrm{HIn}]/[\mathrm{In}^-] \propto [\mathrm{H}^+] \qquad (1)$$

By making the assumption that the concentration and activity of the hydrogen ion are approximately equal (i.e., [H^+] is low), the above relationship can be used to determine the pH of a solution.

To probe the pH variation in methanol/H_2O/CO_2 mixtures, the relationship between the $A_{\mathrm{HIn}}/A_{\mathrm{In}^-}$ ratio of a pH indicator and [H^+] must be established first. This implies knowledge of weak acid dissociation in methanol/H_2O/CO_2 mixtures, which is not available in the literature.

It is obvious that carbonic acid will form in methanol/H_2O/CO_2 mixtures. Because it is nonpolar, the addition of liquid CO_2 will lower the dielectric constant of the resultant mixture as well. The Born equation (eq 2) is often used[15,17,19] to described the net

$$\Delta G^\circ = \frac{C}{\epsilon}\left[\frac{1}{r_{\mathrm{H_3O^+}}} + \frac{z_{\mathrm{A}}^{\;2}}{r_{\mathrm{A}}} - \frac{z_{\mathrm{HA}}^{\;2}}{r_{\mathrm{HA}}}\right] \qquad (2)$$

change in Gibbs energy per mole in an ionization equilibrium of an acid, HA, where z_i is the charge of the ion, C is a constant, r is the radius of the respective solvated species, and ϵ is the dielectric constant of the solvent. Since the Gibbs energy of a reaction is related to its equilibrium constant, the variation of the dissociation constant, K_a, in mixed solvents is a function of the dielectric constant of the mixture using eq 3, where R is the gas

$$-RT \ln K_A = \frac{C}{\epsilon}\left[\frac{1}{r_{\mathrm{H_3O^+}}} + \frac{z_{\mathrm{A}}^{\;2}}{r_{\mathrm{A}}} - \frac{z_{\mathrm{HA}}^{\;2}}{r_{\mathrm{HA}}}\right] \qquad (3)$$

constant and T is absolute temperature. Therefore, at constant temperature, a linear relationship between the pK_a of weak acids ($-\log K_a$) and $1/\epsilon$ (dielectric constant) of methanol/H_2O mixtures is expected and was reported previously.[20]

Experimentally measured dielectric constants of methanol/H_2O/CO_2 mixtures are not available in the literature. However, previous studies of mixtures containing a limited proportion of a nonpolar alkane (less than 50 mol %) added into alcohol showed that the dielectric constant of the mixture varies linearly with the mole percent of the alkane at constant temperature.[21−23] Similar trends were also observed when CO_2 was added into methanol and ethanol.[24,25] That is, the decrease in dielectric constant was proportional to the mole fraction of CO_2 in the mixture.

It is therefore reasonable to believe that changes in dielectric constant will follow the same pattern for methanol/H_2O/CO_2 mixtures. Using dielectric constants of methanol/H_2O mixtures in the literature[26] and the mole fraction of CO_2 in the mixture, the dielectric constants for the studied methanol/H_2O/CO_2 mixtures were calculated. Since no more than 20 mol % CO_2 was added into methanol/H_2O, the dissociation of a weak acid in methanol/H_2O/CO_2 can be approximated by that in methanol/H_2O of the same dielectric constant.

Bosch et al.[27] generated equations that allow the calculation of pK_a values in methanol/H_2O mixtures for commonly used buffers. The pH value of a buffer in a given methanol/H_2O mixture could then be readily determined using the Henderson−Hasselbach equation.

$$\mathrm{pH} = \mathrm{p}K_{\mathrm{a}} + \log[\mathrm{conjugate}]/[\mathrm{acid}] \qquad (4)$$

Calibration curves, plots of $A_{\mathrm{HIn}}/A_{\mathrm{In}^-}$ for a given indicator versus [H^+], were made using methanol/H_2O mixtures with the same dielectric constant as the studied methanol/H_2O/CO_2 mixtures and were used to determine the [H^+] of the methanol/H_2O/CO_2 mixtures.

EXPERIMENTAL SECTION

Materials. HPLC-grade methanol was obtained from J. T. Baker (Phillipsburg, NJ). H_2O was distilled and deionized by a NANOpure II system (Sybron/Barnstead, Boston, MA). The resistivity of the deionized H_2O was 17.3−17.8 MΩ. SFE/SFC-grade CO_2 was obtained from Air Product and Chemicals (Allentown, PA).

Tetrabromophenolphthalein ethyl ester potassium salt, thymol blue, and bromophenol blue (ACS reagent) from Aldrich Chemical Co. (Milwaukee, WI), potassium dihydrogen phosphate (HPLC grade, 99.6%) and dipotassium hydrogen phosphate (ACS certified, 99.2%) from Fisher Scientific (Fairlawn, NJ), glacial acetic acid (99.8%) and phosphoric acid (85%) from Mallinckrodt Chemical (St. Louis, MO), and sodium acetate (ACS reagent, 99.8%) from Jenneile Enterprises (Cincinnati, OH) were used as received.

Sodium carbonate from Jenneile Enterprises was dried at 200 °C for 2 h before use. Stock HCl(aq) solutions were diluted from concentrated HCl(aq) (36.5−38.0%) from J. T. Baker (Phillipsburg, NJ) and standardized with sodium carbonate to give a concentration of 0.9985 M.

Equipment. Two ISCO 260D syringe pumps (Lincoln, NE) were used to mix methanol, H_2O/aqueous buffer, and liquid CO_2 by volume to make the desired methanol/H_2O/CO_2 mixtures.

A Lambda 20 UV/visible spectrophotometer (Perkin-Elmer Co., Norwalk, CT) was used to perform spectroscopic experiments. The sample compartment was modified to accommodate two custom-made, stainless steel, high-pressure view cells with internal volumes of 10 mL and optical path length of 3.5 cm.[28] At each end of the view cell, a quartz window with a diameter of 3.18 cm and thickness of 1.75 cm (ESCO Products Inc., Oak Ridge, NJ)

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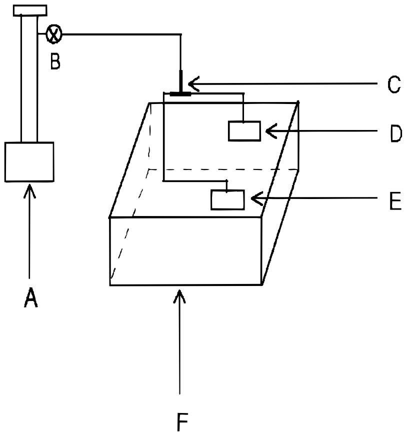

Figure 1. Schematic view of the UV/visible experiment setup: A, pump; B, valve; C, tee; D, reference cell; E, sample cell; F, spectrometer.

was sealed by compression of a Teflon O-ring (1.90 cm i.d. × 2.38 cm o.d. × 0.32 cm). UV/visible spectra were recorded from 200 to 900 nm at 240 nm/min. Data were collected by UV WinLab software (Perkin-Elmer) using a Gateway2000 486/33C computer. The experimental setup is illustrated in Figure 1.

Buffer Preparation. Three aqueous buffer solutions were used in this study. They included the following: HCl(aq)/NaCl solutions with a pH range of 1.12−1.75, H_3PO_4/KH_2PO_4 solutions with a pH range of 1.50−2.50, and acetic acid/sodium acetate solutions with a pH range of 2.68−3.20. The ionic strength of these solutions was maintained at 10 mM. Acetic acid solutions and phosphoric acid solutions were made by dilution of glacial acetic acid and the concentrated phosphoric acid solution, respectively. HCl(aq) solutions were prepared by serial dilution of the stock HCl(aq) solution (0.9985 M). Aqueous buffer solutions were made by dissolving a salt into the corresponding acid solution and diluting to the desired volume. An aqueous phosphate buffer of pH 6.62 was prepared by dissolving an appropriate amount of potassium dihydrogen phosphate and dipotassium hydrogen phosphate in water to the desired concentration. The pH values of aqueous buffer solutions were determined using an Accumet model 10 pH meter, obtained from Fisher Scientific (Pittsburgh, PA), that was standardized with primary pH standards, pH 4.00 potassium acid phthalate (Baxter Diagnostics Inc., Deerfield, IL) and pH 7.00 potassium phosphate monobasic, potassium phosphate dibasic (Mallinckrodt-Baker Inc., Paris, KY).

Procedure. An appropriate amount of a pH indicator (tetrabromophenolphthalein ethyl ester potassium salt, thymol blue, or bromophenol blue) was weighed and dissolved in methanol to make indicator stock solution with a molar concentration of approximately 10^{-4} M. Throughout this study, experiments were conducted at 23 °C. UV/visible spectra of these pH indicators, which were freshly diluted to 1×10^{-5} M, were recorded at ambient pressure using quartz cuvettes.

Methanol/aqueous solution/CO_2 mixtures were prepared by the following steps. First, a specific volume of methanol was premixed with a known volume of aqueous solution, which was either H_2O or a buffer solution. Then the mixture was transferred into an ISCO 260D syringe pump. A known volume of liquid CO_2, which was stored in another ISCO 260D syringe pump that was maintained at 204 atm, was delivered into the pump containing the methanol/H_2O mixtures. The resulting mixture was then pressurized to 204 atm and allowed to equilibrate for at least 12 h. The methanol/aqueous solution composition was maintained at 69.0/31.0 mole ratio, while the amount of CO_2 varied from 5.6 to 19.2 mol % in the mixtures. Previous studies[29] showed that these mixtures with CO_2 content up to 20 mol % were well within the single phase region under these experimental conditions.

The high-pressure view cell was sealed at one end first, and 1 mL of indicator stock solution was placed on the quartz window surface. A gentle argon gas (99.995%, Linde Specialty Gases, Columbus, OH) flow was introduced to the cell to evaporate methanol to dryness. Next, the enhanced-fluidity liquid mixture was transferred into the high-pressure view cell. The final concentration of indicator in the cell was 1×10^{-5} M. A tee was placed in the transfer line between the pump and view cells allowing the reference cell to contain exactly the same solvent as the sample cell. Each UV/visible experiment of a pH indicator in enhanced-fluidity liquids was performed at least in duplicate.

UV/visible spectra of tetrabromophenolphthalein ethyl ester potassium salt revealed that its acidic form has an electronic transition at 428 nm, while its basic form has an electronic transition at 599 nm. For thymol blue, the acidic form has its absorbance maximum at 549 nm, whereas the basic form has its absorbance maximum at 410 nm. UV/visible spectra of bromophenol blue showed the maximum absorbance at 426 nm for the acidic form and maximum absorbance at 596 nm for the basic form. Throughout the experiment, the absorbance maximum displayed wavelength variation less than or equal to 2 nm. As the absorbance peaks for the acidic and basic forms of each pH indicator were virtually baseline separated, deconvolution was not attempted (Figure 2).

Safety Precautions. All work was done with instrumentation specially designed for studies involving pressures up to 500 atm. Only instrumentation with similar pressure ratings should be used for studies similar to these.

RESULTS AND DISCUSSION

Calibration. As stated previously, when a nonpolar compound (alkane or CO_2) is introduced into a solution enriched with alcohol, the dielectric constant of the mixture reduces approximately linearly with the mole percent of the nonpolar component.[21−25] When CO_2 is added into the methanol/H_2O (69.0/31.0 mole ratio) mixture that has a dielectric constant of 42.4,[26] the dielectric constant of the resulting methanol/H_2O/CO_2 enhanced-fluidity liquid should decrease proportionally with the mole percent of CO_2. By varying the methanol/H_2O ratio, the dielectric constant of a methanol/H_2O mixture was matched to that of a methanol/H_2O/CO_2 enhanced-fluidity liquid. For example, a methanol/H_2O/CO_2 enhanced-fluidity liquid of 68.2/30.6/1.2 mole ratio and a methanol/H_2O mixture of 70.0/30.0 mole ratio share a dielectric constant value of 42. A methanol/H_2O/CO_2 enhanced-fluidity liquid of 65.1/29.3/5.6 mole ratio and a methanol/H_2O mixture of 75.0/25.0 mole ratio share a dielectric constant value of 40. A methanol/H_2O/CO_2 enhanced-fluidity liquid of 61.7/27.7/10.6 mole ratio and a methanol/H_2O mixture of 81.4/18.6 mole share a dielectric constant value of 38; while a methanol/H_2O/CO_2

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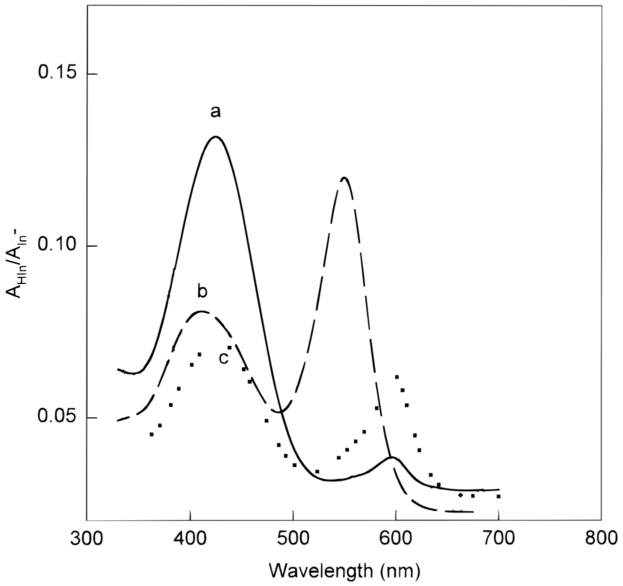

Figure 2. Typical spectra of pH indicators in methanol/aqueous solution/CO_2 mixtures (55.7/25.1/19.2 mole ratio) at 204 atm: (a) bromphenol blue in methanol/acetate buffer, pH 3.00, ionic strength 10 mM/CO_2 mixture; (b) thymol blue in methanol/HCl solution, pH 2.02/CO_2 mixture; (c) tetrabromophenolphthalein ethyl ester potassium salt in methanol/phosphate buffer, pH 2.43, ionic strength 10 mM/CO_2 mixture.

enhanced-fluidity liquid of 55.7/25.1/19.2 mole ratio and a methanol/H_2O mixture of 95.6/4.4 mole ratio share a dielectric constant value of 34.

The acid−base behavior in methanol/H_2O mixtures is well defined.[27,30−33] In this study, the pH was calculated using eq 4 and pK_a values of weak acids that are available in the literature.[27] UV/visible experiments of pH indicators in methanol/aqueous buffer mixtures revealed the A_{HIn}/A_{In^-} ratio. The relationship between A_{HIn}/A_{In^-} and [H^+] was readily established. As an example, the calibration established in methanol/aqueous buffer 95.6/4.4 mole ratio mixtures was used to measure [H^+] of enhanced-fluidity liquids methanol/aqueous solution/CO_2 55.7/25.1/19.2 mole ratio (Figure 3). Linear correlation was obtained between A_{HIn}/A_{In^-} and [H^+] with $r^2 \geq 0.99$ for the fitted curve.

Precision and Accuracy. Throughout the experiments in this study, the measured A_{HIn}/A_{In^-} ratios had uncertainties less than 2% at the 95% confidence level, which resulted in a pH deviation less than 0.03 pH unit.

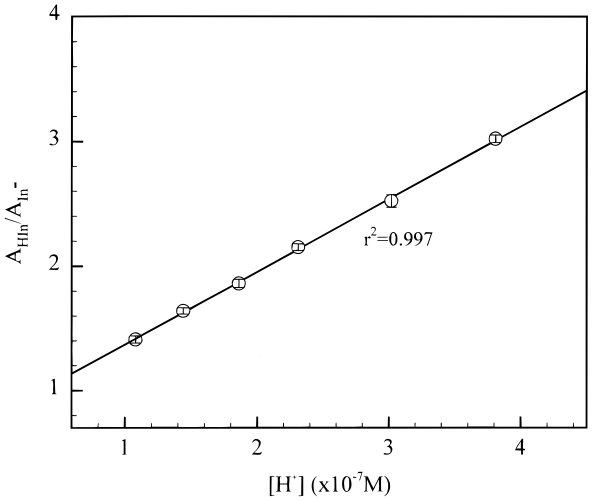

Figure 3. Calibration curves established by the UV/visible experiments of bromophenol blue in methanol/acetate buffer (0.956/0.044 mole ratio) mixtures.

Table 1. pH Measurements of Methanol/HCl/CO_2 Mixtures by the UV/Visible Spectra of Thymol Blue at 204 atm

	pH	
methanol/HCl/CO_2 (mole ratio)	calcd	measd
65.1/29.3[a]/5.6	2.20	2.21 ± 0.02
61.7/27.7[b]/10.6	2.45	2.48 ± 0.01
55.7/25.1[c]/19.2	2.96	3.02 ± 0.01

[a] 3.80×10^{-2} M HCl solution. [b] 2.29×10^{-2} M HCl solution. [c] 9.55×10^{-3} M HCl solution.

The pH measurement of methanol/aqueous HCl solution/CO_2 mixtures was used to evaluate the accuracy of the pH measurements. Strong electrolytes will completely dissociate in solvents with high dielectric constant (i.e., >30).[20,34] As shown in the previous section, the dielectric constants for all the enhanced-fluidity liquid mixtures in this study were greater than 30. So, a strong acid, such as HCl(aq), is expected to dissociate fully in these mixtures. The pH of methanol/aqueous HCl solution/CO_2 mixtures was calculated from the concentration of HCl(aq) in solution and the total volume of the mixture. This value was then compared to that determined by UV/visible experiment. Table 1 shows the resulting data. Methanol/aqueous HCl solution/CO_2 mixtures with 5.6, 10.6, and 19.2 mol % CO_2 had deviations between calculated and measured pH values of 0.01, 0.03, and 0.06 pH units, respectively. These data thus validate the use of UV/visible spectra as an acceptable pH measurements for the purpose of this study.

pH Determination of Methanol/H_2O/CO_2 Mixtures. With the calibration curves established, the pH variation in methanol/H_2O/CO_2 liquid mixtures caused by formation of carbonic acid was investigated from the UV/visible spectra of the pH indicator tetrabromophenolphthalein ethyl ester potassium salt. The results are listed in Table 2.

When small proportions of CO_2 are added, the pH of methanol/H_2O/CO_2 mixtures decreases. The pH of a methanol/H_2O/CO_2 (68.2/30.6/1.2 mole ratio) mixture was 4.54. With 5.6 mol % CO_2, the pH for methanol/H_2O/CO_2 (65.1/29.3/5.6 mole ratio) mixture was reduced further to 4.22. However, a lower pH value was not produced when more CO_2 was present in the mixture. For the 61.7/27.7/10.6 mole ratio methanol/H_2O/CO_2 mixture, a higher pH value, 4.38, was determined; and when 19.2 mol % CO_2 was added, the pH for methanol/H_2O/CO_2 (55.7/25.1/19.2 mole ratio) mixture increased to 4.73.

As stated before, there are two consequences of adding CO_2 into a methanol/H_2O mixture: the formation of carbonic acid and

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Table 2. pH Measurements of Methanol/H_2O/CO_2 Mixtures by the UV/Visible Spectra of Tetrabromophenolphthalein Ethyl Ester Potassium Salt at 204 atm

methanol/H_2O/CO_2 (mole ratio)	pH
68.2/30.6/1.2	4.54 ± 0.01
65.1/29.3/5.6	4.22 ± 0.03
61.7/27.7/10.6	4.38 ± 0.02
55.7/25.1/19.2	4.73 ± 0.03

Table 3. Buffer Capacity of Methanol/H_2O/CO_2 Mixtures at 204 atm

methanol/H_2O/CO_2 (mole ratio)	$\Delta C_a/\Delta pH$
65.1/29.3/5.6	1.9×10^{-2}
61.7/27.7/10.6	1.2×10^{-2}
55.7/25.1/19.2	5.6×10^{-3}

the reduction of the dielectric constant of the mixture. When small amounts of CO_2 are added, there is no significant change in dielectric constant for the mixture. Under these conditions, more carbonic acid is formed and the pH of the mixture decreases with added CO_2. With higher proportion of CO_2, the dielectric constant of the mixture reduces to such a point that the dissociation of carbonic acid is significantly suppressed. As a result, the pH of the mixture increases. This postulation matches well with the experimental results of pH determination for methanol/H_2O/CO_2 enhanced-fluidity liquids.

Due to the formation of carbonic acid, a methanol/H_2O/CO_2 mixture can be considered a buffer system. The buffer capacity, β, defined as the number of moles of strong acid per liter (C_a)

$$\beta = -(\Delta C_a/\Delta pH) \qquad (5)$$

necessary to produce one pH unit change in the buffer,is an important property of a buffer system. By monitoring the pH values in methanol/H_2O/CO_2 mixtures when a strong acid is added, the buffer capacity for methanol/H_2O/CO_2 mixtures can be determined. Using thymol blue as the pH indicator, pH for methanol/aqueous HCl solution/CO_2 mixtures was measured and the buffer capacity for the methanol/H_2O/CO_2 mixtures was determined (Table 3). As shown in Table 3, the buffer capacity of methanol/H_2O/CO_2 mixtures decreases with the addition of liquid CO_2. When the CO_2 proportion increased from 5.6 to 19.2 mol %, the buffer capacity of methanol/H_2O/CO_2 mixtures decreased from 1.9×10^{-2} to 5.6×10^{-3}.

For single-phase buffer systems, the buffer capacity is greatest when the pH of the solution is equal to the pK_a of the acid. Bosch et al.[27] and Ong et al.[33] have shown that the pK_a of weak acids increases when more methanol is added to methanol/H_2O mixtures (equivalent to reducing dielectric constant). For acetic acid, its pK_a value increased more than 2 units (4.77 to 6.69) as the solvation medium changed from pure water to a methanol/H_2O (69.0/31.0 mole ratio) mixture. Accordingly, the pK_a of carbonic acid in methanol/H_2O/CO_2 mixtures probably increases significantly as the dielectric constant of the mixture is reduced by the addition of CO_2. However, the pH of methanol/H_2O/CO_2 mixtures does not change much with the addition of more CO_2 (Table 2). It is reasonable to believe that, with more liquid CO_2 added, the pK_a of carbonic acid is drifting away from the pH of methanol/H_2O/CO_2 mixtures, which will result in a weaker buffer capacity.

Table 4. pH of Acetate-Buffered Enhanced-Fluidity Liquids Determined by the UV/Visible Spectra of Bromophenol Blue and the Comparison with pH of Methanol/H_2O/CO_2 Mixtures at 204 atm

enhanced-fluidity liquid[a]	ionic strength (mM)	pH	ΔpH[b]
methanol/acetate buffer I/CO_2 (65.1/29.3/5.6 mole ratio)	1.7	4.89 ± 0.02	0.19
methanol/acetate buffer II/CO_2 (65.1/29.3/5.6 mole ratio)	1.7	5.11 ± 0.01	0.41
methanol/acetate buffer I/CO_2 (55.7/25.1/19.2 mole ratio)	1.4	6.36 ± 0.03	1.51
methanol/acetate buffer II/CO_2 (55.7/25.1/19.2 mole ratio)	1.4	6.41 ± 0.01	1.5

[a] Acetate buffers: I, aqueous solution of pH 3.00; II, aqueous solution of pH 3.45. [b] Difference between pH of acetate buffered enhanced fluidity liquids and methanol/H_2O/CO_2 mixtures at 204 atm.

pH Determination of Methanol/Aqueous Buffer/CO_2 Mixtures. To control the pH variation caused by the formation of carbonic acid, aqueous buffer solutions were introduced into mixtures of methanol/H_2O/CO_2. [H^+] was determined from the UV/visible spectra of bromophenol blue. With the increased proportion of ions in solution caused by the use of buffers, the ionic strength of the mixture may influence the pH of the solution (i.e., the original assumption that $A = [H^+]$ may no longer hold). The activity coefficient should be considered. Since the ionic strength of the mixtures was maintained under 0.02 M, the Debye−Hückel equation was used to calculate the activity coefficient.

$$\log y = -Az^2\sqrt{I}/(1 + Ba_0\sqrt{I}) \qquad (6)$$

where z is the charge of the ion, I is the ionic strength of the solution, a_0 has a constant value of 4.56 Å by Bates−Guggenheim convention, and A and B are parameters that are functions of temperature and dielectric constant.[27,35,36]

$$A = (1.8246 \times 10^6)/(\epsilon T)^{3/2} \qquad (7)$$

$$B = 50.29/(\epsilon T)^{1/2} \qquad (8)$$

Table 4 lists the pH values of enhanced-fluidity liquid mixtures when H_2O was replaced by aqueous acetate buffer solutions of a fixed ionic strength of 10 mM and pH values of 3.00 and 3.45. With 5.6 mol % CO_2, the pH values for methanol/acetate buffer/CO_2 enhanced-fluidity liquids are 4.89 and 5.11, respectively. While with 19.2 mol % CO_2, the corresponding measured pH values were 6.36 and 6.41, respectively, which is only a difference of 0.05 pH unit between the two measured values.

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Table 5. pH of Phosphate-Buffered Enhanced-Fluidity Liquids Determined by the UV/Visible Spectra of Bromophenol Blue and the Comparison with pH of Methanol/H_2O/CO_2 Mixtures at 204 atm

enhanced-fluidity liquid[a]	ionic strength (mM)	pH	ΔpH[b]
methanol/phosphate buffer I/CO_2 (65.1/29.3/5.6 mole ratio)	12.0	5.55 ± 0.02	0.71
methanol/phosphate buffer II/CO_2 (65.1/29.3/5.6 mole ratio)	9.6	5.48 ± 0.03	0.64
methanol/phosphate buffer III/CO_2 (65.1/29.3/5.6 mole ratio)	4.8	5.29 ± 0.01	0.51
methanol/phosphate buffer I/CO_2 (55.7/25.1/19.2 mole ratio)	9.9	6.82 ± 0.02	1.79
methanol/phosphate buffer II/CO_2 (55.7/25.1/19.2 mole ratio)	7.9	6.73 ± 0.02	1.74
methanol/phosphate buffer III/CO_2 (55.7/25.1/19.2 mole ratio)	4.0	6.59 ± 0.01	1.6

[a] Phosphate buffers: I, aqueous solution of pH 6.62, ionic strength 71.9 mM; II, aqueous solution of pH 6.62, ionic strength 57.5 mM: III, aqueous solution of pH 6.62, ionic strength 28.8 mM. [b] Difference between pH of phosphate-buffered enhanced-fluidity liquids and methanol/H_2O/CO_2 mixtures at 204 atm.

Table 6. pH of Methanol/H_2O/CO_2 Mixtures as a Function of Pressure

methanol/H_2O/CO_2 (mole ratio)	pH	
	119 atm	204 atm
68.2/30.6/1.2	4.54 ± 0.01	4.52 ± 0.01
65.1/29.3/5.6	4.62 ± .02	4.60 ± 0.03
61.7/27.7/10.6	4.39 ± 0.01	4.38 ± 0.02
55.7/25.1/19.2	4.74 ± 0.03	4.73 ± 0.03

The dissociation of weak acid (HA) and the hydrolysis of its conjugated base (A^-) in aqueous solution occur simultaneously. A weak dissociation process is always accompanied by a strong hydrolysis process, and vice versa. The collective effect of these two equilibria dictates the pH of the solution. As shown in Bosch et al.,[27] the pK_a of acetic acid increases from 6.90 to 8.59 when the solvent is changed from 75.0/25.0 mole ratio methanol/H_2O to 95.6/4.4 mole ratio methanol/H_2O. However, the pK_{aw} (autoprotolysis constant) only increases from 14.89 to 15.82. It is clear that, with the addition of methanol, the dissociation of acetic acid is weakened while the hydrolysis of the acetate ion is strengthened. Therefore, similar results are expected when the dielectric constant of the methanol/H_2O/CO_2 is reduced by the addition of CO_2 The dissociation of acetic acid should be weakened in methanol/H_2O/CO_2 mixtures as the dielectric constant reduces. Meanwhile, the hydrolysis of the acetate ion should be strengthened. Higher pH values should be obtained for methanol/acetate buffer/CO_2 with more CO_2 content (Table 4). As stated in the Experimental Section, the ionic strength of the two acetate buffers was maintained at 10.0 mM. Therefore, approximately the same number of moles of acetate ions should be present in the methanol/acetate buffer/CO_2 mixtures. As the contribution to the pH from the hydrolysis of acetate ion increases with added CO_2, the difference in pH between methanol/acetate buffer/CO_2 mixtures with different acetate buffers should go down, which was observed (Table 4).

Table 5 lists the pH values for methanol/aqueous solution/CO_2 mixtures when water was replaced by a pH 6.62 phosphate buffer solutions of different concentrations. As the concentration of the aqueous phosphate buffer solution decreased, the pH of methanol/phosphate buffer/CO_2 mixtures also decreased. Noticeable pH differences were observed among the mixtures that contained buffers of differing ionic strength. The effect of ionic strength variation was similar for mixtures containing 5.6 and 19.2 mol % CO_2. The overall pH variation was 0.26 and 0.23 pH unit, respectively. The effect of aqueous buffer concentration on the acidity of enhanced-fluidity liquids was also noticed from the chromatographic study in our laboratory. Yuan[6] noticed that the retention time for hydroxyatrazine varied when the aqueous buffer concentration was changed in the enhanced-fluidity liquid used as a mobile phase. Changing buffer concentration more effectively manipulates the acidity of enhanced-fluidity liquids than varying the buffer pH.

Replacing H_2O with aqueous buffer can also be regarded as a way to disturb a methanol/H_2O/CO_2 buffer system. The magnitude of this disturbance is reflected in the pH difference between methanol/H_2O/CO_2 and methanol/aqueous buffer/CO_2 mixtures. Larger differences have been observed with more CO_2 content (Tables 4 and 5). For both buffer systems studied, with 5.6 mol % CO_2, the pH difference between methanol/H_2O/CO_2 and methanol/aqueous buffer/CO_2 mixtures varies between 0.2 and 0.7; and with 19.2 mol % CO_2, the pH difference varies between 1.5 to 1.8 pH units. The ability to resist this disturbance is related to the buffer capacity of methanol/H_2O/CO_2 mixtures. Greater differences in pH would imply weaker buffer capacity. This conclusion is consistent with the buffer capacity estimate of methanol/H_2O/CO_2 mixtures, which showed methanol/H_2O/CO_2 enhanced-fluidity mixtures with 5.6 mol % CO_2 had stronger buffer capacity than those with 19.2 mol % CO_2 (Table 3).

Pressure Effect. pH variation due to pressure change was potentially a concern for this study. Throughout this study, pH measurements for methanol/H_2O/CO_2 mixtures were performed at two different pressures, 119 and 204 atm. Previously, Toews et al.[16] illustrated that the molar volume of liquid CO_2 does not change substantially over this pressure range. Since the molar volumes of methanol and H_2O vary to a lesser extent than that of CO_2, the pH of the system was not expected to change substantially with pressure over this pressure range. Table 6 shows the pH for four different methanol/H_2O/CO_2 mixtures at 119 and 204 atm. At the 95% confidence level, the differences in pH values at two pressures were not statistically significant.

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