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High-temperature and high-pressure water solubility in ethylbenzene to 200°C and 1 kbar and the acetic acid effect

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Abstract—Water solubility in hydrocarbon systems is of great interest for deep oil fields. A new autoclave has been designed to measure phase equilibria in water–hydrocarbon systems up to 400°C and 1.5 kbar. It has been applied for the measurement of water solubility in ethylbenzene with or without acetic acid to 200°C and 1 kbar in the two-phase field. Water solubility was measured by the Karl Fisher method. The acetic acid concentration was measured by FT-IR microspectroscopy. Both the experimental procedure and analytical techniques were validated by showing the consistency of our data with those of Heidman et al. (“High-temperature mutual solubilities of hydrocarbons and water,” *AIChE J.* **31**, 376–384, 1995) along the liquid–liquid–vapor curve. At constant pressure, the solubility of water in ethylbenzene increases significantly with temperature. On the other hand, at constant temperature, the solubility of water is constant to 1 kbar at 100°C, and decreases slightly with pressure at 150 and 200°C. Data were regressed by the Krichevsky–Kasarnovsky equation to obtain estimates of the Henry’s law constant and estimates of the molar volume of water at infinite dilution. Acetic acid increases the solubility of water in ethylbenzene and fractionates preferentially into the aqueous phase. Copyright © 2001 Elsevier Science Ltd

1. INTRODUCTION

Interaction between water and organic components is important for evaluating the role of water in the formation petroleum because water is the main component of diagenetic fluids. First, water is involved in chemical processes such as hydrogen transfer during maturation (e.g., Landais et al., 1994; Lewan, 1997), oil migration, and alteration in reservoirs by water washing and biodegradation (Hunt, 1995). Second, these interactions are facilitated by mutual solubilities that are governed by the laws of phase equilibria. The solubility of water in hydrocarbons was studied mainly at high temperatures and pressures (Groschuff, 1911; Alwani et al., 1967; Danneil et al., 1967; De Loos et al., 1980, 1982; Hilder, 1971; Skripka and Boksha, 1976; Yiling et al., 1991). In the pressure (P) and temperature (T) conditions of conventional oil fields (T < 100°C, P < 500 bar), the solubility of water in hydrocarbons is very low. It was studied experimentally (Schatzberg, 1963; Thompson and Snyder, 1964; Tsonopoulos and Wilson, 1983; Heidman et al., 1985; Anderson and Prausnitz, 1986; Hooper et al., 1988; Chen and Wagner, 1994a,b) and calculated by use of equations of state (Haschets et al., 1994; Michel et al., 1989). A tendency for oil prospecting is to consider deeper fields corresponding to higher temperatures (up to 200°C) and higher pressures (up to 1000 bar). The solubility of water in hydrocarbon phases cannot be neglected under those conditions. For instance, the water solubility in benzene along the liquid–liquid–vapor (L–L–V) equilibrium curve increases from 2.135×10^{-2} mole fraction at 101°C to 18.86×10^{-2} mole fraction at 204°C (Anderson and Prausnitz, 1986). Few experimental data are available to quantify the water solubility in hydrocarbons under pressure and temperature conditions rep-

resentative of deep oil fields (T from 100–200°C and P from 250–1000 bar); Anthony and McKetta (1967) studied the mutual solubility of water and ethylene in the temperature range 104 to 138°C and at pressure up to 344 bar, and Sanchez and Lentz (1973) studied the water–propene system in the temperature range 168 to 350°C and in the pressure range 126 to 2500 bar.

Study of the water solubility in ethylbenzene was chosen for two main reasons. The first reason deals with oil composition. Ethylbenzene, made up of an aromatic ring and an alkylside chain, could be considered a model molecule for a light oil of a medium composition. The second reason is that validation of our experimental setup and analytical procedure is possible with previous experimental data (Heidman et al., 1985) dealing with the water solubility in ethylbenzene along the L–L–V curve up to 300°C. The water–ethylbenzene system has two critical lines (Heidman et al., 1985): one joins the critical point of pure ethylbenzene (P = 3.609 MPa; T = 647.09 K) to the three-phase critical end point of the L–L–V curve (P = 10.68 MPa; T = 568.1 K). An upper critical curve starts from the critical point of pure water (P = 22.12 MPa; T = 647.30 K) toward an unknown upper end critical point and has a minimum temperature point (P = 19.5 ± 2.0 MPa; T = 592 ± 2 K). Experiments are carried out in the two-phase field (L–L) at pressures above the L–L–V curve.

The objective of this article is to provide new experimental data on water solubility in ethylbenzene in the L–L equilibrium phase field for temperatures between 100 and 200°C and pressures from 450 to 1000 bar. The low solubility of water in pure hydrocarbons is the result of molecular interactions which are not favorable for the water molecule (no hydrogen bonding, weak dipole–dipole interactions). Acetic acid has been recognized as an ubiquitous organic acid in oil fields (Helgeson et al., 1993). The effect of acetic acid on the water solubility and the

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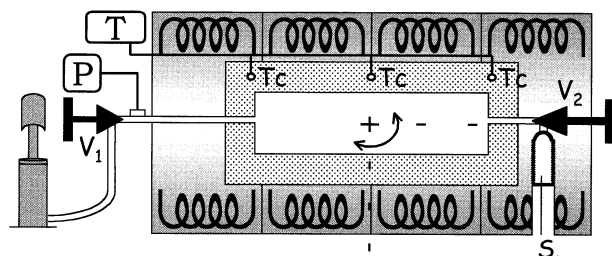


Fig. 1. Autoclave with four independently regulated furnaces. Temperature T is measured with three thermocouples (T_c) along the autoclave body. Pressure P is measured by a pressure transducer. Sampler S is inserted inside one of the furnaces at the experimental temperature. $+$ = rotation axis of the autoclave; V_1 and V_2 = inlet and outlet valves, respectively.

fractionation of acetic acid between the ethylbenzene and aqueous solution are quantified in the same P - T conditions.

2. EXPERIMENTAL DEVICES AND PROCEDURES

2.1. Starting Chemical Products

Water was taken from the laboratory distilled water supply (Millipore Milli-Q Reagent water system). Ethylbenzene (98% minimum purity) was supplied by Fluka Chemika, acetic acid (99.9% minimum purity, $H_2O < 0.05\%$) by Prolabo-Chromanorm and methanol (99.9% minimum purity, $H_2O < 0.05\%$) by Carlo Erba Reagenti.

2.2. Autoclave

The experimental device was designed for use up to 400°C and 1.5 kbar (Fig. 1). It consists of a 100-cm^3 titanium autoclave, with an inlet valve used for the charge of solutions and an outlet valve for the sampling. The autoclave was placed in the middle of four ring furnaces separately regulated to minimize any thermal gradient. The temperature was controlled in the autoclave with three thermocouples placed in its body. They were calibrated by the manufacturer (JUMO) at 100, 150, and 200°C . The maximum error is $\pm 1.5^\circ\text{C}$. The pressure in the autoclave was measured with a pressure transducer placed between the inlet valve and the autoclave body. It was calibrated against a dead weight manometer up to 2500 bar at the Institute of Experimental Mineralogy (Russian Academy of Sciences, Chernogolovka). The maximum error is ± 1.5 bar. A manual press (Novaswiss) was used to increase the experimental pressure. A 1-cm^3 titanium sampler was screwed on the outlet valve and was placed in one of the furnaces at the experimental temperature to avoid any condensation during sampling. This whole system can rotate around a horizontal axis perpendicular to the cylinder axis. The sampler was in the top or bottom position, depending on the relative density of the coexisting liquids and on the phase that was sampled.

2.3. Experimental Procedures

The apparatus was evacuated with a pump connected to the inlet valve. About 90 cm^3 of ethylbenzene was then charged in the autoclave via a syringe connected to the inlet valve. The autoclave was heated until the temperature was stable at the desired experimental temperature. Pressure was then adjusted to ~ 1000 bar by charging water by means of the manual pump connected to the inlet valve. The autoclave was horizontal during experiments to create a larger contact surface between the two liquid phases to accelerate the approach to equilibrium. Equilibrium between the two liquid phases was reached after 5 h in the water–ethylbenzene system at 25°C up to 4000 bar (Sawamura et al., 1989). However, sampling always was carried out after 48 h, and the experiments at 100°C were repeated after a 5-d waiting period. No significant differences in solubility were observed.

The titanium sampler was evacuated and connected to the outlet

valve 12 h before sampling so that it was equilibrated at the experimental temperature. The sampling valve was briefly opened so that the higher pressure in the autoclave pushed 1 cm^3 of solution into the sampler container. The mass of solution sampled was well defined by successive weighing of the sampler with a 10^{-4}-g precision. The sample was two phase at room temperature, which made it difficult to collect and analyze without loss. Therefore, the sample was rehomogenized into a single phase by adding a weighed amount of methanol (1 g) with a syringe. The final sample was collected with a syringe connected to the sampler. Each sampling produced a drop in pressure of ~ 150 bar. Experiments were thus carried out isothermally with decreasing pressure. The same experimental procedure was used to study the effect of acetic acid on water solubility in ethylbenzene. The initial concentration of acetic acid was 1 molal both in the aqueous and in the ethylbenzene phase.

3. ANALYTICAL PROCEDURE

3.1. Water Solubility Measurement

Water solubility was measured by the Karl Fisher method by means of the two-component system (Hydranal-Titrant and Hydranal-Solvent). A weighed amount of the sample was analyzed and the solubility was corrected for the added methanol. Each measurement was repeated. The relative analytical uncertainty depends on the water concentration and consequently on the experimental temperature: 20% for experiments at 100°C , 10% for experiments at 150°C , and 5% for experiments at 200°C .

3.2. Acetic Acid Solubility Measurement in Ethylbenzene

Acetic acid solubility in ethylbenzene was measured via Fourier Transfer infrared (FT-IR) microspectroscopy (Bruker IFS 55). A sample of the solution is placed between two NaCl slides and examined under the IR beam to choose appropriate thickness of liquid such as the absorbance remains lower than 1.5. Two characteristic bands of the absorbance spectrum for acetic acid ($\text{C}=\text{O}$ bending vibration, 1715 cm^{-1} ; Bellamy, 1975) and ethylbenzene (aromatic core vibration, 1610 cm^{-1} ; Bellamy, 1975) were used for the calibration curve (Fig. 2). The baseline was subtracted, and the integrated area of the bands was measured for the calculation of the absorbance ratios. The standard solutions used were the pure components and ethylbenzene solutions containing acetic acid at various molalities (0.53, 0.16, 0.05, 0.016, 0.006, and 0.0015). The calibration curve is a straight line following the Beer Lambert law (Fig. 3a).

3.3. Acetic Acid Solubility Measurement in Water

The acetic acid concentration in aqueous solution was also measured with FT-IR microspectroscopy. A solution sample was placed between two CaF_2 slides that are IR transparent and not water soluble. The characteristic bands used for the calibration curve were, respectively, the stretching vibration band for water in the $3000\text{- to }4000\text{-cm}^{-1}$ region and the $\text{C}=\text{O}$ bending vibration at 1715 cm^{-1} (Bellamy, 1975) for acetic acid (Fig. 2). The ratio of the integrated intensities was plotted vs. the acetic acid molality in the solution at 10, 5, 2, 1.5, 1, 0.5, and 0.1 molal (Fig. 3b).

4. EXPERIMENTAL RESULTS

Experimental data are given in Table 1 and plotted in Figures 4, 5, and 6. Water solubility in ethylbenzene was studied at 100, 150, and 200°C between 300 and 1000 bar in 18 samples.

4.1. Validation of the Experimental Device and Analytical Procedure

Our experimental data for the water–ethylbenzene system can be compared with those of Heidman et al. (1985) obtained at L-L-V equilibrium between 38 and 300°C . Our data at 100,

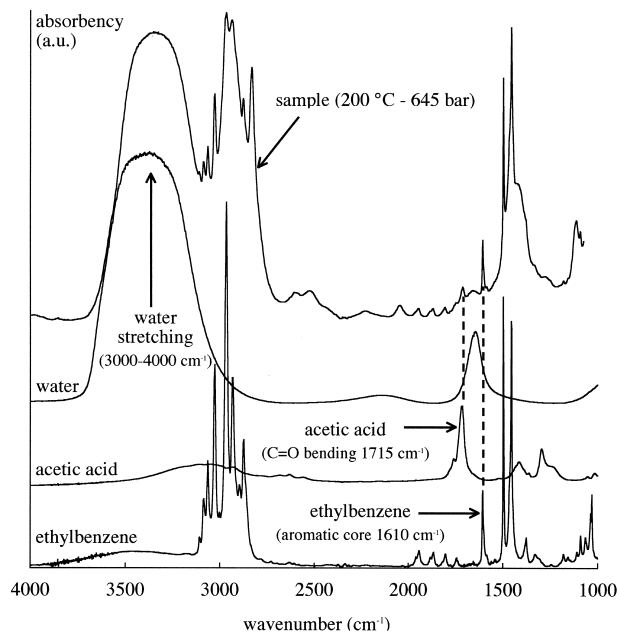


Fig. 2. Infrared spectra of pure water, ethylbenzene, and acetic acid with the bands used to establish the calibration curves. The upper spectrum was obtained from an experiment at 200°C and 645 bar.

150, and 200°C in the L-L field extrapolate along the L-L-V curve at values that are consistent within the experimental precision with the data of Heidman et al. (1985) (Fig. 4). This confirms the validity of our experimental procedure and analytical techniques.

4.2. Effect of Temperature and Pressure on Water Solubility

The effect of pressure on the solubility of water in liquid ethylbenzene (L-L equilibrium) at 100, 150, and 200°C is presented in Figure 4. At 100°C, the experimental uncertainty of 20% is significant. However, the data are consistent within the experimental error. At this temperature, the solubility of water in ethylbenzene does not vary (~ 0.23 molal) with pressure from 1000 bar to 1 bar. At 150°C, the solubility of water decreases very slightly from 0.57 molal at 6 bar to 0.51 molal at 1 kbar, with a mean variation of -0.06 molal/kbar. At 200°C, the effect of pressure is more important. The solubility of water decreases from 1.39 molal at 20 bar to 1.07 molal at 1 kbar with a mean variation of -0.33 molal/kbar. The pressure effect increases with increasing temperature. At constant pressure, we note that the water solubility increases exponentially with increasing temperature.

The solubility of water inside the ethylbenzene-rich phase can be rationalized with the Henry law,

$$f_{\text{H}_2\text{O}}^{\text{T,P,m}} = K_{\text{h,H}_2\text{O,Eb}}^{\text{T,P}} \cdot x_{\text{H}_2\text{O}}, \quad (1)$$

where $f_{\text{H}_2\text{O}}^{\text{T,P,m}}$ is the water fugacity at the P-T conditions, $x_{\text{H}_2\text{O}}$ is the mole fraction of water inside the ethylbenzene-rich phase, and $K_{\text{h,H}_2\text{O,Eb}}^{\text{T,P}}$ is the Henry constant at T and P. The Henry constant at T and P is related to the Henry constant at T and

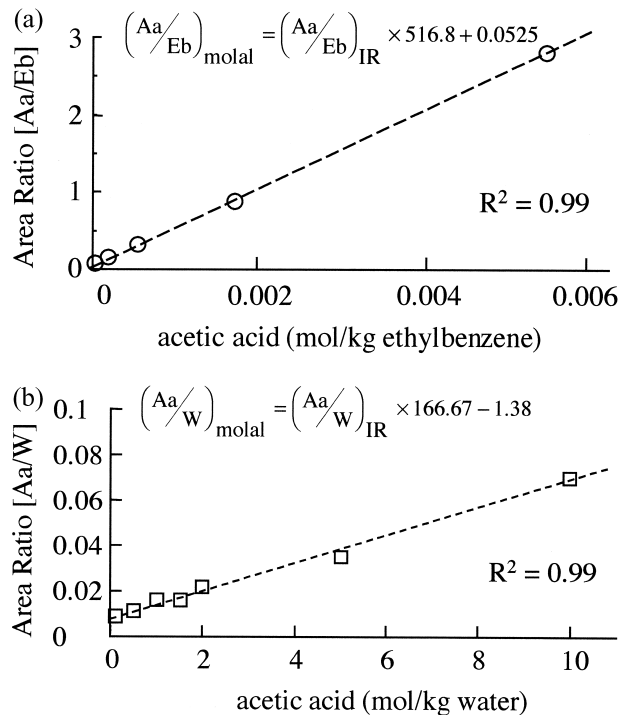


Fig. 3. (a) Calibration curve for the analysis of acetic acid (Aa) in ethylbenzene (Eb) established via infrared microspectroscopy. Aa/Eb = integrated area ratio of the acetic acid band (CO at 1715 cm^{-1}) and the ethylbenzene band (aromatic core vibration at 1610 cm^{-1}). Maximum uncertainties are inside the points size. (b) Calibration curve for the analysis of acetic acid (Aa) in water (W). Aa/W : integrated area ratio of acetic acid band (CO at 1715 cm^{-1}) and water stretching massif ($3000\text{--}4000 \text{ cm}^{-1}$). Maximum uncertainties are inside the point size.

saturation pressure of ethylbenzene ($K_{\text{h,H}_2\text{O,Eb}}^{\text{T,P}}$) by the equation of Krichevsky-Kasarnovsky (Prausnitz et al., 1986):

$$\ln K_{\text{h,H}_2\text{O,Eb}}^{\text{T,P}} = \ln K_{\text{h,H}_2\text{O,Eb}}^{\text{T,P,(T),Eb}} + \frac{\overline{v}_{\text{H}_2\text{O}}^{\infty,\text{T}} (P - P_{\text{s}(T),Eb})}{RT}, \quad (2)$$

where $\overline{v}_{\text{H}_2\text{O}}^{\infty,\text{T}}$ is the molar volume of water at infinite dilution in ethylbenzene at temperature T and is assumed to not vary with pressure.

$P_{\text{s}(T),Eb}$ is the saturation pressure of pure ethylbenzene at temperature T calculated with the Wagner equation (Ambrose, 1978) given in the Appendix. Because the solubility of hydrocarbons in the aqueous phase is low (Heidman et al., 1985), the water fugacity was assumed to be identical to the water fugacity of pure water in the same P-T conditions:

$$f_{\text{H}_2\text{O}}^{\text{T,P,m}} = f_{\text{H}_2\text{O}}^{\text{T,P,pure}}. \quad (3)$$

Water fugacity was calculated from the equation of state of Saul and Wagner (1989). Regression of the data at each temperature allows the calculation of the Henry's law constant at ethylbenzene saturation pressure ($K_{\text{h,H}_2\text{O,Eb}}^{\text{T,P,(T),Eb}}$) and of the molar volume of water at infinite dilution in ethylbenzene ($\overline{v}_{\text{H}_2\text{O}}^{\infty,\text{T}}$) at temperature T (Table 2).

4.3. Acetic Acid Fractionation

Starting conditions of the experiments were 10 cm^3 of water, 90 cm^3 of ethylbenzene, and 1 molal of acetic acid in both

Table 1. Water concentration and acetic acid concentration (molality and mole fraction scales) in ethylbenzene to 200°C and 1 kbar.

P (bar)	T (°C)	Water solubility		Acetic acid solubility	
		(molal)	(mol fraction)	(molal)	(mol fraction)
1009.5	100	0.25	0.026		
1006.9		0.21	0.022		
1000.1		0.19	0.020		
786.8		0.24	0.025		
666.6		0.27	0.028		
607.9		0.26	0.027		
458.1		0.22	0.023		
1012.3	150	0.51	0.051		
844.3		0.54	0.054		
699.8		0.56	0.056		
551.8		0.55	0.055		
1005.6	200	1.07	0.102		
867.6		1.11	0.105		
750.0		1.12	0.106		
639.0		1.17	0.110		
541.1		1.21	0.114		
457.2		1.25	0.117		
853.6	150 ^a	0.73	0.072	0.131	0.014
653.2		0.80	0.078	0.083	0.009
522.1		0.81	0.079	0.096	0.010
1012.5	200 ^a	1.52	0.139	0.113	0.012
880.1		1.59	0.144	0.134	0.014
756.6		1.66	0.150	0.134	0.014
644.7		1.67	0.151	0.136	0.014
541.0		1.79	0.159	0.151	0.016

^a Experiments with acetic acid. Relative uncertainties of water concentrations are respectively, 20% for 100°C experiments, 10% for 150°C experiments, and 5% for 200°C experiments. Relative uncertainties of acetic acid concentrations are 5%.

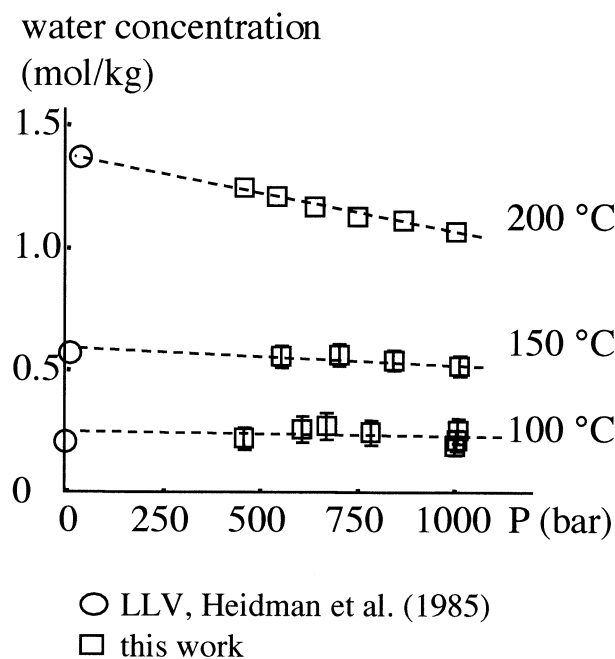


Fig. 4. Water solubility in liquid ethylbenzene in the two liquid phase field (this work, squares) and along the liquid–liquid–vapor curve (LLV, Heidman et al., 1985; circles).

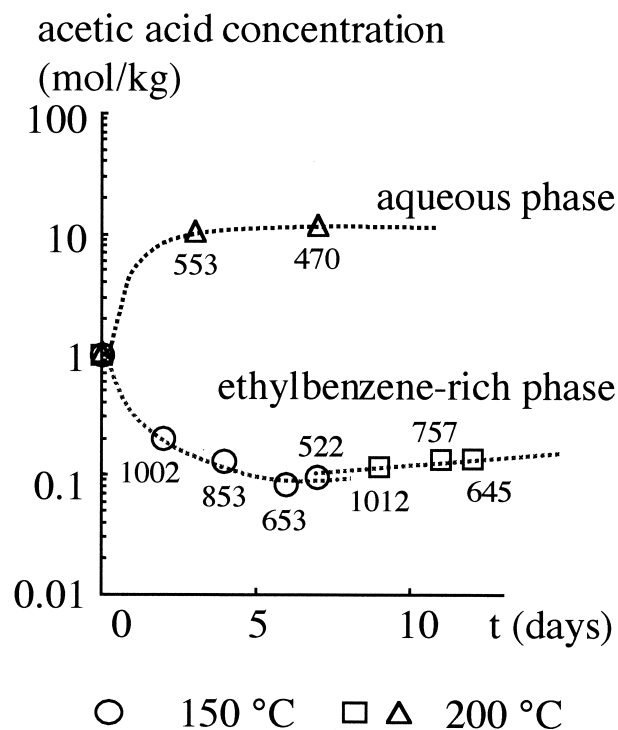


Fig. 5. Evolution vs. time of the acetic acid concentration in the aqueous phase and in the ethylbenzene-rich phase. Labels are pressure in bar.

phases. The acetic acid concentration decreased in the hydrocarbon rich phase and stabilized after 5 d at 0.096 molal (150°C experiments) 0.113 molal (200°C experiments) and increased in the aqueous phase and stabilized at 11.1 molal (Fig. 5). The partition coefficient of acetic acid at equilibrium between the two liquid phases can be deduced for experiments above 5 d (Fig. 5): it is around 100 and its precision is $\pm 10\%$. This value is similar to the value of the partition coefficient of acetic acid between benzene and water at room temperature and pressure (Leo et al., 1971; Lewan and Fisher, 1994).

4.4. Acetic Acid Effect on Water Solubility

Figure 6 compares the solubility of water in ethylbenzene in the presence of acetic acid when equilibrium is reached, with data obtained without acetic acid. The solubility of water increases in the presence of acetic acid, and this effect is more pronounced at 200°C than at 150°C. The dependence of water solubility with pressure is also more important in the presence of acetic acid.

The approximation $f_{\text{H}_2\text{O}}^{\text{P,T,m}} = f_{\text{H}_2\text{O}}^{\text{P,T,pure}}$ cannot be applied because the acetic acid concentration in the water is high (10 molal). Therefore, determination of water solubility in the ethylbenzene-rich phase after the data treatment made for the binary system water–ethylbenzene is carried out with the three following assumptions:

- (i) $f_{\text{H}_2\text{O}}^{\text{P,T,m}} = f_{\text{H}_2\text{O}}^{\text{P,T,pure}} \cdot x_{\text{H}_2\text{O}}^{\text{P,T,aq}}$, which assumes that the activity of water in the aqueous phase is equal to its concentration;
- (ii) the Henry's law constant is relative to the pseudosolvent made of the mixture ethylbenzene–acetic acid (0.1 molal acetic acid in ethylbenzene); and

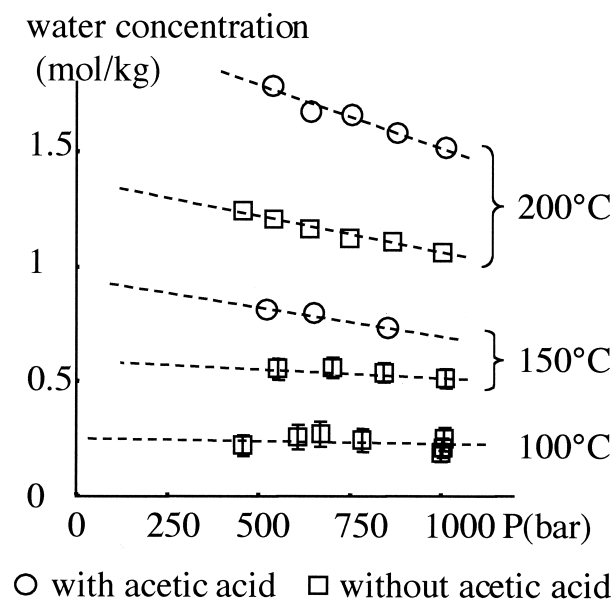


Fig. 6. Comparison of the water concentration in ethylbenzene-rich phase in absence (squares) and in presence (circles) of acetic acid (0.1 molal) at equilibrium conditions.

(iii) the saturation pressure of the pseudosolvent ethylbenzene–acetic acid (0.1 molal acetic acid in ethylbenzene) is assumed to be equal to the saturation pressure of pure ethylbenzene.

The values of $\bar{v}_{H_2O}^{\infty,T}$ and $K_{h,H_2O,Eb}^{T,P_s(T),Eb}$ calculated with these assumptions are given in Table 2. At the same temperature, the presence of acetic acid does not change significantly the values of $\bar{v}_{H_2O}^{\infty,T}$ inside the ethylbenzene-rich phase. However, acetic acid decreases the value of the Henry's constant ($K_{h,H_2O,Eb}^{T,P_s(T),Eb}$) compared with its value in the system without acetic acid; this variation takes into account the increase of water solubility due to acetic acid.

4.5. Kinetics

The evolution of the acetic acid concentration vs. time in the aqueous and ethylbenzene liquid phases is shown in Figure 5. There is a decrease of acetic acid concentration in ethylbenzene from 1 molal (initial condition) to 0.1 molal after 5 d. In the same time, acetic acid concentration in aqueous solution increases from 1 molal (initial condition) to 10 molal. Equilibrium condition is reached in 5 d. This time is much longer than the 5 h required for water to equilibrate in the H_2O –ethylbenzene system (Sawamura et al., 1989). Figure 7 shows the evolution of the concentration of water between 2 and 4 d. Water concentration in ethylbenzene decreases after the decrease of the acetic acid concentration. The kinetics of fractionation of acetic acid between aqueous solution and ethylbenzene phase controls the concentration of water. The difference of diffusion coefficient of water and acetic acid could result from the different sizes of the molecules. The positive slopes observed on the concentrations of water and acetic acid after 5 d is due to the effect of decreasing pressure (Figs. 5 and 7).

GEOLOGICAL IMPLICATIONS AND CONCLUSIONS

The solubility of water in ethylbenzene cannot be neglected in the pressure and temperature range of deep oil fields: it

Table 2. Thermodynamic data obtained from the experiments.^a

T (°C)	$\bar{v}_{H_2O}^{\infty,T}$	$K_{h,H_2O,Eb}^{T,P_s(T),Eb}$ (bar)
100	16.76	0.12
150	20.92	1.15
200	25.51	5.79
150 ^b	22.87	0.96
200 ^b	21.50	4.43

^a $\bar{v}_{H_2O}^{\infty,T}$ is the molar volume of water at infinite dilution of water in ethylbenzene at temperature T. $K_{h,H_2O,Eb}^{T,P_s(T),Eb}$ is the Henry's constant of water solubility in ethylbenzene at temperature T and saturation pressure of ethylbenzene ($P_{s(T),Eb}$).

^b Experiments with acetic acid.

increases significantly with temperature at constant pressure. The effect of pressure is weak; it decreases slightly with increasing pressure at high temperature (e.g., 200°C). These effects are more pronounced in the presence of acetic acid. However, because acetic acid strongly fractionates in favor of water-rich phase, the effect observed on water solubility (shown in Fig. 6) occurs only for high concentrations of acetic acid in the water-rich phase, around 10 molal. Such compositions are not relevant for geological fluids. Acetic acid has been observed in aqueous fluids associated with oil basins but at much lower concentrations (up to 10000 ppm acetate [0.166 molal] in waters associated to oil fields; Helgeson et al., 1993). This means that acetic acid would have an insignificant effect on the solubility of water in hydrocarbons in geological environments if the concentration of acetic acid in the hydrocarbon phase is as low as in ethylbenzene. However, monocarboxylic acids with number of carbon atoms higher than four partitions favorably into oils (Leo et al., 1971; Lewan and Fisher, 1994), suggesting that such acids may also increase the solubility of water in oils.

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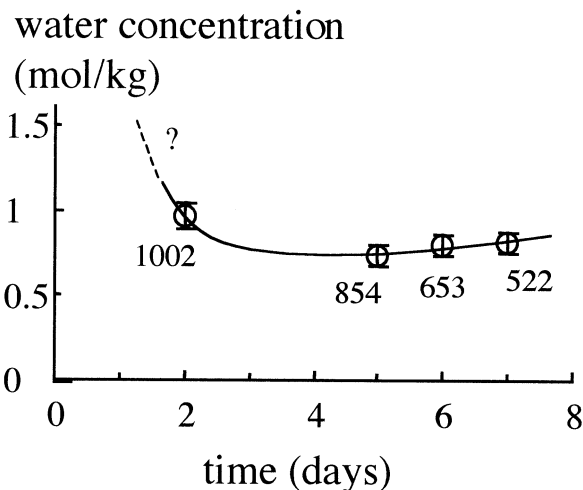


Fig. 7. Evolution vs. time of the water solubility in the ethylbenzene-rich phase for preliminary experiments at 150°C. Starting composition is 1 molal acetic acid both in ethylbenzene and pure water. Pressures are indicated in labels.

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Associate editor: R. C. Burruss

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APPENDIX

The Wagner equation used for the calculation of the vapor pressure of ethylbenzene is the following (Ambrose, 1978):

$$\ln\left(\frac{P}{P_c}\right) = (A \times F + B \times F^{1.5} + C \times F^3 + D \times F^6)/T_r$$

with $T_p = T/T_c$ and $F = 1 - T_p$

$P_c = 3.598$ MPa; $T_c = 617.2$ K

$A = -7.43681$; $B = 1.3332$; $C = -3.1259$, $D = -2.9903$

This equation is valid from -73 to 344°C and from 1 to 3.597 MPa.