Solubility of Solid Ferrocene in Pressurized Hot Water

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Aqueous solubilities of ferrocene (bis(cyclopentadienyl)iron(II), $C_{10}H_{10}Fe$) were measured at temperatures within (313 to 433) K along a 5 MPa isobar. The activity coefficients of ferrocene in aqueous solutions at saturation were obtained employing three different approximations of the solute heat capacity difference, ΔC_{P2}. The relative rate of increase in aqueous solubility of ferrocene with temperature, $(\partial \ln x_2/\partial T)_{P,\sigma}$, is distinctly lower than the corresponding values in aromatic hydrocarbons naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$) possibly because of less endothermic solute−water interactions because of less contact surface of the ferrocene molecule.

Introduction

Park et al.[1] have recently shown that the oxidation of ferrocene by hydrogen peroxide in supercritical water can be used for the one-pot synthesis of nanoparticles with an iron-oxide core and graphitic carbon shell. Such nanoparticles promise to become important in a wide variety of applications, especially if they show suitable magnetic properties. As the use of metallocenes for the hydrothermal synthesis of nanoparticles may increase in the future, aqueous solubilities of metallocenes at elevated temperatures may possibly become of interest.

To date, the aqueous solubility of ferrocene has not received much attention. Wu et al.[2] reported that the solubility of ferrocene in pure water at 298.15 K was $4.25 \cdot 10^{-5}$ $mol \cdot dm^{-3}$, corresponding to a mole fraction solubility of $7.68 \cdot 10^{-7}$. Reports of ferrocene solubilities in water−ethanol mixtures are also available.[3,4] However, our searches have not revealed any published data on the aqueous solubility of ferrocene at an elevated temperature.

The purpose of this work was to determine the aqueous solubility of solid ferrocene within a wide interval of temperature. Activity coefficients of ferrocene in saturated aqueous solutions were estimated employing three different approximations of the difference between the heat capacities of the liquid and the solid ferrocene.

Experimental Section

Materials. Ferrocene (99 %, CAS Registry No. 102-54-5) was purchased from Alfa Aesar (Karlsruhe, Germany). Analysis of calibration solutions of ferrocene in hexane by gas chromatography/mass spectrometry (GC/MS) did not show the presence of any major impurities. Hexane (> 95 %) was obtained from Riedel deHaën (Prague, Czech Republic), and diamantane to be used as an internal standard for GC/MS was purchased from Lachema (Brno, Czech Republic). Water was purified with a reverse osmosis system Ultra Clear UV (SG Wasseraufbereitung and Regenerierstation, Barsbüttel, Germany).

Apparatus and Procedure. The aqueous solubilities were measured by the dynamic method employing the apparatus described before.[5] The dynamic method was employed to prepare the aqueous solution of the solute at the particular temperature and pressure, and a known mass of the solution was allowed to cool down to room temperature. Ferrocene was then extracted with hexane, and the organic solution was analyzed by GC/MS employing diamantane as the internal standard. Any errors caused by the residual amount of the solute in the aqueous phase were within the experimental uncertainty as indicated by repeated aqueous−organic equilibration experiments. At 298.15 K, the mole fraction solubility of ferrocene in hexane ($x_2 = 0.0258$)[6] is about 34 000 times higher than the mole fraction solubility in water.[2]

The operating procedure was the same as in our previous studies of solid solubilities in pressurized hot water (PHW).[5,7] In the present work, the dimensions of fused-silica tubing used as the flow restrictor were 1.3 m in length and 75 μm in i.d. The mass of individual samples of the aqueous solution ranged within (3 to 6) g, and the mass flow rate of water through the system did not exceed $0.016\ g \cdot s^{-1}$. An initial test of the flow-rate dependence of the measured solubility was carried out at 333.2 K and 5 MPa using fused-silica restrictors of various lengths and diameters. The results of the test did not indicate any significant variation in the composition of the aqueous effluent as the flow rate of water varied within (0.007 to 0.026) $g \cdot s^{-1}$. The standard uncertainty[8] in the measurement of the extraction cell temperature was ± 0.10 K, and the standard uncertainty in the measurement of pressure was ± 0.1 MPa.

GC/MS Operating Conditions. A TraceGC gas chromatograph fitted with a TriPlus AS autosampler was equipped with a DB-5 capillary column (30 m × 0.25 mm i.d., polymer film thickness 0.25 μm, J&W Scientific, Folsom, CA) and coupled to a PolarisQ mass spectrometer (TraceGC + PolarisQ, Thermo Finnigan, San Jose, CA). The carrier gas was helium (99.995 %, SIAD, Braňany u Mostu, Czech Republic), and the ionization energy (EI mode) was 70 eV. The splitless injection technique was employed. The GC oven temperature was programmed from 323 K (6 s) at $0.17\ K \cdot s^{-1}$ to 473 K (6 s).

Results and Discussion

Solubility Data. The aqueous solubilities (equilibrium mole fractions, x_2) of ferrocene are listed in Table 1. The GC/MS analyses of the organic extracts of the aqueous solutions did not indicate any noticeable decomposition under the present experimental conditions. Considering the data in Table 1 and

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10.1021/je901028h

Table 1. Aqueous Solubilities of Ferrocene x_2 and Their Standard Deviations (SDs) as Functions of Temperature T and Pressure P

T/K	P/MPa	$10^9\ x_2$	10^9 SD[a]
313.2	5.2	1170	18.2
333.2	5.1	2670	69.3
353.2	5.1	6690	196
373.2	5.1	16200	513
393.2	5.0	38800	884
413.2	5.1	96700	2200
433.2	6.4	227000	9230

[a] Standard deviations (SDs) are based on five fractions collected at each condition.

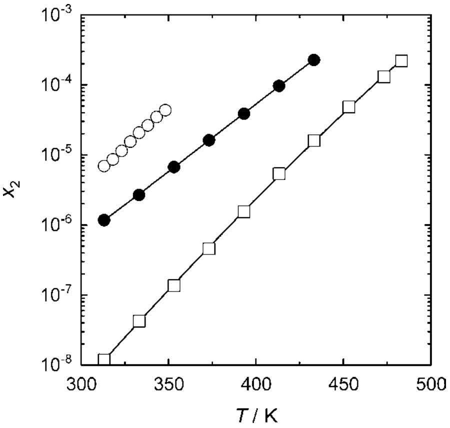

Figure 1. Aqueous solubility of ferrocene, ●. Solubilities[5] of naphthalene, ○, and anthracene, □, are shown for comparison. The lines show the best fits with eq 1.

Table 2. Least-Squares Estimates of the Coefficients a_1, a_2, and a_3 of Equation 1 and the SDs of the Estimates, with T_{min} and T_{max} Indicating the Minimum and the Maximum Temperatures of the Solubility Measurements, Respectively

T_{min}/K	T_{max}/K	a_1	SD a_1	a_2	SD a_2	a_3	SD a_3
313.2	433.2	−35.67	1.80	21.37	1.83	33.68	1.49

the standard uncertainties in temperature and pressure mentioned above, we conclude that the relative expanded uncertainty[8] in the resultant solubilities is ± 12 % (confidence level of 95 %).

Variation of Solubility with Temperature. A simple linear fit of the data from Table 1 indicates that the mean value of the relative increase in solubility with temperature, $(\partial \ln x_2/\partial T)_\sigma$, is 0.044 K^{-1}. This value is distinctly lower than those reported before for the polycyclic aromatic hydrocarbons (PAHs), although the two cyclopentadienyl rings in the ferrocene molecule also have aromatic character as each of them contains six π-electrons.[5] A more detailed insight into the effect of temperature on solubility results from fitting the data from Table 1 with

$$\ln x_2 = a_1 + a_2(T_0/T) + a_3 \ln(T/T_0) \qquad (1)$$

where $T_0 = 298.15$ K. Figure 1 shows a comparison of the fit of the data from Table 1 with previous results for naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$).[5] Together with the lack of other solubility data for ferrocene in PHW, the partly aromatic character of ferrocene was the reason for comparing ferrocene solubilities with those of PAHs. The least-squares estimates of the coefficients a_1, a_2, and a_3 are listed in Table 2. In all coefficients, the ratio of the coefficient estimate to the standard deviation (SD) of the coefficient estimate can be compared to the pertinent critical values of the Student's t-distribution[9] to test the hypothesis that "the coefficient equals zero". In all coefficients, the hypothesis is rejected at a confidence level of 98 %, indicating that the coefficients are statistically significant.

Table 3. Values of $RT^2(\partial \ln x_2/\partial T)_{P,\sigma}$/kJ·mol^{-1} Calculated from Equation 3

T/K	$RT^2(\partial \ln x_2/\partial T)_{P,\sigma}$/kJ·mol^{-1}
313.2	34.7
333.2	40.3
353.2	45.9
373.2	51.5
393.2	57.1
413.2	62.7
433.2	68.3

The temperature dependence of solid solubility is related to the enthalpy of solution by

$$\bar{H}_2 - H_2^{s0} = RT^2\left(\frac{\partial \ln x_2}{\partial T}\right)_{P,\sigma}\left[1 + \left(\frac{\partial \ln \gamma_2}{\partial \ln x_2}\right)_{T,P}\right] \qquad (2)$$

where $\bar{H}_2$ is the partial molar enthalpy of the solute in the solution, H_2^{s0} is the molar enthalpy of the pure solid solute, R is the molar gas constant, P is the pressure, γ_2 is the Raoult law activity coefficient of the solute referred to the pure subcooled liquid solute at the particular T and P, and the subscript σ denotes saturation. The values of $RT^2(\partial \ln x_2/\partial T)_{P,\sigma}$ can be estimated by differentiating eq 1 and using the coefficients from Table 2,

$$RT^2\left(\frac{\partial \ln x_2}{\partial T}\right)_{P,\sigma} = R(a_3T - a_2T_0) \qquad (3)$$

and they are listed in Table 3. Although the relationship between the transfer enthalpy $\bar{H}_2 - H_2^{s0}$ and the slope $(\partial \ln x_2/\partial T)_{P,\sigma}$ is complicated by the quotient $(\partial \ln \gamma_2/\partial \ln x_2)_{T,P}$, eq 2 may provide some clue to the lower value of $(\partial \ln x_2/\partial T)_{P,\sigma}$ in ferrocene as compared to naphthalene and anthracene (see Figure 1). Possibly, the lower value of $(\partial \ln x_2/\partial T)_{P,\sigma}$ in ferrocene reflects a lower value of $\bar{H}_2 - H_2^{s0}$ that could arise from a more compact shape and lower surface-to-volume ratio of the ferrocene molecule compared to the planar molecules of naphthalene and anthracene. Consequently, the formation of a cavity to accommodate the solute molecule within the water structure would require less energy in ferrocene compared to the PAH molecules.

An extrapolation of the present solubility data to 298.15 K via eq 1 with the constants from Table 2 yields $x_2 = 6.16 \cdot 10^{-7}$, a value somewhat lower than the result of Wu et al.[2] mentioned above. The difference can partly be explained by the effect of elevated pressure in the present study.

Estimation of Activity Coefficients. The solubility x_2 of a solid solute (2) in a liquid solvent (1) can be described by

$$x_2 = \frac{f_2^{s0}}{\gamma_2^{sat} f_2^{l0}} \qquad (4)$$

where f_2^{s0} and f_2^{l0} are the fugacities of the pure solid solute and the pure subcooled liquid solute, respectively, and γ_2^{sat} is the Raoult-law activity coefficient of the solute in the saturated solution. The activity coefficient is referred to the pure subcooled liquid solute at the particular temperature and pressure. Equation 4 applies if the solid phase in equilibrium with the solution is pure solute. The fugacity ratio in eq 4 can be expressed as[10]

$$\ln\frac{f_2^{s0}}{f_2^{l0}} = \frac{\Delta H_2^{fus}}{RT_{t2}}\left(1-\frac{T_{t2}}{T}\right) + \frac{\Delta C_{P2}}{R}\left(\frac{T_{t2}}{T}-1\right) - \frac{\Delta C_{P2}}{R}\ln\frac{T_{t2}}{T} + \frac{(V_2^{s0}-V_2^{l0})P}{RT} \qquad (5)$$

where T_{t2} is the triple-point temperature of the solute, ΔH_2^{fus} is the molar enthalpy of fusion of the solute at T_{t2}, ΔC_{P2} is the difference between the molar isobaric heat capacities of the pure subcooled liquid solute and the pure solid solute ($= C_{P2}^{l0} - C_{P2}^{s0}$), and V_2^{s0} and V_2^{l0} are the molar volumes of the pure solid solute and the pure subcooled liquid solute, respectively. Equation 5 applies if there are no solid−solid phase transitions in the pure solute within the temperature interval from T to T_{t2}. The last term on the right-hand side of eq 5 accounts for the effect of elevated pressure on f_2^{s0} and f_2^{l0} assuming that both the solid solute and the subcooled liquid solute are incompressible and that their respective vapor pressures are negligible with respect to the total pressure P.

In this contribution, the triple-point temperature of ferrocene was approximated by the normal melting temperature of 448.7 K,[11] and the enthalpy of fusion at the melting temperature was 18.3 kJ·mol^{-1}.[11] The last term on the rhs of eq 5 was neglected here because of the lack of experimental values of the molar volumes and also because of the lack of critical point data needed to estimate the molar volumes. In view of numerous previous reports in the literature regarding the significance of ΔC_{P2} in the x_2-to-γ_2^{sat} conversion,[12−17] three different values of ΔC_{P2} were employed here to visualize the effect of ΔC_{P2} on the resultant activity coefficients. The first of these was the difference $C_{P2}^{l0} - C_{P2}^{s0} = 46.4$ J·mol^{-1}·K^{-1}, with $C_{P2}^{l0} = 238.9$ J·mol^{-1}·K^{-1} [18] and $C_{P2}^{s0} = 192.5$ J·mol^{-1}·K^{-1}.[19] The second value was the approximation of ΔC_{P2} by the entropy of fusion ΔS_2^{fus} ($= 40.78$ J·mol^{-1}·K^{-1}) calculated from the enthalpy of fusion and the melting temperature mentioned above. Finally, the value $\Delta C_{P2} = 0$ J·mol^{-1}·K^{-1} was also adopted because, following the conclusion of Pappa et al.,[17] we have used it before in the conversion of aqueous solubilities of PAHs to γ_2^{sat}.[20]

Figure 2 compares the estimates of the activity coefficients of ferrocene in saturated aqueous solutions with the corresponding values for naphthalene and anthracene. All activity coefficient data shown in Figure 2 were obtained assuming $\Delta C_{P2} = 0$ J·mol^{-1}·K^{-1} and suggest that the decrease in γ_2^{sat} of ferrocene with temperature is less steep as compared to PAHs. The effect of ΔC_{P2} on the resultant activity coefficients is illustrated by Figure 3. In accordance with previous reports in the literature,[12−17] the effect of ΔC_{P2} becomes more important with decreasing temperature of the solution (i.e., with increasing difference $T_{t2} - T$). At the lower limit of the temperature range of the present measurements, the differences among γ_2^{sat} values coming from different approximations of ΔC_{P2} reach up to 50 % of the lower value. Values of the activity coefficients plotted in Figure 3 are available as Supporting Information.

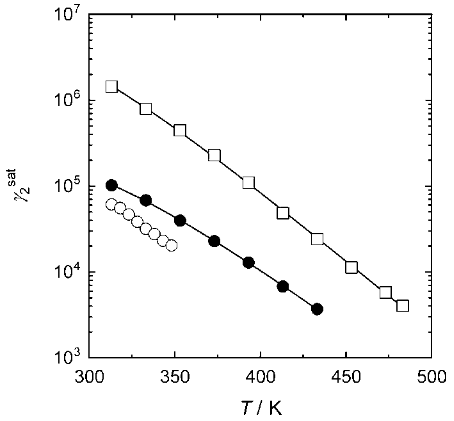

Figure 2. Estimates of the activity coefficients of ferrocene, ●, in saturated aqueous solutions. Naphthalene, ○, and anthracene, □, values[20] are shown for comparison. The approximation ΔC_{P2}/J·mol^{-1}·K^{-1} = 0 was adopted in all solutes. The lines serve just to guide the eye.

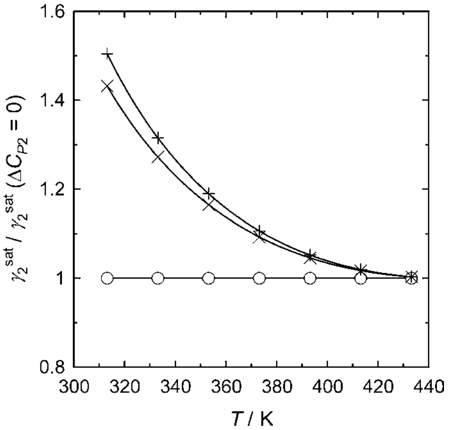

Figure 3. Effect of ΔC_{P2} on the estimates of the activity coefficients of ferrocene in saturated aqueous solutions. +, $\Delta C_{P2} = C_{P2}^{l0} - C_{P2}^{s0}$; ×, $\Delta C_{P2} = \Delta S_2^{fus}$; ○, ΔC_{P2}/J·mol^{-1}·K^{-1} = 0. The data are expressed relatively to γ_2^{sat} values calculated with ΔC_{P2}/J·mol^{-1}·K^{-1} = 0.

Conclusion

Aqueous solubilities of ferrocene were determined within (313 to 433) K along a 5 MPa isobar. The average relative change in solubility with temperature, $(\partial \ln x_2/\partial T)_\sigma$, appears to be lower in ferrocene (0.044 K^{-1}) than in the PAHs naphthalene (0.054 K^{-1}) and anthracene (0.058 K^{-1}).[5] At a particular temperature, the aqueous solubility of ferrocene exceeds that of anthracene by a factor ranging from 15 to 100. The measured solubilities were employed to estimate the activity coefficients of ferrocene in saturated aqueous solutions.

Supporting Information Available:

Activity coefficients of ferrocene in aqueous solutions at saturation calculated with the three different values of ΔC_{P2} as mentioned above (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review December 3, 2009. Accepted February 1, 2010. We thank the Czech Science Foundation (Projects GA203/07/0886, GA203/08/1465, and GA203/08/1536) and the Academy of Sciences of the Czech Republic (Institutional Research Plan No. AV0Z40310501) for financial support of this work.

JE901028H