1092 *J. Chem. Eng. Data* **2006,** *51,* 1092−1096

Vapor−Liquid Equilibrium of Ferrocene in Some Organic Solvents Using Spectroscopic Methods

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Isobaric vapor−liquid equilibrium (VLE) data were measured at $p = 1.01325$ bar for the mixtures of ferrocene in ethanol, toluene, hexane, and 2,2,4-trimethylpentane (isooctane). A dynamical equilibrium apparatus has been used to establish the equilibrium between the phases. The spectrophotometric method has been used to measure the compositions of vapor and liquid phases. Ferrocene is only weakly soluble in these solvents. The experimental binary data were correlated with the NRTL and UNIQUAC models, and the parameters were determined.

Introduction

Chemical vapor deposition (CVD) processes are widely used to deposit thin, highly uniform solid films that are used as mechanical or optical coatings for various purposes. In general, a reactive gas mixture flows continuously through the controlled environment of a reactor process chamber, which contains the substrates on which deposition takes place. Chemical reactions in the gas phase and at the surfaces are activated thermally, by light, or by a glow discharge plasma and lead to the deposition of the bulk material. Solutions of metalorganic compounds are sometimes used to evaporate the metal containing substances (= precursors) in order to produce nanoparticles or thin solid films in chemical vapor deposition (CVD).[1] The precursors used are mostly organometallic compounds.[2] The thermodynamic properties of such compounds are scarce, even for such long-known molecules as ferrocene ($Fe(C_5H_5)_2$). We have, therefore, started a program to study the vapor pressures, thermal stability, and phase equilibrium properties of these compounds. Ferrocene is also used as a catalyst in many chemical process industries; hence, its vapor−liquid equilibrium (VLE) behavior in different solvents is also interesting.

In the present paper, the VLE of ferrocene in some organic solvents is reported, which should allow the calculation of the vapor composition in a simple way. Both UV/VIS and FTIR spectroscopy have been used successfully for several years in our department to study vapor−liquid and chemical equilibrium of diverse systems.[3−5] For this study, a dynamical equilibrium apparatus has been used to establish the equilibrium between the phases. The samples of the vapor phase and the liquid phase are then taken and analyzed by using UV/VIS spectroscopic methods. Ferrocene absorbs in the range of 300 nm to 650 nm. If any decomposition takes place in the boiling process, the spectra will clearly show this.

The VLE of ferrocene in ethanol, toluene, hexane, and 2,2,4-trimethylpentane (isooctane) has been measured under atmospheric conditions. Ferrocene is only weakly soluble in these solvents. After the equilibrium is established, small samples of the liquid phase and the vapor phase are taken and analyzed by UV/VIS spectroscopy. The spectra did not indicate any decomposition or complex formation for the concentrations studied here. So the distribution of ferrocene in the liquid and the vapor phase were measured, and activity coefficients for the liquid phase were determined. Since ferrocene is a solid at the investigated temperatures, one can either use the hypothetical liquid reference state or the easily measurable solid reference state.[6] The two reference states for the activity coefficients are discussed. The activity coefficients for ferrocene in solution were much higher throughout than expected from ideal solution behavior (i.e., 1), even if the hypothetical liquid ferrocene reference state is used for calculations. The deviations from ideal behavior are very strong in ethanol and hexane (activity coefficients between 10 and 20) but are also obvious in toluene ($\gamma = 1.5$ to 2). The data have been fitted to some common activity coefficient models (NRTL and UNIQUAC), and the corresponding parameters were determined.

Experimental Section

Materials. Ferrocene (purity > 98 %) purchased from Fluka was used without further purification as the measured sublimation pressures at different temperatures were the same as those obtained with the sample purified by sublimation. Ethanol (purity > 99.8 %), hexane (purity > 99 %), and toluene (purity > 99.7 %) were supplied by Riedel de Haen, and 2,2,4-trimethylpentane (purity > 99.5 %) was obtained from Merck. The densities and the normal boiling points of the solvents were checked and found to match with established literature values.

Apparatus and Procedure. The VLE measurements were performed using a dynamic equilibrium still shown in Figure 1. The heating coil (4) immersed into the still (1) (boiling chamber) takes care for the uniform vapor formation. The rising vapor bubbles stir up effectively the contents of the still and convey a considerable quantity of liquid when going through the Cotrell tube (2) so that a vapor−liquid mixture is discharged over the temperature measurement device (Pt-100 thermometer) inserted through the opening (6). The liquid and the vapor phases are separated. The liquid flows back to the still while the vapor is condensed in the cooler and then flows back into the still. The volume of the boiling chamber is about 100 cm^3, 80 cm^3 of which is occupied by the liquid. Hence the liquid composition is constant during the experiment.

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10.1021/je060002k CCC: $33.50

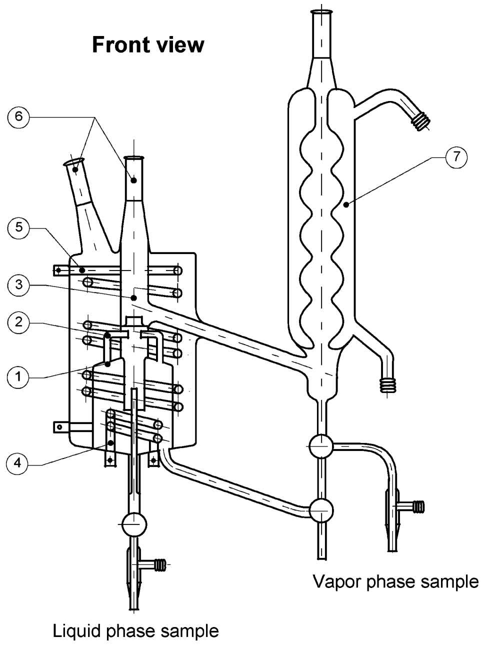

Figure 1. Equilibrium recirculation apparatus for the measurement of VLE (see text for explanations).

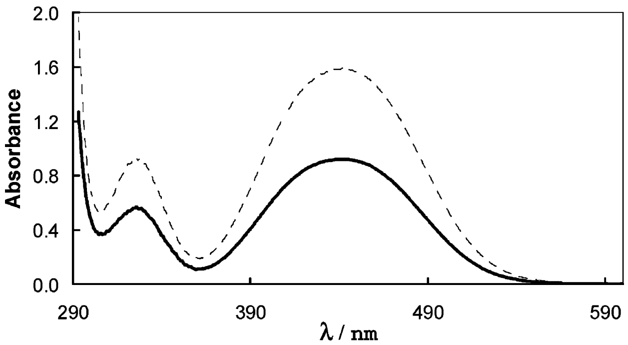

Figure 2. Absorption spectra of ferrocene in toluene solution: - - -, solution 1; —, solution 2.

To start the measurement, a liquid of known composition is introduced into the boiling room (1). It is filled with mixture to the extent that during boiling a mixture of vapor and liquid phases flows against the platinum resistance thermometer fixed at (6). Care is to be taken that the liquid level lies always under the Cotrell tube (2). This is necessary for the proper functioning of the pump. Also during the boiling process this condition should be held. The boiling room (1) is separated from the vapor room (3) through a hydraulic seal. The vapor is thus forced to follow the path through the Cotrell pump to reach the vapor room. The liquid taken along with the vapor is separated in the vapor room and falls back to the boiling room crossing the hydraulic seal. The rising vapor is totally condensed in the condenser (7) and goes back to the boiling room through the connecting tube. The boiling room is heated with the help of a glass-covered heating coil (4). The outer room is also heated with another glass-covered heating coil (5) to avoid an earlier condensation of the vapor. Its temperature has to be adjusted accordingly so that neither condensation of the vapor nor overheating occurs. The two heating coils are controlled by a heater controller.

After attainment of equilibrium, the boiling temperature and the compositions of the vapor and the liquid phases are determined. Very small samples were drawn from the liquid phase and the condensate vapor phase without disturbing the equilibrium. As the solutions are very dilute, the boiling point temperatures do not change much and have to be measured with great care. The boiling point temperatures shown in Table 2 are the average values of two measurements.

Atmospheric pressure was measured by a mercury column barometer with a maximum uncertainty of 0.05 kPa. The boiling point temperature was measured using a Pt-100 thermometer, which was already calibrated against a quartz thermometer. The uncertainty in temperature measurement did not exceed ± 0.05 K.

As the measurements were done at atmospheric pressure, which varied a little from day to day, it was necessary to correct the boiling temperatures to 101.325 kPa.[7] This was done using the relation:

$$t = t^{*} + \frac{\mathrm{d}t}{\mathrm{d}p}(101.325 - p/\mathrm{kPa}) \tag{1}$$

where the coefficient dt/dp for the mixture was evaluated as

$$\frac{\mathrm{d}t}{\mathrm{d}p} = \left(\frac{\mathrm{d}t}{\mathrm{d}p}\right)_1 x_1 + \left(\frac{\mathrm{d}t}{\mathrm{d}p}\right)_2 x_2 \tag{2}$$

$(\mathrm{d}t/\mathrm{d}p)_1$ and $(\mathrm{d}t/\mathrm{d}p)_2$ were obtained by differentiating the vapor pressure equation (e.g., Antoine equation):

$$\log(p_i/\mathrm{kPa}) = A_i - \frac{B_i}{(t_i/°\mathrm{C} + C_i)}. \tag{3}$$

or

$$t_i/°\mathrm{C} = \frac{B_i}{A_i - \log(101.325)} - C_i \tag{4}$$

and

$$\left(\frac{\mathrm{d}t}{\mathrm{d}p}\right)_i/(°\mathrm{C/kPa}) = \frac{(t_i/°\mathrm{C} + C_i)^2}{2.303(101.325B_i)} \tag{5}$$

A, B, and C are Antoine constants in eqs 3, 4, and 5; t is the boiling temperature.

Ferrocene absorbs in UV/VIS region; hence, the concentration of ferrocene in a mixture may be determined using absorption spectroscopy. The molar absorption coefficients at the two main peaks are $\epsilon(440\ \mathrm{nm}) = 97\ \mathrm{L{\cdot}mol^{-1}{\cdot}cm^{-1}}$ and $\epsilon(325\ \mathrm{nm}) = 55\ \mathrm{L{\cdot}mol^{-1}{\cdot}cm^{-1}}$. The solvents ethanol, toluene, hexane, and isooctane do not absorb in this region. Figure 2 shows the absorption spectra of two ferrocene solutions in toluene. The spectra in other solvents are exactly the same.

Both vapor- and liquid-phase compositions for the four systems were determined by measuring the concentration of ferrocene in the mixture by evaluating the UV/VIS spectra obtained with a Shimadzu UV 2102 PC spectrophotometer. It was necessary to use cuvettes with optical lengths (1 to 100) mm to cover the whole concentration range. The spectra over the whole UV/VIS absorption range were evaluated using partial least squares (PLS) method. The equilibrium compositions of mixtures were determined with an uncertainty less than ± 0.000002 mole fraction of ferrocene.

Results and Discussion

The experimental values (T, x_1, and y_1) at 101.3 kPa are given in Table 1 in columns 1 to3. The fugacity of a component i in the vapor phase is given by

$$f_i^{\mathrm{V}} = y_i \phi_i^{\mathrm{V}} p = y_i p \quad \text{(considering the vapor phase as ideal gas)} \tag{6}$$

Table 1. VLE Data for Some Ferrocene Systems at 1.01325 Bar

EXPT					NRTL				
x_1	y_1	t/°C	γ_1*	γ_2*	y_1	t/°C	γ_1*	γ_2*	γ_1
Ferrocene (1) + Ethanol (2)									
0.000000	0	78.3		1.00	0.000000	78.28	40.51	1.00	16.14
0.000733	0.000025	78.4	38.20	1.00	0.000026	78.33	40.11	1.00	15.97
0.000914	0.00003	78.4	36.76	1.00	0.000032	78.33	40.02	1.00	15.94
0.001076	0.000038	78.5	39.27	0.99	0.000038	78.38	39.90	1.00	15.89
0.001504	0.000055	78.5	40.67	0.99	0.000053	78.38	39.69	1.00	15.81
0.001955	0.000069	78.6	38.97	0.99	0.000069	78.43	39.43	1.00	15.71
0.002355	0.000086	78.6	40.32	0.99	0.000083	78.44	39.24	1.00	15.63
0.003370	0.000126	78.7	40.99	0.99	0.000117	78.50	38.72	1.00	15.42
0.003900	0.000140	78.7	39.36	0.99	0.000135	78.50	38.46	1.00	15.32
0.005669	0.000192	78.8	36.87	0.98	0.000193	78.57	37.61	1.00	14.98
0.006315	0.000198	78.9	33.89	0.98	0.000214	78.62	37.28	1.00	14.85
Ferrocene (1) + Toluene (2)									
0.000000	0	110.6		1.00	0.000000	110.61	2.07	1.00	1.03
0.005934	0.000083	110.8	1.91	1.00	0.000089	110.81	2.06	1.00	1.02
0.011869	0.000170	111.0	1.94	1.00	0.000179	111.01	2.04	1.00	1.01
0.022763	0.000366	111.4	2.12	1.00	0.000346	111.40	2.00	1.00	0.99
0.035052	0.000524	111.8	1.93	1.00	0.000536	111.81	1.97	1.00	0.97
0.044450	0.000683	112.1	1.95	1.00	0.000683	112.12	1.94	1.00	0.96
0.055010	0.000850	112.5	1.91	1.00	0.000852	112.50	1.91	1.00	0.95
0.062880	0.001022	112.6	2.00	1.01	0.000973	112.69	1.89	1.00	0.94
0.068506	0.001250	112.9	2.20	1.01	0.001067	112.93	1.88	1.00	0.93
0.070100	0.001101	113.0	1.89	1.00	0.001095	113.01	1.87	1.00	0.93
0.080030	0.001270	113.3	1.87	1.01	0.001256	113.33	1.85	1.00	0.91
0.086349	0.001360	113.5	1.84	1.01	0.001360	113.54	1.83	1.01	0.91
Ferrocene (1) + Hexane (2)									
0.000000	0	68.7		1.00	0.000000	68.71	18.33	1.00	7.10
0.001110	0.000008	68.8	16.25	1.00	0.000009	68.78	18.16	1.00	7.04
0.002240	0.000017	68.8	17.11	1.00	0.000018	68.80	18.00	1.00	6.98
0.003190	0.000024	68.8	16.96	1.00	0.000025	68.81	17.87	1.00	6.93
0.005680	0.000043	68.9	16.94	1.00	0.000044	68.90	17.53	1.00	6.79
0.011620	0.000090	69.1	17.07	1.00	0.000088	69.09	16.74	1.00	6.49
0.017000	0.000125	69.2	16.09	1.00	0.000125	69.21	16.08	1.00	6.23
0.018770	0.000140	69.3	16.20	1.00	0.000137	69.29	15.86	1.00	6.15
0.021570	0.000161	69.3	16.21	1.00	0.000155	69.32	15.54	1.00	6.02
0.023000	0.000170	69.3	16.05	1.00	0.000163	69.34	15.38	1.00	5.96
0.023390	0.000180	69.4	16.59	1.00	0.000166	69.40	15.33	1.00	5.94
Ferrocene (1) + 2,2,4-Trimethylpentane (2)									
0.000000	0	99.2		1.00	0.000000	99.22	8.22	1.00	3.68
0.001790	0.000050	99.3	7.73	1.00	0.000053	99.30	8.15	1.00	3.65
0.002680	0.000081	99.3	8.36	1.00	0.000079	99.31	8.11	1.00	3.63
0.003500	0.000111	99.3	8.77	1.00	0.000102	99.32	8.08	1.00	3.62
0.004830	0.000141	99.4	8.02	1.00	0.000141	99.40	8.02	1.00	3.59
0.006470	0.000184	99.4	7.82	1.00	0.000188	99.42	7.96	1.00	3.57
0.007110	0.000182	99.5	6.99	1.00	0.000206	99.49	7.93	1.00	3.55
0.008670	0.000252	99.5	7.94	1.00	0.000250	99.51	7.87	1.00	3.53
0.010200	0.000290	99.6	7.72	1.00	0.000293	99.59	7.81	1.00	3.50
0.011300	0.000315	99.6	7.57	1.00	0.000324	99.61	7.77	1.00	3.48
0.011770	0.000354	99.7	8.11	1.00	0.000337	99.67	7.75	1.00	3.47

The fugacity of component *i* in the liquid phase is generally normalized with reference to the standard fugacity of pure liquid and written as

$$f_i^{\mathrm{L}} = x_i \gamma_i f_i^{0,\mathrm{L}} \tag{7}$$

where γ_i is the liquid-phase activity coefficient.

For systems with ferrocene (component 1) that exist as a solid at room temperature, it will be convenient to use as a reference standard state fugacity the fugacity of pure solid. Hence

$$f_1^{\mathrm{S}} = f_1^{\mathrm{L}} = x_1 \gamma_1^* f_1^{0,\mathrm{S}} = x_1 \gamma_1^* p_1^{\mathrm{sat}} \tag{8}$$

From eqs 6 and 8, it follows then that

$$x_1 \gamma_1^* p_1^{\mathrm{sat}} = y_1 p \tag{9}$$

where p_1^{sat} is the sublimation pressure of ferrocene and γ_1* is the activity coefficient with reference to fugacity of pure solid.

Table 2. Constants for the Antoine Equation log(p/kPa) = A_i − B_i/(t/°C + C_i)

substance	A_i	B_i	C_i	T_b °C	dt/dp K·kPa^{-1}
ferrocene	9.78	3805.00	273.15	216.28	0.26979
toluene	6.05043	1327.62	217.625	110.61	0.34777
hexane	6.00139	1170.875	224.317	68.72	0.31428
ethanol	7.33675	1648.22	230.918	78.26	0.24853
2,2,4-trimethylpentane	5.93646	1257.85	220.767	99.24	0.34887

The relation between the two activity coefficients is given as

$$\gamma_1 f_1^{0,\mathrm{L}} = \gamma_1^* f_1^{0,\mathrm{S}} \tag{10}$$

The pure solute fugacity ratio $f_i^{0,\mathrm{L}}/f_i^{0,\mathrm{S}}$ may be expressed in terms of measurable thermodynamic properties $\Delta_{\mathrm{fus}}H$, the enthalpy of fusion at the melting point; $\Delta C_p = C_{p(\mathrm{liquid})} - C_{p(\mathrm{solid})}$, the heat capacity difference; and T_t, the triple point as derived in many text books:[6]

$$\ln \frac{f_i^{0,\mathrm{L}}}{f_i^{0,\mathrm{S}}} = \frac{\Delta_{\mathrm{fus}}H}{RT_t}\left(\frac{T_t}{T} - 1\right) - \frac{\Delta C_p}{R}\left(\frac{T_t}{T} - 1\right) + \frac{\Delta C_p}{R} \ln \frac{T_t}{T} \tag{11}$$

For ferrocene, the following data are available in the literature:[8]

$$\Delta_{\mathrm{fus}}H = 17322\ \mathrm{J{\cdot}mol^{-1}}$$

$$C_p(\mathrm{l}) = 326.77\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$$

$$C_p(\mathrm{s}) = 4.184(50.32 + 0.1627(T/\mathrm{K} - 325))\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$$

$$T_t = 456.15\ \mathrm{K}$$

The value of $f_i^{0,\mathrm{S}}/f_i^{0,\mathrm{L}} = x_i$ (x_i is the ideal mole fraction solubility) depends only upon temperature and thus is different for different ferrocene solutions. The mean values of ideal solubilities (= $f_i^{0,\mathrm{S}}/f_i^{0,\mathrm{L}}$) are 0.3983, 0.4945, 0.3875, and 0.4480 for ferrocene + ethanol, ferrocene + toluene, ferrocene + hexane, and ferrocene + 2,2,4-trimethylpentane, respectively, at the boiling point of the mixture. Hence, the activity coefficients γ_1 may be calculated using eq 10 and γ_1*. The values of γ_1 are thus lower than γ_1* by the factor given above.

The activity coefficients γ_1* have been evaluated from the measured VLE data from eq 9 and using the vapor pressures calculated from the Antoine equation constants given in Table 2. The measured boiling point temperatures for pure ethanol, toluene, hexane, and 2,2,4-trimethylpentane agreed very well with those calculated from the literature values of Antoine equation constants.[9] It should be mentioned that ferrocene evaporates without leaving any residues, so that it appears to be a physical evaporation process without decomposition. The sublimation pressure for ferrocene were measured at our laboratory at different temperatures and fitted to obtain Antoine equation constants. The enthalpy of sublimation calculated from these vapor pressure values is (72659 ± 800) J·mol^{-1} in the temperature range 295 to 325 K, which is in very good agreement with the literature values[10] varying from 71900 to 73400 with uncertainties between 700 and 2720. These activity coefficients are also listed in Table 1. The experimental VLE data have been correlated using NRTL[11] and UNIQUAC[12] models. The pure component parameters have been taken from the literature.[11,12] For the NRTL model, the value of α (non-randomness parameter) has been kept as 0.3. The volume and

Table 3. Parameters for NRTL and UNIQUAC Models[a]

	NRTL		UNIQUAC	
system	Δg_{12}/J·mol	Δg_{21}/J·mol	a_{12}/K	a_{21}/K
ferrocene (1) + ethanol (2)	5909.13	7594.95	209.56	
ferrocene (1) + toluene (2)	1330.77	1154.10	140.45	−47.68
ferrocene (1) + hexane (2)	5160.38	5273.24	160.61	59.49
ferrocene (1) + 2,2,4-trimethylpentane (2)	3588.24	3989.14	79.43	61.53

[a] $a_{12} = a_{12} = 0.3$; $z = 10$.

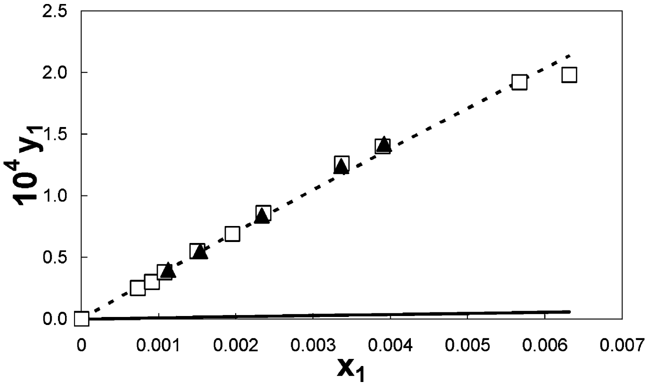

Figure 3. VLE diagram for the ferrocene (1) + ethanol (2) system at 101.3 kPa: □, experimental; - - -, calculated NRTL; —, ideal; ▲, ref 11.

surface area parameters (R and Q) for Fe needed for UNIQUAC model are not available in the literature; these were taken as 1.047 and 0.04099, respectively (similar as those for Si).

The vapor phase has been taken as an ideal gas mixture. The activity coefficients for the non-ideal liquid phase have been calculated. Because of the non-linearity of the VLE and activity coefficients more than one set of binary parameters will fit the experimental data to the same degree of accuracy. The parameters obtained can depend on the initial guesses, the objective function, and the minimization procedure used. The binary interaction parameters have been determined through the minimization of the objective function F:

$$F = \sqrt{\sum_{j=1}^{N} \left(\frac{y_j^{\text{cal}} - y_j^{\text{exp}}}{y_j^{\text{exp}}} \right)^2}$$

where N is the total number of the data points. The parameters are shown in Table 3.

The isobaric VLE data for the ferrocene (1) + ethanol (2) system is shown in Figure 3. The only available literature data[13] and the calculated data using ideal solution model and NRTL model are also shown. The very high values for the activity coefficients, γ_1*, for ferrocene show that the behavior of the system is far from ideal. Figure 4 shows the results for the ferrocene (1) + toluene (2) system, which is nearly ideal (the values for γ_1* nearly 2 and of γ_1 nearly 1). The results for ferrocene (1) + hexane (2) and for ferrocene (1) + isooctane (2) are shown in Figure 5. The UNIQUAC model furnishes almost the same results as NRTL. It is observed that three out of the four mixtures studied in this investigation show strong non-ideality.

The mean values for the solubilities (in terms of mole fractions) calculated at the boiling temperatures considering the real behavior (i.e., taking into account the respective activity coefficients) are 0.010, 0.247, 0.023, and 0.056 for ferrocene + ethanol, ferrocene + toluene, ferrocene + hexane, and ferrocene + 2,2,4-trimethylpentane, respectively. These values are much lower than the ideal solubility values. These solubility values are of similar order as those determined experimentally at room temperature (25 °C) in the laboratory by measuring the concentration of ferrocene in saturated solutions spectrophotometrically. The Henry's constants calculated for ferrocene in ethanol, toluene, hexane, and 2,2,4-trimethylpentane are (3.47, 1.58, 0.75, and 2.92) kPa, respectively.

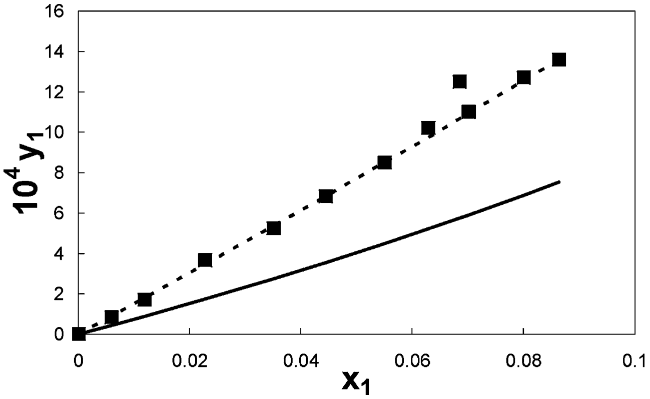

Figure 4. VLE diagram for the ferrocene (1) + toluene (2) system at 101.3 kPa: ■, experimental; - - -, calculated NRTL; —, ideal.

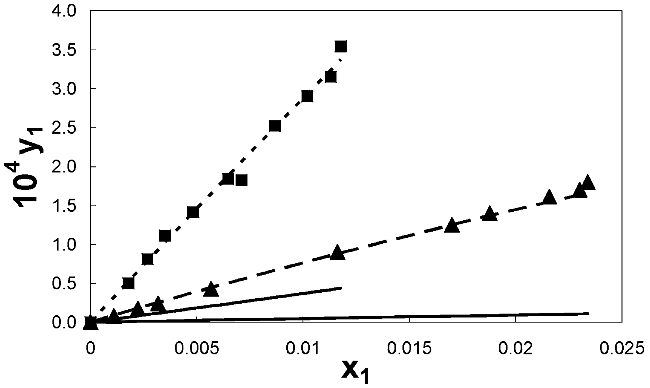

Figure 5. VLE diagram at 101.3 kPa for ferrocene (1) + 2.2.4-trimethylpentane (2): ■, experimental; - - -, calculated NRTL; —, ideal; and ferrocene (1) + hexane(2): ▲, experimental; - - -, calculated NRTL; —, ideal.

In summary, the VLE behavior of ferrocene in three solvents was measured for the first time while a good agreement with literature values was found for its solution in ethanol. In all cases, large differences from ideal solution behavior was found. This finding makes further studies for other organometallic compounds desirable and important. Such measurements are under way.

Acknowledgment

The authors thank A. Görnt for technical assistance and H. Wang for some measurements.

Literature Cited

(1) Jones, A. C.; O'Brien, P. *CVD of Compound Semiconductors: Precursor Synthesis, Development and Applications*; VCH: Weinheim, 1997.

(2) Pflitsch, C.; Muhsin, A.; Bergmann, U.; Atakan, B. Growth of thin aluminium oxide films on stainless steel by MOCVD at ambient pressure and by using a hot-wall CVD setup. *Surf. Coat. Technol.* (accepted for publication).

(3) Siddiqi, M. A.; Petersen, J.; Lucas, K. Influence of nitrogen monxide on the complex phase and chemical equilibria in wet flue gas cleaning processes. *Ind. Eng. Chem. Res.* **2003**, *42*, 1406−1413.

(4) Krissmann, J.; Siddiqi, M. A.; Lucas, K. Improved thermochemical data for computation of phase and chemical equilibria in flue-gas/water systems. *Fluid Phase Equilib.* **2000**, *169*, 223−236.

(5) Siddiqi, M. A.; Krissmann, J.; Peters-Gerth, P.; Luckas, M.; Lucas, K. Spectrophotometric measurement of the vapour−liquid equilibria of (sulphur dioxide + water). *J. Chem. Thermodyn.* **1996**, *28*, 685−700.
(6) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice Hall: Upper Saddle River, NJ, 1999.
(7) Yoshikawa, Y.; Takagi, A.; Kato, M. Indirect determination of vapor−liquid equilibria by small ebulliometer. Tetrahydrofuran−alcohol binary systems. *J. Chem. Eng. Data* **1980**, *25*, 344−346.
(8) *Gmelin Handbuch der Anorganischen Chemie*; Band 14 Eisen-Organische Verbindungen Teil A Ferrocen 1; Springer-Verlag: Berlin, 1974.
(9) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 2000.
(10) Sabbah, R.; Xu-wu, A.; Chickos, J. S.; Planas Leitao, M. L.; Roux, M. V.; Torres, L. A. Reference materials for calorimetry and differential thermal analysis. *Thermochim. Acta* **1999**, *331*, 93−204.
(11) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135−144.
(12) Abrams, D. S.; Prausnitz. J. M. Thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116−128.
(13) Kodama, D.; Tanaka. H.; Kato. M. Vapor−liquid equilibrium of ferrocene in methanol or ethanol. *J. Chem. Eng. Data* **1999**, *44*, 1252−1253.

Received for review January 3, 2006. Accepted February 14, 2006.

JE060002K