1504 *J. Chem. Eng. Data* **2001,** *46,* 1504−1505

Experimental Determination of the Oxygen Solubility in Benzene

Kai Fischer,[†] Olliver Noll,[‡,§] and Jürgen Gmehling*,[‡]

Laboratory for Thermophysical Properties LTP GmbH, Institute at the University of Oldenburg, and
Carl von Ossietzky Universität Oldenburg, FB9 - Technische Chemie, Postfach 2503,
D-26111 Oldenburg, Germany

Oxygen solubility in benzene was measured at pressures up to 0.4 MPa in the temperature range between 302.85 K and 332.63 K using a static synthetic method. The *P*,*x* data were correlated with the Soave−Redlich−Kwong equation of state and the Huron−Vidal mixing rule combined with the UNIQUAC model. From this correlation the Henry coefficients were derived and compared to data from literature. The experimental results were used together with literature data for fitting the interaction parameters between oxygen and the aromatic CH group of the predictive Soave−Redlich−Kwong (PSRK) model.

Introduction

The simultaneous oxygen and nitrogen solubilities in organic solvents (alkanes, alkenes, aromatics, alcohols, ketones, and ethers) reflect the air solubility, which is important to determine the amount of dissolved air in contact with any of these liquids. Several gas solubility measurements were performed by Fischer and Wilken,[1] because the oxygen solubility data retrieved from the literature were found to be insufficient to adjust the desired interaction parameters for the predictive Soave−Redlich−Kwong (PSRK) model.[2−5] Gas solubility data are usually published in terms of solubility coefficients, which superpose linearity between the solubility and the partial pressure at low concentrations. Most of the published data have been obtained at atmospheric pressure, whereas our measurements were performed at pressures up to 0.4 MPa. The Henry coefficients derived from the *P*,*x* data obtained in this work have already been published, together with the values for various other systems, elsewhere.[6]

Experimental Section

Materials. Oxygen with a purity 99.995 mol % was purchased from Messer Griesheim and used without further purification. Benzene supplied by Fluka with an initial purity of 99.7 mass % was distilled and degassed after drying over molecular sieve by vacuum distillation as described before.[7] Its final purity was >99.9 mass %, as checked by gas chromatography and Karl Fischer titration.

Apparatus and Procedure. The apparatus used was described in detail by Fischer and Gmehling.[7] Modifications of the experimental setup, as well as the raw data treatment, which is required for the indirect experimental method for determining the gas solubility in the liquid phase, have been outlined by Fischer and Wilken.[1] The indirect experimental method provides the system pressure *P* of a mixture with known composition charged into a thermostated equilibrium cell at the temperature *T*. The global feed composition is known precisely, whereas the composition of the liquid phase is obtained by subtracting the molar amount in the vapor from the total molar amount loaded in the equilibrium cell. Further details about the raw data treatment method may be found elsewhere.[1] The uncertainty introduced by this evaluation method depends mainly on the relative molar amount in the vapor phase; therefore, the equilibrium cell was charged almost completely full with benzene, leaving a relatively small vapor space. The overall uncertainty of the liquid phase composition was estimated to be $x_1 = \pm 0.000005$, taking into account the uncertainties of the feed composition by using the DIPPR correlation[8] for charging liquid benzene and adding gaseous oxygen and accounting also for the accuracy limited by the raw data exploitation method. The temperature was measured with an absolute uncertainty of ±0.02 K and the pressure with an estimated relative precision of ±0.05% and an uncertainty of ±0.05 kPa.

Table 1. Experimental Isothermal *P*,*x* Data for the System Oxygen (1) + Benzene (2)

$T = 302.85$ K		$T = 317.71$ K		$T = 332.63$ K	
x_1	P/MPa	x_1	P/MPa	x_1	P/MPa
0.000000	0.01577	0.000000	0.02937	0.000000	0.05132
0.000080	0.02669	0.000087	0.04086	0.000094	0.06327
0.000653	0.09793	0.000706	0.11573	0.000765	0.14070
0.001001	0.14068	0.001085	0.15960	0.001170	0.18737
0.001825	0.24122	0.001976	0.26438	0.002135	0.29597
0.002242	0.29183	0.002424	0.31776	0.002618	0.35136
0.002783	0.35987	0.003011	0.38863	0.003252	0.42528

Results and Discussion

The solubility measurements have been performed at (302.85, 317.71, and 332.63) K. The isothermal *P*,*x* data are listed in Table 1 and plotted in Figure 1. For each temperature the Henry coefficient was derived from the *P*,*x* data correlated with the SRK equation of state and the Huron−Vidal mixing rule[9] combined with the UNIQUAC model. The values are given in Table 2. According to Figure 2, the Henry coefficients, obtained from the phase equilibrium data measured in this work up to superatmospheric pressure, are in a reasonable agreement with most of the literature values[10−23] taken from the Dortmund Data Bank mainly determined at atmospheric or subatmospheric pressure. The scattering of the literature data is not caused

---

* Corresponding author (telephone ++49-441-798-3831; fax ++49-441-798-3330; e-mail gmehling@tech.chem.uni-oldenburg.de).

[†] Laboratory for Thermophysical Properties LTP GmbH.

[‡] Carl von Ossietzky Universität Oldenburg.

[§] Present address: Krupp Uhde GmbH, Oil & Gas, Friedrich-Uhde-Str. 15, D-44128 Dortmund, Germany.

10.1021/je010163i CCC: $20.00

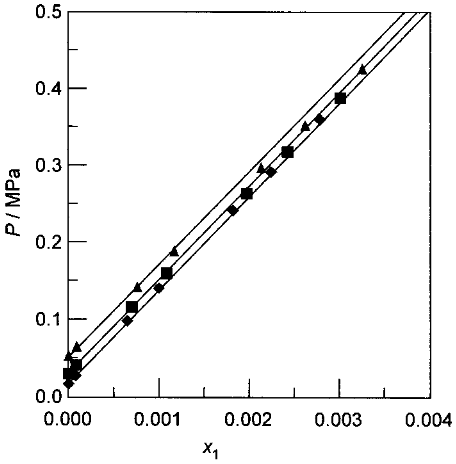

Figure 1. Experimental isothermal *P*,*x* data for the system oxygen (1) + benzene (2): ◆, 302.85 K; ■, 317.71 K; ▲, 332.63 K; —, calculations using the PSRK method.

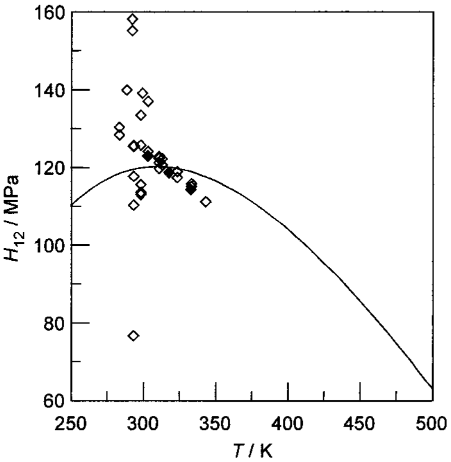

Figure 2. Experimental Henry coefficients for oxygen (1) in benzene (2): ◇, taken from the literature;[10–23] ◆, derived from isothermal *P*,*x* data; —, calculations using the PSRK method.

Table 2. Henry Coefficients for the Solubility of Oxygen (1) in Benzene (2) Derived from Experimental Isothermal *P*,*x* Data Applying the SRK Equation of State and the UNIQUAC Model with Huron–Vidal Mixing Rule[9]

T/K	H_{12}/MPa
302.85	122.9
317.71	118.6
332.63	114.3

by the effect of different pressures as the data from this work show that the imposed linearity between the gas solubility and its partial pressure is valid for oxygen solubilities in benzene even for moderately high pressures. The experimental data were obtained at temperatures close to the maximum of the Henry coefficient at 315 K; thus, the solubility changes only slightly, as shown in Figure 1, within the temperature interval investigated experimentally.

Additionally, the experimental *P*,*x d*ata and Henry coefficients are compared with the calculated results from the PSRK method. The required PSRK interaction parameters were fitted to a larger database with oxygen solubilities in aromatic compounds, including our *P*,*x* data. The values are given elsewhere.[1] A good agreement between the experimental values and the calculated results is obtained.

Literature Cited

(1) Fischer, K.; Wilken, M. Experimental Determination of Oxygen and Nitrogen Solubility in Organic Solvents up to 10 MPa at Temperatures between 298 K and 398 K. *J. Chem. Thermodyn.* **2001**, in press.

(2) Holderbaum, T.; Gmehling, J. PSRK: A Group Contribution Equation of State Based on UNIFAC. *Fluid Phase Equilib.* **1991**, *70*, 251–265.

(3) Fischer, K.; Gmehling, J. Further Development, Status and Results of the PSRK Method for the Prediction of Vapor-Liquid Equilibria and Gas Solubilities. *Fluid Phase Equilib.* **1996**, *121*, 185–206.

(4) Gmehling, J.; Li, J.; Fischer, K. Further Development of the PSRK Model for the Prediction of Gas Solubilities and Vapor-Liquid Equilibria at Low and High Pressures II. *Fluid Phase Equilib.* **1997**, *141*, 113–127.

(5) Horstmann, S.; Fischer, K.; Gmehling, J. PSRK Group Contribution Equation of State: Revision and Extension III. *Fluid Phase Equilib.* **2000**, *167*, 173–186.

(6) Fischer, K.; Wilken, M.; Gmehling, J. Correlation, Prediction and Experimental Determination of Gas Solubilities. *Proceedings of GVC–Fachausschuβ High-Pressure Chemical Engineering*, March 3rd–5th, Karlsruhe, Germany; GVC, Dusseldorf, 1999.

(7) Fischer, K.; Gmehling, J. *Px*- and γ^∞-data for the Different Binary Butanol–Water Systems at 50 °C. *J. Chem. Eng. Data* **1994**, *39*, 309–314.

(8) Daubert, T. E.; Danner, R. P.; Sibul, H. M.; Stebbins, C. C. *Physical and Thermodynamic Properties of Pure Chemicals, Data Compilation*; Taylor and Francis Publishing: New York, 1998.

(9) Huron, M. J.; Vidal, J. New Mixing Rules in Simple Equations of State for Representing Vapour-Liquid Equilibria of Strongly Non-Ideal Mixtures. *Fluid Phase Equilib.* **1979**, *3*, 255–271.

(10) Naumenko, N. K.; Mukhin, N. N.; Aleskovsky, V. B. Investigation of the Solubility of Oxygen in Liquid Derivatives of the Aromatic Series. *J. Appl. Chem. U.S.S.R.* **1969**, *42*, 2376–2381.

(11) Schlaepfer, P.; Audykowski, T.; Bukowiecki, A. Untersuchungen über das maximale Sauerstoffaufnahmevermögen organischer Flüssigkeiten und die jodometrische Bestimmung des aufgenommenen Sauerstoffes. *Schweizer Arch.* **1949**, *15*, 299–307.

(12) Byrne, J. E.; Battino, R.; Danforth, W. F. The Solubility of Gases in Liquids. 7. The Solubilities of N_2, O_2, Ar, CO, CO_2, and c-C_3H_6 in Benzene and Isobutanol Solutions of Cholesterol, Lecithin, and Cephalin at 310.65 K. *J. Chem. Thermodyn.* **1974**, *6*, 245–250.

(13) McKeown, A. B.; Hibbard, R. R. Determination of Dissolved Oxygen in Hydrocarbons. *Anal. Chem.* **1956**, *28*, 1490–1492.

(14) Sinn, E.; Matthes, K.; Naumann, E. Experimentelle Untersuchungen über die Löslichkeit von Sauerstoff in flüssigen organischen Substanzen. *Wiss. Z. Friedrich-Schiller-Univ. Jena, Math.-Naturwiss. R.* **1967**, *16*, 523–529.

(15) Jakubicek, J. Bestimmung der Löslichkeit des Sauerstoffs in Isopren, Hexan und Isopentan. *Collect. Czech. Chem. Commun.* **1963**, *28*, 3430–3434.

(16) Fischer, F.; Pfleiderer, G. Über die Löslichkeit von Sauerstoff in verschiedenen organischen Lösungsmitteln. *Z. Anorg. Chem.* **1922**, *124*, 61–69.

(17) Horiuti, J. On the Solubility of Gas and Coefficient of Dilatation by Absorption. *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)* **1931**, *17*, 125–265.

(18) Naumenko, N. K.; Mukhin, N. N.; Aleskovsky, V. B. *Determination of the Solubility of Oxygen in Organic Liquids*; Plenum Publishing: New York, 1959–1962, 1969.

(19) Ford, P. T. Determination of Dissolved Oxygen in Hydrocarbon Solvents Using Gas–Liquid Chromatography with Electron Capture Detection. *Anal. Chem.* **1969**, *41*, 393–395.

(20) Gorbachev, V. M.; Tretyakov, T. V. Determination of the Solubility of Oxygen and Nitrogen in CH_3SiCl_3, $SiCl_4$ and $GeCl_4$ Using Gas–Liquid Chromatography. *Zavod. Lab.* **1966**, *32*, 796–798.

(21) Luehring, P.; Schumpe, A. Gas Solubilities (H_2, He, N_2, CO, O_2, Ar, CO_2) in Organic Liquids at 293.2 K. *J. Chem. Eng. Data* **1989**, *34*, 250–252.

(22) Livingston, J.; Morgan, R.; Pyne, H. R. Solubility Relations in Gas–Liquid Systems. III. The Solubility of Oxygen in Benzene. *J. Phys. Chem.* **1930**, *34*, 2045–2048.

(23) Neumann, M.; Hild, M.; Brauer H.-D. The [4+2]-Cycloaddition of Singlet Oxygen ($^1\Delta_g$) to Aromatic Hydrocarbons: An Easy Method for Determination of Oxygen Concentrations in Organic Solvents. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 999–1001.

Received for review May 25, 2001. Accepted July 25, 2001. We thank the Bundesministerium für Wirtschaft for financial support via Arbeitsgemeinschaft industrieller Forschungsvereinigungen (AiF Project 10931N).

JE010163I