

Measurement and Prediction of Oxygen Solubility in Toluene at Temperatures from 298.45 K to 393.15 K and Pressures up to 1.0 MPa

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Oxygen solubility in toluene at temperatures from 298.45 K to 393.15 K and pressures up to 1.0 MPa was measured in an autoclave type phase equilibrium apparatus using the total pressure method. Henry coefficients were derived from the mole fractions at experimental pressures and temperatures. A model based on predictive Soave–Redlich–Kwong (PSRK) equation and modified-Huron Vidal (MHV1) mixing rule combined with the UNIQUAC model was used to predict oxygen solubility in toluene. Both experimental and predicted data are in good agreement, which shows that the oxygen solubility increases with increasing temperature and pressure. The results indicate that the solubilization of oxygen in toluene is an endothermic process. An empirical equation of the Henry coefficient was obtained in this work.

Introduction

Because it has many advantages, such as, moderate reaction conditions, higher yield and selectivity, pollution prevention, and energy saving, the liquid-phase oxidation of toluene is an environmental benign technique to produce benzoic acid and benzaldehyde; both of them are important intermediates for organic synthesis.¹ For the concern of safety, oxygen partial pressure in the industrial reactors must be controlled under a very low concentration (volume fraction is less than 7 % in off gas).² For this reason, local shortage of oxygen and oxygen transfer limiting often occur inside the oxidation reactors, which usually leads to the low conversion of toluene (mass fraction is less than 15 %). To solve this problem, using pure oxygen or rich oxygen air instead of air as the oxidant is an efficient method to enhance the oxidation reaction, which was occasionally reported in publication.^{1,2} Hence, the solubility of oxygen is essential information for the design and optimization of this gas–liquid oxidation reactor,³ especially the solubility data under reaction pressure and temperature. Unfortunately, the solubility of oxygen in toluene at high temperatures is rarely reported in literatures.^{4,5} So, it is necessary to study the solubility of oxygen in toluene.

A good way to predict the oxygen solubility in toluene is by using a thermodynamic method when experimental data are not available. It is well known that a group contribution equation of state called the predictive Soave–Redlich–Kwong (PSRK), which is based on the SRK (Soave–Redlich–Kwong) equation and the UNIFAC method, has yielded good results for predicting vapor–liquid-equilibria and gas–liquid-equilibria of nonpolar or slightly polar mixtures from binary information only.^{5,6} The fundamental rule of the PSRK has been utilized to predict phase equilibrium data when experimental data are not available. The PSRK equation is especially used for the prediction of phase equilibria and their thermophysical mixture properties required for the development, design, and optimization of chemical processes, such as thermal separation process.^{7–9} As demon-

strated in the literature,^{5–10} the predicted values of the PSRK equation are in good agreement with experimental data.

Modified-Huron Vidal (MHV1) mixing rule based on the zero-pressure reference state is one of the few mixing rules working quite successfully in phase equilibrium calculations for a large number of systems.^{7,8} Because the empirical mixing parameter A_1 in MHV1 is calculated at atmospheric pressure, it is not very accurate for the calculations at higher pressures. To improve the precision of MHV1-mixing rule at higher pressures, the previous researcher⁶ recommended changing the value of parameter A_1 from -0.593 to -0.64663 . It has yielded better results at higher pressures. Hence, in this work it is reasonable to choose the MHV1-mixing rule to calculate the phase equilibria at low and moderate pressures.

The aim of this investigation is to measure oxygen solubility in toluene at reaction pressures and higher temperatures. The results measured were compared with those predicted by the combination of the PSRK group contribution equation of state (EOS) with the MHV1 mixing rule.^{6–12} On the basis of both experimental and calculating results, we developed an empirical equation for the oxygen solubility in toluene.

Experimental Section

Materials. Oxygen (purity 99.99 %, Chengdu Tianyi Co. Ltd, China) was used without further purification. Toluene (analytical grade, Chengdu Kelong Chemical Reagent Co. Ltd, China) was degassed by vacuum degasification at a vacuum degree of $P = 0.092$ MPa and room temperature.

Experimental Method. The solubility of oxygen in toluene was measured with a method of pressure measurement, as described by Cukor et al.,¹³ Olson,¹⁴ Graaf et al.,¹⁵ d'Angelo et al.,¹⁶ and Breman et al.¹⁷ In the saturation technique, a known quantity of gaseous solute (e.g., oxygen) was introduced into a vessel in which a precisely weighed solvent (e.g., toluene) was filled. Before introducing the gaseous solute, the vessel with solvent was degassed and heated to given temperatures. Because the volume of the vessel is constant, the pressure inside the vessel dropped with the solution of oxygen, and it decreased to a constant value when the phase equilibrium was reached. By

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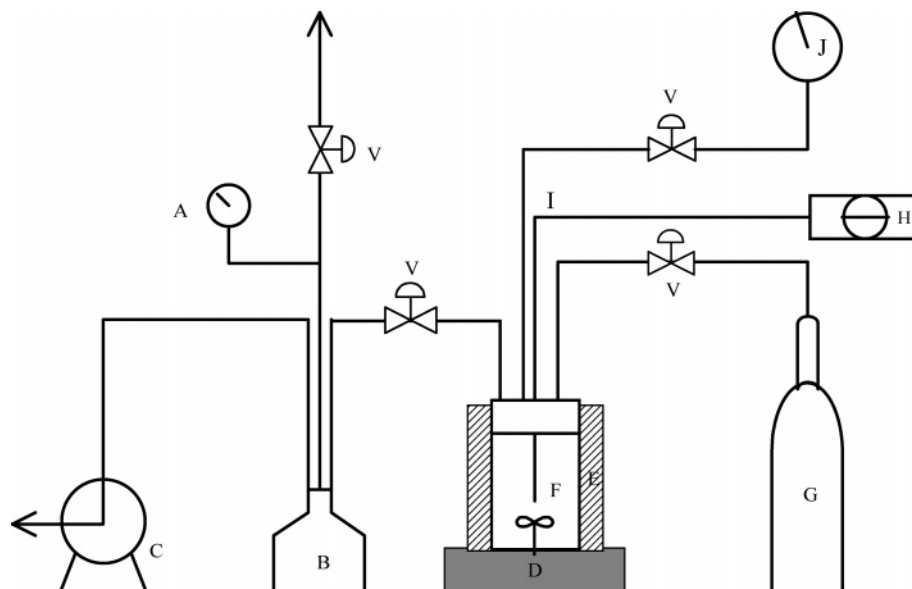


Figure 1. Scheme of experimental equilibrium apparatus: A, vacuum manometer; B, buffer flask; C, vacuum pump; D, mechanical agitator; E, electric oven; F, equilibrium vessel; G, oxygen cylinder; H, temperature controller; I, thermocouple; J, pressure manometer; V, valve.

Table 1. Uncertainties of the Measurement for Experimental Parameters

variable	uncertainty
pressure	± 0.01 MPa
temperature	± 0.1 K
volume	± 0.5 mL
mass	± 0.1 g

recording the pressure drop, we can measure the solubility of oxygen.

Apparatus and Procedure. The experimental schematic is shown in Figure 1. A 218.5 mL cylindrical stainless steel autoclave was used as the equilibrium vessel, which was stirred with a mechanical agitator and heated with an electric oven. Inside the autoclave, a K-type thermocouple was installed to measure the temperature. The thermocouple was connected with an intelligent temperature controller. A precise manometer ranging from 0 MPa to 2.4 MPa was connected with the autoclave to measure the pressure of the equilibrium cell. The measurement uncertainties of temperature, pressure, etc. are listed in Table 1.

First, a precisely weighed amount of toluene was filled into the vessel. Then, the vessel was vacuumed by a vacuum pump to clean up all gases in the equilibrium apparatus. During the vacuum-pumping process, little solvent (only mass fraction 0.42 %) was lost. After that, the toluene was heated to given temperatures with the electric oven. Oxygen was introduced into the vessel in a few seconds, and the initial pressure and temperature were recorded. When the agitator (1225 rpm) was turned on, the pressure dropped immediately as the toluene was stirred. After about 30 min to 50 min, the pressure became constant. When the pressure and temperature were stable within the experimental uncertainty for at least 10 min, the equilibrium in the system was considered established. The equilibrium pressure and temperature of the system were recorded.

Experimental Data Processing. The solubility of oxygen in toluene was expressed in the mole fraction^{17–22} as the following:

$$x_{\text{O}_2} = \frac{n_{\text{O}_2}^{\text{L}}}{n_{\text{T}}^{\text{L}} + n_{\text{O}_2}^{\text{L}}} \quad (1)$$

where $n_{\text{O}_2}^{\text{L}}$ is the moles of oxygen dissolved in toluene; n_{T}^{L} is the moles of toluene in the liquid phase. The quantity of oxygen dissolved in toluene was calculated from the pressure difference between the initial oxygen partial pressure when oxygen was first introduced and the final oxygen partial pressure after the phase equilibrium reached. It is expressed as

$$V_{\text{O}_2} = V_{\text{reactor}} - V_{\text{T}}^{\text{L}} \quad (2)$$

$$n_{\text{O}_2}^{\text{L}} = \frac{P_1 V_{\text{O}_2}}{Z_1 R T_1} - \frac{P_2 V_{\text{O}_2}}{Z_2 R T_2} \quad (3)$$

where V_{reactor} is the vessel volume; V_{T}^{L} is the toluene volume at final temperature T_2 . P_1 is the initial oxygen partial pressure when oxygen was first introduced; P_2 is the final oxygen partial pressure when the equilibrium reached. Z_1 is the compressibility factor of pure oxygen at initial temperature T_1 and the initial oxygen partial pressure P_1 ; Z_2 is the compressibility factor of oxygen at the final temperature T_2 and the final oxygen partial pressure P_2 .

The partial pressure of oxygen P_1 and P_2 can be given as the following:

$$P_1 = P_{\text{total},1} - P_{\text{T}}^{\text{sat}} \quad \text{and} \quad P_2 = P_{\text{total},2} - P_{\text{T}}^{\text{sat}}$$

where $P_{\text{total},1}$ and $P_{\text{total},2}$, respectively, are the total pressures in the equilibrium vessel at the beginning and end of the solubilization process; $P_{\text{T}}^{\text{sat}}$ is the saturated vapor pressure of toluene at experimental temperature.

According to the definition of Henry's law, the Henry constant was considered as being independent of pressure in the present case and calculated from the solubility given by eq 01 above. Therefore, the Henry coefficient is presented by eq 04

$$H = P_2/x_{\text{O}_2} \quad (4)$$

Thermodynamic Model

Pure Compound Properties. The critical temperatures (T_{C}), critical pressures (P_{C}), critical volumes (V_{C}), and acentric factors (ω) for both oxygen and toluene are listed in Table 2.

Table 2. Critical Properties and Acentric Factors^{23–25}

compound	P_C /MPa	T_C /K	V_C /m ³ ·kmol ⁻¹	ω
oxygen	5.04	154.58	0.0734	0.021
toluene	4.05	591.85	0.316	0.257

Description of the Model. Briefly, a general phase equilibrium model based on the uniformity of the fugacity of each component throughout all phases is used to calculate gas solubility. In this model, the PSRK equation and the MHV1 mixing rules are employed in calculating fugacity in both gas and liquid phases. This combination is an efficient tool for systems with both polar and nonpolar compounds. In the PSRK model, the EOS combines the advantages of both local composition concept and group contribution approach UNIQUAC.^{26–29}

The PSRK equation is a modified model of the SRK equation of state, which gives good prediction for the gas solubility of nonpolar or slight polar mixtures only based on binary data.⁸ The PSRK equation is given by

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \quad (5)$$

where P , T , V are the system pressure, temperature, and molar volume, respectively; R is the universal gas constant; and both a and b are the parameters used in the PSRK equation of state.

According to MHV1 mixing rules

$$a = b \left[\frac{g_0^E}{A_1} + \sum x_i \frac{a_i}{b_i} + \frac{RT}{A_1} \sum x_i \ln \frac{b_i}{b} \right] \quad (6)$$

$$b = \sum b_i x_i \quad (7)$$

The coefficients A_1 , a_i , and b_i of component i are given by

$$A_1 = -0.64663$$

$$g_0^E = RT \sum x_i \ln \gamma_i \quad (8)$$

$$a_i = 0.42748 \frac{R^2 T_{c,i}^2}{P_{c,i}} f(T) \quad (9)$$

$$b_i = 0.08664 \frac{RT_{c,i}}{P_{c,i}} \quad (10)$$

$$f(T) = [1 + C_1(1 - T_{r,i}^{0.5})] \quad T_r > 1 \quad (11)$$

The parameter C_1 is given by eq 12 as

$$C_1 = 0.48 + 1.574\omega - 0.176\omega^2 \quad (12)$$

$$f(T) = [1 + c_3(1 - T_{r,i}^{0.5}) + c_4(1 - T_{r,i}^{0.5}) + c_5(1 - T_{r,i}^{0.5})] \quad T_r < 1 \quad (13)$$

$$T_{r,i} = \frac{T}{T_{c,i}} \quad (14)$$

The pure component parameters of toluene recommended by Dortmund and Data Bank (Gmehling, 1991)⁶ are given by eq 15

$$c_3 = 0.9469, \quad c_4 = -0.5896, \quad c_5 = 1.213 \quad (15)$$

where P_C , T_C are the critical pressure and temperature; ω is the acentric factor; g_0^E is the excess Gibbs energy; x is the mole fraction; γ is the activity coefficient; and c_3 , c_4 , and c_5 are parameters of pure toluene used in the PSRK state equation.⁶

The PSRK state equation combined with MHV1 mixing rules can determine the mixture volumes of both gas and liquid phases. Then, the fugacity of component i in both gas and liquid phases are calculated from eq 16

$$f_i^G = y_i \varphi_i^G P \quad f_i^L = x_i \varphi_i^L P \quad (16)$$

where

$$\ln \varphi_i^G = \frac{b_i}{b} \left(\frac{PV^G}{RT} - 1 \right) - \ln \frac{P(V^G - b)}{RT} - \alpha_i \ln \left(\frac{V^G + b}{V^G} \right) \quad (17)$$

$$\ln \varphi_i^L = \frac{b_i}{b} \left(\frac{PV^L}{RT} - 1 \right) - \ln \frac{P(V^L - b)}{RT} - \alpha_i \ln \left(\frac{V^L + b}{V^L} \right) \quad (18)$$

The α_i parameter is expressed by

$$\alpha_i = \frac{1}{A_1} \left(\ln \gamma_i + \ln \frac{b}{b_i} + \frac{b_i}{b} - 1 \right) + \frac{a_i}{b_i RT} \quad (19)$$

According to phase equilibrium rule, the phase equilibrium of component i is expressed by fugacity in eq 20:

$$f_i^L = f_i^G \quad (20)$$

Therefore, Henry coefficient is obtained by eq 21:

$$H = \frac{\varphi_i^L}{\varphi_i^G} P \quad (21)$$

where φ_i^L and φ_i^G are the fugacity coefficients of component i in liquid and gas phases, respectively and P is the system pressure.

Additionally, in a multicomponent mixture, the UNIQUAC equation for the activity coefficient of component i can be described by eq 22 as

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (22)$$

where γ^C is the combinatorial activity coefficient and γ^R is the residual activity coefficient, then

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \quad (23)$$

and

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1); \quad z = 10 \quad (24)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad \phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad (25)$$

In these equations, x_i is the mole fraction of component i , and the summation in eq 23 is over all components, including component i ; θ_i is the area fraction, and ϕ_i is the segment fraction that is similar to the volume fraction.

The subscripts i and j denote both component oxygen and toluene.

Pure component parameters r_i and q_i are sizes of molecular Van der Waals volumes and molecular surface areas, respectively. Only pure component properties are involved

Table 3. All Group Parameters R_k and Q_k

group	R_k	Q_k
ACH	0.5313	0.4
ACCH ₃	1.2663	0.968
O ₂	0.733	0.849

Table 4. Molecular Volumes and Surface Areas of Oxygen and Toluene³⁰

component	r	q
oxygen	0.733	0.849
toluene	3.9228	2.968

Table 5. Group Interaction Parameters in Equation PSRK^{9,11}

m	n	a_{mn}	a_{nm}	b_{mn}	b_{nm}
ACH	ACCH ₃	167.0	-146.8		
ACH	O ₂	285.26	-0.6989		
ACCH ₃	O ₂	130.37	384.98	63.323	-2.1163

in this equation. Parameters r_i and q_i are calculated as the sum of the group volume and area parameters, R_k and Q_k , are given in Table 3 as

$$r_i = \sum_k \nu_k^{(i)} R_k \quad \text{and} \quad q_i = \sum_k \nu_k^{(i)} Q_k \quad (26)$$

where $\nu_k^{(i)}$, always an integer, is the number of groups of type k in molecule i .

The molecular Van der Waals volumes and molecular surface areas of oxygen and toluene are listed in Table 4. They were employed to calculate the activity coefficients of oxygen and toluene in the group contribution approach UNIQUAC.

The residual activity coefficient is calculated by eq 27 as

$$\ln \gamma_i^R = \sum_k \nu_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \quad (27)$$

$$\ln \Gamma_k = Q_k [1 - \ln(\sum_m \Theta_m \Psi_{mk}) - \sum_m (\Theta_m \Psi_{km} / \sum_n \Theta_n \Psi_{nm})] \quad (28)$$

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (29)$$

$$\Psi_{mn} = \exp \left[-\frac{a_{mn} + b_{mn} T}{T} \right] \quad (30)$$

where Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in the molecule i . Θ_m is the area fraction of group m , and the sums are over all different groups. X_m is the mole fraction of group m in the mixture. Ψ_{mn} is the group interaction parameter given by eq 30, and the group interaction parameters a_{mn} , a_{nm} , b_{mn} , and b_{nm} are the parameters per binary mixture of groups given in Table 5. In conclusion, the calculation of Henry coefficient for given temperature and pressure is performed as the following procedures:

- (1) Calculate the pure component parameters.
- (2) Calculate the mixture parameter b from the linear mixing rule.
- (3) Determine the activity coefficient γ and the excess Gibbs energy g_0^E from the UNIQUAC model.
- (4) Calculate the mixture parameter a from MHV1 mixing rule.
- (5) Determine the mixture volumes of gas and liquid phases by solving the PSRK equation.

Table 6. Comparison of Solubility Data of Oxygen in Toluene

literature data ^{4,5}			experimental data		
T/K	P/MPa	x	T/K	P/MPa	x
283.71	0.101	0.000922	283.45	0.250	0.00197
313.20	0.101	0.00096	313.15	0.379	0.00358
323.30	0.8908	0.000916	323.15	0.828	0.00842

Table 7. Experimental Isothermal P, x data for the System Oxygen (1) +Toluene (2)

$T = 283.45 \text{ K}$		$T = 313.15 \text{ K}$		$T = 333.15 \text{ K}$	
x	P/MPa	x	P/MPa	x	P/MPa
0.00197	0.250	0.00358	0.379	0.00380	0.358
0.00254	0.320	0.00419	0.455	0.00429	0.410
0.00278	0.357	0.00460	0.514	0.00492	0.488
0.00353	0.457	0.00528	0.601	0.00542	0.529
0.00392	0.524	0.00539	0.621	0.00606	0.603
0.00457	0.630	0.00680	0.738	0.00676	0.669
0.00525	0.691	0.00751	0.821	0.00790	0.795
0.00586	0.769	0.00764	0.848	0.00866	0.847
0.00689	0.941	0.00771	0.852	0.00901	0.908

Table 8. Experimental Isothermal P, x data for the System Oxygen (1) +Toluene (2)

$T = 353.15 \text{ K}$		$T = 373.15 \text{ K}$		$T = 393.15 \text{ K}$	
x	P/MPa	x	P/MPa	x	P/MPa
0.00358	0.296	0.00303	0.181	0.00321	0.221
0.00421	0.357	0.00375	0.290	0.00359	0.309
0.00509	0.448	0.00456	0.331	0.00541	0.407
0.00548	0.478	0.00503	0.379	0.00655	0.512
0.00630	0.558	0.00593	0.463	0.00793	0.601
0.00675	0.578	0.00671	0.533	0.00846	0.641
0.00727	0.678	0.00819	0.670	0.0101	0.783
0.00875	0.829	0.0105	0.857	0.0103	0.823

6) Calculate fugacity coefficient φ .

7) Calculate Henry coefficient H .

Results and Discussion

Table 6 gives the comparison of experimental solubility data obtained in this work with those reported previously.^{4,5} Considering the difference of experimental method as well as data processing, the observed deviations between the experimental and literature data are acceptable.

The solubility measurements were performed at temperatures range from 283.45 K to 393.15 K and pressures up to 1.0 MPa. The isothermal P, x data are presented in Tables 7 and 8 and plotted in Figures 2 and 3, respectively. From Figures 2 and 3, the pressure (P) linearly increased with the mole fraction of oxygen (x).

For each temperature, the Henry coefficient was derived from the experimental isothermal P, x data. The Henry coefficient decreases with temperature. The results suggest that the solubility of oxygen in toluene increases with temperature. Fischer et al.⁵ previously reported the Henry coefficients of oxygen in toluene at low temperatures. A comparison with some data published by Fischer⁵ is shown in Figure 4. Even though some perceptible deviation exists between the two sets of data, we also can see the same tendency of the Henry coefficients.

Both calculating and experimental data of the Henry coefficients are compared and their relative deviations are also presented in Table 9. The fractional relative deviations ($100 - (\Delta H/H_{\text{expt}})$) within the 0 % to 16 % range demonstrate a good consistency. Thus, the predicted values based on the above gas solubility model are acceptable when the experimental data are not available (such as, at high temperatures and high pressures). Because the MHV1 mixing rule employs the parameters of

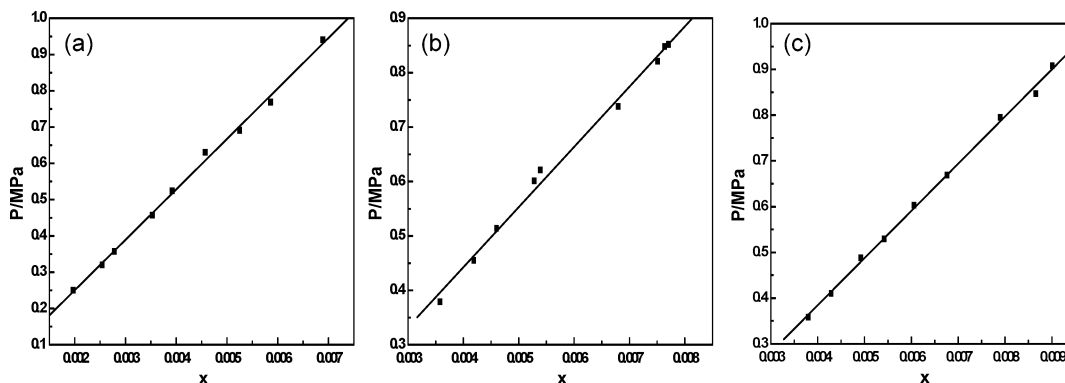


Figure 2. Experimental pressure (P) against mole fraction of oxygen (x) at (a) $T = 283.45$ K; (b) $T = 313.15$ K; (c) $T = 333.15$ K. ■, experimental data; □, linear fit of experimental data.

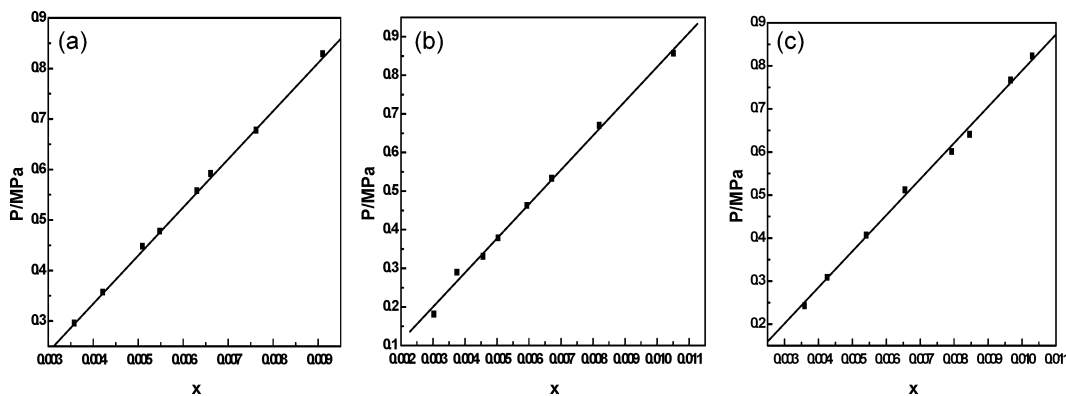


Figure 3. Experimental pressure (P) against mole fraction of oxygen (x) at (a) $T = 353.15$ K; (b) $T = 373.15$ K; (c) $T = 393.15$ K. ■, experimental data; □, linear fit of experimental data.

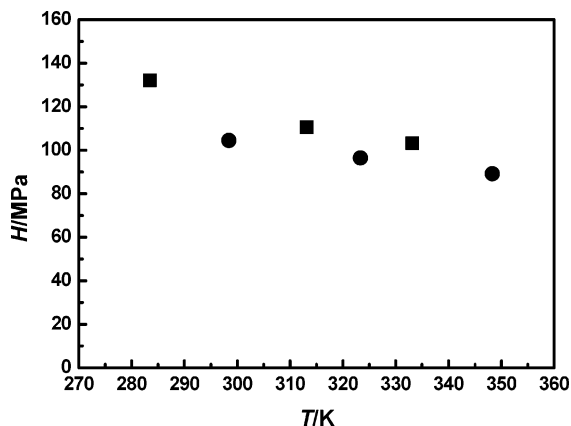


Figure 4. Comparison of Henry coefficients between this work and literature work. ■, experimental data in this work; ●, literature data in reference 5

Table 9. Henry Coefficients for the Solubility of Oxygen in Toluene Derived from Experimental Isothermal P , x Data and Thermodynamic Model

T/K	H/MPa (expt data)	H/MPa (calc data)	$100(\Delta H/H_{\text{(expt)}})/\%$
283.45	132.1	132.7	0.45
313.15	110.6	127.5	15.3
333.15	103.2	117.1	13.5
353.15	95.4	109.2	14.5
373.15	88.4	101.5	14.8
393.15	83.8	92.4	10.3

G^E model at low temperature, the predicted data are not identical with the experimental data at high temperatures.

Figure 5 demonstrates that plotting the natural logarithm of experimental Henry coefficients versus the reciprocal of the

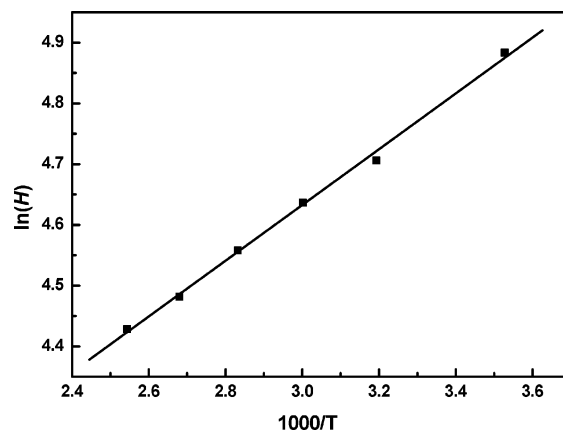


Figure 5. Experimental Henry coefficients versus the reciprocals of experimental temperature. ■, experimental data; □, linear fit of experimental data.

temperatures appears a linear relationship and the $\ln H$ increases with decreasing temperature. The increase of solubility with temperature indicates that the solubilization is an endothermic process.

Hypothesizing the Henry constant being independent of pressure, the relationship between temperature and Henry coefficient can be expressed as eq 31

$$\ln H = \frac{\Delta H}{RT} + C \quad (31)$$

where $\Delta H/J$ denotes the absorption heat of the solubilization; $R/(J \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$ is the universal gas constant; T/K is the system temperature; and C is an equation parameter. Thus, absorption heat ΔH is obtained from the slope of the straight line in Figure

5. Similarly, parameter C is the intercept of the straight line. Hence, an empirical equation of Henry coefficient as a function of temperature is described by eq 32 as

$$\ln H = \frac{3816}{RT} + 3.256 \quad (32)$$

Conclusions

In this paper, the solubility data for oxygen–toluene systems at temperatures from 289.45 K to 393.15 K and pressures up to 1.0 MPa were measured. Henry coefficients were derived from the experimental pressures and mole fractions of oxygen in toluene. A resulting thermodynamic model was used to calculate the Henry coefficient of oxygen in toluene. Both calculation and experimental data show that Henry coefficient of oxygen in toluene decreases with increasing temperature and suggest the oxygen-dissolving process in toluene is endothermic. Finally, an empirical equation of Henry coefficient as a function of temperature was obtained as the following:

$$\ln H = \frac{3816}{RT} + 3.256$$

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