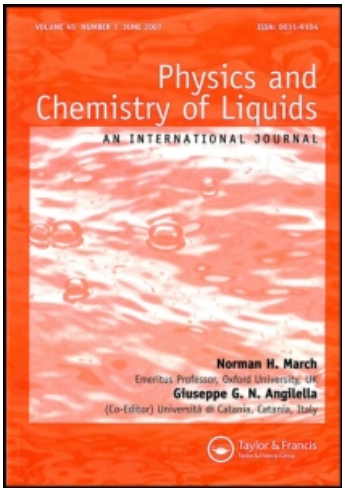


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# Solubility of $SO_2$, $CO_2$ in DMSO+$Mn^{2+}$ mixture solvents and EOS model

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# Solubility of $SO_2$, $CO_2$ in DMSO + $Mn^{2+}$ mixture solvents and EOS model

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The electrolyte equation of state (EOS) in [*Phys. Chem. Liq.*, **44**(1), 83, 2006] has been applied which describes the solubility of $SO_2$ in DMSO + $Mn^{2+}$ mixture solvents. With the assumptions used in previous applications of our model to $SO_2$ system, the EOS in this study is extended to the system of $SO_2$ and $CO_2$. In this article, on the basis of solubility measurement of dilute $SO_2$, $CO_2$ in DMSO + $Mn^{2+}$ mixture solvents, an extended EOS model is described. In order to test the correctness of our model, the data of gas–liquid equilibrium of such a multicomponent system have been fitted with the binary interaction parameters in the model, and the solubilities calculated by the model show good agreement with the experimental data.

*Keywords*: Solubility; Gas–liquid equilibrium; Sulfur dioxide; Carbon dioxide; EOS

## 1. Introduction

Removal of $SO_2$, $CO_2$, and other acidic gas from flue gas is one of the most important research projects in recent times. In a previous paper [1], the solubility of $SO_2$ in DMSO + $Mn^{2+}$ mixture solvents and equation of state (EOS) model has been described. In this article, we extend them to the system containing $SO_2$ and $CO_2$. Therefore, on the basis of solubility measurement of dilute $SO_2$ and $CO_2$ in DMSO + $Mn^{2+}$ mixture solvents (temperature ranging from 293.15 to 313.15 K, partial pressure of $SO_2$ from 0.279 to 1.68 kPa, and partial pressure of $CO_2$ from 6.69 to 13.34 kPa), we applied the previous EOS model to this new system. The model and the determination of the adjustable parameters shall be discussed below. The solubility of dilute $SO_2$, $CO_2$ in DMSO + $Mn^{2+}$ mixture solvents is listed in table 1.

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Table 1a. The experimental data of solubilities for $SO_2$, $CO_2$ in mixture absorbent.

| $T$ (K) | $P_{SO_2}$ (kPa) | $P_{CO_2}$ (kPa) | $y_{SO_2}$ | $y_{CO_2}$ | $y_{O_2}$ | $y_{DMSO}$ | $y_{N_2}$ | $x_{DMSO}$ | $x_{SO_4^{2-}}$ | $x_{H^+}$ | $x_{Mn^{2+}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 293.15 | 1.68 | 13.32 | 0.0168 | 0.133 | 0.120 | 0.00184 | 0.729 | 0.809 | 0.102 | 0.200 | 0.00167 |
| 293.15 | 1.56 | 18.81 | 0.0156 | 0.188 | 0.0828 | 0.00181 | 0.712 | 0.818 | 0.0979 | 0.192 | 0.00169 |
| 293.15 | 1.39 | 12.08 | 0.0139 | 0.121 | 0.0801 | 0.00183 | 0.784 | 0.832 | 0.0907 | 0.178 | 0.00172 |
| 293.15 | 0.925 | 9.14 | 0.00924 | 0.0913 | 0.0609 | 0.00182 | 0.837 | 0.867 | 0.0765 | 0.150 | 0.00179 |
| 293.15 | 0.571 | 6.69 | 0.00571 | 0.0670 | 0.0382 | 0.00183 | 0.887 | 0.920 | 0.0478 | 0.0918 | 0.00190 |
| 293.15 | 0.336 | 11.46 | 0.00338 | 0.115 | 0.0225 | 0.00183 | 0.857 | 0.943 | 0.0356 | 0.0672 | 0.00195 |
| 298.15 | 1.57 | 13.34 | 0.0157 | 0.133 | 0.119 | 0.00259 | 0.729 | 0.800 | 0.117 | 0.231 | 0.00165 |
| 298.15 | 1.47 | 18.83 | 0.0147 | 0.188 | 0.0824 | 0.0026 | 0.712 | 0.808 | 0.114 | 0.225 | 0.00167 |
| 298.15 | 1.34 | 12.07 | 0.0134 | 0.121 | 0.0798 | 0.0026 | 0.784 | 0.822 | 0.106 | 0.208 | 0.00170 |
| 298.15 | 0.877 | 9.13 | 0.00877 | 0.0913 | 0.0605 | 0.00260 | 0.837 | 0.854 | 0.0936 | 0.184 | 0.00177 |
| 298.15 | 0.481 | 6.68 | 0.00483 | 0.0670 | 0.0380 | 0.00260 | 0.888 | 0.918 | 0.0515 | 0.0991 | 0.00190 |
| 298.15 | 0.319 | 11.43 | 0.00321 | 0.115 | 0.0225 | 0.0026 | 0.857 | 0.940 | 0.0401 | 0.0763 | 0.00194 |
| 303.15 | 1.56 | 13.31 | 0.0155 | 0.133 | 0.119 | 0.00366 | 0.729 | 0.797 | 0.125 | 0.247 | 0.00165 |
| 303.15 | 1.38 | 18.81 | 0.0138 | 0.188 | 0.0820 | 0.00361 | 0.712 | 0.804 | 0.123 | 0.243 | 0.00166 |
| 303.15 | 1.30 | 12.05 | 0.0130 | 0.121 | 0.0795 | 0.00365 | 0.783 | 0.819 | 0.114 | 0.224 | 0.00169 |
| 303.15 | 0.811 | 9.12 | 0.00813 | 0.0913 | 0.0602 | 0.00365 | 0.837 | 0.849 | 0.103 | 0.202 | 0.00176 |
| 303.15 | 0.480 | 6.67 | 0.00482 | 0.0670 | 0.0379 | 0.00365 | 0.887 | 0.915 | 0.0569 | 0.110 | 0.00189 |
| 303.15 | 0.315 | 11.41 | 0.00317 | 0.115 | 0.0224 | 0.00366 | 0.856 | 0.934 | 0.0472 | 0.0906 | 0.00193 |
| 308.15 | 1.50 | 13.34 | 0.0150 | 0.133 | 0.118 | 0.00506 | 0.729 | 0.782 | 0.150 | 0.296 | 0.00162 |
| 308.15 | 1.41 | 18.80 | 0.0141 | 0.188 | 0.0807 | 0.00507 | 0.712 | 0.789 | 0.148 | 0.292 | 0.00163 |
| 308.15 | 1.22 | 12.04 | 0.0122 | 0.121 | 0.0790 | 0.00507 | 0.783 | 0.804 | 0.137 | 0.271 | 0.00166 |
| 308.15 | 0.807 | 9.11 | 0.00808 | 0.0912 | 0.0600 | 0.00507 | 0.836 | 0.842 | 0.115 | 0.227 | 0.00174 |
| 308.15 | 0.446 | 6.65 | 0.00448 | 0.0669 | 0.0376 | 0.00507 | 0.886 | 0.909 | 0.0655 | 0.127 | 0.00188 |
| 308.15 | 0.294 | 11.39 | 0.00296 | 0.115 | 0.0223 | 0.00507 | 0.855 | 0.932 | 0.0515 | 0.0992 | 0.00193 |
| 313.15 | 1.49 | 13.32 | 0.0149 | 0.133 | 0.118 | 0.00694 | 0.727 | 0.776 | 0.169 | 0.335 | 0.00160 |
| 313.15 | 1.35 | 18.82 | 0.0134 | 0.188 | 0.0811 | 0.00702 | 0.71 | 0.781 | 0.167 | 0.331 | 0.00162 |
| 313.15 | 1.22 | 12.04 | 0.0122 | 0.121 | 0.0786 | 0.00694 | 0.782 | 0.797 | 0.155 | 0.307 | 0.00165 |
| 313.15 | 0.778 | 9.10 | 0.00777 | 0.0911 | 0.0596 | 0.00695 | 0.835 | 0.831 | 0.134 | 0.265 | 0.00172 |
| 313.15 | 0.434 | 6.65 | 0.00437 | 0.0668 | 0.0374 | 0.00695 | 0.884 | 0.902 | 0.0778 | 0.152 | 0.00186 |
| 313.15 | 0.279 | 11.38 | 0.00281 | 0.115 | 0.0221 | 0.00695 | 0.854 | 0.928 | 0.0592 | 0.114 | 0.00192 |



## 2. The EOS model

The model used in the present study is an electrolyte EOS [1–7] and has already been described in a previous paper [1]. Here, we describe the differences of the model employed in the present study, with respect to ref. [1].

### 2.1. *Pure component parameters*

The values of pure molecular component parameters of system containing $SO_2$ and $CO_2$ in our model are listed in table 2. The molecular diameter is reported in table 3. The diameter of the ions is reported in table 4.

### 2.2. *Binary interaction parameters*

The optimized binary parameters $\tau_{ij}$ by fitting the solubility data at various temperatures and pressures for DMSO–$SO_2$ binary systems and DMSO–$CO_2$ systems are listed in table 5. The other binary parameters are for interactions between ions and molecules or between cations and anions, that is $W_{kl}$ parameters, the obtained interaction parameters $W_{kl}$ in our previous paper [1] are shown in table 6. In this system

Table 1b. The comparison of experimental data and calculation values for $SO_2$, $CO_2$ solubilities in mixture absorbent.

| $x_{SO_2}$ | | $x_{CO_2}$ | |
|---|---|---|---|
| Experimental value | Calculated value | Experimental value | Calculated value |
| 0.0887 | 0.0879 | 0.00105 | 0.00110 |
| 0.0823 | 0.0832 | 0.00150 | 0.00157 |
| 0.0761 | 0.0763 | 0.000982 | 0.00100 |
| 0.0555 | 0.0538 | 0.000774 | 0.000785 |
| 0.0320 | 0.0339 | 0.000601 | 0.000613 |
| 0.0203 | 0.0194 | 0.000948 | 0.000957 |
| 0.0825 | 0.0810 | 0.000991 | 0.00100 |
| 0.0764 | 0.0772 | 0.00141 | 0.00140 |
| 0.0707 | 0.0720 | 0.000923 | 0.000917 |
| 0.0514 | 0.0506 | 0.000725 | 0.000724 |
| 0.0300 | 0.0293 | 0.000570 | 0.000571 |
| 0.0190 | 0.0197 | 0.000892 | 0.000874 |
| 0.0769 | 0.0762 | 0.000950 | 0.000953 |
| 0.0711 | 0.0707 | 0.00135 | 0.00133 |
| 0.0659 | 0.0678 | 0.000885 | 0.000872 |
| 0.0478 | 0.0466 | 0.000693 | 0.000690 |
| 0.0280 | 0.0282 | 0.000546 | 0.000544 |
| 0.0177 | 0.0178 | 0.000854 | 0.000831 |
| 0.0675 | 0.0664 | 0.000615 | 0.000628 |
| 0.0624 | 0.0638 | 0.000875 | 0.000879 |
| 0.0578 | 0.0579 | 0.000571 | 0.000573 |
| 0.0424 | 0.0421 | 0.000452 | 0.000454 |
| 0.0248 | 0.0245 | 0.000357 | 0.000359 |
| 0.0157 | 0.0161 | 0.000554 | 0.000545 |
| 0.0546 | 0.0540 | 0.000541 | 0.000545 |
| 0.0504 | 0.0507 | 0.000771 | 0.000758 |
| 0.0468 | 0.0474 | 0.000503 | 0.000498 |
| 0.0341 | 0.0335 | 0.000396 | 0.000395 |
| 0.0201 | 0.0200 | 0.000314 | 0.000313 |
| 0.0128 | 0.0130 | 0.000487 | 0.000475 |



Table 2. The values of pure molecular component properties and parameters.

| Solvent | DMSO | $SO_2$ | $CO_2$ |
|---|---|---|---|
| $T_c$ (K) | 707 [9,10] | 430.8 [11] | 304.1 [11] |
| $P_c$ (kPa) | 5850 [9,10] | 7880 [11] | 7380 [11] |
| $\omega$ | 0.414 [9,10] | 0.256 [11] | 0.239 [11] |
| $m_1$ | $m_1 = 0.48344 + 1.58597\omega - 0.3758\omega^2 + 0.23194\omega^3$ | | |
| $m_2$ | 0 [11] | −1.9446 [8] | −1.9446 [11] |
| $m_3$ | 0 [11] | 15.2851 [11] | 15.2851 [11] |

Table 3. The parameters of pure substance.

| Substance | $b_i$ | Diameter $\sigma$ (Å) |
|---|---|---|
| $SO_2$ | $3.938 \times 10^{-5}$ | 4.112 [11] |
| DMSO | $8.7055 \times 10^{-5}$ | 5.267 [11] |
| $CO_2$ | $2.968 \times 10^{-5}$ | 3.94 [11] |

Table 4. The diameters of ion.

| Substance | $b_i$ | Diameter $\sigma$ (Å) | Stocks radius (Å) | Pauling radius (Å) |
|---|---|---|---|---|
| $H^+$ | $5.4458 \times 10^{-7}$ | 1.20 [12] | 0.73 | |
| $Mn^{2+}$ | $1.2909 \times 10^{-6}$ | 1.60 [12] | 2.48 | |
| $SO_4^{2-}$ | $2.7771 \times 10^{-5}$ | 4.45 [12] | 2.3 [13] | 2.815 [13] |

Table 5. Optimized $\tau_{ij}$ parameters for binary systems.

| System | $\tau_{ij}$ |
|---|---|
| $SO_2$–DMSO | 1.85 |
| DMSO–$SO_2$ | −4.35 |
| $CO_2$–DMSO | 0.4869 |
| DMSO–$CO_2$ | 0.4195 |

containing $SO_2$ and $CO_2$, subscripts 0–5 below refer to $SO_2$, DMSO, $Mn^{2+}$, $SO_4^{2-}$, $H^+$, and $CO_2$, respectively. Therefore, in our extended EOS model, the specific expressions of the various parameters are as follows:

$$b = b_m + x_2 b_2 + x_3 b_3 + x_4 b_4 \tag{1}$$

$$b_m = \frac{x_0^2(b-(a/RT))_{00} + x_1^2(b-(a/RT))_{11} + x_5^2(b-(a/RT))_{55} + f}{1-(x_0(a_0/b_0RT) + x_1(a_1/b_1RT) + x_5(a_5/b_5RT)) + (A_\infty^E/RT)} \tag{2}$$

$$f = 2x_0x_1\left(b - \frac{a}{RT}\right)_{01} + 2x_0x_5\left(b - \frac{a}{RT}\right)_{05} + 2x_1x_5\left(b - \frac{a}{RT}\right)_{15} \tag{3}$$

$$a^{SR} = b_m\left(\frac{a_0}{b_0} + \frac{x_1a_1}{b_1} + \frac{x_5a_5}{b_5} - A_\infty^E(x)\right) \tag{4}$$

$$\frac{A_\infty^E}{RT} = \frac{x_0(x_1\tau_{10}g_{10} + x_5\tau_{50}g_{50})}{x_0 + x_1g_{10} + x_5g_{50}} + \frac{x_1(x_0\tau_{01}g_{01} + x_5\tau_{51}g_{51})}{x_0g_{01} + x_1 + x_5g_{50}} + \frac{x_5(x_0\tau_{05}g_{05} + x_1\tau_{15}g_{15})}{x_0g_{05} + x_1g_{15} + x_5} \tag{5}$$

$$\zeta_3 = \frac{N \times 3.14}{6}\frac{x_0\sigma_0^3 + x_1\sigma_1^3 + x_2\sigma_2^3 + x_3\sigma_3^3 + x_4\sigma_4^3 + x_5\sigma_5^3}{v} \tag{6}$$

$$a_{LR}^2 = \frac{e^2N}{\varepsilon_0 DRT} \tag{7}$$

$$D = 1 + (D_s - 1)\left(\frac{1-\zeta_3}{1+\frac{\zeta_3}{2}}\right) \tag{8}$$

$$D_s = \frac{x_0D_0 + x_1D_1 + x_5D_5}{x_0 + x_1 + x_5} \tag{9}$$

The dielectric constants for $SO_2$, $CO_2$, DMSO in equation (9) are listed in table 7.

### 2.3. *The fitting results by experiment data correlation*

The model used in the present system relates to six components of $SO_2$, $CO_2$, DMSO, $Mn^{2+}$, $SO_4^{2-}$, $H^+$, contains eight adjustable parameters $W_{kl}$. The known interaction

Table 6. Interaction parameters, $W_{kl}$.

| Ion–molecule or ion–ion pair | $W_{kl}$ |
|---|---|
| $H^+$–$SO_2$ | 0.00152 |
| $H^+$–DMSO | 0.132 |
| $Mn^{2+}$–$SO_2$ | −7.63 |
| $Mn^{2+}$–DMSO | $1.51 \times 10^2$ |
| $H^+$–$SO_4^{2-}$ | $-3.85 \times 10^{-4}$ |
| $Mn^{2+}$–$SO_4^{2-}$ | $-7.92 \times 10^{-4}$ |

Table 7. The dependence of the dielectric constant of pure substance and temperature.

| Substance | Expression | Temperature range (K) | Source |
|---|---|---|---|
| $SO_2$ | $D = 36.67 - 0.077T$ | 287.15–373.15 | [14] |
| $CO_2$ | $D = 0.50 + 34.97/T + 1.37 \times 10^{-3}T$ | 298.15–623.15 | [13,15] |
| DMSO | $D = 91.21 - 0.15T$ | 293.15–328.15 | [14,15] |



parameters $W_{kl}$ between the ionic and molecular species and the ionic species of $SO_2$ system [1,15] are listed in table 6. Using these known parameters in this model, two interaction parameters $W_{54} = 0.00453$, $W_{52} = -6.00$ are obtained by experimental data correlation.

### 2.4. *Optimization calculation*

In order to test the accuracy of our model, we inserted the above values for $W_{kl}$ into our model EOS, and show the comparison between the theoretical and the experimental results in table 1. The comparison of $SO_2$, $CO_2$ solubilities calculated by the model and the experimental data at different $SO_2$, $CO_2$ partial pressures are shown in figures 1 and 2. The solubilities calculated by the model show good agreement with the experimental data.

## 3. Conclusions

(1) According to the measured solubilities of dilute $SO_2$, $CO_2$ in $DMSO + Mn^{2+}$ mixture solvent from 294.15 to 313.15 K and partial pressure of $SO_2$ from 0.279 to 1.68 kPa, $CO_2$ from 6.69 to 13.34 kPa, as well as in our previous papers [1,15–20], a suitable electrolyte solution model based on the gas–liquid phase equilibrium principles of electrolyte solution has been applied to represent $SO_2$ and $CO_2$ solubility in $DMSO + Mn^{2+}$ mixture solvent. Which takes into account the interactions between the ions and molecules or between the cations and anions to the contribution of the Helmholtz energy. Taking into account the Helmholtz energy arising from the repulsive forces and the attractive forces between the molecules through the improved SRK EOS by Wang and Gmehling [8].

(2) From figures 1 and 2, we can find that the solubilities calculated by the model show good agreement with the experimental data.

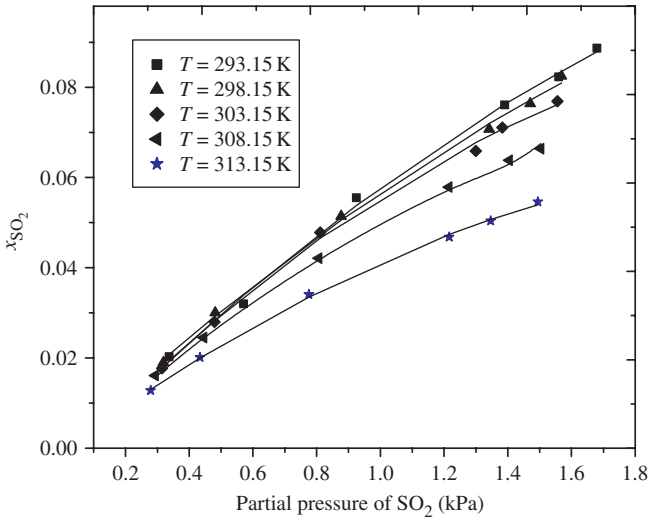


Figure 1. The comparison of experimental data and calculated values for $SO_2$ solubilities in mixture absorbent at different $SO_2$ partial pressure.



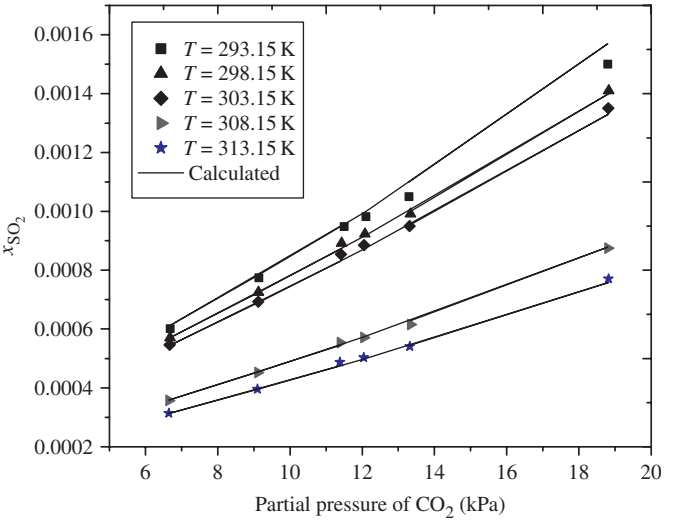


Figure 2. The comparison of experimental data and calculated values for $CO_2$ solubilities in mixture absorbent at different $CO_2$ partial pressure.

(3) The resulting model uses only two adjustable ionic parameters for the representation of $SO_2$ and $CO_2$ solubility in DMSO + $Mn^{2+}$ mixture solvent. Compared with other models, this model is simple and applicable and the model accuracy is consistent with the experimental deviation.
(4) The model could easily be extended to the calculation of the solubility of other gases and could therefore be a useful tool for column design and optimization. Modelings could also be useful as a guide for the analysis of data consistency.

## References

[1] H. Li, W.R. Chen. *Phys. Chem. Liq.*, **44**(1), 83 (2006).
[2] W. Furst, H. Renon. *A.I.Ch.E. J.*, **39**(2), 335 (1993).
[3] Y.X. Zuo, W. Furst. *Fluid Phase Equilibria*, **138**(1–2), 87 (1997).
[4] Y.X. Zuo, T.M. Guo. *J. Chem. Indus. Eng. (China)*, **42**(3), 318 (1991).
[5] C.X. Li, Y.G. Li, J.F. Lu. *J. Chem. Indus. Eng. (China)*, **47**(3), 295 (1996).
[6] W.B. Liu, Y.G. Li, J.F. Lu. *J. Chem. Indus. Eng. (China)*, **49**(4), 389 (1998).
[7] Y.X. Zuo, W. Furst. *Fluid Phase Equilibria*, **150–151**(Sep), 567 (1998).
[8] L.S. Wang, J. Gmehling. *A.I.CH.E J.*, **45**(5), 1125 (1999).
[9] H.Z. Lu. *Manual of Basic Data Petrochemical Industry*, Chemical Industry Press, Peking (1984).
[10] P.S. Ma, S.Q. Xia. *Petrochem. Tech.*, **30**(1), 37 (2001).
[11] R.C. Reid, J.M. Prausnitz, B.E. Poling. *The Properties of Gases and Liquids*, 4th Edn, McGraw-Hill, New York (1987).
[12] Y.X. Zuo, T.M. Guo. *J. Chem. Indus. Eng. (China)*, **41**(1), 1 (1990).
[13] R.A. Robinson, R.H. Stokes (Eds). *Electrolyte Solutions*, Butterworths, London (1970).
[14] J.A. Dean. *Lange's Handbook of Chemistry*, 15th Edn, P S.6, McGraw-Hill, New York (1999).
[15] H. Li, W.R. Chen, D.Zh. Liu. *J. Environ. Sci.*, **15**(1), 92 (2003).
[16] H. Li. *Phys. Chem. Liq.*, **42**(2), 195 (2004).
[17] H. Li, W.R. Chen. *Phys. Chem. Liq.*, **43**(3), 289 (2005).
[18] H. Li, W.R. Chen. *Phys. Chem. Liq.*, **43**(4), 343 (2005).
[19] H. Li, W.R. Chen. *Phys. Chem. Liq.*, **43**(5), 467 (2005).
[20] H. Li, D.Zh. Liu, F.A. Wang. *J. Chem. Eng. Data.*, **47**(4), 772 (2002).