



Thermodynamic property prediction for high molecular weight molecules based on their constituent family



Hideo Nishiumi*

Chemical Engineering Laboratory, Faculty of Bioscience and Applied Chemistry, Hosei University, 3-7-2 Kajino-cho, Koganei, Tokyo 184-8584 Japan

ARTICLE INFO

Article history:

Received 9 September 2015

Received in revised form

5 December 2015

Accepted 9 December 2015

Available online 12 December 2015

Keywords:

Group contribution methods

Critical properties

Joback correlation

Equations of state

ABSTRACT

A method for predicting the critical temperature of high molecular weight molecules is proposed. The method is based on a modification of the functional form of the Joback method and the use of constituent functional group trends. To demonstrate the predictive capability of the method several pure fluids and their binary mixtures with CO₂ are studied. In particular, diglyme, triglyme and tetraglyme whose molecular weights range from 134 to 222, are shown to reveal excellent predictions between 3 and 9% deviation for saturated liquid densities. Application to vapor–liquid phase equilibria for CO₂–glyme systems exhibit 4–8% deviation in saturated liquid densities and 1% for vapor densities. For the system of oleic acid + CO₂, pure component parameters from the method allow the correlation of the vapor pressure of oleic acid and the solubility of H₂ in oleic acid with a BWR type of equation of state and temperature dependent interaction parameters. Solubility of CO₂ in triolein is also well correlated. The critical temperature of a polyalkylene glycol with a molecular weight of 1100 is predicted to be 842 K, whereas the prediction by of the Joback method predicts 8541 K, and so cannot be used in equation of state calculations. The pure component properties predicted with the new functional form of the Joback method also allow reliable correlation of CO₂–polyalkylene glycol vapor–liquid equilibria.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

When the critical properties of a pure substance are known, it is possible to predict thermodynamic properties using corresponding state theories such as equations of state (EoS). For the substances in which the critical properties are unknown, simple predictive methods based on molecular group contributions such as those of Joback and Reid [1], Constantinou and Gani [2], Marrero and Gani [3] or Valderrama and Robles [4] methods are effective. However, in all of these group contribution methods, the uncertainty of the predictions becomes higher as the molecular weight (M_w) increases and at values of $M_w = 1000$ or more, the relationships may not give physically realistic results. Moreover, for big molecules such as polyalkylene glycols (PAGs), glymes or other molecules for which data are unavailable and are generally not included in databases for group contribution methods, the applicability of the method may be doubtful even though data exist for small molecules having the same constituent families (e.g., ether, di-ol).

To predict the thermodynamic properties of higher molecular weight molecules, the method of Joback and Reid [1] is taken as an example and two observations are made. First, the Joback method [1] becomes unsuitable for predicting the properties of high molecular weight molecules because it uses a quadratic function that has a maximum at some value of molecular weight. Second, the Joback method has linear contribution increments for the critical temperature (T_c), critical pressure (P_c), critical volume (V_c) and boiling point (T_b) that combines all constituent families and does not take advantage of specific trends of constituent families. To address these limitations, the following approach was developed:

- (i) First, a monotonically increasing functional ratio T_b/T_c is introduced with the sum of contribution increments for the molecule being obtained from the Joback correlation.
- (ii) Second, the correlation is based on constituent family trends (hydrocarbons, ethers, esters).

A 15-constant BWR EoS [8–12] with predicted parameters is used as an equation of state and the properties of pure substances or mixture properties [8–12,14–18] are predicted and compared with experimental data. Large molecules and molecules that are

* Tel./fax: +81-425835956.

E-mail address: nishi@hosei.ac.jp.

generally unfamiliar to property databases (glymes, PAG, etc.) are considered. The prediction of the properties of high molecular weight molecules from their relationships with their constituent families of small molecules is considered along with the appropriate functional forms and a methodology for group contribution methods that can predict the properties of large molecules thus demonstrated.

2. Prediction of critical temperature developing Joback method

2.1. Relationship between $\sum \Delta_T$ of Joback correlation and T_b/T_c

According to the Joback correlation [1], the critical temperature T_c is obtained from the following relation:

$$T_c [K] = T_b \left[0.584 + 0.965 \sum \Delta_T - \left(\sum \Delta_T \right)^2 \right]^{-1} \quad (1)$$

$$T_b [K] = 198 + \sum \Delta_b \quad (2)$$

where T_b is the boiling point, Δ_T and Δ_b are contribution increments for the critical temperature and boiling point, respectively. Since Eq. (1) has a linear relationship, T_c approaches a very large value at high molecular weights according to Eq. (2). For example, T_c of triolein is 4019 K and that of PAG-1 (a polyalkylene glycol) is 8581 K. From these values, predictions cannot be reliably made with an equation of state.

To avoid the direct T_b calculation, the value of T_b/T_c from Eq. (1) is written as follows,

$$\frac{T_b}{T_c} = 0.584 + 0.965 \sum \Delta_T - \left(\sum \Delta_T \right)^2 \quad (3)$$

For about 400 substances [5], the experimental values of T_b/T_c were plotted against $\sum \Delta_T$ from the Joback correlation as shown in Fig. 1. Except for higher alcohols, the trends are similar for all constituent families and excellent correlations can be made.

For a large molecules, however, the value of T_b/T_c decreases with molecular weight when using eq. (3), which is undesirable. As the molecular weight increases, the value of T_b/T_c should increase monotonically and have a maximum value of unity at best. For higher alcohols, the effect of hydrogen bonding (effect of OH-increment) can probably be neglected. To address these issues,

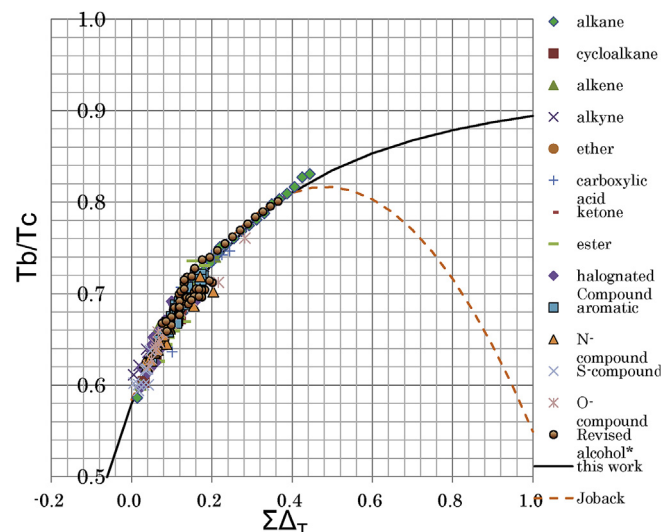


Fig. 2. Correlation between T_b/T_c and $\sum \Delta_T$ applicable to high molecular weight molecules considered in this work. Revised alcohol: contribution of OH increment is neglected for higher alcohols.

the following function form is employed (Fig. 2)

$$\frac{T_b}{T_c} = \frac{1}{(1.3 + \sum \Delta_T)^4} + 0.93 \quad (4)$$

The above expression shows that a maximum value of T_b/T_c is 0.93.

2.2. Method of calculating T_c that avoids direct calculation of T_b

The next step in the proposed method is to obtain a relationship between T_c and T_b/T_c . For about 400 substances [5], the experimental values of T_b/T_c are plotted against T_c as shown in Fig. 3. Although there appears to be no clear trends in the data, excellent correlations for the constituent families can be obtained. For example, chain hydrocarbons (alkane, alkene and alkyne) and esters can be correlated by the same function,

$$T_b/T_c = 4.639 \times 10^{-7} T_c^2 - 6.783 \times 10^{-5} T_c + 0.5840 \quad (5)$$

While chain alcohols and carboxylic acids can be expressed by

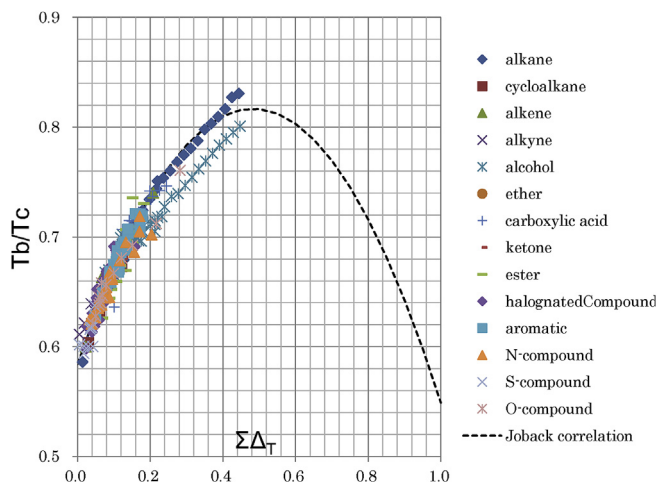


Fig. 1. Relation between T_b/T_c and $\sum \Delta_T$ obtained by Joback [1].

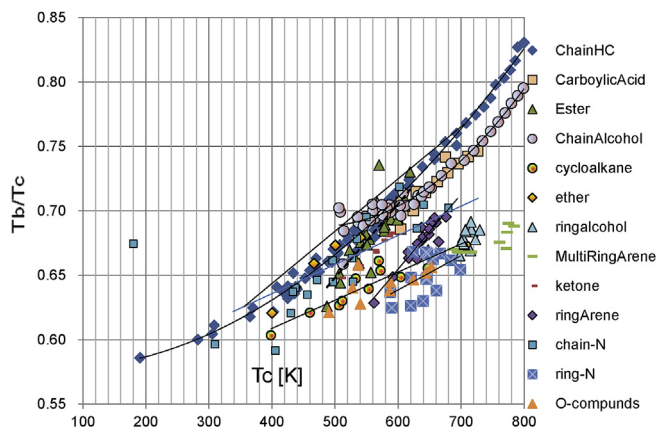


Fig. 3. Relationship between T_c and T_b/T_c depending for constituent families.

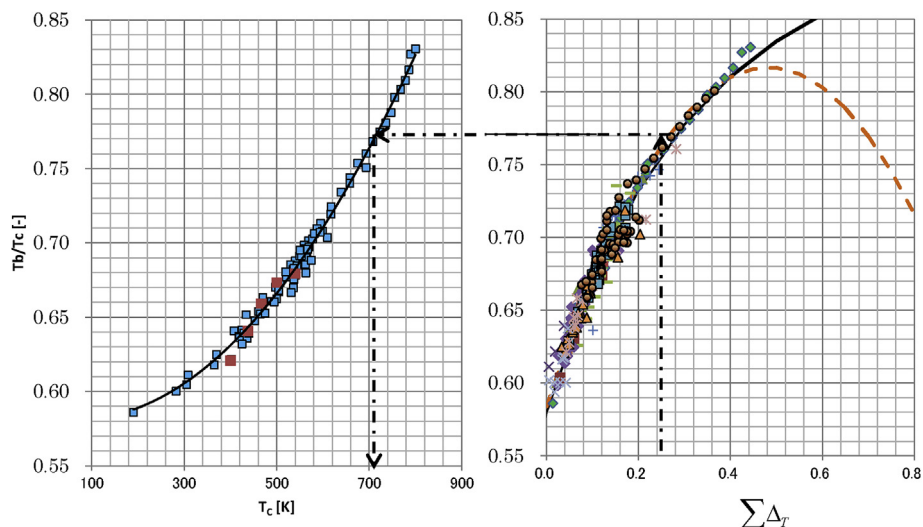


Fig. 4. Methodology to obtain T_c (chain hydrocarbon and ester) from $\sum \Delta_T$ of the Joback correlation [1] through T_b/T_c .

$$T_b/T_c = 1.201 \times 10^{-6} T_c^2 - 9.724 \times 10^{-4} T_c + 0.917 \quad (6)$$

where T_c is given in [K].

Therefore in the proposed method T_c can be calculated while avoiding the direct prediction of T_b . Fig. 4 illustrates the method to obtain T_c from $\sum \Delta_T$ of the Joback correlation [1] through T_b/T_c . The method predicts a T_c for triolein of 835 K and a T_c of 842 K for PAG-1 (1105 molecular weight polyalkylene glycol). This method succeeds in reducing the T_c value as a prediction parameter and allows the calculation of thermodynamic properties of large molecules as shown in the next section.

3. Prediction of thermodynamic properties using the proposed method

3.1. Glymes

Polyethylene glycol ethers (glymes) are expected to be promising solvents for carbon dioxide gas in high-pressure absorption towers. Kodama et al. [6] measured the solubility of carbon dioxide in glymes such as diglyme, triglyme, and tetraglyme at 313.15 K and the densities of pure glymes between 273.15 and 363.15 K at atmospheric pressure. Table 1 shows a summary of the predicted results for glymes using the proposed method and a BWR EoS with 15 coefficients [8–12] as described below.

This work is concerned with critical temperature calculation and so the selection of the EoS to be used does not have a strong bearing

on the conclusions. As shown in Table 1, the T_c values of glymes predicted in this work are similar to those by Joback [1]. Liquid density predictions at atmospheric pressure subsequently give 2.8, 6.2 and 9.0% deviations for di-, tri- and tetra-glyme, respectively and, as shown in Fig. 5, the vapor prediction compared with NIST data [7] exhibits a 3.9% deviation. We note that this is better than that obtained from the Joback method, though both methods produce reasonable results.

To calculate mixture properties, binary interaction parameters m_{ij} that determine the deviation of the interactions between species i and j from ideal behavior are needed and are defined as $T_{cij} = m_{ij} \sqrt{T_{ci} T_{cj}}$. Note m_{ij} is written as $(1 - \delta_{ij})$ in the Peng-Robinson EoS [13].

Generalized values of have been reported in the literature [14–18] for the BWR EoS and for the Peng-Robinson EoS [13,19–21]. Using $m_{12} = 0.90$ and the BWR EoS ([14–18]), Figs. 6 to 8 show that the solubility of CO₂ in diglyme and the liquid and vapor prediction are well correlated.

We find that as long as the molecular weight is below 250, the Joback method and the method proposed herein provide similar T_c values and therefore the calculated results will be similar.

3.2. Higher molecular weight molecules - oleic acid, triolein and PAG-1

Table 2 provides a summary of the predicted results for higher molecular weight molecules. Comparing the Joback correlation

Table 1
Summary of prediction results for glymes.

		Calc. deviation [%]		
		Diglyme	Triglyme	Tetraglyme
Chemical formula		C ₆ H ₁₄ O ₃	C ₈ H ₁₈ O ₄	C ₁₀ H ₂₂ O ₅
Molecular weight		134	178	222
T_c prediction	T_c (this work) [K]	592	652	698
	T_c (Joback) [K]	570	636	703
Pure	Vapor pressure	3.9 (Fig. 5)		
	Liquid density at atmospheric pressure	2.8	6.2	9.0
Mixture	Optimal m_{ij} for solubility of CO ₂	0.90 (Fig. 6)	0.89	0.845
	Saturated liquid density	3.8 (Fig. 7)	6.5	8.4
	Saturated vapor density	0.9 (Fig. 8)	1.1	1.1

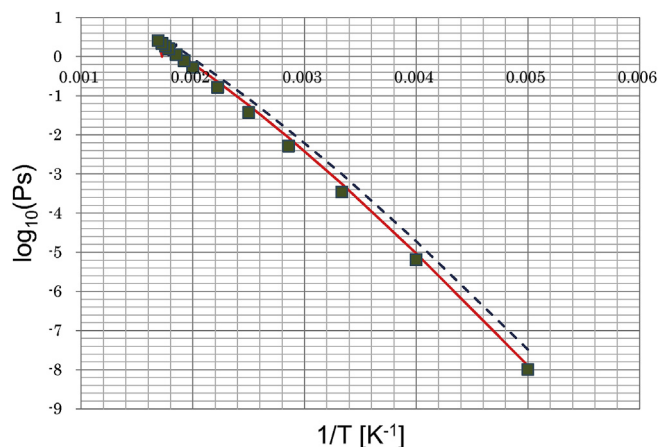


Fig. 5. Comparison of vapor pressure prediction for diglyme from this work and that of Joback. Solid lines: this work, broken line: using T_c of Joback correlation [1], square: NIST data [7].

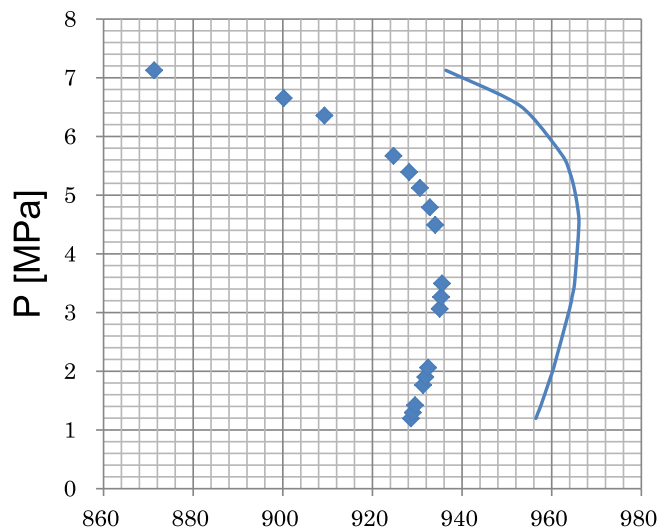


Fig. 7. Liquid density calculation for the system of CO_2 + diglyme. Diamonds correspond to the experimental data of Kodama et al. [6], solid line: calculation with BWR EoS and $m_{12} = 0.90$ [14–18].

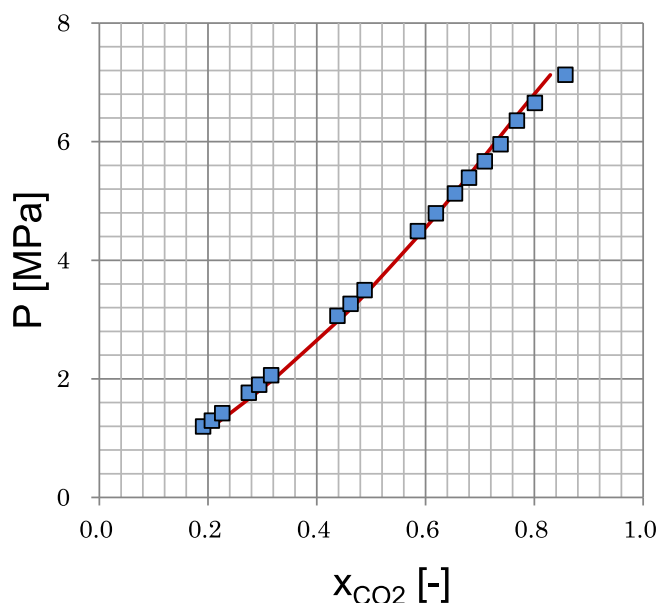


Fig. 6. Solubility of CO_2 in diglyme at 313.15 K. Squares experimental data from Kodama et al. [6], solid line: calculation with BWR EoS and $m_{12} = 0.90$ [14–18].

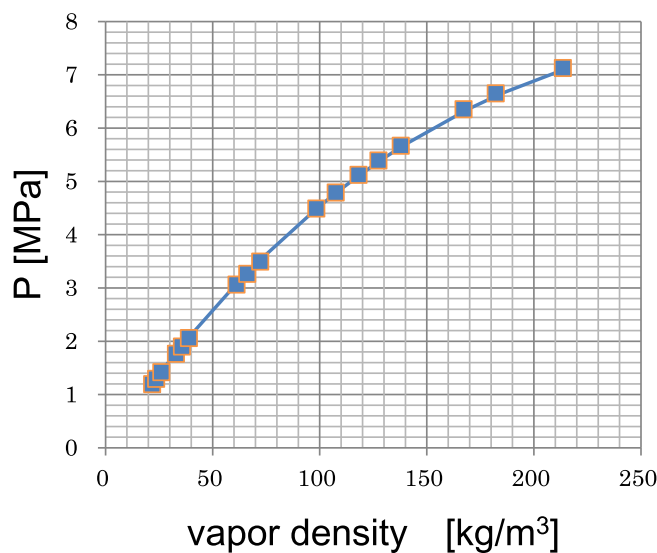


Fig. 8. Vapor density calculation for the system of CO_2 + diglyme. Diamonds correspond to the experimental data of Kodama et al. [6], solid line: calculation with BWR EoS and $m_{12} = 0.90$ [14–18].

with this work, the value of the critical temperatures are reduced dramatically in the new method, which enables one to calculate thermodynamic properties with equations of state. However, as even these values are hypothetical, it may be more appropriate to treat the property as a fitted parameter.

Fig. 9 shows a comparison of the experimental vapor

Table 2
Summary of prediction results for big molecules.

		Oleic acid	Triolein	PAG-1
Chemical formula		$\text{C}_{18}\text{H}_{34}\text{O}_2$	$\text{C}_{57}\text{H}_{104}\text{O}_6$	$\text{C}_{55}\text{H}_{108}\text{O}_{21}$
Molecular weight		284	885	1105
T_c	T_c (this work) [K]	815.2	835	910
prediction	T_c (Joback) [K]	as acid 942.9	as ester 4019	as ester 8541
Pure	Boiling temperature	3.8% dev. (Fig. 9)		
Mixture	Optimal m_{ij} for solubility of H_2	-2.0: -0.9 (Fig. 10a–b)	-1.8 (Fig. 11)	
	Optimal m_{ij} for solubility of CO_2	0.	-0.8	0.60 (Fig. 12)

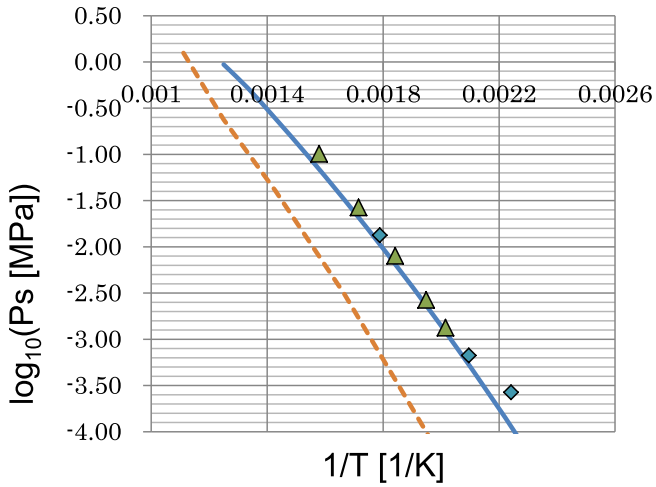


Fig. 9. Vapor pressure calculation for oleic acid. Solid line: prediction with BWR EoS [8–12], dotted line: prediction with Joback method, experimental data (triangles [24] and diamonds [25]).

pressure for oleic acid with the predicted values from the BWR EoS [8–12]. As can be seen by the figure, the results are

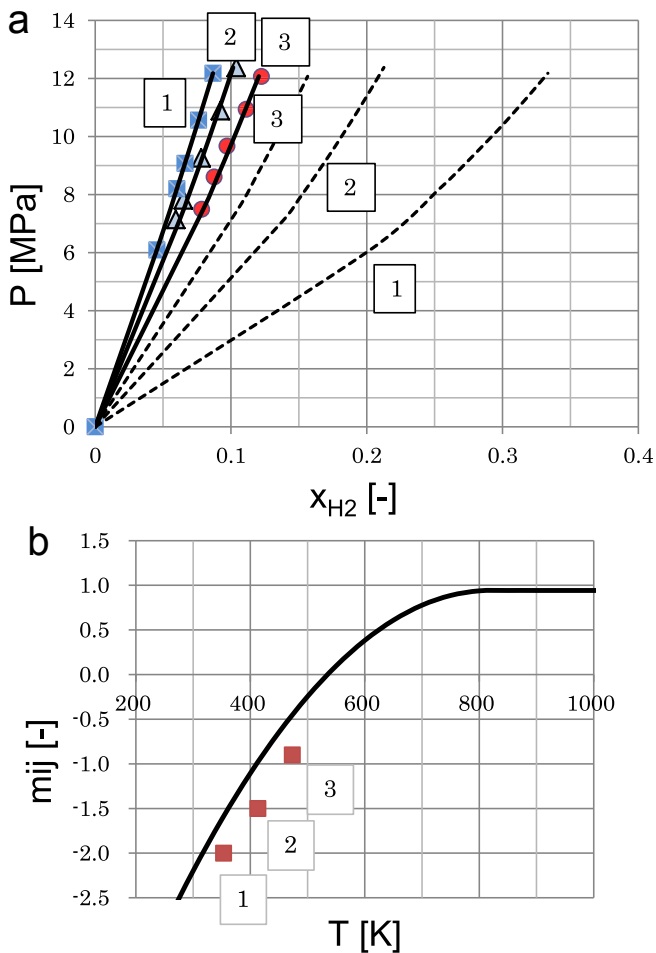


Fig. 10. A Solubility of H₂ in oleic acid. Dotted line: the generalized correlation containing H₂ [18] (Eq. (6)), solid line: optimized value of m_{ij} in this work, temperature 1: 353.2 K ($m_{ij} = -2.0$), 2: 413.2 K ($m_{ij} = -1.5$), 3: 473.18 K ($m_{ij} = -0.9$). Symbols are the experimental data [22]. Fig. 10b Comparison of m_{ij} for the generalized correlation (solid line) containing H₂ [14–18] with this work [square].

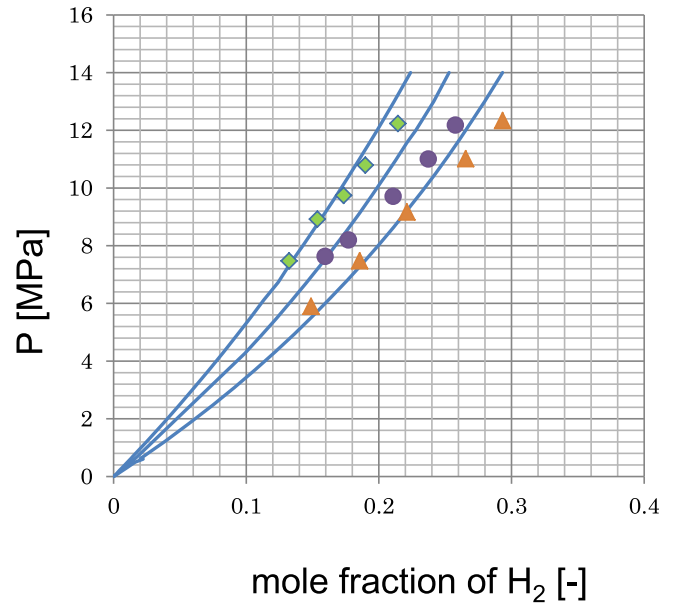


Fig. 11. Fitted solubilities of H₂ in triolein. diamonds: 353.19 K, circles: 413.19 K, triangles: 473.2 K, solid lines: optimal $m_{ij} = -1.8$ for the BWR EoS in this work.

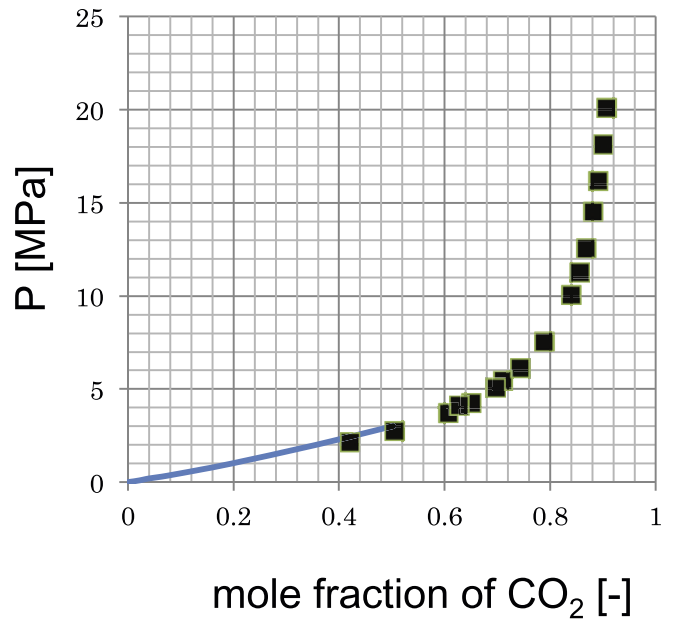


Fig. 12. Fitted solubility of CO₂ in polyalkylene glycol-1 at 313.15 K. Solid line: from the BWR EoS with $m_{ij} = 0.60$ and symbols are experimental data [23].

significantly more accurate than those obtained from the Joback method.

In Fig. 10a and b the results for the solubility of H₂ in oleic acid between 353.2 K and 473.18 K are presented. A generalized binary interaction parameter m_{ij} correlation for mixtures containing H₂ for BWR EoS has been developed in the literature and is as follows [18]:

$$m_{ij} = a T_c^2 (1 - T_r)^2 + b \quad \text{for } T_r \leq 1$$

$$= b \quad \text{for } 1 < T_r \quad (7)$$

where

$$a = -1.250 \times 10^{-5} / (V_c - 0.065)^{0.4} + 0.118 \times 10^{-5}$$

$$b = 0.940 + 3.13 V_c \quad \text{for } V_c \leq 0.15 \text{ [L/mol]}$$

$$= 1.492 - 0.55 V_c \quad 0.15 < V_c$$

Therefore m_{ij} can be calculated at a given temperature for a given V_c and T_c [14–18].

However, as shown in Fig. 10b, the binary interaction parameters fitted in this work for m_{ij} as a function of temperature (2.0 for 353.2 K, -1.55 for 413.21 K and -0.90 for 473.18 K) are slightly smaller than the generalized values [18] and naturally provide significantly better results.

On the other hand, fitting of H_2 solubility in triolein between 353.19 K and 473.2 K [22] gives good correlation for an m_{ij} value of -1.8 as shown in Fig. 11. The Joback correlation does not converge because the T_c value of triolein is too large.

Fig. 12 shows results for the solubility of CO_2 in PAG-1 at 313.15 K [23] using the fitted m_{ij} value of 0.60. We find that although the calculations converge to pressures of 3 MPa, at higher pressures the calculations fail since only a single liquid phase is predicted to exist. When the T_c value of PAG-1 is reduced, a P - x diagram of the CO_2 - PAG-1 system can be completely calculated. In the future, the effect of T_c as a prediction parameter should be studied. As the value of the critical temperature of PAG-1 with the Joback correlation is too large, calculations do not converge for this mixture and so the results cannot be compared.

4. Conclusions

In this work, instead of using T_c prediction through T_b as is done in the Joback method, a relationship between T_b/T_c and T_c is developed from the data for constituent chemical families. Using a 15 constant BWR EoS with the predicted parameters obtained in this work, properties of pure substances or mixture properties can be predicted and in the systems studied are shown to compare well with experimental data. Some of the specific conclusions for the chemical systems studied are:

1. Application of the method to diglymes, triglymes and tetraglymes, whose molecular weights range from 134 to 222, gives excellent vapor pressure prediction with 3–9% deviations in saturated liquid densities. Moreover, predicted critical parameter values gave excellent vapor–liquid phase equilibria correlations for CO_2 -glyme systems with 4–8% deviation in saturated liquid density and 1% deviation in vapor density.
2. For the system of oleic acid and its mixtures with CO_2 , the proposed method allows excellent prediction of the vapor pressure of oleic acid compared to the Joback method and the solubility of H_2 in oleic acid can be calculated over a wide range of conditions.
3. Solubility of CO_2 in triolein is also well correlated between 353.19 K and 413.19 K. Calculations made with the critical parameters obtained from the Joback method did not converge, whereas parameters predicted with the proposed method provide good correlations of the vapor–liquid equilibria
4. For polyalkylene glycol-1 with a molecular weight of 1100 the critical temperature of PAG-1 is found to be 842 K, whereas it is estimated to be 8541 K with the Joback method. Parameters obtained from the proposed method allow the determination of PAG-1 - CO_2 vapor liquid equilibria.

The formulation and functional form of the proposed method has therefore been shown to allow the reliable determination of the critical parameters of high molecular weight molecules. The proposed method is successful as it does not require the calculation of the normal boiling point of the pure substance and compensates for the nonlinearity of the Joback method.

References

- [1] K.G. Joback, R.C. Reid, Estimation of pure-component properties from group-contributions, *Chem. Eng. Commun.* 57 (1987) 233–243.
- [2] L. Constantinou, R. Gani, New group contribution method for estimating properties of pure compounds, *AIChE J.* 40 (1994) 1697–1709.
- [3] J. Marrero, R. Gani, Group-contribution based estimation of pure component properties, *Fluid Phase Equilibria* 183–184 (2001) 183–208.
- [4] J.O. Valderrama, P.A. Robles, Critical properties, normal boiling temperatures, and acentric factors of fifty ionic liquids, *Indus. Eng. Chem. Res.* 46 (2007) 1338–1344.
- [5] Poling, Prausnitz, O'Connell, *Properties of Gases and Liquids*, fifth ed., McGraw-Hill, 2001.
- [6] D. Kodama, M. Kanakubo, M. Kokubo, S. Hashimoto, H. Nanjo, M. Kato, Density, viscosity, and solubility of carbon dioxide in glymes, *Fluid Phase Equilibria* 302 (2011) 103–108.
- [7] NIST data for diglyme: Thermodynamic Properties of Fluid Systems <http://webbook.nist.gov/chemistry/fluid/>.
- [8] H. Nishiumi, S. Saito, Improved generalized BWR equation of state applicable to low reduced temperatures, *J. Chem. Eng. Jap* 8 (1975) 356–360.
- [9] H. Nishiumi, Thermodynamic property prediction of C_{10} to C_{20} paraffins and their mixtures by the generalized BWR equation of state, *J. Chem. Eng. Jpn.* 13 (1980) 74–76.
- [10] H. Nishiumi, Extended BWR Equation of State for Five Polar Substances, *Bulletin of the College of Engineering, Hosei University*, 1984, pp. 13–27.
- [11] T. Arai, H. Nishiumi, Vapor Pressure Calculation for Non-polar Substances Using Generalized Equations of State, *Bulletin of the College of Engineering, Hosei University*, 1986, pp. 19–30.
- [12] H. Nishiumi, S. Kura, T. Yokoyama, Extended BWR equation of state for fluorocarbons, chloroform and carbon tetrachloride, *Fluid Phase Equilibria* 69 (1991) 141–153.
- [13] D.-Y. Peng, D.B. Robinson, *Ind. Eng. Chem., Fundam.* 15 (1976) 59–64.
- [14] H. Nishiumi, S. Saito, Correlation of the binary interaction parameter of the modified generalized BWR equation of state, *J. Chem. Eng. Jpn.* 10 (1977) 176–180.
- [15] H. Nishiumi, Vapor-liquid equilibrium calculation of systems containing hydrogen by extended BWR equation of state, *J. Chem. Eng. Jpn.* 16 (1983) 449–453.
- [16] H. Nishiumi, Vapor-liquid equilibrium calculation of systems containing hydrogen by extended BWR equation of state, *Organ. by Korean Inst Chem. Eng.* (1983) 297–302.
- [17] H. Nishiumi, Pressure determination of vapor-liquid equilibrium using successive substitution method, *J. Chem. Eng. Jpn.* 21 (1988) 210–214.
- [18] H. Nishiumi, M. Fukushima, Correlation of binary interaction parameters of the extended BWR equation of state for systems containing hydrogen, *J. Chem. Eng. Jpn.* 22 (1989) 205–207.
- [19] T. Arai, H. Nishiumi, Correlation of the binary interaction parameter of the Peng-Robinson equation of state, *Hosei Daigaku Kogakubu kenkyu shuho* (1987) 1–20.
- [20] H. Nishiumi, T. Arai, K. Takeuchi, Generalization of the binary interaction parameter of the Peng-Robinson equation of state by component family, *Fluid Phase Equilibria* 42 (1988) 43–62.
- [21] H. Nishiumi, H. Gotoh, Generalization of binary interaction parameters of Peng-Robinson equation of state for systems containing hydrogen, *Fluid Phase Equilibria* 56 (1990) 81–88.
- [22] T. Tsuji, K.H. Ohya, T.A. Hoshina, T. Hiaki, K. Maeda, H. Kuramochi, M. Osako, Hydrogen solubility in triolein, and propane solubility in oleic acid for second generation BDF synthesis by use of hydrodeoxygenation reaction, *Fluid Phase Equilibria* 362 (2014) 383–388.
- [23] T. Tsuji, S. Tanaka, T. Hiaki, R. Saito, Measurements of bubble point pressure for CO_2 + decane and CO_2 + lubricating oil, *Fluid Phase Equilibria* 219 (2004) 87–92.
- [24] Kagaku Benran (Japanese), Maruzen, 2000.
- [25] *Encyclopedia Chimica* (Japanese), Kyouritu Shuppan, 2000.