Journal of Thermal Analysis and Calorimetry, Vol. 95 (2009) 2, 393–396

MEASUREMENT AND PREDICTION OF INFINITE DILUTION ACTIVITY COEFFICIENTS FOR ALKANE IN ALKANE WITHIN WIDE TEMPERATURE

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The infinite dilution activity coefficients of alkane (hexane, octane, decane and dodecane) in alkane (hexadecane and octadecane) were measured in the region of 313–470 K using a gas stripping method. The experimental results were predicted by the modified ASOG previously proposed.

Keywords: *activity coefficient, alkane, ASOG, gas stripping method, infinite dilution, prediction*

Introduction

The accurate design of separation processes requires the knowledge of phase equilibrium behavior. Correlation and prediction of vapor-liquid equilibria (VLE) are usually performed by using activity coefficients for liquid phase. In our previous studies, the infinite dilution activity coefficients were measured for binary systems (alkanol, alkane, alkene, ether, fluoroether and water) using a gas stripping method [1–6]. There are four fundamental techniques for the experimental determination of infinite dilution activity coefficients. They are chromatographic method (gas–liquid chromatography (GLC), Headspace GLC, liquid–liquid chromatography (LLC)), differential ebulliometry method, dew point method and gas stripping method. This gas stripping method is rapid and exact without calibration of the chromatographic detector. In this study, the infinite dilution activity coefficients of alkane (hexane, octane, decane, dodecane) in alkane (hexadecane, octadecane) were measured at 313–470 K using a gas stripping method. This purpose is development for measurement of infinite dilution activity coefficients within wide temperature range.

Previously the Flory–Huggins (FH) part of modified ASOG [7] was examined by using the infinite dilution activity coefficient data of *n*-alkane binary mixtures. The group-interaction (G) part of modified ASOG [7] was improved by introducing the contact probability between groups to give a good correlation for the infinite dilution activity coefficients of binary systems (alkane, alkanol, ether, fluoroether and water) [3–5, 7]. In this study, the modified ASOG was applied to predict the infinite dilution activity coefficients of alkane in alkane.

Experimental

The experimental study was carried out by using the gas stripping method, which is similar to that described by Leroi *et al.* [8]. In the previous papers [1–6], the experimental apparatus and procedure were reported in detail. In this study, the sampling valve (Valco, A4C6UWE) was placed in column oven gas chromatograph and diluter glass cell was connected to

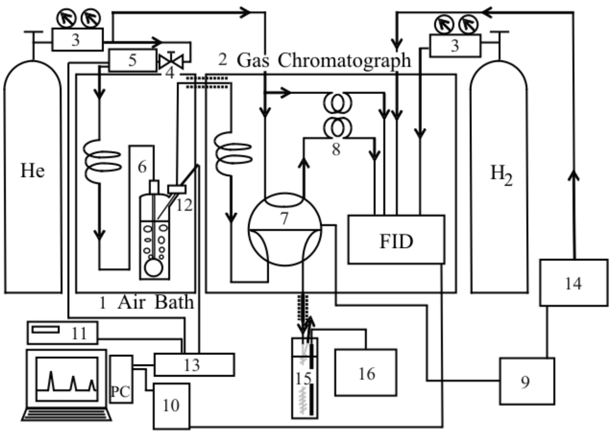

Fig. 1 Experimental apparatus (3 – flow control valve, 4 – heat exchanger, 5 – mass flow meter, 6 – dilutor, 7 – sampling tube, 8 – column, 9 – remote control timer, 10 – PC integrator, 11 – digital barometer, 12 – thermo sensor, 13 – PVT remote scanner, 14 – air compressor, 15 – cold trap, 16 – refrigerator)

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1388–6150/$20.00

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stainless column by the reducing union (Swagelok) with the Teflon ferrule as shown in Fig. 1. The equilibrium cell was thermostatically controlled within ±0.1 K. Temperatures in equilibrium cell and air bath (Koyo, KLO-30M) were measured by thermo sensor (PT100). The inert gas (helium) flow rate was controlled by flow control valve and measured by a mass flow meter (Kofloc, Model 3100) with integrating unit (Kofloc, CR-500). The amount of solute carried with helium was analyzed by using a gas chromatograph with FID (GL Sciences, GC-4000) and an integrator (Hitachi, D-7000i). The PVT remote scanner (NEC, Jr DC3100) was connected to thermo sensor, flow meter and the digital barometer (Okano Works, AVG134N11) with personal computer. The present data are considered to be accurate to within 3%.

The organic compounds used in this study were of guaranteed reagent grade and their purities are reported by the supplier (Nacalai Tesque Co.) to be better than 99%. They were used as received because no significant impurities were detected on gas chromatography. The purities of carrier gas (He) and hydrogen are reported by the supplier (Sumitomoseika Co.) to be better than 99.995%.

The infinite dilution activity coefficient for a volatile solute (1) in a volatile or non volatile solvent (2) can be determined by the following equation [8].

$$\ln(S_1/S_0)=(\gamma_1^\infty p_1^0/p_2^0-1)\ln[1-\{P/(P-p_2^0)\}\{Dp_2^0/(N_2)_0RT\}t] \qquad (1)$$

where S, p^0, P, D, N_2, R, T and t are peak area of solute (m^2), vapor pressure of pure substance (Pa), total pressure (Pa), flow rate of carrier gas ($m^3\ s^{-1}$), amount of solvent (mol), gas constant ($J\ mol^{-1}\ K^{-1}$), temperature (K) and time (s) respectively. A detail procedure to determine the infinite dilution activity coefficient, γ_1^∞, has been shown in elsewhere [1, 2]. p^0 was calculated by the Antoine equation (Table 1) [9]. The experimental infinite dilution activity coefficients of alkane (hexane, octane, decane and dodecane) are presented in Tables 2 and 3, and illustrated in Fig. 2. As shown in Fig. 2, the literature experimental

Table 1 Constants of Antoine equation

Component	A	B	C	Ref.
Hexane	15.8366	2697.55	–48.78	[9]
Octane	15.9426	3120.29	–63.63	[9]
Decane	16.0114	3456.80	–78.67	[9]
Dodecane	16.1134	3774.56	–91.31	[9]
Hexadecane	16.1841	4214.91	–118.7	[9]
Octadecane	16.1232	4361.79	–129.9	[9]

$\ln(p^0)=A-B/(T+C)$; T(K), p^0 (mmHg)

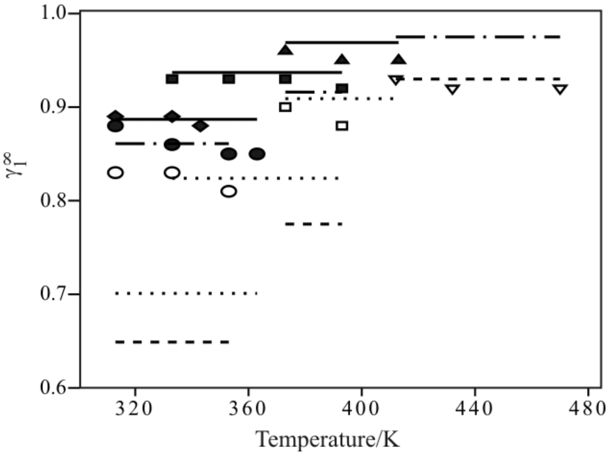

Fig. 2 Infinite dilution activity coefficients γ_1^∞ of alkane in alkane (● – hexane in hexadecane, ◆ – hexane in hexadecane [10], ■ – octane in hexadecane, ▲ – decane in hexadecane, ○ – hexane in octadecane, □ – octane in octadecane, ▽ – dodecane in octadecane, solid line – modified ASOG [7] for alkane in hexadecane, dot-dash line – modified ASOG for alkane in octadecane, dotted line – original ASOG [11] for alkane in hexadecane, broken line – original ASOG for alkane in octadecane)

Table 2 Infinite dilution activity coefficients of alkane in hexadecane

Solute	313 K	333 K	353 K	363 K	373 K	393 K	413 K
Hexane	0.88	0.86	0.85	0.85			
Octane		0.93	0.93		0.93	0.92	
Decane					0.96	0.95	0.95

Table 3 Infinite dilution activity coefficients of alkane in octadecane

Solute	313 K	333 K	353 K	373 K	393 K	412 K	432 K	470 K
Hexane	0.83	0.83	0.81					
Octane				0.90	0.88			
Dodecane						0.93	0.92	0.92

data [10] at 313–343 K show good agreement with the present experimental values.

Prediction by ASOG and modified ASOG

ASOG (Analytical Solution Of Groups) [11] is widely applied to predict the liquid phase activity coefficients. The activity coefficient of component *i* is given as

$$\ln\gamma_i = \ln\gamma_i^{FH} + \ln\gamma_i^{G} \tag{2}$$

where the first term of right-hand side is the combinatorial part due to the entropy of mixing which is given by the Flory–Huggins (FH) equation and the second term is the interaction part between group pairs (*G*).

An improvement of FH part and *G* part were derived in previous study [7]. In present study (alkane in alkane), *G* part is zero. That is $\gamma_i^G=1$. The Flory–Huggins (FH) part is usually expressed by

$$\ln\gamma_i^{FH} = \ln\left(v_i^{FH}/\sum_j v_j^{FH}x_j\right)+1-\left(v_i^{FH}/\sum_j v_j^{FH}x_j\right) \tag{3}$$

where v_i^{FH} and x_j are number of atoms other than hydrogen atom in molecule *i* and mole fraction of molecule *j*. Then, the FH part at infinite dilution condition for alkane binary mixtures can be reduced as

$$\ln\gamma_1^{FH\infty} = \ln(C_1^*/C_2^*)+1-(C_1^*/C_2^*) \tag{4}$$

where C_i^* denotes the modified carbon number and is given by

$$C_i^* = 1+\alpha(C_i-1)+(1-\alpha)(C_i-1)^{\beta} \tag{5}$$

Equation (5) is essentially empirical and α=0.1 and β=0.5 are found for alkane binary mixtures. In case of alkane in alkane, the original ASOG [11] can use the carbon number as group number. The modified ASOG model [7] applied the modified carbon number C_i^* using Eq. (5) instead of the carbon number. The carbon number, C_i, adopted in Eq. (5) should be replaced by the effective carbon number (ECN) [12] to apply Eq. (6) to components other than alkane [7].

$$ECN = -0.11630-0.019376T_b+1.1596\cdot10^{-4}T_b^2 -1.5491\cdot10^{-7}T_b^3+1.3513\cdot10^{-10}T_b^4+0.19102T_b^{1/2} \tag{6}$$

where T_b is the normal boiling point in Table 4 [9]. The calculated results are presented Figs 2 and 3 with a good prediction performance. This modified ASOG is better than original ASOG without dodecane in octadecane. This model should be re-examined when many data can be available in the future work.

Table 4 Normal boiling point T_b [9], effective carbon number *ECN*, modified carbon number C^*

Compound	T_b/K	*ECN*	C^*
Hexane	341.85	6	3.51
Octane	398.75	8	4.08
Decane	447.3	10	4.60
Dodecane	489.5	12	5.08
Tetradecane	526.66	14	5.54
Hexadecane	559.95	16	5.99
Octadecane	589.5	18	6.41

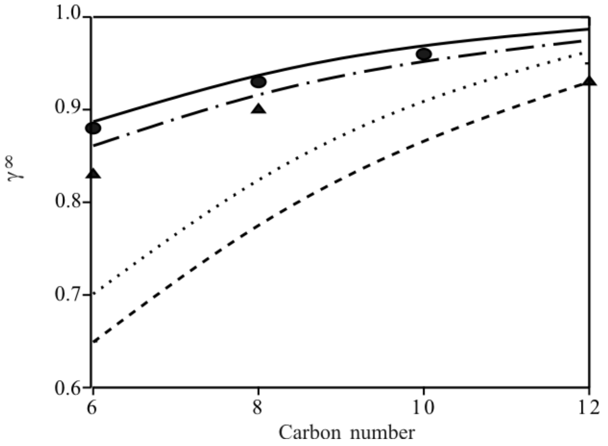

Fig. 3 Infinite dilution activity coefficients γ^∞ of alkane in hexadecane and octadecane (● – hexadecane, ▲ – octadecane, solid line – modified ASOG [7] for alkane in hexadecane, dot-dash line – modified ASOG for alkane in octadecane, dotted line – original ASOG [11] for alkane in hexadecane, broken line – original ASOG for alkane in octadecane)

Conclusions

The infinite dilution activity coefficients of alkane (hexane, octane, decane and dodecane) in alkane (hexadecane and octadecane) were measured in the region of 313–470 K using the gas stripping method. The apparatus was made for accurate measurement of infinite dilution activity coefficients within wide temperature. The experimental results were predicted by the modified ASOG previously proposed. Predicted results by the modified ASOG show good agreement with the experimental infinite dilution activity coefficients. A modified ASOG previously proposed seems to be useful.

Acknowledgements

The authors would like to acknowledge Mr. Norio Sunamachi for his helpful experimental work and preparing this manuscript.

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DOI: 10.1007/s10973-008-9244-3