

Measurement of Infinite-dilution Activity Coefficients of Alcohols in Water Using Relative Gas-liquid Chromatographic Method

Katsumi Tochigi, Masanori Uchiyama and Kazuo Kojima

College of Science and Technology, Nihon University, 1-8 Surugadai, Kanda, Chiyoda-ku, Tokyo, Japan

(Received 30 September 1999 • accepted 20 July 2000)

Abstract—Infinite-dilution activity coefficients of n-alcohols (C_1 - C_8) in water were measured by using the relative gas-liquid chromatographic method proposed by Orbey and Sandler [1991]. The temperature range of measurement was 298 to 343 K. The γ^∞ values at 298.15 K varied from 1.72 (methanol) to 1970 (n-heptanol). ASOG, UNIFAC, modified UNIFAC (Dortmund), modified UNIFAC (Lyngby) group contribution methods could predict γ^∞ to within 16.9, 28.8, 23.9 and 31.8 average percent error, respectively, for all systems and temperatures.

Key words: Measurement, Infinite-Dilution Activity Coefficients, Relative Gas-Liquid Chromatography, ASOG, UNIFAC

INTRODUCTION

Contaminants in ground water have become an increasing concern in environmental and waste management. Infinite-dilution activity coefficients (γ^∞) represent an important property for estimating the extent of contamination and for developing processes for contaminant removal. For measuring γ^∞ , various methods have been proposed, namely, gas-liquid chromatographic (GLC) method, dilutor method, liquid-liquid chromatography, vapor-liquid equilibrium and Rayleigh distillation method [Gmehling et al., 1994]. Among these methods, GLC seems to offer a convenient method of determining γ^∞ . However, application of the GLC method for solutes in volatile solvents has some practical difficulties. Orbey and Sandler [1991] proposed a relative gas-liquid chromatographic method (RGLC) that can be applied reliably to volatile solvents. In this method, the ratio of the infinite dilution activity coefficients is related to the ratio of the pure component saturated fugacities multiplied by a relative retention time factor.

This paper deals with the measurement of γ^∞ of n-alcohols (C_1 - C_8) in water by RGLC. The temperature range of measurement is 298 to 343 K. The experimental values are then compared with the predicted values by using ASOG, UNIFAC and modified UNIFAC group contribution methods [Tochigi et al., 1990; Hansen et al., 1991; Gmehling et al., 1993; Larsen et al., 1987].

CALCULATING EQUATION OF γ^∞ BY RELATIVE GAS-LIQUID CHROMATOGRAPHIC METHOD

The infinite-dilution activity coefficient of solute 1 in solvent 2 is obtained by the following equation [Gmehling et al., 1994],

$$\gamma_1^\infty = RT\phi_1 Z / V_g^0 M_2 \phi_1^s P_1^s \quad (1)$$

where P_1^s is vapor pressure of solute 1, ϕ_1^s is fugacity coefficient of pure component 1, and V_g^0 is specific retention volume obtained from the retention times of solute and of inert gas.

We note that for two solutes, A and B, that are injected into the gas chromatograph simultaneously and are completely separated by the column, the following relation can be written for the ratio of their infinite-dilution activity coefficients [Orbey and Sandler, 1991];

$$\gamma_A^\infty / \gamma_B^\infty = (\phi_B^s P_B^s / \phi_A^s P_A^s) \alpha_{BA} \quad (2)$$

$$\text{where } \alpha_{BA} = (t_B - t_{ref}) / (t_A - t_{ref}) \quad (3)$$

In Eq. (3), t_A , t_B and t_{ref} are the retention times of two solutes A, B and a reference substance. Here t_{ref} is the value necessary for correcting the apparent retention times of solutes A and B according to the hold-up time of carrier gas.

If one assumes that the column pressure is so low that the gas-phase nonidealities can be completely neglected, then Eq. (2) becomes.

$$\gamma_A^\infty / \gamma_B^\infty = (P_B^s / P_A^s) \alpha_{BA} \quad (4)$$

From Eq. (2), it can readily be seen that when the net retention times of two components are determined simultaneously and with precise knowledge of the activity coefficient at infinite dilution of one of the solutes, the unknown γ^∞ -values can be determined. With this method, measurements of the mass of the stationary phases of the solvent and the velocity of the carrier gas, which are necessary to obtain V_g^0 , are no longer needed. For evaluation of γ^∞ , only chromatographic retention times of the solutes and reference are needed along with the vapor pressures of the solutes and second Virial coefficients at the given experimental conditions.

EXPERIMENTAL

1. Apparatus and Procedure

The apparatus used is schematically shown in Fig. 1 [Uchiyama et al., 1996] and is similar to that which was used by Orbey and Sandler [1991]. The apparatus is composed of a gas chromato-

¹To whom correspondence should be addressed.

E-mail: tochigi@chem.cst.nihon-u.ac.jp

This paper was presented at The 8th APCChE (Asia Pacific Confederation of Chemical Engineering) Congress held at Seoul between August 16 and 19, 1999.

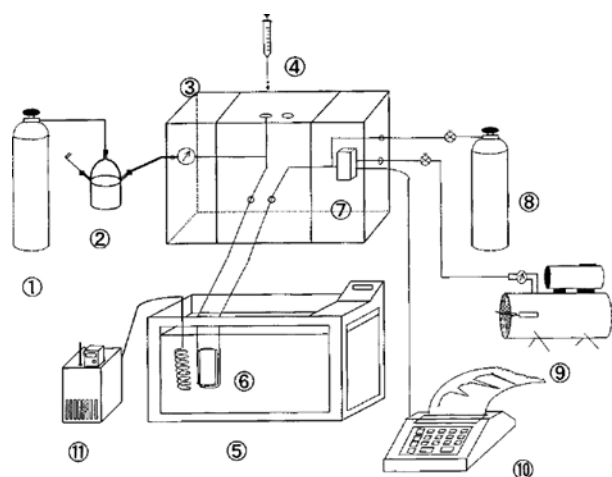


Fig. 1. Apparatus for measuring γ^{∞} of alcohol+water systems.

1. Helium gas
2. Presaturator
3. GC12APF
4. Sample injection port
5. Water bath
6. SUS column
7. Flame ionization detector
8. Hydrogen gas
9. Air compressor
10. Chromatopack (Recorder)
11. Cooler

graph (SHIMAZU GC-12APF equipped with a flame ionization detector), the presaturator to saturate the carrier gas with water, a cooler (YAMATO BK-33) used to control the temperature and a recorder (Shimazu Chromatopack CR-6A).

The experimental procedure was as follows. A 50 cm (or 100 cm) stainless steel GC column (3 mm i.d.) was filled with chromosorb DMCS-80/100 mesh. The column was then filled with

water. Water-saturated helium gas was flowed through the column. A liquid mixture of two solutes and reference substance was injected after a certain period of time and then the retention times of each substance were measured. The pressures at outlet and inlet of the column were measured by an Hg-pressure gauge and a primary pressure gauge in the gas chromatograph. Retention time measurements were carried out 5 or 6 times for each data set and the average values were used. The standard deviations of typical values were 1.4×10^{-3} to 2.1×10^{-2} .

2. Materials

All solutes (methanol, ethanol, n-propanol, n-butanol, n-pentanol, n-hexanol, n-heptanol, n-octanol) and n-pentane used as the reference substance were reagent grade supplied by Wako Chemicals, Ltd. (Japan), and were used in this experiment without further purification processes. The water was passed through an ion exchanger and distilled.

DATA REDUCTION

Ethanol was selected as solute B, because the reliable γ_B^{∞} data shown in Table 1 were available. Experimental data of normal pressure, column pressure at entrance and α_{BA} are shown in Table 1. Table 1 shows the $\gamma_A^{\infty}/\gamma_B^{\infty}$ and γ_A^{∞} in the case that nonideality of vapor phase is calculated using the procedure of Tsonopoulos [1974]. The experimental values are shown in Fig. 2 with literature values [Butler et al., 1935; Kojima et al., 1968; Ochi et al., 1987; Orbey and Sandler, 1991]. From Fig. 2, $\ln \gamma_A^{\infty}$ of methanol and n-propanol decreases with the increase of $1/T$, and this agrees with the signs of partial molar excess enthalpies at infinite dilution obtained from the literature h^E data [Uchiyama et al., 1996].

Table 1. Experimental data of α_{BA} , $\gamma_A^{\infty}/\gamma_B^{\infty}$ and γ_A^{∞} of solute (A) in Water

Solute (A)	Temperature [K]	Normal pressure [mmHg]	Column pressure at entrance [kg/cm ²]	α_{BA}	Non ideal gas		Ideal gas	
					$\gamma_A^{\infty}/\gamma_B^{\infty}$	γ_A^{∞}	$\gamma_A^{\infty}/\gamma_B^{\infty}$	γ_A^{∞}
Methanol	298.2	761.0	3.12	0.915	0.427	1.72	0.425	1.71
	323.2	760.0	2.00	0.772	0.413	2.07	0.410	2.05
	333.2	760.0	2.00	0.722	0.403	2.26	0.400	2.24
n-Propanol	298.2	760.5	2.33	1.22	3.42	13.8	3.44	13.8
	323.2	760.0	2.00	1.38	3.32	16.6	3.35	16.8
	333.2	760.0	2.00	1.42	3.24	18.1	3.28	18.3
n-Butanol	298.2	760.7	1.76	1.43	13.7	55.2	13.8	55.7
	323.2	760.0	2.00	1.79	11.7	58.7	11.9	59.6
	333.2	760.0	2.00	1.87	10.9	61.1	11.1	62.2
n-Pentanol	298.2	756.9	1.76	1.73	41.4	167	41.8	168
	333.2	760.6	0.99	2.53	33.7	189	34.5	193
	343.2	771.5	1.05	2.64	31.2	174	32.1	180
n-Hexanol	298.2	763.2	2.08	2.04	137	552	139	558
	333.2	763.9	1.18	3.11	102	571	105	585
	343.2	765.0	1.09	3.42	95.7	534	98.6	553
n-Heptanol	298.2	759.9	1.69	1.91	490	1970	496	2000
	333.2	762.2	1.14	3.74	321	1800	330	1850
	343.2	751.8	1.20	4.01	273	1530	282	1580
n-Octanol	333.2	762.9	1.44	3.43	833	4660	851	4760

γ_B^{∞} : 298.15 K: 4.03 [Landau et al., 1991]

333.15 K: 5.59 [Pividal et al., 1992]

323.15 K: 5.01 [Prausnitz, 1990]

343.15 K: 5.61 [Prausnitz, 1990]

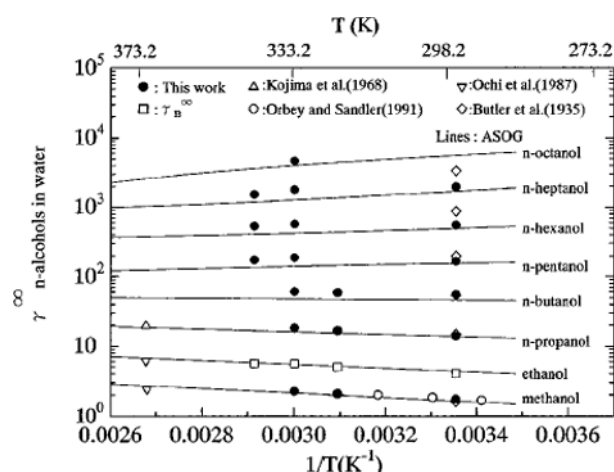


Fig. 2. ASOG predicted infinite-dilution activity coefficient for alcohol+water systems.

PREDICTION OF γ^∞ USING ASOG, UNIFAC AND MODIFIED UNIFAC

Infinite-dilution activity coefficients of n-alcohols in water can be predicted by group contribution methods such as ASOG, UNIFAC and modified UNIFAC. The fundamental equation for activity coefficient is given by the following:

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r \quad (5)$$

where γ_i^c and γ_i^r are the combinatorial and residual parts, respec-

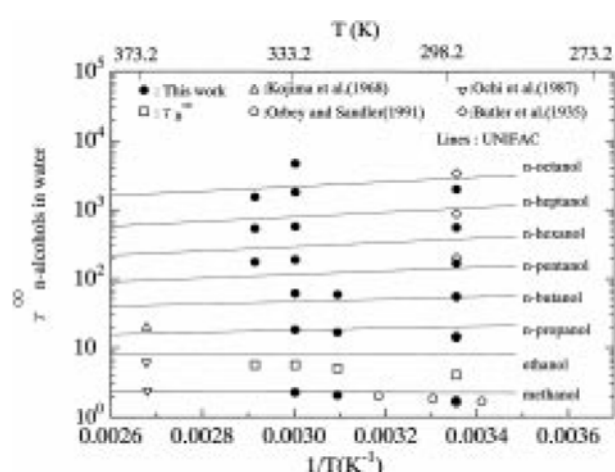


Fig. 3. UNIFAC predicted infinite-dilution activity coefficient for alcohol+water systems.

tively. The residual part is given by the following group activity coefficients:

$$\ln \gamma_i^r = \sum_k v_k (\ln \Gamma_k - \ln \Gamma_k^0) \quad (6)$$

The four models are given by the difference between equations for γ_i^c and Γ_k .

The group pair parameters necessary for Eqs. (5) and (6) have been collected from the literature [Tochigi, 1990; Hansen et al., 1991; Gmehling et al., 1993; Larsen et al., 1987]. The absolute arithmetical deviations between predicted and measured values are

Table 2. Comparison of predicted results of γ_i^∞ using group contribution methods

Solute (A)	Temperature [K]	Experimental data γ^∞	ASOG		UNIFAC		Mod.UNIFAC (Do.)		Mod.UNIFAC (Ly.)	
			γ^∞	$\Delta\gamma$ (%)*	γ^∞	$\Delta\gamma$ (%)*	γ^∞	$\Delta\gamma$ (%)*	γ^∞	$\Delta\gamma$ (%)*
Methanol	298.15	1.72	1.50	12.7	2.24	30.2	1.67	2.9	1.82	5.8
	323.15	2.07	1.86	10.1	2.27	9.7	1.94	7.7	2.13	2.9
	333.15	2.26	2.02	10.6	2.28	0.9	2.05	9.3	2.22	2.2
n-Propanol	298.15	13.8	14.1	2.2	20.1	45.6	14.0	1.4	12.5	9.4
	323.15	16.6	15.3	7.8	18.5	11.4	14.9	10.2	15.9	4.2
	333.15	18.1	15.9	12.2	17.9	1.1	15.1	16.6	17.0	6.1
n-Butanol	298.15	55.3	45.7	17.4	54.0	2.41	41.0	24.1	30.2	45.4
	323.15	58.7	46.4	21.0	47.9	18.4	43.0	26.7	40.5	31.0
	333.15	61.1	46.8	23.4	45.8	25.0	42.9	29.8	43.9	28.2
n-Pentanol	298.15	167	150	10.2	148	11.4	129	22.7	75.6	54.7
	323.15	189	140	25.9	119	37.0	124	34.4	117	38.1
	343.15	174	138	20.7	113	35.1	120	31.0	126	27.6
n-Hexanol	298.15	552	494	10.5	408	26.1	403	27.0	195	64.7
	323.15	571	421	26.3	311	45.5	364	36.2	322	43.6
	343.15	534	407	23.8	291	45.6	346	35.2	349	34.6
n-Heptanol	298.15	1970	1630	17.3	1130	42.6	1280	35.0	512	74.0
	333.15	1800	1270	29.4	818	54.6	1080	40.0	900	50.0
	343.15	1530	1200	21.6	755	50.7	1010	34.0	982	35.8
n-Octanol	333.15	4660	3840	17.6	2160	53.6	3230	30.7	2560	45.1
Average dev.				16.9		28.8		23.9		31.8

$$*\Delta\gamma = \left| \frac{\gamma_{exp}^\infty - \gamma_{pred}^\infty}{\gamma_{exp}^\infty} \right| \times 100$$

shown in Table 2. Of the four methods, ASOG provided the most accurate predictions. The predicted results using ASOG and UNIFAC are shown in Figs. 2 and 3, respectively.

CONCLUSIONS

Infinite dilution activity coefficients were measured for n-alcohols in water in the temperature range of 298 to 343 K. Few data exist for these systems that are important for environmental analysis, design and assessment. The ASOG method can predict infinite dilution activity coefficients of alcohol+water systems to within 17% over a moderate (298-343 K) temperature range.

NOMENCLATURE

M_2	: molecular weight of solvent 2
P_A^S, P_B^S	: vapor pressure of solutes A and B
R	: universal gas constant
T	: temperature
t_A, t_B, t_{ref}	: retention time of solutes A, B, and reference substance
V_g^0	: specific retention volume
Z	: compressibility factor
$\alpha_{B,A}$	: ratio of retention times given by Eq. (3)
Γ_k	: group activity coefficient of group k
$\Gamma_k^{(i)}$	: group activity coefficient of group k in pure component i
γ_i	: activity coefficient of component i
γ_i^C	: combinatorial part of activity coefficient of component i
γ_i^R	: residual part of activity coefficient of component i
$\gamma_A^\infty, \gamma_B^\infty$	: infinite dilution activity coefficients of solutes A, B in water
ϕ_A, ϕ_B	: fugacity coefficients of component A and B at pressure in the gas phase
ϕ_A^S, ϕ_B^S	: fugacity coefficients of pure components A and B at

their saturation pressure
 v_k : number of group k in molecule i

REFERENCES

- Butler, J. A., Ramchandani, C. N. and Thomson, D. W., "The Solubility of Non-electrolytes. Part I. The Free Energy of Hydration of Some Aliphatic Alcohols," *J. Chem. Soc.*, 280 (1935).
- Gmehling J., Li, J. and Schiller, M., "A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties," *Ind. Eng. Chem. Res.*, **32**, 178 (1993).
- Gmehling, J., Menke, J. and Schiller, M., "Activity Coefficients at Infinite Dilution C₁-C₉," DECHEMA Chemistry Data Series, Vol. IX, Part 3, Frankfurt (1994).
- Hansen, H. K., Rasmussen, P., Fredenslund, Aa., Schiller, M. and Gmehling, J., *Ind. Eng. Chem. Res.*, **30**, 2352 (1991).
- Kojima, K., Tochigi, K., Seki, H. and Watase, K., "Determination of Vapor-Liquid Equilibrium from Boiling Point Curve," *Kagaku Kagaku*, **32**, 149 (1968).
- Larsen, B. L., Rasmussen, P. and Fredenslund, Aa., "A Modified UNIFAC Group-Contribution Model for Prediction of Phase Equilibria and Heats of Mixing," *Ind. Eng. Chem. Res.*, **26**, 2274 (1987).
- Ochi, K. and Kojima, K., "A Measurement of Vapor-Liquid Equilibria at Extreme Dilution," *J. Chem. Eng. Jpn.*, **20**, 6 (1987).
- Orbey, H. and Sandler, S. I., "Relative Measurements of Activity Coefficients at Infinite Dilution in Volatile Solvents by Gas-Liquid Chromatography," *Ind. Eng. Chem. Res.*, **30**, 2006 (1991).
- Tochigi, K., Tiegs, D., Gmehling, J. and Kojima, K., "Determination of New ASOG Parameters," *J. Chem. Eng. Jpn.*, **23**, 453 (1990).
- Tsonopoulos, C., "An Empirical Correlation of Second Virial Coefficients," *AIChE J.*, **33**, 263 (1974).
- Uchiyama, M., Tochigi, K. and Kojima, K., "Measurement of Infinite-Dilution Activity Coefficients of Alcohols in Water Using Relative Gas-Liquid Chromatograph Method," Preprints of 61st annual meeting of SCEJ, paper no. G203, Nagoya (1996).