J. Chem. Eng. Data **2003,** *48,* 167−170 **167**

Infinite Dilution Activity Coefficients in Ethylene Glycol and Ethylene Carbonate

Suojiang Zhang,*,[†] Akio Tsuboi,[‡] Hiroaki Nakata,[‡] and Takeshi Ishikawa[‡]

Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100080, China, and Process Engineering Research Center, Mitsubishi Chemical Corporation (MCC), Kurashiki 712-8054, Japan

Infinite dilution activity coefficients (γ^∞) have been determined by using a gas−liquid chromatography (GLC) technique for benzene, toluene, methanol, ethanol, 2-propanol, and acetaldehyde in ethylene glycol and ethylene carbonate in a range of temperatures from 50 to 110 °C. In the literature, there were no reported data for γ^∞ for any of the studied solutes in ethylene carbonate or for acetaldehyde in ethylene glycol. A few γ^∞ data were available for benzene, toluene, methanol, and 2-propanol in ethylene glycol, but they were limited to a low-temperature range (<70 °C). The measured γ^∞ data in this work therefore provide a good source of γ^∞ data in the higher temperature region.

Introduction

Infinite dilution activity coefficients (γ^∞) are very useful for process synthesis and design. For example, infinite dilution activity coefficients can be directly used for the selection of solvents for azeotropic/extractive distillation, liquid extraction, solvent-aided crystallization, and even chemical reaction.[1] γ^∞data for each species in the other can be used to determine g^E model parameters and predict VLE over the whole composition range. Also, γ^∞ data provide valuable information for testing predictive models[2−4] or computer simulation methods, because values of γ^∞ give a direct measure of interactions between unlike molecules in the absence of solute−solute interactions.

A number of experimental techniques are available for direct measurement of γ^∞, including gas−liquid chromatography (GLC), relative GLC,[5] differential ebulliometry, headspace, gas-stripping, and dew point. Each of these techniques has some limitations,[6] and therefore one may be most suitable within certain regions, as shown approximately in Figure 1. In a practical application, it is certainly important to choose the most suitable technique for a specific problem.

Gas−liquid chromatography was chosen in this work due to its characteristics. For example, it is fast and accurate and requires only a small amount of the required agent. In fact, a large amount of the γ^∞ data has been determined with the GLC technique in the literature; however, most of them are limited in the temperature range from 20 to 50 °C. There is a serious lack of experimental data of γ^∞ in a higher temperature range, for example, 50 to 150 °C. In this work, infinite dilution activity coefficients for six solutes (benzene, toluene, methanol, ethanol, 2-propanol, and acetaldehyde) in ethylene glycol and ethylene carbonate have been determined in the higher temperature region from 50 to 110 °C. The measured data in this work, to some extent, compensate for the lack of γ^∞data in the higher temperature range.

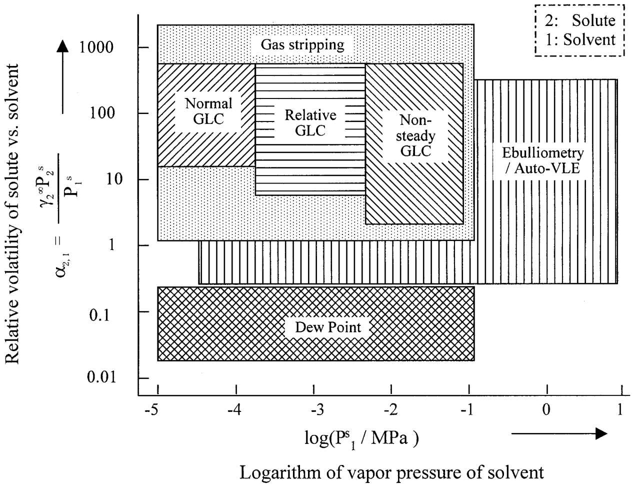


Figure 1. Approximate applicable range of a variety of techniques for determination of γ^∞.

Experimental Section

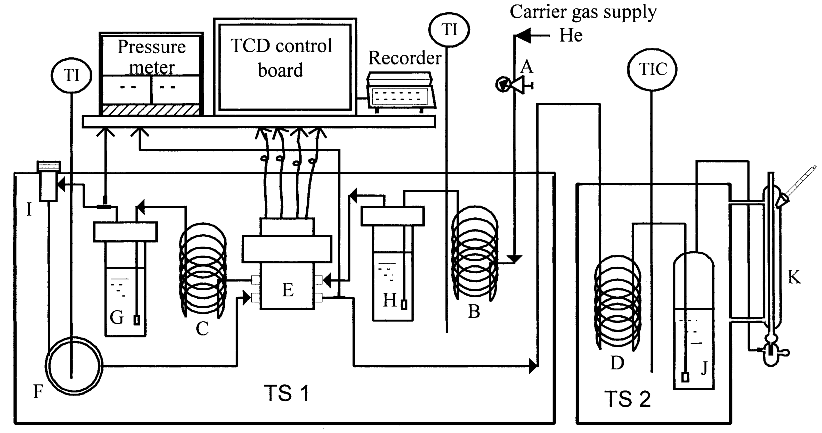
A schematic diagram of the GLC apparatus is shown in Figure 2. To prevent solvent loss and correct for solvent loss during the measurements, the following procedures are carried out: (1) The carrier gas is saturated with the solvent by passing it through two presaturators H and G. (2) The column F is kept as short as possible to minimize the pressure drop. (3) To determine the actual mass of solvent in the stationary phase, an interpolation is carried out between the beginning and the end of a series of measurements over an interval of time. Such an interpolation method is verified by injecting a test solute with a known value of γ^∞ and then back-calculating the solvent amount. The results obtained are in good agreement by using both approaches. (4) Solvent loading is about 20 wt % on Chromosorb W (45/60 meshes), and the injection amount of solute is varied over a wide range of 0.005 to 1 μL to ensure operation at equilibrium and at infinite dilution.

The infinite dilution activity coefficients are obtained from eqs 1 and 2:[15]

---

* To whom correspondence should be addressed. Telephone/Fax: +86-10-8262-7080. E-mail: sjzhang@home.ipe.ac.cn; zhangsj_0@yahoo.com.
[†] Chinese Academy of Sciences.
[‡] Mitsubishi Chemical Corporation (MCC).

10.1021/je0102107 CCC: $25.00



A	- needle valve	F	- G.C. column	K	- soap bubble flowmeter
B	- preheating coil	G,H	- solvent saturator	TS 1	- G.C. air thermostat
C,D	- tempering coil	I	- injector	TS 2	- water thermostat bath
E	- TCD detector	J	- water saturator	TI,TIC	- temp. sensor or control

Figure 2. Schematic diagram of the GLC apparatus for measurement of γ^∞.

$$\gamma_2^\infty = \frac{273.15R}{v_g^\circ p_2^s \varphi_2^s M_1} \qquad (1)$$

$$v_g^\circ = \frac{F}{w_1}\frac{P_{fm} - P_w^s}{P_{out}}\frac{273.15}{T_{fm}}\frac{3}{2}\frac{(P_{in}/P_{out})^2 - 1}{(P_{in}/P_{out})^3 - 1}(t_r - t_a) \qquad (2)$$

where R is the gas constant, M_1 is the molecular weight of the solvent, w_1 is the total amount of the coated solvent in the stationary phase, and P_2^s is the saturated vapor pressure of the solute calculated by using the Antoine equation with the parameters taken from the Dortmund Data Bank (DDB). The saturation fugacity coefficient φ_2^s is calculated by using the truncated virial equation.[7] v_g° is known as the specific net retention volume corrected to 0 °C. The quantity t_r is the retention time of the solute, and t_a is the dead time required for an inert gas to pass through the column. F is the volume flow rate of carrier gas at the soap bubble flow meter, where T_{fm} and P_{fm} are the temperature and pressure. P_{in} and P_{out} are the column inlet and outlet pressures, and P_w^s is the saturation vapor pressure of water at T_{fm}.

The contributions from the measurement of solvent mass in the stationary phase and the net retention time to the error in V_g° are important, whereas the contributions of the operating parameters, including carrier gas flow rate, column inlet and outlet pressures, temperature, and pressure at the flow meter, are comparatively negligible. The mean error in the determination of the infinite dilution activity coefficients is estimated from a consideration of all sources of errors to be about 3.04% in this work. This lies within the range of the normal errors in the measurement of γ^∞ by using the gas chromatography technique.[15]

By following the above procedures with the GLC, the infinite dilution activity coefficients were measured for several solutes including benzene, toluene, methanol, ethanol, 2-propanol, and acetaldehyde in ethylene glycol and ethylene carbonate in the temperature range from 50 to 110 °C. One exception should be noted here: that the measurement has not been carried out for ethanol in ethylene glycol.

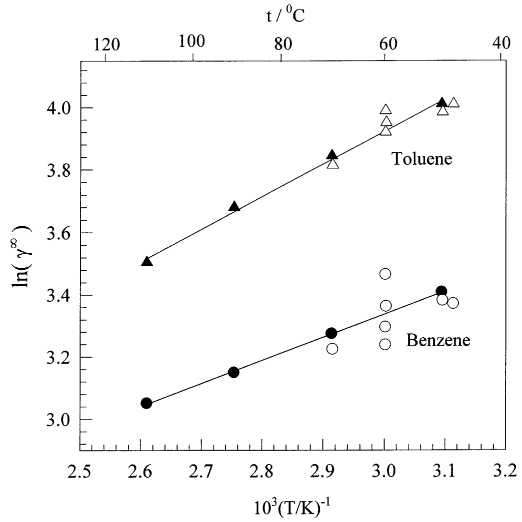


Figure 3. Infinite dilution activity coefficients for benzene and toluene in ethylene glycol: ●, benzene, this work; ○, benzene;[8−10] ▲, toluene, this work; △, toluene.[8−12]

Table 1. Experimental γ^∞ Values of Various Solutes in Ethylene Glycol

	γ^∞				
T/°C	benzene	toluene	acetaldehyde	methanol	2-PrOH
50	30.23	55.15	5.927	1.230	3.019
70	26.44	46.71	5.053	1.241	2.803
90	23.34	39.65	4.221	1.320	2.590
110	21.14	33.26	3.490	1.271	2.371

Table 2. Experimental γ^∞ Values of Various Solutes in Ethylene Carbonate

	γ^∞					
T/°C	benzene	toluene	acetaldehyde	methanol	ethanol	2-PrOH
50	5.081	6.624	2.238	3.208	4.362	5.625
70	4.831	6.360	1.984	3.033	4.090	5.058
90	4.618	6.110	1.752	2.718	3.821	4.657
110	4.417	5.790	1.514	2.460	3.357	4.360

Results and Discussion

The experimental values of γ^∞ are presented in Tables 1 and 2. In Figures 3−6, linear relationships were shown between the natural logarithm of γ^∞ and the inverse temperature for all the studied systems, and the values of γ^∞ were shown to decrease with increasing temperature for most of the studied systems. One exception is the system for methanol in ethylene glycol, where the values of γ^∞ slightly increase with increasing temperature.

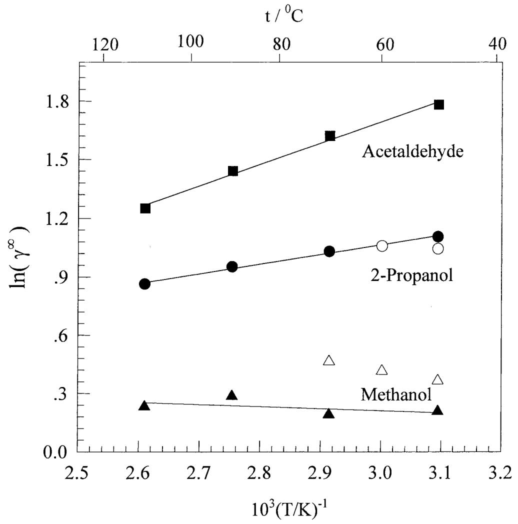


Figure 4. Infinite dilution activity coefficients for acetaldehyde, methanol, and 2-propanol in ethylene glycol: ▲, methanol, this work; △, methanol;[14] ●, 2-propanol, this work; ○, 2-propanol.[13]

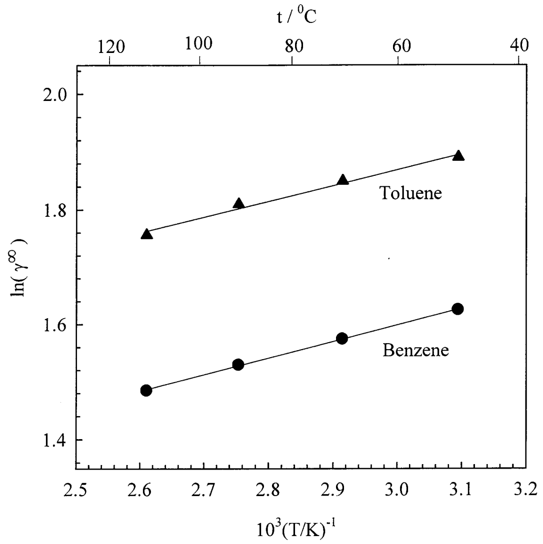


Figure 5. Infinite dilution activity coefficients for benzene and toluene in ethylene carbonate.

There are a few published γ^∞ data for benzene, toluene, methanol, and 2-propanol in ethylene glycol in the lower temperature range (<70 °C).[8-14] These data are plotted in the figures for comparison. It can be seen that our measured data show good accuracy and consistency when compared to the data reported in the literature. For methanol in ethylene glycol, the measured data show a similar temperature dependency, although the absolute values in our measurements are slightly lower than those reported in the literature.[14] The comparisons are not possible for acetaldehyde in ethylene glycol and for all the studied solutes in ethylene carbonate, because there are no γ^∞ data to be found for these systems in the open literature.

Conclusions

Infinite dilution activity coefficients for six solutes (benzene, toluene, methanol, ethanol, 2-propanol, and acetaldehyde) in ethylene glycol and ethylene carbonate have been measured at different temperatures by using the GLC method. The natural logarithms of the measured data of γ^∞ show a good linear relationship with the inverse temperatures. Also, our measured data show good accuracy and consistency when compared to literature data. In fact, the experimental data of γ^∞ in the higher temperature range (e.g., 50 to 150 °C) are extremely scarce; therefore, the measured data in this work provide a good source of data in the higher temperature region.

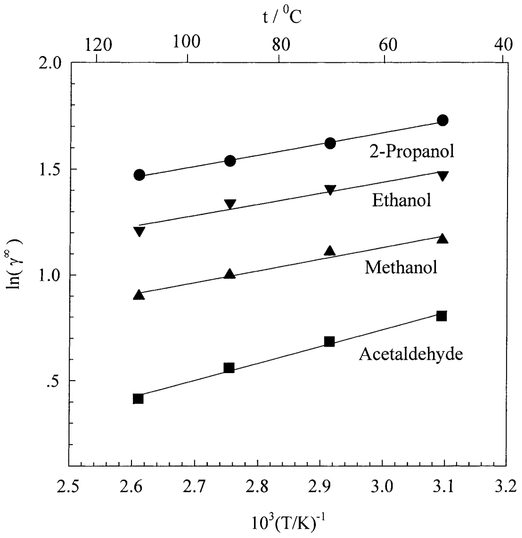


Figure 6. Infinite dilution activity coefficients for acetaldehyde, methanol, ethanol, and 2-propanol in ethylene carbonate.

Literature Cited

(1) Wong, K. F.; Eckert, C. A. Dilute Solution Behavior of Two Cyclic Anhydrides. *Ind. Eng. Chem. Fundam.* **1971**, *1*, 20−23.
(2) Zhang, S.; Hiaki, T.; Kojima, K. Prediction of Infinite Dilution Activity Coefficients in Aqueous Solutions by Group Contribution Models. A Critical Evaluation. *Fluid Phase Equilib.* **1998**, *144*, 97−112.
(3) Zhang, S.; Hiaki, T.; Kojima, K. Prediction of Infinite Dilution Activity Coefficients for Systems Including Water Based on Group Contribution Method with Mixture-Type Groups. I. Alkane-H_2O and Alkanol-H_2O. *Fluid Phase Equilib.* **1998**, *149*, 27−40.
(4) Zhang, S.; Hiaki, T.; Kojima, K. Prediction of Infinite Dilution Activity Coefficients for Systems Including Water Based on Group Contribution Method with Mixture-Type Groups. II. Extension and Application. *Fluid Phase Equilib.* **2002**, *198*, 15−27.
(5) Orbey, H.; Sandler, S. I. Relative Measurements of Activity Coefficients at Infinite Dilution by Gas Chromatography. *Ind. Eng. Chem. Res.* **1991**, *30*, 2006−11.
(6) Kojima, K.; Zhang, S.; Hiaki, T. Measuring Methods of Infinite Dilution Activity Coefficients and Database for Systems Including Water. *Fluid Phase Equilib.* **1997**, *131*, 145−179.
(7) Hayden, J. G.; O'Connel, J. P. Generalized Method for Predicting Second Virial Coefficient. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209−16.
(8) Sarius, A.; Lempe, D.; Bittrich, H. J. Studies on Selective Material Separation. Part III. Limiting Activity Coefficients of Hydrocarbons in Various Selective Solvents. *Chem. Tech. (Leipzig)* **1978**, *30*, 585−6.
(9) Bender, A. O.; Zainel, H. A.; Sarkissian, T. M.; Talib, E. K. A Study of the Effect of Ethylene Glycol on the Extraction Properties of N-Formylmorpholine by GLC. *J. Pet. Res.* **1988**, *7*, 131−44.
(10) Pavlova, O. P.; Gaile, A. A.; Proskuryokov, V. A. Effect of the Structure of Solvents and Separable Components on Selectivity. XII. Selectivity and Solvent Action in Relation to Hydrocarbons on Azeotropic Mixtures of Solvents. *Zh. Fiz. Khim.* **1971**, *45*, 76−81.
(11) Van Aken, A. B.; Broersen, J. M. Selectivity and Solvency Properties of Extraction Solvents and Their Mixtures. *CIM Spec.* **1979**, *21* (2, Proc. Int. Solvent Extr. Conf., 1977), 693−700.
(12) Oveckova, J.; Graczova, E.; Surovy, J. Influence of Nonideality of a Ternary Solvent on its Extraction Characteristics. *Collect. Czech. Chem. Commun.* **1990**, *55*, 1465−71.
(13) Gmehling, J. *Dortmund Databank (DDB)*; Electronic version (2001).
(14) Zhao, C.; Chen, M.; Zhao, C. Relative Volatility and Selectivity of Salt-Containing System. *J. Chem. Eng. (China)* **1992**, *20*, 58−60.
(15) Knoop, C.; Tiegs, D.; Gmehling, J. Measurement of γ^∞ Using Gas−Liquid Chromatography. 3. Results for the Stationary Phases 10-

Nonadecanone, N-Formylmorpholine, 1-Pentanol, *m*-Xylene, and Toluene. *J. Chem. Eng. Data* **1989**, *34*, 240−247.

Received for review July 23, 2001. Accepted September 21, 2002. All the authors acknowledge gratefully the financial support of Mitsubishi Chemical Co. S.Z. also acknowledges sincerely the financial support of the National Science Foundation of China and Multiphase Reaction Laboratory of CAS (Chinese Academy of Sciences).

JE0102107