J. Chem. Eng. Data **2004,** *49,* 1429−1432 **1429**

Measurement of Activity Coefficients at Infinite Dilution of Benzene, Toluene, Ethanol, Esters, Ketones, and Ethers at Various Temperatures in Water Using the Dilutor Technique

Zadja Atik,[†] Detlef Gruber,[‡,§] Michael Krummen,[‡,||] and Jürgen Gmehling[*,‡]

University of Sciences and Technology Houari Boumediene, Faculty of Chemistry,
P. O. Box 32 El-Alia, 16111 Bab-Ezzouar, Algeria, and Carl von Ossietzky-Universität Oldenburg,
Institute for Pure and Applied Chemistry, Technische Chemie, D-26111 Oldenburg, Germany

This paper reports experimental activity coefficients at infinite dilution for 16 solutes (benzene, toluene, ethanol, esters, ketones, and ethers) at different temperatures ($308 \le T/\mathrm{K} \le 343$) measured with the help of a dilutor technique (inert gas stripping). The activity coefficients obtained are in good agreement with data derived from LLE data. Furthermore, the partial molar excess enthalpies derived from these data are in agreement with the values derived from enthalpy of mixing data.

Introduction

The existence of water as a unique and the most abundant solvent is characterized by ever-renewed interest in obtaining experimental thermophysical properties of aqueous solutions. The mixture behavior of aqueous solutions is essentially influenced by differences in the size and polarity of water and solutes with very different values of activity coefficients at infinite dilution, making their measurement and correlation challenging.[1]

In recent years, thermodynamic studies at infinite dilution have been devoted to improvements in the knowledge of the phase equilibrium involved in thermal separation processes. For example, for extraction processes a solvent is required, which is characterized by sufficient capacity and high selectivity. Moreover, the elimination of the last traces of a component from a solution requires accurate information about the separation factor at high dilution; these parameters are obtained from activity coefficients at infinite dilution. In G^E models and group contribution methods, activity coefficients at infinite dilution are important quantities for a precise description of the real behavior in the dilute region and an adequate description and the adjustment of reliable group-interaction parameters of modified UNIFAC (Dortmund), thus contributing directly to the development of software tools used for the synthesis and separation processes. [2,3]

Different techniques have been used for the measurement of activity coefficients at infinite dilution: static methods, differential ebulliometry, gas−liquid chromatography, Rayleigh distillation, and the dilutor technique. The dilutor technique combines inert gas stripping and gas−liquid chromatography.[4−9] The dilutor technique has various potential advantages because this technique is capable of measuring small and large values of activity coefficients in pure or mixed solvents with good reproducibility.

In this work, the dilutor technique was used to measure activity coefficients at infinite dilution of aqueous solutions with 16 solutes: benzene, toluene, ethanol, esters (methyl acetate, ethyl acetate, propyl acetate, methyl formate, ethyl formate), ketones (acetone, 2-butanone, and 2-pentanone) and branched ethers (diethyl ether, diisopropyl ether, dipropyl ether, *tert*-amyl methyl ether (TAME), and methyl *tert*-butyl ether (MTBE)).

Experimental Section

Ultrapure-grade helium (Messer-Griesheim, purity of 99.996%) is used as a carrier gas and for line flushing. The solvent was ionized, doubly distilled water. The investigated solutes were all of the highest purities (GC > 99.8%).

A complete description of the dilutor and the experimental procedure has been published.[1,12,13] For a single experiment, up to four solutes can be injected into the measuring cell, whose temperature was measured with a Pt-100 thermometer (model Mesurix 2002A-RC) with a resolution of 0.01 K. The mole fractions of the injected solutes are in the infinite dilution range ($x_i < 10^{-3}$). To be in the homogeneous region, the initial composition was still smaller ($x_i \approx 10^{-4}$) in the case of solutes benzene and toluene.

Decreases in the concentrations of solutes leaving the measuring cell are measured with the help of gas chromatography (United Technologies Packard, model 438A; FID detector, Porapak P column: mesh $^{80}/_{100}$, $^{1}/_{8}$” diameter, 0.66-m length). Only the variation of solute peak areas with time (A_i, t) is required to compute the activity coefficient at infinite dilution.[10] The (A_i, t) chromatograms were recorded and integrated over a period of time via a computer. Typically, 20 concentration recordings are needed to ensure the reliable determination of the solute concentration decrease with time over the whole run. To obtain reliable results, at least 15% of the solute has to be stripped from the solution during a single run.

Results and Discussion

The thermodynamic fundamentals of the dilutor technique have been well described by Krummen et al.[9] The

---

[*] Corresponding author. E-mail: gmehling@tech.chem.uni-oldenburg.de. Fax: +49-441-7983330.

[†] University of Sciences and Technology Houari Boumediene.

[‡] Carl von Ossietzky-Universität Oldenburg.

[§] Present address: Nordland Papier GmbH, P.O. Box 1160, D-26888 Dörpen, Germany.

[||] Present address: Thermo Electron, Barkhausenstrasse 2, D-28197 Bremen, Germany.

10.1021/je049875+ CCC: $27.50

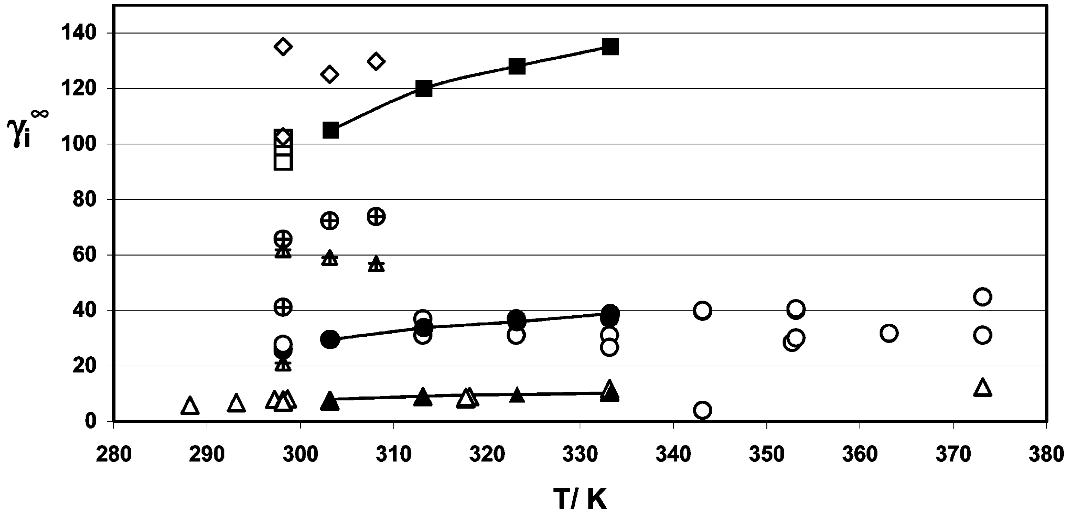

Figure 1. Experimental activity coefficients at infinite dilution of different ketones in water as a function of temperature. Acetone: ▲, new data; △, published data;[17] triangle with cross, published data (LLC).[17] 2-Butanone: ●, new data; ○, published data;[17] ⊕, published data (LLC).[17] 2-Pentanone: ■, new data; □, published data;[17] ◇, published data (LLC).[17]

vapor−liquid equilibrium of component *i* in a real solution is governed by the thermodynamic equation

$$x_i \gamma_i \varphi_i^{s} P_i^{s} \mathrm{Poy}_i = y_i \varphi_i^{V} P \tag{1}$$

where x_i is the mole fraction in the liquid phase, γ_i is the activity coefficient, φ_i^s is the fugacity coefficient in the saturation state, P_i^s is the vapor pressure, Poy_i is the Poynting factor, y_i is the mole fraction in the vapor phase, φ_i^V is the fugacity coefficient in the vapor phase, and P is the total equilibrium pressure. Because the concentration of the solute is at infinite dilution ($x_i < 10^{-4}$, $\gamma_i = \gamma_i^\infty$, $\mathrm{Poy}_i \approx 1.0$, $\phi_i^V \approx 1.0$ (helium as carrier gas)), eq 1 can be simplified to

$$x_i \gamma_i^\infty \varphi_i^s P_i^s = y_i P \tag{2}$$

The concentration decrease (i.e., area decrease A_i (gas chromatogram)) of a solute is linear with time and has a slope of $m = \{\ln(A_i/A_o)\}/t$. Neglecting the solubility of helium in the liquid phase leads to[9]

$$\gamma_i^\infty = -\frac{RTn_j}{((F_{\mathrm{He}}/m) + V_g)\phi_i^s P_i^s} \tag{3}$$

where F_{He} is the helium flow rate, V_g is the vapor volume in the measuring cell, R is the general gas constant, and T is the absolute temperature. The experimental results (T, γ_i^∞) for all solutes investigated are summarized in Table 1. As discussed in different papers, the uncertainty of the γ_i^∞ values derived depends on the pure-component properties (e.g., vapor pressure, second virial coefficients) used, the gas flow rate, temperature, pressure, mass of the solvent, and slope m, whereby the main source of error is the flow rate F_{He}. Thus, the uncertainty of the activity coefficients at infinite dilution given in Table 1 is approximately ±2.5%.[9] This means, for example, that the listed γ^∞ value for toluene at 303.25 K (8570) can vary from 8355 to 8785.

Table 1. Experimental Activity Coefficients at Infinite Dilution γ_i^∞ of Various Solutes in Water at Different Temperatures

	T/K				
solute	303.25	313.25	323.25	333.25	343.25
ethanol	5.03	5.33	5.54	5.76	5.96
acetone	8.02	9.2	9.81	10.3	
2-butanone	29.5	33.8	35.9	38.9	
2-pentanone	105	120	128	135	
diethyl ether	90.1	113	135	158	
diisopropyl ether	737	965	1140	1310	
dipropyl ether	2520	2880	3230	3230	
MTBE	153	195	235	278	
TAME	643	796	942	1080	
methyl acetate	26.2	28.4	29.8	31.2	31.6
ethyl acetate	76.5	85	90.1	94.7	96.2
propyl acetate	297	325	341	351	348
methyl formate	18.7	19.1	19.5	19.8	
ethyl formate	53.79	55.7	57.1	57.7	

	T/K			
solute	308.95	313.25	318.25	323.15
benzene	2470	2370	2250	2140
toluene	8570	8090	7720	7110

In the temperature range covered for all oxygenated solutes, the activity coefficients increase with rising temperature. The data for the ketones and selected ethers are shown in Figures 1 and 2 together with the scattering literature data measured with the help of different techniques[1] . The new γ_i^∞ values are in good agreement with most of the published data obtained by different techniques,[10,11] but it can be recognized that the data are in disagreement with the values measured by liquid−liquid chromatography,[18,19] a fact that has been well known for a long time[1]. Using the new γ_i^∞ values, we can estimate the partial excess molar enthalpies at infinite dilution $H_i^{E\infty}$ of the solutes using the Gibbs−Helmholtz equation:

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial 1/T}\right)_{P,x} = \frac{H_i^{E\infty}}{R} \tag{4}$$

The computed partial molar excess enthalpies at infinite dilution for the solutes are listed in Table 2 together with the values derived from excess enthalpy data. As can be seen, good agreement with the partial molar excess enthalpy data derived from excess enthalpies[12−14] is obtained. Whereas for the oxygenated solutes exothermal values are obtained, for the systems with aromatics (e.g., benzene) endothermal partial molar excess enthalpies are obtained from the γ_i^∞ values measured and the available excess enthalpies. The partial molar excess enthalpies are strongly temperature-dependent, as shown in Table 2 for ethanol. To derive reliable values, in particular, for experimental

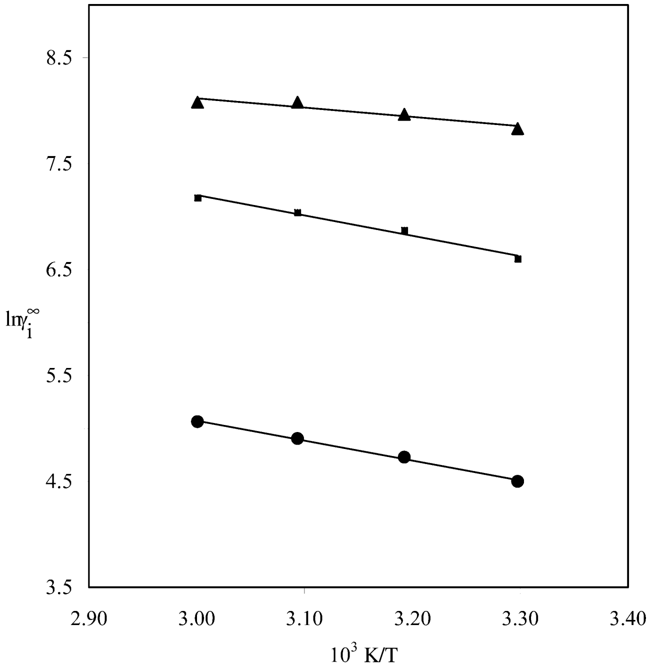

Figure 2. Experimental activity coefficients at infinite dilution of ethers in water as a function of temperature: ▲, dipropyl ether; ■, diisopropyl ether; ●, diethyl ether.

Table 2. Partial Molar Excess Enthalpies Derived from the Experimental γ^∞ Data (h^E Data)

solute	temperature range γ^∞, K	$h_i^{E\infty}$ J/mol	temperature h^E data, K	$h_i^{E\infty}$ J/mol
ethanol	303−343	−3620	298	−10 300
			323	−6400
			343	−4200
acetone	303−333	−6890	318	−5770
2-butanone	303−333	−7500	328	−5770
2-pentanone	303−333	−6910	298	−7190
diethyl ether	303−333	−15 680	308	−16 000
diisopropyl ether	303−333	−15 960		
dipropyl ether	303−333	−7290		
MTBE	303−333	−16 650	303	−16 270
TAME	303−333	−14 520		
methyl acetate	303−343	−4090	323	−3510
ethyl acetate	303−343	−4950	298	−8550
propyl acetate	303−343	−3460		
methyl formate	303−333	−1620		
ethyl formate	303−333	−1990		
benzene	309−323	8410	303	4660
toluene	309−323	10 580		

excess enthalpy, data in the dilute homogeneous region are required. In a few cases, these data were not available for the solute toluene. For systems with a large miscibility gap, for example, for systems with benzene and toluene, starting from the isoactivity criterion the solubility of the hydrocarbon can be estimated by the following simple thermodynamic relation: $x_i = 1/\gamma_i^\infty$. This means that the temperature dependence of the γ_i^∞ measurements can also be confirmed by liquid−liquid equilibrium data. In Figure 3, the calculated and experimental solubilities of benzene and toluene in water are shown. As can be seen, nearly perfect agreement is observed.[15,16]

The investigated oxygenated solutes are quite polar, have good proton-accepting abilities, and form linear and branched C═O⋯O−H or O⋯H−O hydrogen bonds in water, giving complex associations (hydrates) with large exothermic energies at infinite dilution. These associations are still sensitive and unstable with rising temperatures, as indicated by the increasing values of activity coefficients at infinite dilution.

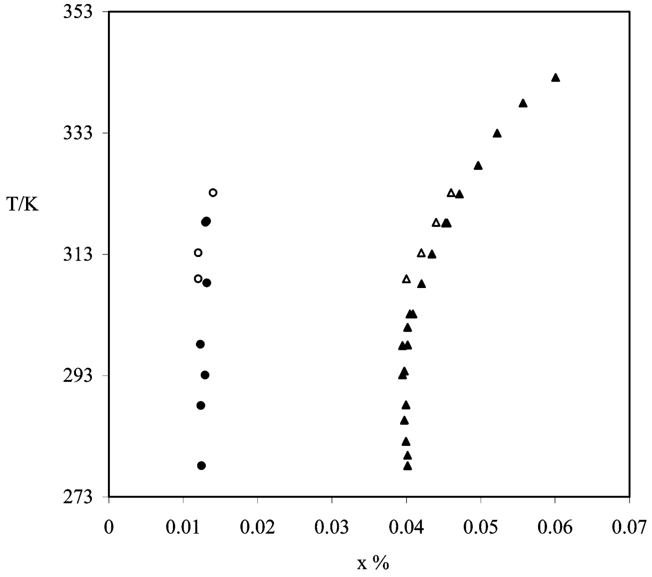

Figure 3. Solubility of benzene and toluene (mol %) in water. Benzene: ○, this work; ●, from ref 15. Toluene: △, this work; ▲, from ref 16.

Conclusions

With the help of the dilutor technique, reliable activity coefficients at infinite dilution for aromatics and selected oxygenated solutes in water have been measured in the temperature range from 303 to 343 K. Depending on the polarity of the solutes and the temperature, the γ_i^∞ values vary from 5 (ethanol) to ∼8.500 (toluene). The accuracy of the values has been approved with the help of published data, excess enthalpies, and LLE data measured for these systems.

Acknowledgment

We thank the DDBST GmbH for permission to use the data bank.

Literature Cited

(1) Gruber, D. Experimentelle Bestimmung von Aktivitätskoeffizienten bei unendlicher Verdünnung als Grundlage für die Entwicklung eines Programmpakets zur Auswahl selektiver Lösungsmittel für Thermische Trennprozesse. Ph.D. Thesis, Universität Oldenburg, Oldenburg, Germany, 1999.

(2) Gmehling, J.; Li, J.; Schiller, M. A Modified UNIFAC Model 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178−193.

(3) Gmehling, J.; Möllmann, C. Synthesis of Distillation Processes Using Thermodynamic Models and the Dortmund Data Bank. *Ind. Eng. Chem. Res.* **1998**, *37*, 3112−3123.

(4) Krummen, M. Unterschiedliche Methoden zur experimentellen Bestimmung der Aktivitätskoeffizienten bei unendlicher Verdünnung als Grundlage für die Auslegung Thermischer Trennprozesse. Diplomarbeit, Universität Oldenburg, Oldenburg, Germany, 1998.

(5) Leroi, J.-C.; Masson, J.-C; Renon, H.; Fabies, H.-J.; Sannier, H. Accurate Measurements of Activity Coefficients at Infinite Dilution by Inert Gas Stripping and Gas Chromatography. *Ind. Eng. Chem. Process Des. Dev.* **1977**, *16*, 139−144.

(6) Duhem, P.; Vidal, J. Extension of the Dilutor Method to Measurement of High Activity Coefficients at Infinite Dilution. *Fluid Phase Equilib.* **1978**, *2*, 231−235.

(7) Richon, D.; Antoine, P.; Renon, H Infinite Dilution Activity Coefficients of Linear and Branched Alkanes from C_1 to C_9 in *n*-Hexadecane by Inert Gas Stripping. *Ind. Eng. Chem. Process Des. Dev.* **1980**, *19*, 144−147.

(8) Gruber, D.; Krummen, M.; Gmehling, J. The Determination of Activity Coefficients at Infinite Dilution with the Help of the Dilutor-Technique (Inert Gas Stripping). *J. Chem. Eng. Technol.* **1999**, *22*, 827−831.

(9) Krummen, M.; Gruber, D.; Gmehling; J. Measurement of Boundary Activity Coefficients at Infinite Dilution in Solvent Mixtures Using the Dilutor Technique. *Ind. Eng. Chem. Res.* **2000**, *39*, 2114−2123.
(10) Fowlis, I. A.; Scott; R. P. W. A Vapour Dilution System for Detector Calibration. *J. Chromatogr.* **1963**, *11*, 1−10.
(11) Sorrentino, F.; Voilley, A.; Richon, D. Activity Coefficients of Aroma Compounds in Model Food Systems. *AIChE J.* **1986**, *32*, 1988−1993.
(12) Villamanan, M. A.; Allawi, A. J.; Van Ness, H. C. *J. Chem. Eng. Data* **1984**, *29*, 431.
(13) Gmehling, J. Unpublished data.
(14) Richon, D.; Viallard, A. Les systèmes Eau/Ester. I. Etude Calorimétrique des Systèmes Eau/Acetate d'Alcoyle, *Can. J. Chem. Eng.* **1976**, *54*, 2584−2593.
(15) Arnold, D. S.;. Plank, C. A.; Erickson, E. E.; Pike, F. P. Solubility of Benzene in Water. *J. Chem. Eng. Data* **1958**, *3*, 253−256.
(16) Pierotti, R. A.; Liabastre, A. A. The Structure and Properties of Water Solutions. Report, 1971, 1−102.
(17) Dortmund Data Bank 2004 (www.ddbst.de).
(18) Janini, G. M.; Qadorra, L. A. Determination of Activity Coefficients of Oxygenated Hydrocarbons by Liquid−Liquid Chromatography. *J. Liq. Chromatogr.* **1986**, *9*, 39−53.
(19) Djerki, R. A.; Laub, R. J. Solute Retention in Column Liquid Chromatography. X. Determination of Solute Infinite-Dilution Activity Coefficients in Methanol, Water, and their Mixtures, by Combined Gas−Liquid and Liquid−Liquid Chromatography. *J. Liq. Chromatogr.* **1988**, *11*, 585−612.

Received for review March 30, 2004. Accepted June 7, 2004. The authors thank the Algerian Ministry of Higher Education for financial support of Z.A.

JE049875+