1526 *J. Chem. Eng. Data* **2001,** *46,* 1526−1529

Thermodynamic Properties of Mixtures Containing Ionic Liquids. 1. Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkylbenzenes in 4-Methyl-*n*-butylpyridinium Tetrafluoroborate Using Gas−Liquid Chromatography

Andreas Heintz,* Dmitry V. Kulikov, and Sergey P. Verevkin

Department of Physical Chemistry, University of Rostock, Hermannstrasse 14, D-18055 Rostock, Germany

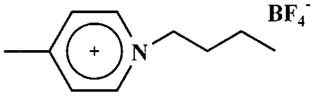
Activity coefficients at infinite dilution γ_i^∞ of 19 alkanes, alkenes, and alkylbenzenes in the ionic liquid 4-methyl-*n*-butylpyridinium tetrafluoroborate ($C_{10}H_{16}BF_4N$) were determined by gas chromatography using the ionic liquid as stationary phase. The measurements were carried out at different temperatures between 313.1 K and 363.1 K. From the temperature dependence of the limiting activity coefficients partial molar excess enthalpies at infinite dilution $H_i^{E,\infty}$ of the organic solutes in the ionic liquids have been derived.

Introduction

The study of ionic liquids that are air and moisture stable has become the subject of an increasing number of scientific investigations.[1−8] Most work has been invested in the elaboration of the synthetic methods and applications of ionic liquids in catalytic processes. However, the physicochemical properties of the ionic liquids have not been studied systematically. For example, ionic liquids are claimed to be potential solvents for many organic, inorganic, and polymeric substances,[1] but even the simple question as to what degree any compound of interest is soluble in any kind of ionic liquid has received almost no answer so far due to the lack of experimental data. Only a few investigations of the liquid−liquid equilibrium[7] and the viscosity[8] of mixtures containing ionic liquids are available in the literature.

Activity coefficients at infinite dilution of a solute *i*, γ_i^∞, provide information about the intermolecular energy between solvent and solute and are used, in particular, for the selection of solvents for extraction and extractive distillation.[9,10] Values of γ_i^∞ are also important for the reliable design of thermal separation processes when the last traces of impurities have to be removed. To avoid an oversizing of distillation columns or stripping processes, reliable information about the separation factor at infinite dilution is also required. Understanding the thermodynamics of mixtures of ionic liquids with organic solvents exhibits a challenge for theoreticians dealing with statistical mechanics of electrolyte solutions. Therefore, experimental data of thermodynamic properties of mixtures consisting of ionic liquids and organic solvents are also of interest for testing theoretical concepts.

Our interest in ionic liquids is focused on providing systematic data on activity coefficients, densities, and viscosities in mixtures with organic solutes. Diverse ionic liquids are commercially available.[7] In this initial work we examine the ionic liquid 4-methyl-*n*-butylpyridinium tetrafluoroborate ($C_{10}H_{16}BF_4N$).



Because ionic liquids have a negligible vapor pressure, the most suitable method for measuring limiting activity coefficients of volatile solutes in ionic liquids is the gas−liquid chromatographic (GLC) method using the ionic liquid as stationary phase. A series of 19 hydrocarbons (see Table 2) including alkanes, alkenes, and alkylbenzenes in 4-methyl-*n*-butylpyridinium tetrafluoroborate has been studied over the temperature range (313−343) K.

Experimental Procedure

Materials. The hydrocarbons were purchased from Aldrich and Merck. GC analysis gave a purity >99.9% in agreement with specifications stated by the suppliers. The ionic liquid 4-methyl-*n*-butylpyridinium tetrafluoroborate was purchased from Solvent Innovation.[11] Before use, the purchased sample of the ionic liquid was dissolved in an excess of methanol and filtered. Then the sample was subjected to vacuum evaporation to remove possible traces of solvents and moisture. The density of the purified sample, (1184.24 ± 0.20) kg·m^{-3} at 298.15 K, was measured using the vibrating tube method. This value was checked regularly in order to test the chemical stability of the sample. Chromosorb W/AW-DMCS 100/120 mesh was used as solid support for the ionic liquid in the GC column. Before use, Chromosorb was subjected to vacuum treatment with heating to remove traces of adsorbed moisture.

Procedure. Coating the solid support material with the ionic liquid was performed by dispersing a certain portion of Chromosorb in a solution of the ionic liquid in dichloromethane followed by evaporation of the solvent using a rotating evaporator. The Chromosorb was weighed before and after the coating process. The experiments were performed with a Carlo Erba Strumentazione 4130 gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator. Nitrogen was used as carrier gas. Two different GC columns with lengths

---

* Author to whom correspondence should be addressed (e-mail andreas.heintz@chemie.uni-rostock.de).

10.1021/je0101348 CCC: $20.00

Table 1. Activity Coefficients γ_i^∞ at Infinite Dilution of Three Solutes in Hexadecane Used as the Stationary Phase and Their Comparison with Literature Data by Castells et al.[14] at 313 K

	$\gamma_{i\ 313}^\infty$ (this work)	$\gamma_{i\ 313}^\infty$ (lit.)[a]	$\gamma_{i\ 313}^\infty$ this work (uncorrected)
hexane	0.911	0.903	0.943
		0.910	
		0.883	
		0.910	
heptane	0.928	0.920	0.949
		0.898	
benzene	1.010	1.005	1.031
		0.995	

[a] Data from different authors cited in ref 14.

of 100 cm and 240 cm, respectively, with an inside diameter of 0.40 cm have been used. The masses of stationary phase (ionic liquid) were 1.112 g for the short column and 2.642 g for the longer one. The masses of the stationary phase were determined with a precision ±0.0005 g. To avoid possible residual adsorption effects of the solvents on Chromosorb, the amount of ionic liquid was ~30 mass % of the support material. Columns were filled with the help of an ultrasound vibrator in order to provide uniform packing of the material in the column.

According to Cruickshank et al.[12] the following equation for the data treatment has been used:

$$\ln \gamma_{i,3}^\infty = \ln\left(\frac{n_3RT}{V_N p_1^0}\right) - \frac{B_{11} - V_1^0}{RT}p_1^0 + \frac{2B_{12} - V_1^\infty}{RT}Jp_0 \quad (1)$$

In eq 1 $\gamma_{i,3}^\infty$ is the activity coefficient of solute i at infinite dilution in the stationary phase (index 3), p_1^0 is the vapor pressure of the pure liquid solute, n_3 is the number of moles of the stationary phase component on the column, and V_N is the standardized retention volume obtained by

$$V_N = JU_0(t_r - t_G)\frac{T_{col}}{T_f}\left[1 - \frac{p_{0w}}{p_o}\right] \quad (2)$$

where t_r is the retention time, t_G is the dead time, U_0 is the flow rate, measured by a soap bubble flow meter, T_{col} is the column temperature, T_f is the flow meter temperature, p_{0w} is saturation pressure of water at T_f, and p_o is the pressure at the column outlet.

The second and third terms in eq 1 are correction terms that arise from the nonideality of the mobile gaseous phase. B_{11} is the second virial coefficient of the solute, B_{12} the mixed virial coefficient of the solute (1) with the carrier gas nitrogen (2), V_1^0 the liquid molar volume of pure solute, and V_1^∞ the partial molar volume of solute in the ionic liquid at infinite dilution.

The factor J appearing in eqs 1 and 2 corrects for the influence of the pressure drop along the column given by[13]

$$J = \frac{3}{2}\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \quad (3)$$

where p_i and p_o are the inlet and outlet pressures of the GC column, respectively.

The outlet pressure p_o was kept equal to the atmospheric pressure. The pressure drop $(p_i - p_o)$ was varied between 20.3 and 101.3 kPa, providing suitable retention times with sharp peaks. The pressure drop and the outlet pressure were measured using a membrane manometer with a precision of ±0.2 kPa.

Volumes of the samples injected into the GC probes were from 0.5 to 2 μL. No differences in retention times t_r were found by injecting individual pure components or their mixtures. Experiments were carried out at four temperatures between 313 K and 363 K. The temperature of the GC column was maintained constant to within ±0.05 K. At a given temperature, each experiment was repeated at least twice to check the reproducibility. Retention times were generally reproducible within (0.01−0.03) min. Absolute values of retention times varied between 3 and ~30 min depending on the individual solute. At each temperature, values of the dead time t_G identical to the retention time of the nonretainable component were measured. Although our GC was equipped with a flame ionization detector, methane[20] was used as nonretainable component

Table 2. Experimental Activity Coefficients γ_i^∞ at Infinite Dilution for Various Solutes in the Ionic Liquid $C_{10}H_{16}BF_4N$ as the Stationary Phase at Temperatures of 313−343 K[a]

solute *i*	313 K	323 K	333 K	343 K
		Alkanes		
hexane	60.44 (312.18)	57.00 (323.11)	54.58 (333.54)	52.31 (343.92)
heptane	86.28 (313.79)	82.81 (323.11)	76.62 (333.54)	73.00 (343.92)
octane	129.3 (313.93)	122.5 (323.12)	113.3 (333.36)	104.2 (343.91)
nonane	195.8 (313.73)	178.1 (323.15)	162.9 (333.54)	149.3 (343.90)
decane	308.0 (313.89)	279.7 (323.16)	258.0 (333.57)	233.3 (344.02)
cyclohexane	29.03 (313.83)	26.72 (323.15)	24.86 (333.54)	23.18 (343.90)
2,2,4-trimethylpentane	98.42 (313.71)	91.34 (323.12)	84.91 (333.51)	78.97 (343.96)
		Alkenes		
cyclohexene	12.52 (313.96)	11.95 (323.16)	11.36 (333.56)	11.11 (344.04)
1-methylcyclohexene	19.93 (313.91)	19.42 (323.16)	18.83 (333.56)	18.30 (344.03)
styrene[b]	1.980 (333.43)	2.019 (343.78)	2.053 (354.06)	2.084 (363.36)
α-methylstyrene[b]	3.938 (333.33)	4.359 (343.79)	4.837 (354.07)	5.322 (363.36)
		Alkylbenzenes		
benzene	1.639 (313.68)	1.645 (322.99)	1.648 (333.36)	1.652 (343.79)
toluene	2.632 (313.79)	2.652 (322.99)	2.671 (333.24)	2.688 (343.55)
ethylbenzene	4.759 (313.69)	4.736 (322.99)	4.713 (333.24)	4.684 (343.55)
o-xylene	3.683 (313.68)	3.716 (322.93)	3.739 (333.23)	3.762 (343.58)
p-xylene	4.074 (313.72)	4.101 (323.47)	4.125 (333.25)	4.150 (343.57)
m-Xylene	4.454 (313.67)	4.455 (322.93)	4.456 (333.23)	4.458 (343.57)
isopropylbenzene	7.794 (313.73)	7.690 (322.94)	7.563 (333.23)	7.453 (343.58)
tert-butylbenzene	10.87 (313.73)	10.56 (322.95)	10.29 (333.23)	10.09 (343.58)

[a] Measured experimental temperatures are given in parentheses. [b] Values are measured in the temperature interval 333−363 K.

Table 3. Coefficients of Equation 4, Correlation Coefficient R^2, γ_i^∞ at 298 K Calculated Using Equation 4, and Values of $H_i^{E,\infty}$ Derived from Equation 4

solute i	a	b	R^2	$\gamma^{\infty\ b}_{i\ 298K}$	$H_i^{E,\infty\ c}$ J·mol^{-1}
		Alkanes			
hexane	2.5441	485.48	0.9982	63.7	4037
heptane	2.4850	620.60	0.9887	93.6	5160
octane	2.3754	783.11	0.9918	143.0	6137
nonane	2.1976	965.58	0.9997	218.1	8028
decane	2.6112	978.58	0.9973	344.0	8136
cyclohexane	0.8094	801.86	0.9982	31.8	6667
2,2,4-trimethylpentene	2.0946	782.4	0.9999	107.9	6505
		Alkenes			
cyclohexene	1.1249	438.82	0.9786	13.2	3649
1-methylcyclohexene	2.0138	307.38	0.9992	20.8	2556
styrene[a]	1.3010	−205.95	0.9998	1.86	−1712
α-methylstyrene[a]	5.0082	−1213.9	0.9985	2.29	−10093
		Alkylbenzenes			
benzene	0.5822	−27.517	0.9741	1.63	−228.8
toluene	1.2100	−75.941	0.9986	2.60	−631.4
ethylbenzene	1.3775	57.363	0.9953	4.80	476.9
o-xylene	1.5419	−74.422	0.9902	3.65	−618.8
p-xylene	1.6153	−66.037	0.9999	4.04	−549.1
m-xylene	1.5034	−3.0138	0.9990	4.45	−25.10
isopropylbenzene	1.5355	162.61	0.9991	7.97	1352
tert-butylbenzene	1.5233	270.05	0.9931	11.2	2245

[a] Measured in the temperature interval 333−363 K. [b] Range of uncertainties is within ±3%. [c] Range of uncertainties is within ±5%.

under the assumption that the effect of the solubility of methane in 4-methyl-*n*-butylpyridinium tetrafluoroborate is negligible. This assumption has been justified by confirmation of our experimental procedure with the reliable data on γ_i^∞ of hexane, heptane, and benzene (see Table 1).

To check the stability of the experimental conditions, such as the possible elution of the stationary phase by the nitrogen stream, the measurements of retention times were repeated systematically every 6−8 h for three selected solutes. No changes of the retention times were observed during 80 h of continuous operation.

Data needed for calculating the correction terms in eq 1 have been obtained in the following way. For all solutes with the exception of α-methylstyrene,[15] values of p_1^0 were taken from the Antoine constants given by Boublik et al.[16]

Molar volumes of solutes V_1^0 were estimated using experimental values of their densities; partial molar volumes of solute at infinite dilution V_1^∞ have been assumed to be equal to V_1^0.

Values of B_{11} have been estimated according to the equations suitable for nonpolar liquids by Tsonopolous's method[17] with an uncertainty of $<\pm 10$ cm^{-3}·mol.$^{-1}$ Critical parameters needed for the calculations were available from the literature.[17] If these data were not available, values of the critical pressure P_c, the critical temperature T_c, and the critical volume V_c were estimated using Lydersen's method.[17] Acentric factors ω_i were calculated by using the Edminster equation.[17]

Values of B_{12} have also been estimated according to Tsonopolous's method. The mixed critical properties P_{cij}, T_{cij}, V_{cij}, and Z_{cij} and mixed acentric factor ω_{ci} were calculated by using equations given in the literature.[17, 18]

Experimental Error Estimation

Retention time, dead time, column temperature, flow meter temperature, flow rate, input and output pressures, and the mass of stationary phase all have experimental errors. For instance, the retention time t_r and the dead time t_G have absolute deviations of ±0.03 min and ±0.01 mim, respectively, and values of $(t_r - t_G)$ lie between 3 and 30 min. Hence, the maximal experimental errors can be 1.3%. In a similar way the error limits of the flow rate U_0 are estimated to be ±0.7% of the column temperature and ±0.01% of the flow meter temperature. Because the input and output pressures may, in principle, be measured as frequently as necessary, it was more important to eliminate short-term fluctuations in pressure and to facilitate achievement of the long-term stability of the experimental conditions. Taking into account this fact, the error limits of the input pressure p_i and the output pressure p_o are estimated to be ±0.9% and ±0.02%, respectively. Then the error of J in eq 3 was estimated to be not larger than ±1%. The experimental error of the saturation pressures is estimated to be (0.01−0.25)%.

Reliable estimation of the experimental error of the mole number n_3 of ionic liquid is rather difficult because of the uncertainty in estimating the amount of the ionic liquid that remained on the walls of the rotational evaporator flask or the adsorption of air moisture during weighing of stationary phase and the filling process of the column. Taking into account the possible influence of these factors, the precision of determining n_3 was estimated to be ±0.5%. Furthermore, the good reproducibility of γ_i^∞ obtained with different amounts of stationary phases justifies the error limits adopted for n_3.

According to the error propagation law γ_i^∞ is estimated to be accurate within ±3.0%.

Attestation of the Experimental Procedure. There exist numerous results on activity coefficients at infinite dilution available from the literature.[19] Appreciable attention has been paid to the investigation of γ_i^∞ for light hydrocarbons in hexadecane used as a stationary phase. To check the validity of our experimental procedure, the values of γ_i^∞ for hexane, heptane, and benzene in hexadecane were measured using the small column (100 cm) with Chromosorb as the solid support. The data obtained here are compared with those available in the literature. Table 1 presents this comparison at 313.1 K. The agreement of the results is satisfactory. The third column in Table 1 demonstrates the effect of neglecting the correction terms in eq 1 containing the second virial coefficients. Uncorrected values of γ_i^∞ are enhanced by ~2−4%, which is in the same order of magnitude as the estimated error limit of γ_i^∞.

Results and Discussion

The values of γ_i^∞ of different solutes (alkanes, alkenes, and alkylbenzenes) in 4-methyl-*n*-butylpyridinium tetrafluoroborate obtained at different temperatures are listed in Table 2. They have been approximated by the linear regression

$$\ln(\gamma_i^\infty) = a + \frac{b}{T} \qquad (4)$$

The coefficients a and b and correlation coefficients R^2 as well as values of $\gamma_{i\ 298\mathrm{K}}^\infty$ calculated with these coefficients are given in Table 3. The quality of the linear regression was very good because the correlation coefficients lie between 0.97 and 0.99.

The activity coefficients of the linear *n*-alkanes increase with increasing chain length. The branching of the alkane skeleton (e.g., cyclohexane or 2,2,4-trimethylpentane) reduces the value of γ_i^∞ in comparison to the corresponding linear alkanes hexane and octane. Introduction of the double bond in the six-membered ring (cyclohexene) also causes a diminishing of γ_i^∞.

Values of γ_i^∞ for benzene and the alkylbenzenes are distinctly lower in comparison with those of the alkanes and alkenes. However, similarly as with the alkanes, γ_i^∞ values increase with increasing size of the alkyl group (see Table 3). No significant effect due to the branching the alkane chain in alkylbenzenes was observed.

According to the Gibbs−Helmholtz equation, the value for the partial molar excess enthalpy at infinite dilution $H_i^{\mathrm{E},\infty}$ can be directly obtained from the slope of a straight line derived from eq 4

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial(1/T)}\right) = \frac{H_i^{\mathrm{E},\infty}}{R} \qquad (5)$$

where R is the gas constant. The values of $H_i^{\mathrm{E},\infty}$ for the compounds studied are listed in Table 3. $H_i^{\mathrm{E},\infty}$ is positive and increases with increasing chain length of the linear alkanes. The introduction of double bonds decreases the positive values of $H_i^{\mathrm{E},\infty}$. For molecules containing the aromatic ring $H_i^{\mathrm{E},\infty}$ becomes negative; however, increasing the size of the alkyl groups in the aromatic ring compensates for this effect and in the case of isopropylbenzene and *tert*-butylbenzene $H_i^{\mathrm{E},\infty}$ is again positive.

The results of γ_i^∞ and $H_i^{\mathrm{E},\infty}$ suggest that the intermolecular interactions between the ionic liquid and the solute become stronger with increasing number of polarizible electrons present in double bonds and aromatic rings, probably due to the increasing strength of ion-induced dipole interactions.

Literature Cited

(1) Wasserscheid, P.; Keim, W. Ionic Liquids—New "Solutions" for Transition Metal Catalysis. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772−3789.
(2) Hussey, C. L. Room temperature haloaluminate ionic liquids. Novel solvents for transition metal solution chemistry. *Pure Appl. Chem.* **1988**, *60*, 1763−1772.
(3) Adams, C. J.; Earle, M. J.; Roberts, G.; Seddon, K. R. Friedel−Crafts reactions in room temperature ionic liquids. *Chem. Commun.* **1998**, 2097−2098.
(4) Laali, K. K.; Gettwert, V. J. Electrophilic Nitration of Aromatics in Ionic Liquid Solvents. *J. Org. Chem.* **2001**, *65*, 35−40.
(5) Larsen, A. S.; Holbrey, J. D.; Tham, F. S.; Reedm, C. A. Designing Ionic Liquids: Imidazolium Melts with Inert Carborane Anions. *J. Am. Chem. Soc.* **2000**, *122*, 7264−7272.
(6) Ngo, H. L.; LeCompte, K.; Hargens, L.; McEwen, A. B. Thermal properties of imidazolium ionic liquids. *Thermochim. Acta* **2000**, *357*−*358*, 97−102.
(7) Selvan, M. S.; McKinley, M. D.; Dubois, R. H.; Atwood, J. L. Liquid−Liquid Equilibria for Toluene + Heptane + 1-Ethyl-3-methylimidazolium Triiodide and Toluene + Heptane + 1-Butyl-3-methylimidazolium Triiodide. *J. Chem. Eng. Data* **2000**, *45*, 841−845.
(8) Liao, Q.; Hussey, C. L. Densities, Viscosities, and Conductivities of Mixtures of Benzene with the Lewis Acidic Aluminum Chloride + 1-Methyl-3-ethylimidazolium Chloride Molten Salt. *J. Chem. Eng. Data* **1996**, *41*, 1126−1130.
(9) Dohnal, V.; Horakova, I. A new variant of the Rayleigh distillation method for the determination of limiting activity coefficients. *Fluid Phase Equilib.* **1991**, *68*, 173−185.
(10) Letcher, T. M.; Jerman, P. Activity coefficients of cyclohexane + *n*-alkane mixtures. *J. Chem. Thermodyn.* **1976**, *8*, 127−131.
(11) Solvent Innovation, http://www.solvent-innovation.de.
(12) Cruickshank, A. J. B.; Windsor, M. L.; Young, C. L. The use of gas−liquid chromatography to determine activity coefficients and second virial coefficients of mixtures. *Proc. R. Soc. London* **1966**, *A295*, 259−270.
(13) Grant, D. W. *Gas−Liquid Chromatography*; van Nostrand Reinhold: London, U.K., 1971.
(14) Castells, R. C.; Arancibia, E. L.; Nardillo, A. M.; Castells, C. Thermodynamics of hydrocarbon solutions using GLC *n*-hexane, *n*-heptane, benzene and toluene as solutes each at infinite dilution in *n*-hexadecane, in *n*-octadecane and *n*-eicosane. *J. Chem. Thermodyn.* **1990**, *22*, 969−977.
(15) Verevkin, S. P. Thermochemical investigation on α-methyl-styrene and parent phenyl substituted alkenes. *Thermochim. Acta* **1999**, *326*, 17−25.
(16) Boublik, T.; Fried, V.; Hala, E. The vapour pressure of pure substances. *Physical Science Data 17*; Elsevier: Amsterdam, The Netherlands, 1984.
(17) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill Chemical Engineering Series: New York, 1977.
(18) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed.; Prentice-Hall: New York, 1986.
(19) PLACID—Prague Limiting Activity Coefficients Inquiry Database. Department of Physical Chemistry, Institute of Chemical Technology, Prague, Czech Republic, 1997; IUPAC STD Project.
(20) Conder, J. R.; Young, C. L. *Physicochemical Measurements by Gas Chromatography*; Wiley: New York, 1979.

Received for review April 24, 2001. Accepted August 8, 2001. D.K. acknowledges gratefully a research scholarship from the DAAD (Deutscher Akademischer Austauschdienst).

JE0101348