

## Supporting Information

### New for Old. Password to the Thermodynamics of the Protic Ionic Liquids

Sergey P. Verevkin, Dzmitry H. Zaitsau, Bo Tong and Urs Welz-Biermann

#### Experimental Section

**Materials.** The samples of solutes studied were of commercial origins. GC analysis gave a purity >99.9 % in agreement with specifications stated by the suppliers. All chemicals were used without further purification. EAN (purity >99 %) was purchased from IoLiTec, Germany.

Chromosorb W/AW-DMCS 100/120 mesh was used as solid support for the ionic liquid in the GC-column. The chromosorb has been subjected to vacuum treatment with heating in order to remove traces of adsorbed moisture.

**Experimental 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 Hewlett Packard gas-chromatograph equipped with a flame ionization detector. Nitrogen was used as carrier gas. GC column (stainless steel) with length 45 cm with an inside diameter of 0.40 cm was used. The amount of stationary phase (ionic liquid) was around 5.4 mmol. The mass of the stationary phase was determined with a precision of  $\pm 0.0003$  g. In order to avoid possible residual adsorption effects of the solutes on chromosorb, the amount of ionic liquid was about 35 mass per cent of the support material.

According to Cruickshank *et. al.*<sup>1</sup> the following equation for the data treatment was used:

$$\ln \gamma_{i,3}^{\infty} = \ln \left( \frac{n_3 \cdot R \cdot T}{V_N \cdot p_1^0} \right) - \frac{B_{11} - V_1^0}{RT} \cdot p_1^0 + \frac{2 \cdot B_{12} - V_1^{\infty}}{RT} \cdot J \cdot p_0 \quad (1)$$

where  $\gamma_{i,3}^{\infty}$  is the activity coefficient of component  $i$  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 (ionic liquid) on the column and  $V_N$  is the standardized retention volume obtained by,

$$V_N = J \cdot U_0 \cdot (t_r - t_G) \cdot \frac{T_{col}}{T_f} \cdot \left[ 1 - \frac{p_{0w}}{p_o} \right] \quad (2)$$

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

The second and third term in eq 1 are correction terms which arise from the non-ideality of 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).  $V_1^0$  is the liquid molar volume of pure solute and  $V_1^{\infty}$  is 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<sup>2</sup>,

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

where  $p_i$  and  $p_o$  are the inlet and the outlet pressure 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 an uncertainty of  $\pm 0.2$  kPa.

Volumes of the samples injected into the GC probes were (0.5 to 2  $\mu$ l). No differences in retention times  $t_r$  were found by injecting individual pure components or their mixtures. This fact indicates that different concentrations of the solute in the stationary phase caused by different ratios of the injected amounts of solute and the amount of stationary phase do not affect the results and it can be concluded that in all cases the state of infinite dilution was realised to a high degree of approximation. Experiments were carried out at 4 to 5 temperatures between 303 K and 353 K. The temperature of the GC column was maintained constant to within  $\pm 0.01$  K. At a given temperature each experiment was repeated at least twice to check the reproducibility. Retention times were generally reproducible within (0.01 to 0.03) min. Absolute values of retention times varied between (3 to 30) min depending on the individual solute. At each temperature values of the dead time  $t_G$  identical to the retention time of a non-retainable component were measured. While our GC was equipped with a flame-ionization detector, methane<sup>1</sup> was used as non-retainable component under the assumption that the effect of solubility of methane in ionic liquid is negligible. This assumption has been justified by attestation of our experimental procedure with the reliable data on  $\gamma_i^\infty$  of hexane, heptane and benzene in hexadecane.<sup>3</sup>

In order 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 (2 to 3) hours for tridecane. No changes of the retention times were observed during 2-3 days of continuous operation.

Data needed for calculating the correction terms in eq 1 have been obtained in the following way. Molar volumes of solutes  $V_1^0$  were estimated using experimental values of their densities, partial molar volumes of solute at infinite dilution  $V_1^\infty$  have been assumed to be equal of  $V_1^0$ . Values of  $B_{11}$  have been estimated according to Tsonopolous' method.<sup>4</sup> Critical parameters needed for the calculations were available from the literature.<sup>5</sup> 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.<sup>6</sup> Acentric factors  $\omega_1$  were calculated by Edmister equation.<sup>6</sup> More details are given in the Supporting information. Values of  $B_{12}$  have also been estimated according to Tsonopolous' method. The mixed critical properties  $P_{cij}$ ,  $T_{cij}$ ,  $V_{cij}$ ,  $Z_{cij}$  and mixed acentric factor  $\omega_{ij}$  were calculated by equations given in the literature.<sup>4,7</sup>

Values of vapor pressures  $p_1^0$  of pure solutes are of a crucial importance for the reliability of  $\gamma_i^\infty$ . For alkanes these values were calculated using parameters of the Cox equation recommended by Ruzicka and Majer.<sup>8</sup> For alkenes values of  $p_1^0$  were calculated using parameters of the Cox equation recommended by Steele and Chirico.<sup>9</sup> Vapor pressures of pure alcohols were calculated using coefficients of Wagner's equation recommended by Ambrose and Walton<sup>10</sup>. Specification of the sources of vapor pressures of other solutes was given in the previous papers of this series.<sup>11-12</sup>

The validity of the experimental procedure has been checked by comparison of our measured values of  $\gamma_i^\infty$  for hexane in hexadecane with those available in the literature.<sup>3</sup> The

procedure of the experimental error estimation was described in our previous work.<sup>3</sup> Values of  $\gamma_i^\infty$  are estimated to be accurate within to  $\pm 3$  %.

**Transpiration method.** Vapor pressures of EAN were determined using the method of transference in a saturated stream of inert gas and applying the Clausius-Clapeyron equation. The method is especially applicable at low pressures. It has been described in detail before<sup>13</sup> and has proven to give results in good agreement with other established techniques. A sample of approximately 0.5 g was mixed with glass beads and placed in a thermostatted U-tube of length 10 cm and diameter 0.5 cm. A preheated helium stream was passed through the U-tube at constant temperature ( $\pm 0.1$  K). The flow rate of the helium stream was measured using a soap film bubble flow meter ( $\pm 0.2$ - $0.3\%$ ) and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. We tested our apparatus at different flow rates of the carrier gas in order to check the lower boundary of the flow, below which, the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transpired one. In our apparatus the contribution due to diffusion was negligible at flow rates down to  $0.5 \text{ dm}^3 \cdot \text{h}^{-1}$ . The upper limit for our apparatus was a flow rate of  $12 \text{ dm}^3 \cdot \text{h}^{-1}$ . Thus, we carried out the experiments using flow rates ranging from 7 to  $10 \text{ dm}^3 \cdot \text{h}^{-1}$  which ensured that the carrier gas was in saturated equilibrium with the coexisting liquid phase in the saturation tube. The material transported was condensed in a cold trap. The amount of condensed product in the trap was determined by weighing ( $\pm 0.0001$  g). The saturated vapor pressure  $p_i^{sat}$  at each temperature  $T_i$  was calculated from the amount of product collected within a definite period of time. Assuming the validity of Dalton's law of partial pressures applied to the helium stream saturated with the substance  $i$  of interest  $i$ , values of  $p_i^{sat}$  were calculated according to the ideal gas law. Experimental vapor pressures of EAN at 379.4 K was 0.99 Pa and at 409.4 K it was 9.5 Pa.

## References

- [1] A.J.B. Cruickshank, M.L. Windsor, C.L. Young, Proc. R. Soc. A295 (1966), 259-270.
- [2] D.W. Grant, Gas-Liquid Chromatography, van Nostrand Reinhold Company, London, 1971.
- [3] A. Heintz, D.V. Kulikov, S. P. Verevkin, J. Chem. Eng. Data 46 (2001), 1526-1529.
- [4] A. Heintz, T.V. Vasiltsova, J. Safarov, E. Bich, S.P. Verevkin, J. Chem. Eng. Data 51 (2006), 648-655.
- [5] R.C. Reid, J.M. Prausnitz, T.K. Sherwood, The properties of gases and liquids, 3<sup>rd</sup> ed., McGraw-Hill Chem. Eng. Series, New York, 1977.
- [6] J.M. Prausnitz, R.N. Lichtenthaler, E.G. Azevedo, Molecular thermodynamics of

- fluid-phase equilibria, 2<sup>nd</sup> ed., Prentice-Hall, New York, 1986.
- [7] J. Safarov, S.P. Verevkin, E. Bich, A. Heintz, *J. Chem. Eng. Data* 51 (2006), 518-525.
- [8] K. Ruzicka, V. Majer, *J. Phys. Chem. Ref. Data* 23 (1994), 1-39.
- [9] W.V. Steele, R.D. Chirico, *J. Phys. Chem. Ref. Data* 22 (1993), 377-430.
- [10] D. Ambrose J. Walton, *Pure and Appl. Chem.* 61 (1989), 1395-1403.
- [11] A. Heintz, S.P. Verevkin, *J. Chem. Eng. Data* 50, (2005), 1515-1519.
- [12] T.V. Vasil'tsova, S.P. Verevkin, E. Bich, A. Heintz, R. Bogel-Lukasik, U. Domanska, *J. Chem. Eng. Data* 51 (2006), 213-218.
- [13] Emel'yanenko, V. N.; Verevkin, S.P.; Heintz, A. *J. Amer. Chem. Soc.* 129 (2007) 3930-3937.

**Table 1.** Experimental activity coefficients at infinity dilution.  $\gamma_i^\infty$  for the solutes in the EAN as the stationary phase at temperatures 303 to 353 K  
 The values of  $\gamma_i^\infty$  have been approximated by the linear regression,  $\ln \gamma_i^\infty = a + b/T$

Solute i	303	308	313	318	323	a	b / K	$r^2$
<i>n</i> -tridecane	$3.34 \cdot 10^3$	$3.18 \cdot 10^3$	$3.02 \cdot 10^3$	$2.88 \cdot 10^3$	$2.78 \cdot 10^3$	$5.1 \pm 0.2$	$910 \pm 62$	0.996
<i>n</i> -tetradecane	$3.89 \cdot 10^3$	$3.40 \cdot 10^3$	$3.09 \cdot 10^3$	$2.80 \cdot 10^3$	$2.42 \cdot 10^3$	$0.84 \pm 0.6$	$2250 \pm 220$	0.993
<i>n</i> -pentadecane	$3.96 \cdot 10^3$	$3.71 \cdot 10^3$	$3.69 \cdot 10^3$	$3.47 \cdot 10^3$	$3.33 \cdot 10^3$	$5.6 \pm 0.6$	$808 \pm 190$	0.960
1-dodecene	$1.95 \cdot 10^3$	$1.97 \cdot 10^3$	$1.98 \cdot 10^3$	$2.00 \cdot 10^3$	$2.02 \cdot 10^3$	$8.1 \pm 0.1$	$-161 \pm 34$	0.999
<i>n</i> -propyl benzene	88.2	87.9	87.7	87.5	87.3	$4.30 \pm 0.01$	$52.3 \pm 1.8$	0.999
<i>n</i> -butyl benzene	$1.60 \cdot 10^2$	$1.59 \cdot 10^2$	$1.57 \cdot 10^2$	$1.56 \cdot 10^2$	$1.54 \cdot 10^2$	$4.48 \pm 0.01$	$181 \pm 4$	0.999
<i>n</i> -pentyl benzene	$2.97 \cdot 10^2$	$2.95 \cdot 10^2$	$2.92 \cdot 10^2$	$2.89 \cdot 10^2$	$2.86 \cdot 10^2$	$5.1 \pm 0.05$	$190 \pm 16$	0.995
methyl propionate	5.5	5.61	5.8	5.9	6.0	$3.1 \pm 0.2$	$-430 \pm 50$	0.992
methyl butyrate	10.0	10.2	10.4	10.5	10.6	$3.3 \pm 0.1$	$-293 \pm 23$	0.996
methyl pentanoate	15.1	15.2	15.4	15.7	15.9	$3.6 \pm 0.1$	$-257 \pm 15$	0.990
methyl hexanoate	29.1	29.4	30.2	30.5	31.2	$4.5 \pm 0.2$	$-333 \pm 52$	0.981
	<b>333</b>	<b>338</b>	<b>343</b>	<b>348</b>	<b>353</b>			
methanol	2.60	2.87	3.06	3.30	3.38	$5.70 \pm 0.9$	$-1576 \pm 310$	0.971
ethanol	2.94	3.04	3.15	3.26	3.35	$3.4 \pm 0.1$	$-773 \pm 42$	0.998
<i>n</i> -propanol	3.30	3.42	3.48	3.56	3.65	$2.9 \pm 0.2$	$-575 \pm 62$	0.991
<i>n</i> -butanol	4.25	4.36	4.42	4.52	4.58	$2.8 \pm 0.1$	$-439 \pm 50$	0.991

**Table 2.** Activity coefficients  $\gamma_i^\infty$  and partial molar excess enthalpy at infinite dilution ( $H_i^{E,\infty}$  / kJ·mol) for the investigated solutes in EAN as the stationary phase.

Solute i	$\gamma_i^\infty$	$H_i^{E,\infty}$ / kJ·mol <sup>b</sup>
<i>n</i> -undecane	2922 <sup>a</sup>	-
<i>n</i> -dodecane	3165 <sup>a</sup>	-
<i>n</i> -tridecane	3498	-7.6 ± 0.5
<i>n</i> -tetradecane	4403	-18.7 ± 1.8
<i>n</i> -pentadecane	4105	-6.7 ± 1.6
1-dodecene	1939	-0.16 ± 0.02
<i>n</i> -propyl benzene	88.2	-0.44 ± 0.02
<i>n</i> -butyl benzene	162	-1.51 ± 0.03
<i>n</i> -pentyl benzene	302	-1.6 ± 0.1
methyl propionate	5.4	3.6 ± 0.4
methyl butyrate	9.9	2.4 ± 0.2
methyl pentanoate	14.9	2.1 ± 0.5
methyl hexanoate	28.5	2.8 ± 0.4
methanol	1.52	13.1 ± 2.6
ethanol	2.25	6.4 ± 0.4
<i>n</i> -propanol	2.69	4.8 ± 0.5
<i>n</i> -butanol	3.63	3.7 ± 0.4

<sup>a</sup> Calculated using the linear dependence  $\ln \gamma_i^\infty = 0.085 \cdot N_C + 7.0$  for *n*-alkanes measured in this work.

<sup>b</sup> The value for the partial molar excess enthalpy at infinite dilution  $H_i^{E,\infty}$  were obtained from

the slope of a straight line derived from equation:  $\left( \frac{\partial \ln \gamma_i^\infty}{\partial (1/T)} \right) = \frac{H_i^{E,\infty}}{R}$

**Table 3.** Critical constants,  $V_c$ ,  $P_c$  and  $T_c$ , and acentric factors of the solutes and the carrier gas required for evaluation activity coefficients.

Solute	$V_c$	$P_c$	$T_c$	$\omega$
	cm <sup>3</sup> mol <sup>-1</sup>	atm	K	
<i>n</i> -tridecane	823	16.8	676	0.582
<i>n</i> -tetradecane	894	15.7	694	0.568
<i>n</i> -pentadecane	966	14.8	708	0.612
1-dodecene	680	19.30	658	0.559
methanol	113	79.9	513	0.564
ethanol	168	63.0	514	0.668
<i>n</i> -propanol	218	52.0	536.9	0.635
<i>n</i> -butanol	274	43.66	563.1	0.591
<i>n</i> -propyl benzene	440	32.0	638.4	0.350
<i>n</i> -butyl benzene	497	28.9	660.5	0.396
<i>n</i> -pentyl benzene	536	32.4	667.6	0.551
methyl propionate	282.5	40.0	531.0	0.362
methyl butyrate	340.3	34.7	554.5	0.379
methyl pentanoate	416.7	31.9	577	0.456
methyl hexanoate	450	35.2	599	0.593
<i>carrier gas</i>				
Nitrogen	89.5	33.5	126.2	0.04