Prediction of Infinite Dilution Activity Coefficients of

Organic Compounds in Ionic Liquids Using

COSMO-RS.

Michael Diedenhofen*, Frank Eckert, and Andreas Klamt

COSMOlogic GmbH & Co. KG, Burscheider Str. 515, D-51381 Leverkusen, Germany

diedenhofen@cosmologic.de

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COSMO-RS, a general and fast method for the prediction of thermophysical data of liquids is used for the calculation of activity coefficients at infinite dilution for 38 compounds in the ionic liquids 1-methyl-3-ethylimidazolium bis((trifluoromethyl)sulfonyl)imide, 1,2-dimethyl-3-ethylimidazolium bis((trifluoromethyl)sulfonyl)imide, and 4-methyl-N-butylpyridinium tetrafluoroborate. Calculated values for (314 and 344) K are presented and compared with experimental data.

Introduction

During the last ten years ionic liquids (ILs) have received increased attention. Their unique physical and chemical properties such as specific solvent abilities, negligible vapor pressures, and broad liquid temperature ranges, have led to promising applications as recyclable and environmentally benign solvents for various reactions.[1] Other applications can be found in areas like chromatography, electrochemistry, and in separation processes.[2] Ionic liquids are organic salts, and their chemical and physical properties can be tailored by the selection of anion and cation. Therefore, it is possible to generate a huge number of different ionic liquids, each with specific properties. In spite of their interest, accurate thermodynamic data of ionic liquids and their mixtures are still rare.

In order to exploit the potential of these new substances it would be of great value to have prediction methods that can reliably predict the thermodynamic properties of ionic liquids and their mixtures. This would help to scan the growing set of already known ILs in order to find suitable candidates for a certain task, or to design new ILs for special applications.

Group contribution methods are not applicable because group parameters are not available at present, and the group contribution concept is not suitable to handle the long range interactions in ionic compounds. Monte Carlo simulations and molecular dynamics need appropriate force-fields for the treatment of ionic liquids, which have to be developed. The development of force-fields together with simulation derived thermodynamic properties of imidazolium IL solutions have been reported recently.[3-6]

This work presents the application of the quantum chemically based thermodynamic prediction model COSMO-RS to ionic liquids mixtures. Activity coefficients at infinite dilution γ_i^{inf} for a variety of organic solvents i in ionic liquids, measured by Heintz and co-workers,[7-9] are valuable data for the validation of COSMO-RS for ionic liquids. γ_i^{inf} values for alkanes, alkenes, alkylbenzenes, alcohols, polar organics, and chloromethanes in the ionic liquids 1-methyl-3-ethylimidazolium bis((trifluoromethyl)sulfonyl)imide ([emim][N(Tf)$_2$]), 1,2-dimethyl-3-ethylimidazolium

bis((trifluoromethyl)sulfonyl)imide ([em$_2$im][N(Tf)$_2$]), and 4-methyl-N-butylpyridinium tetrafluoroborate ([bmpy][BF$_4$]) have been studied at (314 and 343) K.

Theory

COSMO-RS is a predictive method for the thermodynamic properties of fluids and liquid mixtures that uses a statistical thermodynamics approach based on the results of quantum chemical calculations. The underlying quantum chemical model, the so called "COnductor-like Screening Model" (COSMO),[10] is an efficient variant of dielectric continuum solvation methods. In this calculations the solute molecules will be calculated in a virtual conductor environment. In such an environment the solute molecule induces a polarization charge density σ on the interface between the molecule and the conductor, i.e. on the molecular surface. These charges act back on the solute and generate a more polarized electron density than in vacuum. During the quantum chemical self-consistency algorithm SCF, the solute molecule is thus converged to its energetically optimal state in a conductor with respect to electron density. The molecular geometry can be optimized using conventional methods for calculations in vacuum. The quantum chemical calculation has to be performed once for each molecule of interest.

In the second step the polarization charge density of the COSMO calculation, which is a good local descriptor of the molecular surface polarity, is used to extend the model towards the "Real Solvents" (COSMO-RS). [11,19] The 3D polarization density distribution on the surface of each molecule X is converted into a distribution-function, the so called σ-profile $p^{X_i}(\sigma)$, which gives the relative amount of surface with polarity σ on the surface of the molecule. The σ-profile for the entire solvent of interest S, which might be a mixture of several compounds, $p_S(\sigma)$ can be built by adding the $p^{X_i}(\sigma)$ of the components weighted by their mole fraction x_i in the mixture.

$$p_S(\sigma) = \sum_{i \in S} x_i p^{X_i}(\sigma) \qquad (1)$$

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The most important molecular interaction energy modes, i.e. electrostatics (E_{misfit}) and hydrogen bonding (E_{HB}) are described as functions of the polarization charges of two interacting surface segments σ and σ' or $\sigma_{acceptor}$ and σ_{donor}, if the segments are located on a hydrogen bond donor or acceptor atom. The less specific van der Waals (E_{vdW}) interactions are taken into account in a slightly more approximate way.

$$E_{misfit}(\sigma, \sigma') = a_{eff} \frac{\alpha'}{2}(\sigma + \sigma')^2 \qquad (2)$$

$$E_{HB} = a_{eff} c_{HB} \min\left(0; \min\left(0; \sigma_{donor} + \sigma_{HB}\right) \max\left(0; \sigma_{acceptor} - \sigma_{HB}\right)\right) \qquad (3)$$

$$E_{vdW} = a_{eff}\left(\tau_{vdW} + \tau'_{vdW}\right) \qquad (4)$$

The eqs. 2-4 contain five adjustable parameters, an interaction parameter α', the effective contact area a_{eff}, the hydrogen bond strength c_{HB}, the threshold for hydrogen bonding σ_{HB}, and the element specific vdW interaction parameter τ_{vdW}. To take into account the temperature dependence of E_{HB} and E_{vdW}, temperature dependent factors are applied, each with one adjustable parameter as defined in ref .12 .

Thus, the molecular interactions in the solvent are fully described by $p_S(\sigma)$ and the chemical potential of the surface segments can be calculated solving a coupled set of non-linear equations.

$$\mu_S(\sigma) = -\frac{RT}{a_{eff}} \ln\left[\int p_S(\sigma') \exp\left(\frac{a_{eff}}{RT}\left(\mu_S(\sigma') - E_{misfit}(\sigma, \sigma') - E_{HB}(\sigma, \sigma')\right)\right) d\sigma' \right] \qquad (5)$$

The distribution function $\mu_S(\sigma)$ is a measure for the affinity of the system S to a surface of polarity σ. The vdW energy, which does not appear in eq. (5), is added to the reference energy in solution (energy of the COSMO calculation). The chemical potential of compound X_i in the system S (the solvent) can now be calculated by integration of $\mu_S(\sigma)$ over the surface of the compound.

$$\mu_S^{X_i} = \mu_{C,S}^{X_i} + \int p^{X_i}(\sigma)\mu_S(\sigma)d\sigma \qquad (6)$$

In order to take into account size and shape differences of the molecules in the system an additional combinatorial term, which depends on the area and volume of all compounds in the mixture and three

adjustable parameters $\mu_{C,S}^{X_i}$, is added. [19] The chemical potential can now be used to calculate a wide variety of thermodynamic properties e.g. the activity coefficient:

$$\gamma_S^{X_i} = \exp\{\frac{\mu_S^{X_i} - \mu_{X_i}^{X_i}}{RT}\} \tag{7}$$

where $\mu_S^{X_i}$ is the potential in the solvent S, and $\mu_{X_i}^{X_i}$ is the potential of the pure compound X_i.

Computational Details

The COSMO calculations have been performed with the TURBOMOLE [13] program package on the density functional theory (DFT) level, utilizing the BP functional [14-16] with a triple zeta valence polarized basis set (TZVP) [17]. All COSMO-RS calculations are performed using the COSMOtherm [18] program, which provides an efficient and flexible implementation of the COSMO-RS method. The latest parameterization BP_TZVP_C12_0402 [18] is used. In such parameterization the very few global parameters (~15) of the COSMO-RS method are optimized based on a set of about 1000 thermodynamic data, mostly partition coefficients and vapor pressures, in combination with DFT/COSMO calculations of a certain quantum chemical method. The temperature dependence of E_{HB} and E_{misfit} [12] is fitted to pure compound vapor pressures and hence does not contain information about the special systems under consideration. It is important to mention that ionic compounds are not included in the optimization data set. The parameter set used in this study is a general one and not fitted for ionic liquids.

The activity coefficients have been calculated using eq 7. The ILs have been described by an equimolar mixture of two distinct ions i.e., the cation and the anion contribute to $P_S(\sigma)$ (eq 1) as two different compounds.

The mole fraction of IL solutions can be defined with respect to distinct ions or with respect to an ion pair (cation plus anion as one compound). Because the experimental data have been obtained using the latter definition, we have to scale the calculated γ_i^{inf} values with the factor 0.5.

Results and Discussion

The $\ln(\gamma_i^{\text{inf}})$ values of 38 compounds in [bmpy][BF$_4$], [emim][N(Tf)$_2$], and [em$_2$im][N(Tf)$_2$] are listed in Tables 1-2 together with the experimental values. A graphical comparison of the calculated versus experimental data at 314 K is given in the Figures 1-3.

The root mean square (rms) deviation for [bmpy][BF$_4$], [emim][N(Tf)$_2$], and [em$_2$im][N(Tf)$_2$] at 314 K are 0.524, 0.426 , and 0.278 ln-units respectively. For normal organic solutes the expected deviations for $\ln(\gamma_i^{\text{inf}})$ are 0.7 ln-units (rms) and 1.0 ln-units (maximal deviation). [19] Thus, the accuracy of all calculated $\ln(\gamma_i^{\text{inf}})$ values in ILs is in the expected range for non ionic organic solvents.

The calculated values for [bmpy][BF$_4$] (Figure 1) show the biggest deviations from the experimental data for the examined ILs. This is mainly due to the underestimation of the activity coefficients of alkanes, polar organics, and alkenes, which cannot be found for the other examined ILs. 2,2,4-trimethylpentane exhibits the largest deviation from experiment (-1.019 ln-units) of this study. Nevertheless, this deviation is still in the range of the expectation for normal organic solvents. Significant positive deviations from the experimental data can be found for tetrachloromethane (0.819 ln-units) and methanol (0.652 ln-units) only, while the other alcohols are in very good agreement with experiment. The quality of the predictions for the examined chloromethanes is strongly depended on the number of chlorine atoms in the molecules. Dichloromethane shows a negative deviation from the experimental data (-0.941 ln-units), tricholormethane is in good agreement, and tetrachloromethane exhibits the mentioned positive deviation from the experimental data.

For [emim][N(Tf)$_2$] (Figure 2) the calculated values exhibit a small constant shift. Most of the examined compounds show positive deviations from the experimental values. Only dichloromethane shows a significant negative deviation (-0.666 ln-units). Because [emim] is the only cation in this study that is able to act as a hydrogen bond donor, this might be a reason for the relatively large shift of the $\ln(\gamma_i^{\text{inf}})$ values. The COSMO-RS parametrization used does not take into account hydrogen bonding for C-H donors. Therefore, the acidic hydrogen at C2 cannot form hydrogen bonds in the model used, but

its polarity is represented by strong, pure electrostatic interactions (eq. 2). Nevertheless, this description seems to be permissible, because compounds with hydrogen bond acceptor moieties e.g. alcohols, show the same deviations as alkanes, which should not be influenced by hydrogen bonding.

The calculated activity coefficients in [em$_2$im][N(Tf)$_2$] (Figure 3) are in very good agreement with the experimental values. The only outlier is dichloromethane with a deviation of –0.925 ln-units.

The $\ln(\gamma_i^{\text{inf}})$ values calculated at 344 K, which are given in the Tables 1-2, exhibit the same trends as the values for 314 K. The rms deviations at 344 K are 0.529 ln-units for [bmpy][BF$_4$], 0.273 ln-units for [emim][N(Tf)$_2$], and 0.330 ln-units for [em$_2$im][N(Tf)$_2$].

A graphical comparison of the calculated versus the measured temperature dependence of $\ln(\gamma_i^{\text{inf}})$ is given in the Figures 4-6. Except for α-methylstyrene, which is an outlier for all examined ILs, the temperature dependent shifts of the activity coefficients in [bmpy][BF$_4$] (Figure 4) agree very well with the experimental data. The rms deviation is 0.098 ln-units. For [emim][N(Tf)$_2$] (Figure 5) larger deviations from the experimental data are found. Again α-methylstyrene shows the largest difference. The calculated temperature dependence for [em$_2$im][N(Tf)$_2$] (Figure 6) is very similar to that for [emim][N(Tf)$_2$], but the rms deviation is substantially lower, 0.166 versus 0.215 ln-units. This is due to the fact that the accuracy of the predicted values is increased at 344 K in the case of [emim][N(Tf)$_2$], whereas it doesn't change significantly for the other ILs.

Conclusion

Although the COSMO-RS model was developed for normal neutral solvents, it predicts the activity coefficients at infinite dilution in various ionic liquids with the same accuracy that is observed for normal organic solvents, without any adjustment of the theory or the use of specific parameters. Thus COSMO-RS and its implementation in the program COSMOtherm are capable of giving a-priori predictions of the thermodynamics of ionic liquids, which may be of considerable value for the exploration of suitable ILs for practical applications.

Acknowledgments

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Table 1. Calculated and Experimental[a] Logarithmic Activity Coefficients at Infinite Dilution $\ln(\gamma_i^{inf})$ for Various Solutes in [bmpy][BF$_4$] at 314 and 344 K[b].

| Compounds i | $\ln(\gamma_i^{inf})$ in [bmpy] [BF$_4$] | | | |
| | 314 K | | 344 K | |
	Exp.	Calc.	Exp.	Calc.
Alkanes				
Hexane	4.102	3.120	3.957	2.917
Heptane	4.458	3.614	4.290	3.385
Octane	4.862	4.103	4.646	3.847
Nonane	5.277	4.590	5.006	4.307
Decane	5.730	5.076	5.452	4.766
Cyclohexane	3.368	2.583	3.143	2.408
2,2,4-trimethylpentane	4.589	3.570	4.369	3.345
Alkenes				
Cyclohexene	2.527	1.788	2.408	1.664
1-methylcyclohexene	2.992	2.363	2.907	2.208
styrene[c]	0.683	0.568	0.734	0.549
α-methylstyrene[c]	1.371	0.979	1.672	0.934
Alkylbenzenes				
Benzene	0.494	0.370	0.502	0.346
Toluene	0.968	0.904	0.989	0.850
Ethylbenzene	1.560	1.351	1.544	1.276
o-xylene	1.304	1.315	1.325	1.236
p-xylene	1.405	1.471	1.423	1.383
m-xylene	1.494	1.457	1.495	1.370
Isopropylbenzene	2.053	1.714	2.009	1.624
tert-butylbenzene	2.386	1.973	2.312	1.870
Alcohols				
Methanol	0.075	0.727	-0.177	0.301
Ethanol	0.562	0.810	0.285	0.411
1-propanol	0.907	1.049	0.611	0.655
1-butanol	1.288	1.353	0.952	0.951
1-pentanol[c]	1.450	1.422	1.133	1.065
isopropyl alcohol	0.871	0.945	0.589	0.589
tert-butyl alcohol	0.994	1.140	0.710	0.809
sec-butanol	1.150	1.132	0.852	0.823
2-methyl-2-butanol	1.242	1.459	1.023	1.112
cyclohexanol[c]	1.206	1.353	1.020	1.033
1-hexanol[c]	1.751	1.764	1.478	1.393
Polar Organics				
Acetonitrile	-0.545	-0.813	-0.573	-0.808
Acetone	-0.097	-0.353	-0.082	-0.375
ethyl acetate	0.977	0.112	0.944	0.070
methyl tert-butyl ether	2.000	1.285	1.933	1.186
methyl tert-amyl ether	2.474	1.706	2.405	1.586
Chloromethanes				
Dichloromethane	-0.290	-1.232	-0.259	-1.061
Trichloromethane	-0.312	-0.386	-0.184	-0.265
Tetrachloromethane	1.317	2.136	1.369	1.981

[a] Experimental values are taken from ref. [7,8]. [b] The exact experimental temperatures are given in ref. 7,8. c Values at 333 and 363 K.

Table 2. Calculated and Experimental[a] Logarithmic Activity Coefficients at Infinite Dilution $\ln(\gamma_i^{\text{inf}})$ for Various Solutes in [emim][N(Tf)$_2$] and [em$_2$im][N(Tf)$_2$] at 314 and 344 K[b].

	$\ln(\gamma_i^{\text{inf}})$ in [em$_2$im] [N(Tf)$_2$]				$\ln(\gamma_i^{\text{inf}})$ in [emim]	
	314 K		344 K		314 K	
Compounds i	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
Alkanes						
hexane	3.229	2.922	3.050	2.516	3.233	3.425
heptane	3.622	3.408	3.391	2.946	3.647	3.974
octane	4.015	3.888	3.738	3.372	4.069	4.518
nonane	4.441	4.365	4.113	3.794	4.521	5.057
decane	4.879	4.841	4.507	4.215	5.019	5.597
cyclohexane	2.699	2.423	2.456	2.069	2.656	2.854
2,2,4-trimethylpentane	3.569	3.352	3.359	2.898	3.587	3.918
Alkenes						
cyclohexene	2.040	1.516	1.874	1.272	2.015	1.866
1-methylcyclohexene	2.520	2.087	2.363	1.780	2.506	2.509
styrene	0.399	0.429	0.426	0.332	0.509	0.770
α-methylstyrene[c]	1.091	0.702	1.354	0.574	1.110	1.120
Alkylbenzenes						
benzene	0.093	0.203	0.100	0.119	0.163	0.467
toluene	0.499	0.649	0.514	0.519	0.551	0.965
ethylbenzene	1.035	1.077	1.000	0.900	1.042	1.452
o-xylene	0.793	1.000	0.809	0.831	0.874	1.358
p-xylene	0.945	1.145	0.938	0.960	0.995	1.519
m-xylene	0.964	1.130	0.959	0.947	1.006	1.501
isopropylbenzene	1.471	1.430	1.401	1.216	1.435	1.857
tert-butylbenzene	1.722	1.675	1.642	1.433	1.663	2.136
Alcohols						
methanol	0.378	0.920	0.073	0.472	0.123	0.839
ethanol	0.714	0.922	0.399	0.476	0.422	0.917
1-propanol	1.015	1.146	0.686	0.676	0.736	1.214
1-butanol	1.359	1.432	0.989	0.927	1.080	1.564
1-pentanol	1.755	1.767	1.316	1.220	1.461	1.963
isopropyl alcohol	0.925	0.962	0.588	0.537	0.658	1.024
tert-butyl alcohol	0.888	1.107	0.591	0.686	0.640	1.234
sec-butanol	1.139	1.065	0.802	0.665	0.885	1.199
2-methyl-2-butanol	1.058	1.393	0.798	0.938	0.796	1.565
cyclohexanol[d]	1.420	1.573	1.157	1.079	1.101	1.583
1-hexanol[c]	1.756	1.717	1.392	1.210	1.659	2.166
Polar Organics						
acetonitrile	-0.772	-0.753	-0.821	-0.755	-0.832	-0.833
acetone	-0.772	-0.742	-0.757	-0.744	-0.919	-0.793
Ethyl acetate	0.066	-0.360	0.068	-0.401	-0.121	-0.310
methyl tert-butyl ether	1.054	0.842	0.990	0.664	0.882	1.058
methyl tert-amyl ether	1.541	1.256	1.469	1.034	1.350	1.530
Chloromethanes						
dichloromethane	-0.095	-1.021	-0.153	-0.944	-0.115	-0.781
trichloromethane	-0.043	-0.408	0.006	-0.386	-0.028	-0.084
tetrachloromethane	1.220	1.448	1.158	1.244	1.178	1.810

[a] Experimental values are taken from ref. 9. [b] The exact experimental temperatures are given in ref. 9. [c] Values at 323/354 K for [emim][N(Tf)$_2$] and 333/364 K for [em$_2$im][N(Tf)$_2$]. [d] Values at 323/354 K for [emim][N(Tf)$_2$]

Figure 1
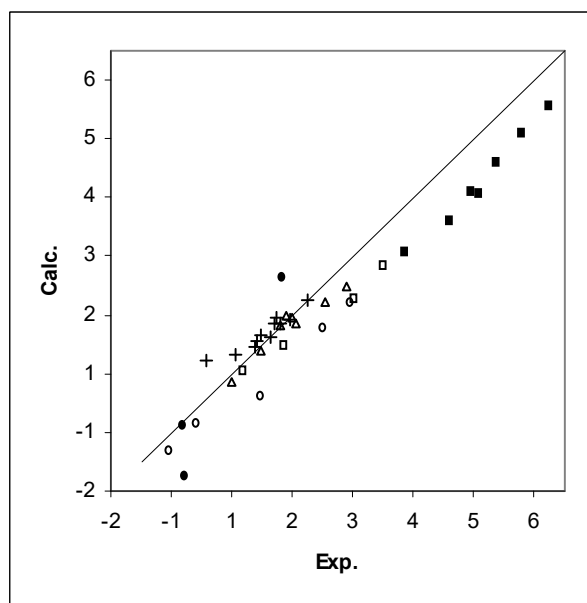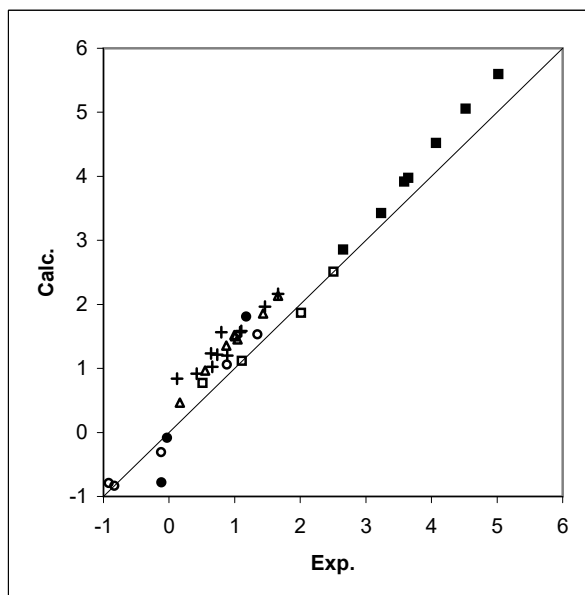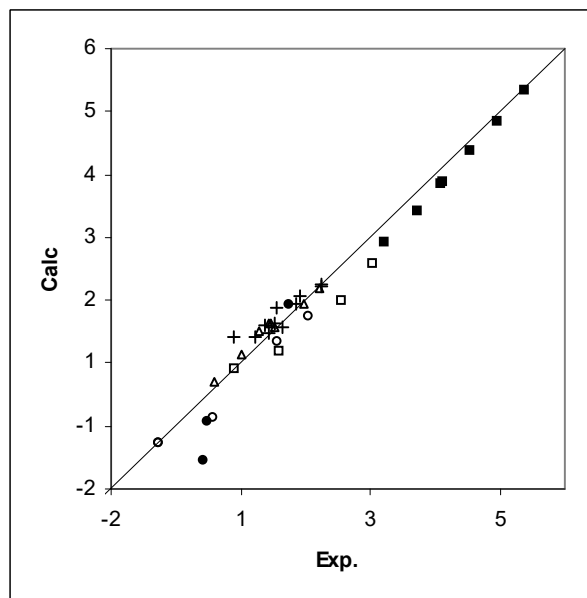

Figure 1. Calculated versus Experimental Logarithmic Activity Coefficients at Infinite Dilution $\ln(\gamma_i^{\text{inf}})$ of Alkanes (▪), Alkenes (▫), Alkylbenzenes (△), Alkohols (+), Polar Organics (○), and Chloromethanes (●) in [bmpy][BF$_4$] at 314 K.

Figure 2

Figure 2. Calculated versus Experimental Logarithmic Activity Coefficients at Infinite Dilution $\ln(\gamma_i^{\text{inf}})$

of Alkanes (·), Alkenes (▫), Alkylbenzenes (△), Alkohols (+), Polar Organics (○), and Chloromethanes

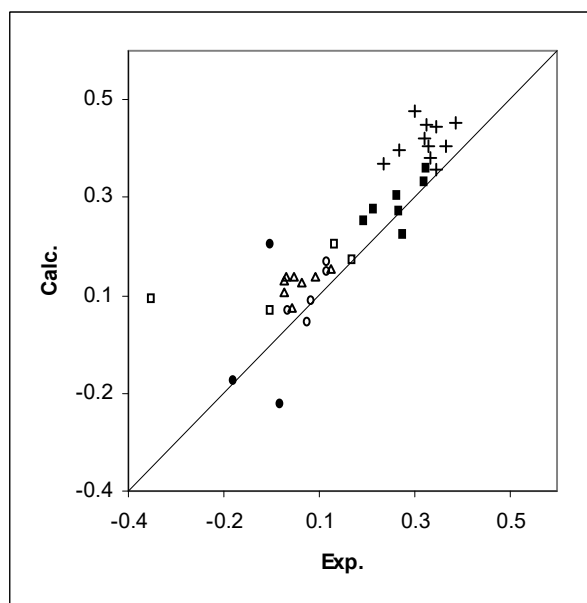(•) in [emim][N(Tf)$_2$] at 314 K.

Figure 3

Figure 3. Calculated versus Experimental Logarithmic Activity Coefficients at Infinite Dilution $\ln(\gamma_i^{\text{inf}})$ of Alkanes (•), Alkenes (▫), Alkylbenzenes (△), Alkohols (+), Polar Organics (○), and Chloromethanes (•) in [em$_2$im][N(Tf)$_2$] at 314 K.

Figure 4
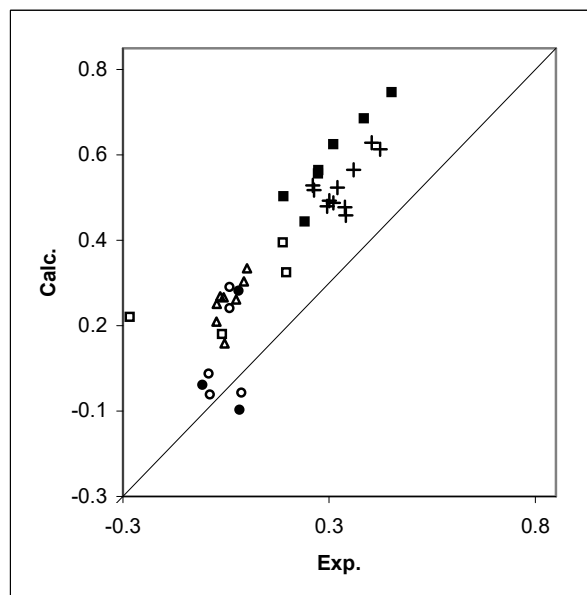

Figure 4. Temperature Dependence of the Logarithmic Activity Coefficients at Infinite Dilution $\ln(\gamma_i^{\inf,314K}) - \ln(\gamma_i^{\inf,344K})$ in [bmpy][BF$_4$]. Alkanes (▪), Alkenes (▫), Alkylbenzenes (△), Alkohols (+), Polar Organics (○), and Chloromethanes (●).

Figure 5
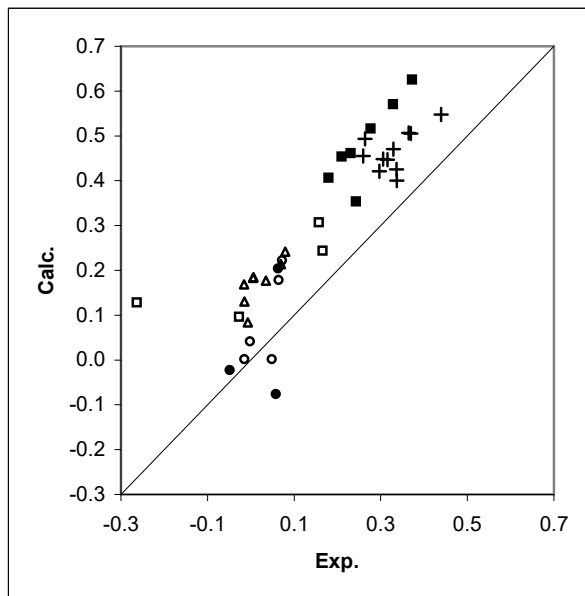

Figure 5. Temperature Dependence of the Logarithmic Activity Coefficients at Infinite Dilution $\ln(\gamma_i^{\inf,314K}) - \ln(\gamma_i^{\inf,344K})$ in [emim][N(Tf)₂]. Alkanes (▪), Alkenes (□), Alkylbenzenes (△), Alkohols (+), Polar Organics (○), and Chloromethanes (●).

Figure 6

Figure 6. Temperature Dependence of the Logarithmic Activity Coefficients at Infinite Dilution $\ln(\gamma_i^{\text{inf},314K}) - \ln(\gamma_i^{\text{inf},344K})$ in [em₂im][N(Tf)₂]. Alkanes (▪), Alkenes (▫), Alkylbenzenes (△), Alkohols (+), Polar Organics (○), and Chloromethanes (●)