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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 Strasse 515, D-51381 Leverkusen, Germany

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 past 10 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 such as chromatography, electrochemistry, and 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. Despite the interest, accurate thermodynamic data of ionic liquids and their mixtures are still rare.

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 has been reported recently.[3−6]

This work presents the application of the quantum chemically based thermodynamic prediction model COSMO-RS to ionic liquid 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 these 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, that is, on the molecular surface. These charges act back on the solute and generate a more polarized electron density than in a 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 a 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 toward 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 $p^{X_i}(\sigma)$ values of the components weighted by their mole fractions x_i in the mixture.

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

The most important molecular interaction energy modes, that is, electrostatics (E_{misfit}) and hydrogen bonding (E_{HB}), are described as functions of the polarization charges of

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* To whom correspondence should be addressed. E-mail: diedenhofen@cosmologic.de.

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two interacting surface segments σ and σ' or σ_{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.

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

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

$$E_{\text{vdW}} = a_{\text{eff}}(\tau_{\text{vdW}} + \tau'_{\text{vdW}}) \tag{4}$$

Equations 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 by solving a coupled set of nonlinear equations.

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

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.

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

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, for example, the activity coefficient:

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

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-ζ 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 parametrization BP_TZVP_C12_0402[18] is used. In such parametrization, 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 is not fitted for ionic liquids.

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

	$\ln(\gamma_i^{\text{inf}})$ in [bmpy] [BF$_4$]			
	314 K		344 K	
compounds *i*	expt	calcd	expt	calcd
	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 refs 7 and 8. [b] The exact experimental temperatures are given in refs 7 and 8. [c] Values at 333 and 363 K.

The activity coefficients have been calculated using eq 7. The ILs have been described by an equimolar mixture of two distinct ions; that is, 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

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

	$\ln(\gamma_i^{\mathrm{inf}})$ in [em$_2$im] [N(Tf)$_2$]				$\ln(\gamma_i^{\mathrm{inf}})$ in [emim] [N(Tf)$_2$]			
	314 K		344 K		314 K		344 K	
compounds *i*	expt	calcd	expt	calcd	expt	calcd	expt	calcd
Alkanes								
hexane	3.229	2.922	3.050	2.516	3.233	3.425	3.093	2.972
heptane	3.622	3.408	3.391	2.946	3.647	3.974	3.423	3.460
octane	4.015	3.888	3.738	3.372	4.069	4.518	3.809	3.943
nonane	4.441	4.365	4.113	3.794	4.521	5.057	4.186	4.421
decane	4.879	4.841	4.507	4.215	5.019	5.597	4.617	4.900
cyclohexane	2.699	2.423	2.456	2.069	2.656	2.854	2.465	2.460
2,2,4-trimethylpentane	3.569	3.352	3.359	2.898	3.587	3.918	3.364	3.411
Alkenes								
cyclohexene	2.040	1.516	1.874	1.272	2.015	1.866	1.869	1.592
1-methylcyclohexene	2.520	2.087	2.363	1.780	2.506	2.509	2.368	2.164
styrene	0.399	0.429	0.426	0.332	0.509	0.770	0.519	0.640
α-methylstyrene[c]	1.091	0.702	1.354	0.574	1.110	1.120	1.343	0.949
Alkylbenzenes								
benzene	0.093	0.203	0.100	0.119	0.163	0.467	0.166	0.358
toluene	0.499	0.649	0.514	0.519	0.551	0.965	0.574	0.806
ethylbenzene	1.035	1.077	1.000	0.900	1.042	1.452	1.018	1.240
o-xylene	0.793	1.000	0.809	0.831	0.874	1.358	0.896	1.157
p-xylene	0.945	1.145	0.938	0.960	0.995	1.519	1.009	1.301
m-xylene	0.964	1.130	0.959	0.947	1.006	1.501	1.012	1.285
isopropylbenzene	1.471	1.430	1.401	1.216	1.435	1.857	1.391	1.604
tert-butylbenzene	1.722	1.675	1.642	1.433	1.663	2.136	1.612	1.852
Alcohols								
methanol	0.378	0.920	0.073	0.472	0.123	0.839	−0.137	0.401
ethanol	0.714	0.922	0.399	0.476	0.422	0.917	0.171	0.474
1-propanol	1.015	1.146	0.686	0.676	0.736	1.214	0.466	0.740
1-butanol	1.359	1.432	0.989	0.927	1.080	1.564	0.771	1.049
1-pentanol	1.755	1.767	1.316	1.220	1.461	1.963	1.088	1.400
isopropyl alcohol	0.925	0.962	0.588	0.537	0.658	1.024	0.369	0.597
tert-butyl alcohol	0.888	1.107	0.591	0.686	0.640	1.234	0.395	0.804
sec-butanol	1.139	1.065	0.802	0.665	0.885	1.199	0.595	0.790
2-methyl-2-butanol	1.058	1.393	0.798	0.938	0.796	1.565	0.582	1.097
cyclohexanol[d]	1.420	1.573	1.157	1.079	1.101	1.583	0.890	1.104
1-hexanol[c]	1.756	1.717	1.392	1.210	1.659	2.166	1.306	1.587
Polar Organics								
acetonitrile	−0.772	−0.753	−0.821	−0.755	−0.832	−0.833	−0.870	−0.826
acetone	−0.772	−0.742	−0.757	−0.744	−0.919	−0.793	−0.879	−0.781
ethyl acetate	0.066	−0.360	0.068	−0.401	−0.121	−0.310	−0.079	−0.347
methyl *tert*-butyl ether	1.054	0.842	0.990	0.664	0.882	1.058	0.874	0.867
methyl *tert*-amyl ether	1.541	1.256	1.469	1.034	1.350	1.530	1.341	1.290
Chloromethanes								
dichloromethane	−0.095	−1.021	−0.153	−0.944	−0.115	−0.781	−0.149	−0.734
trichloromethane	−0.043	−0.408	0.006	−0.386	−0.028	−0.084	0.029	−0.095
tetrachloromethane	1.220	1.448	1.158	1.244	1.178	1.810	1.147	1.578

[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)$_2$].

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

The root-mean-square (rms) deviations 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 $\ln(\gamma_i^{\mathrm{inf}})$ are 0.7 ln-units (rms) and 1.0 ln-units (maximal deviation).[19] Thus, the accuracy of all calculated $\ln(\gamma_i^{\mathrm{inf}})$ values in ILs is in the expected range for nonionic 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 strongly depends on the number of chlorine atoms in the molecules. Dichloromethane shows a negative deviation from the experimental data (−0.941

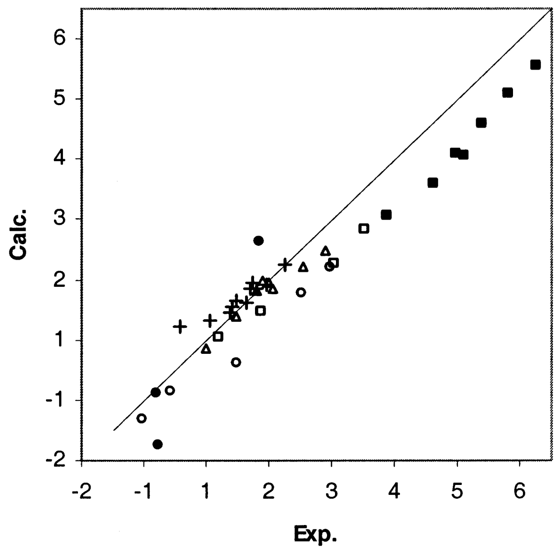

Figure 1. Calculated versus experimental logarithmic activity coefficients at infinite dilution $\ln(\gamma_i^{\mathrm{inf}})$ in [bmpy][BF$_4$] at 314 K: ■, alkanes; □, alkenes; △, alkylbenzenes; +, alcohols; ○, polar organics; ●, chloromethanes.

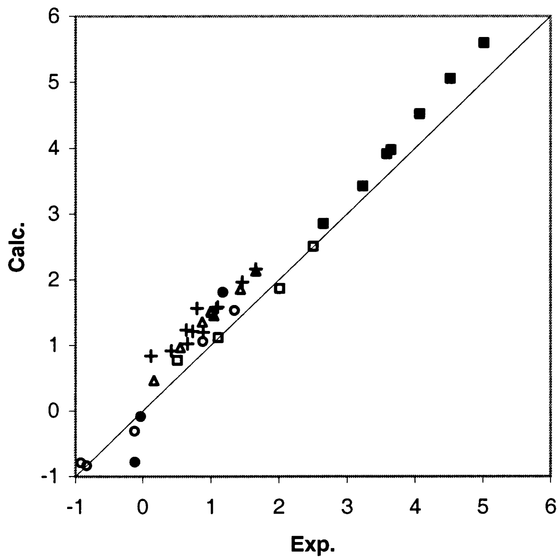

Figure 2. Calculated versus experimental logarithmic activity coefficients at infinite dilution $\ln(\gamma_i^{\mathrm{inf}})$ in [emim][N(Tf)$_2$] at 314 K: ■, alkanes; □, alkenes; △, alkylbenzenes; +, alcohols; ○, polar organics; ●, chloromethanes.

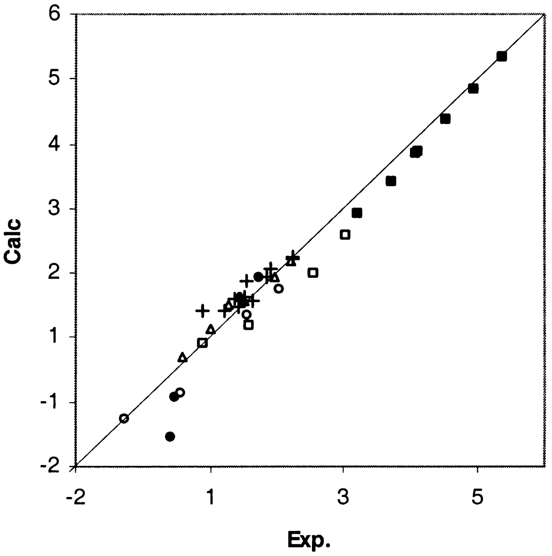

Figure 3. Calculated versus experimental logarithmic activity coefficients at infinite dilution $\ln(\gamma_i^{\mathrm{inf}})$ in [em$_2$im][N(Tf)$_2$] at 314 K: ■, alkanes; □, alkenes; △, alkylbenzenes; +, alcohols; ○, polar organics; ●, chloromethanes.

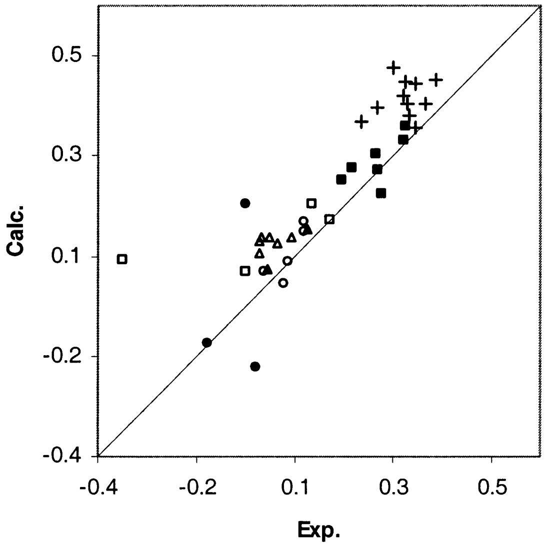

Figure 4. Temperature dependence of the logarithmic activity coefficients at infinite dilution $\ln(\gamma_i^{\mathrm{inf,314K}}) - \ln(\gamma_i^{\mathrm{inf,344K}})$ in [bmpy][BF$_4$]: ■, alkanes; □, alkenes; △, alkylbenzenes; +, alcohols; ○, polar organics; ●, chloromethanes.

ln-units), trichloromethane 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 $\ln(\gamma_i^{\mathrm{inf}})$ 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, for example, 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 $\ln(\gamma_i^{\mathrm{inf}})$ values calculated at 344 K, which are given in Tables 1 and 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 $\ln(\gamma_i^{\mathrm{inf}})$ is given in 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),

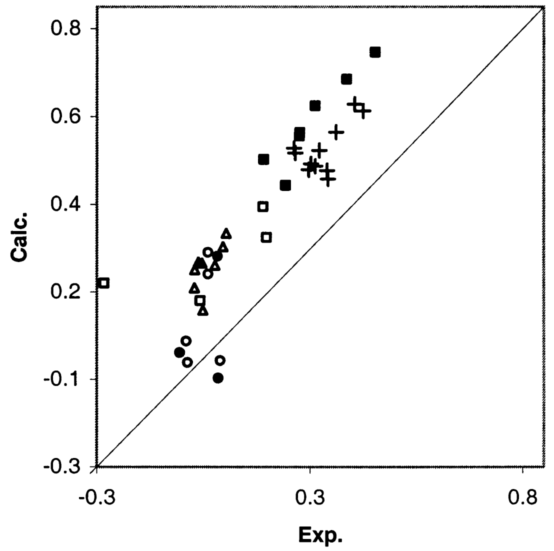

Figure 5. Temperature dependence of the logarithmic activity coefficients at infinite dilution $\ln(\gamma_i^{\mathrm{inf},314\mathrm{K}}) - \ln(\gamma_i^{\mathrm{inf},344\mathrm{K}})$ in [emim]-[N(Tf)$_2$]: ■, alkanes; □, alkenes; △, alkylbenzenes; +, alcohols; ○, polar organics; ●, chloromethanes.

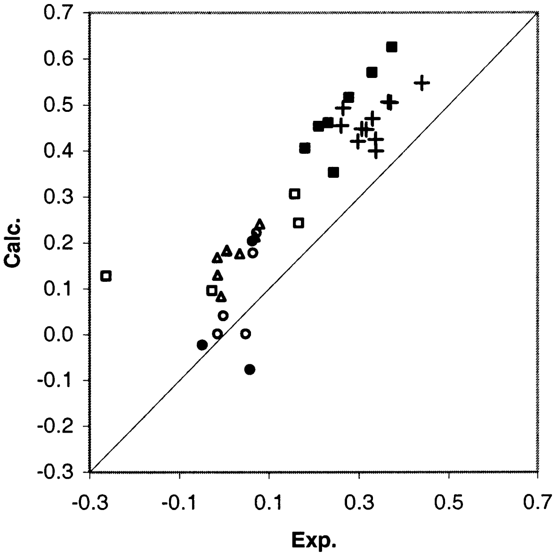

Figure 6. Temperature dependence of the logarithmic activity coefficients at infinite dilution $\ln(\gamma_i^{\mathrm{inf},314\mathrm{K}}) - \ln(\gamma_i^{\mathrm{inf},344\mathrm{K}})$ in [em$_2$im][N(Tf)$_2$]: ■, alkanes; □, alkenes; △, alkylbenzenes; +, alcohols; ○, polar organics; ●, chloromethanes.

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 does not 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.

Acknowledgment

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