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Theoretical Study of Ion Pairing in Protic Ionic Liquids of ΔpK_a Range 6 to 18

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Studies on "poor" protic ionic liquids, having proton-transfer strength $\Delta pK_a = pK_a(base) - pK_a(acid) = 0$-6, have shown the need to make corrections to the Fuoss equation for prediction of ΔG_{ioniz} and K_{ioniz} for ion-pairing equilibria in these systems. Recent work built empirical functions to replace the Fuoss equation for this ΔpK_a region, based on *ab initio* ion-pairing energies, but the functions did not perform well at the higher end of this range. Here, we extend the study to the range $\Delta pKa = 6$-18, examining hypothetical mixtures of trimethylamine (TEA) with acids from weak (CH_3COOH) to quite strong (CF_3SO_3H). *Ab initio* pairing energies were obtained for these systems, followed by refitting. Preliminary comparisons with experimental ionicities appear to show inaccuracies in the *ab initio* dataset, not in the fitting function form. Future work is planned to include dataset shifts, empirical or theoretical, to allow the goal of a predictive function for ionicity as a function of ΔpK_a and acid:base mixing ratio.

Introduction

Protic ionic liquids (PILs) can be made by anhydrous mixing of Bronsted acids with Bronsted bases, generating high ion concentrations via proton transfer (1-4). Some have particularly limited ionicity (5-7). It is of considerable interest to understand and predict the ionicity of PILs.

An experimental measure of ionicity is $\alpha = \sigma/\sigma_{ideal} = \Lambda/\Lambda_{ideal}$ where σ and Λ are respectively the specific (S cm^{-1}) and equivalent or molar (S cm^2 mol^{-1}) ionic conductivities. Ideal conductivity in liquids is normally defined with the idea that it should be limited only by viscosity η or the often-but-not-always-viscosity-controlled ion self-diffusion coefficients D_j. A summary of such definitions has been recently published (8). Here, we shall take Angell's simple Walden-plot choice (1) of $\Lambda_{ideal} = \eta^{-1}$, with the units for Λ_{ideal} being S cm^2 mol^{-1} if η is in Poise and the ion radii r are in Angstroms. Hence,

$$\alpha_{expt} = \alpha_{Angell} = \Lambda/\eta^{-1} \qquad [1]$$

Angell's ionicity metric was not α, but $\Delta\hat{W} = \log \Lambda_{ideal} - \log \Lambda = \log \eta^{-1} - \log \Lambda$, which can be converted into an ionicity via $\alpha_{Angell} = 10^{-\Delta\hat{W}}$. Example values for PILs appear in Table 1.

Table 1. Limited ionicities α of room-temperature 1:1 (n=1, x_{acid} = 0.5) ionic liquids from experiment (1,9), listed with acid-base proton transfer strength $\Delta pK_a = pK_a(base)-pK_a(acid)$.

ionic liquid	ΔpK_a	$\Delta\hat{W}$	$\alpha_{\eta,AW}$
dema CF_3SO_3H	16.54	0.21	0.62
α-pic CF_3SO_3H	12.15	0.35	0.45
dema CH_3SO_3H	12.97	0.37	0.43
dema CF_3COOH	10.25	0.83	0.15
α-pic CF_3COOH	5.86	0.93	0.12
dema CH_3COOH	5.62	1.75	0.02
α-pic CH_3COOH	1.23	3.20	0.001

Kite theory (8,10) offers a means of predicting ion concentrations (c_{ions}) in PIL, as a function of acid/base mixing ratio n and proton-transfer strength ΔpK_a, by predicting ion-pairing equilibrium constants K_{ioniz} from first principles. To relate its ion concentrations to conductivity, it uses a Walden's Rule formalism:

$$\sigma = W\frac{c_{ions}}{\eta} = W\frac{2\alpha\rho}{M\eta} \quad [2]$$

$$\alpha = \frac{c_{ions}}{c_{ions,ideal}} = \frac{c_{ions}}{2c_{kites}} = \frac{c_{ions}}{(2\rho/M_{kites})} \quad [3]$$

where W is the Walden constant, α is the degree of ionization, c = molar concentration, ρ = liquid mass density, and M_{kite} = molar mass of the stoichiometric electrolyte, envisaged as a parent "kite" molecule. For instance, for the more common case of acid/base ratios n ≥ 1, the electrolyte is written as $BH^+(A^-_nH^+_{n-1})^-$ (B = base e.g. trialkylamine, A^- = acid anion e.g. acetate or triflate). Simpler abbreviate kite notations are $B(HA)_n$ or BA_n.

Now, since Angell's Λ_{ideal} corresponds to fully dissociated aqueous potassium chloride, its $c_{ions,ideal}$ would be $2c_{salt}$, entirely analogous to the choice $2c_{kites}$ in kite theory, Thus, in kite theory, the Angell ionicity (eq. 1) is the degree of ionization (eq. 2). We have been actively pursuing the development of kite theory as a means of explaining and predicting the experimentally determined ionicities (8,10-12).

Two difficulties, addressed in 2023 (8), were (i) the need to replace the Fuoss equation for predicting the *association Gibbs energy of ion pairing*, $\Delta G_{A,+-}$, and (ii) the need to predict *additional association Gibbs energies* ($\Delta G_{A,+0}$, $\Delta G_{A,0-}$, $\Delta G_{A,00}$), due to the need to account for triple ions $[BH{\cdot}A{\cdot}HB]^+$, $[BH{\cdot}AHA{\cdot}HB]^+$ observed (10,11) in *ab initio* molecular dynamics simulations of "weak PILs" ($0 < \Delta pK_a < 6$). In 2023 such equations were presented, built by considering dipole and induced-dipole terms and requiring fitting to a generated *ab initio* dataset of association Gibbs energies. However, this was only done for the range $0 < \Delta pK_a < 6$, and the resulting ionicities at the upper half of this range were too low compared to experiment (12). Hence, here we wished to extend these equations to a broader ΔpK_a range ($0 < \Delta pK_a < 18$), by extending the *ab initio* dataset to include strong PILs ($6 < \Delta pK_a < 18$) and refitting the empirical (induced-dipole motivated) association Gibbs energy equations.

Computational Methods

As before (8) for the weak PIL systems (various amines with acetic acid), Gaussian09 (13) was used to optimize the geometries and compute energies of several hydrogen-bonded complexes, but now for strong-PIL systems: triethylamine (TEA) paired with CF_3COOH, HNO_3, CH_3SO_3H, and CF_3SO_3H (ΔpK_a = 10.61, 12.15, 13.35, 16.91). The system TEA with CH_3COOH (ΔpK_a = 5.99) was redone, due to the decision to switch to the use of lower-energy cis-HOXO acid conformers (the previous study used only trans-HOCO acid conformers). The quantum chemistry ESM (electronic structure method) used for "opt+freq" calculations (geometry optimization and vibrational frequencies for Gibbs energy) was B3LYP/6-31+G(d,p), one of the methods used in the weak PIL study (8). Again, the opt+freq calculations were performed in 3 solvation environments: the gas phase (equivalent to a dielectric constant $\varepsilon = 1$), and with SCRF(solvent=aceticacid) and SCRF(solvent=water), which employs $\varepsilon = 6.2528$ and 78.3553 (respectively) within Gaussian09's default continuum solvation model (IEFPCM with UFFx1.1 cavity radii, here "CSM=def").

Later, when the accuracy of CSM=def came into question, we obtained a second *ab initio* dataset, with single-point energies (using B3LYP/6-31G(d,p)/def geometries), still using B3LYP/6-31G(d,p) but with the alternative CSM=SMD.

As usual (8), the CSM-specific Gibbs energy computation for 1 molar concentration is:

$$G^* = G_{el,\varepsilon}^* + G_{freq}^\circ + \Delta G^{\circ\rightarrow *}$$

where ° indicates gas-phase standard-state conditions of T° = 298 K and P° = 1 atm. $G_{el,\varepsilon}^*$ is the electronic energy with the solvation correction. G_{freq}° is the set of thermal motion (nuclear-motion degree-of-freedom) corrections, including zero-point vibrational energy, to convert electronic energy to Gibbs energy. A Gaussian09 SCRF frequency run reports a Gibbs energy that is conventionally understood to be only the sum $G_{el,\varepsilon}^* + G_{freq}^\circ$, and thus the researcher must add the $\Delta G^{\circ\rightarrow *}$ cratic (concentration-change) term RT ln (c*/c°) = RT ln ([1 M]/[P°/RT°]) = +1.89 kcal mol^{-1} *a posteriori*. For the CSM=SMD dataset we used the CSM=def opt+freq run for G_{freq}° and the CSM=SMD single-point run for $G_{el,\varepsilon}^*$.

From these G* values, the association Gibbs energies for the following associations were computed (H atoms omitted in notation):

$\Delta G_{A,+-}(n)$: $B^+ + A_n^- \rightarrow BA_n$
$\Delta G_{A,+0}(n)$: $B^+ + BA_n \rightarrow BA_nB^+$
$\Delta G_{A,0-}(n)$: $A + A_n^- \rightarrow A_{n+1}^-$
$\Delta G_{A,00}(n)$: $A + BA_n \rightarrow BA_{n+1}$

This data will be presented in a forthcoming full paper. This data was then fit via least-squares regression (Excel SOLVER algorithm) to the same empirical functions published in 2023 (8). Table 2 summarizes the parameter values obtained.

Table 2. Parameter values for kite-theory functions for association Gibbs energies.

Parameter	DEF0[a]	DEF2[b]	SMD2[c]	AVG2[d]
-TΔS	5.00	3.700	6.027	4.863
zeta	0.0020	0.0038	0.0042	0.0040
r_{+1}	4.08	19.535	17.811	18.673
r_{+2}	-0.33	-0.587	-0.175	-0.381
r_{+3}	-2.29	-17.262	-15.545	-16.403
r_{+4}	4.21	19.358	16.955	18.157
r_{+5}	-0.14	-0.038	0.147	0.055
r_{+6}	-2.88	-18.641	-16.219	-17.430
r_{01}	2.15	4.885	2.827	3.856
r_{02}	-0.37	-0.582	-0.544	-0.563
r_{03}	0	-1.883	0.308	-0.787
r_{04}	1.62	1.904	1.992	1.948
r_{05}	-0.27	-0.142	-0.049	-0.096
r_{06}	0	-0.924	-1.191	-1.057
μ_{+1}	2.90	21.902	21.625	21.763
μ_{+2}	0.13	-0.096	0.291	0.097
μ_{+3}	-2.49	-21.403	-21.057	-21.230
μ_{+4}	0.27	0	0	0
μ_{+5}	0	0	0	0
μ_{+6}	0	0	0	0
μ_{01}	2.53	21.902	21.625	21.763
μ_{02}	0.19	-0.096	0.291	0.097
μ_{03}	-2.43	-21.403	-21.057	-21.230
μ_{04}	1.05	0	0	0
μ_{05}	-0.16	0	0	0
μ_{06}	0	0	0	0

[a] from fit to B3LYP/def 2022 dataset (8,12) (trans-acid conformers, weakIL only)
[b] from fit to B3LYP/def 2024 dataset (cis-acid conformers, weakIL + strongIL)
[c] from fit to B3LYPSMD 2024 dataset (cis-acid conformers, weakIL + strongIL)
[d] "averaged" function, from averaging the DEF2 and SMD2 parameter values.

Results and Discussion

Figure 1 shows the plots of $\Delta G_{A,+-}$, versus mixing ratio n, from the two datasets and their resulting fitting functions. Results for the additional association Gibbs energies ($\Delta G_{A,+0}$, $\Delta G_{A,0-}$, $\Delta G_{A,00}$) will be shown in the follow-up full paper.

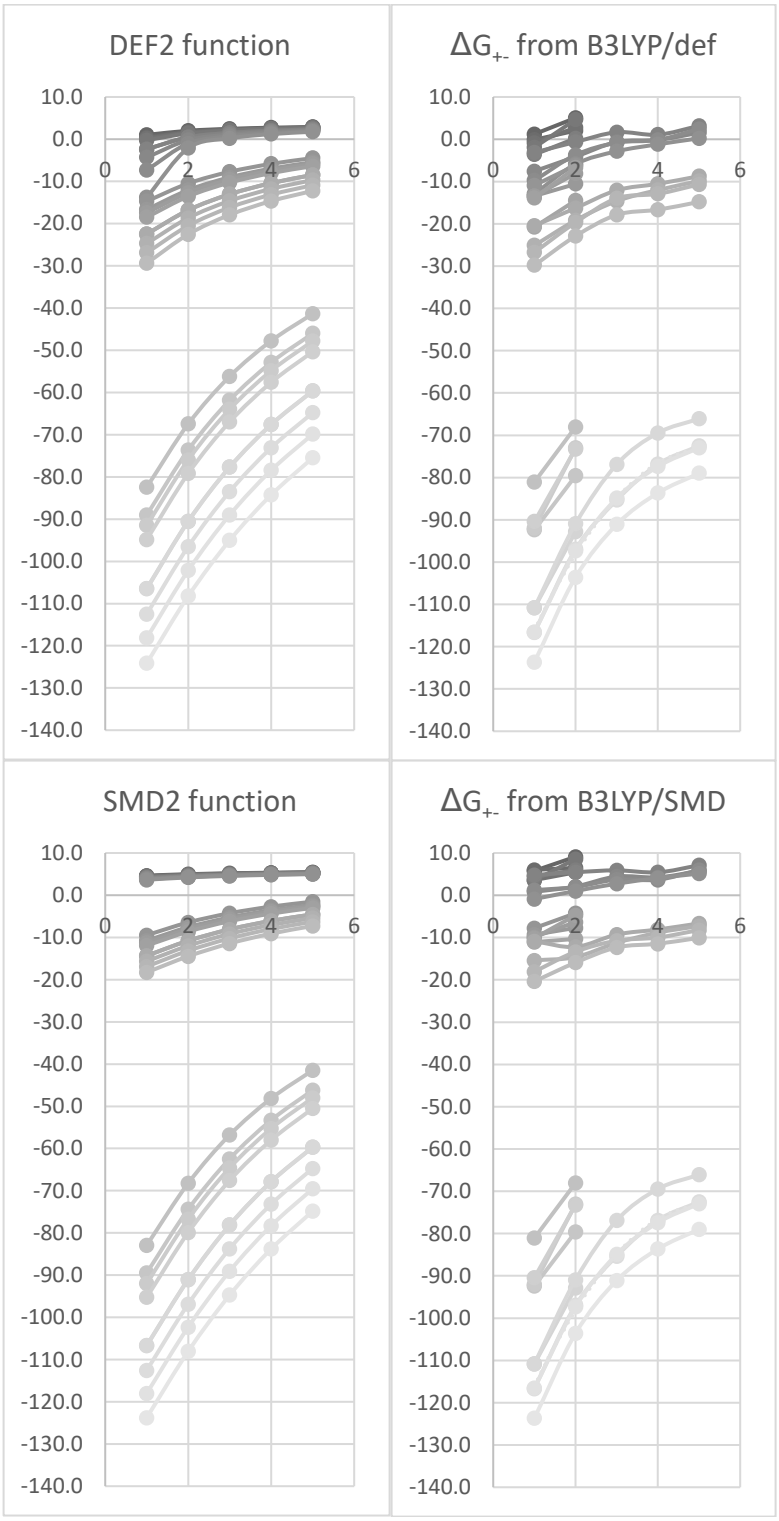

Figure 1. Association Gibbs energies (kcal/mol) for PIL ion pairing $B^+ + A_n^- \rightarrow BA_n$, versus mixing ratio (= kite length) n. Upper curves: 8 PIL systems, ε=78. Medium curves: 8 systems, ε=6. Light curves: 8 systems, ε=1. Right side: dataset results, from the new B3LYP *ab initio* computations. Left side: from the 2023 empirical function (8) refitted to each of these datasets.

We then took these ΔG_A's empirically fitted functions and generated ionization Gibbs energies, for arbitrary values of ΔpK_a, ε, and n, for the two ion-generating equilibria considered before (12):

$\Delta G_{ioniz}(2{:}2) = \Delta G_{A,+0} - \Delta G_{A,+-}$, for $2\ B(HA)_n \rightleftharpoons B(HA)_nHB^+ + A(HA)_{n-1}^-$

$\Delta G_{ioniz}(1{:}2) = -\Delta G_{A,+-}$, for $B(HA)_n \rightleftharpoons HB^+ + A(HA)_{n-1}^-$

$K_{2:2} = e^{-\Delta G_{2:2}/RT}$

$K_{1:2} = e^{-\Delta G_{1:2}/RT}$

The results appear in the following figures. It is seen that the functions DEF2 and SMD2, fit to different datasets, give differing results. Although the SMD2 results for n=1 (the 1:1 mixtures) appear to give surprisingly good ionicities α (compare to Table 1), it does not predict the cation identities well, since they produce very few triple ions, in qualitative disagreement with results from simulations (10, 11).

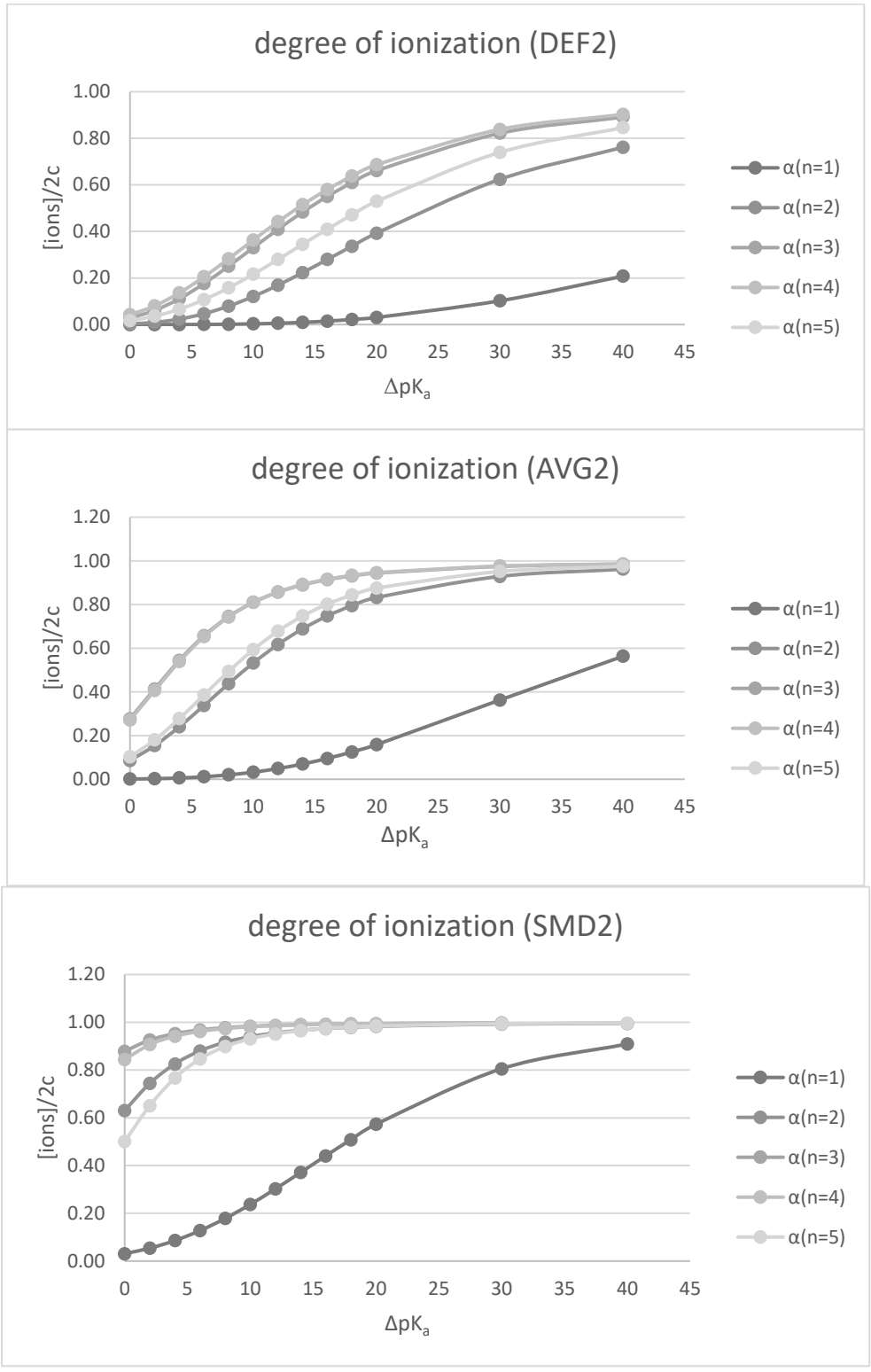

Figure 2. Ionicity α from the predictive functions.

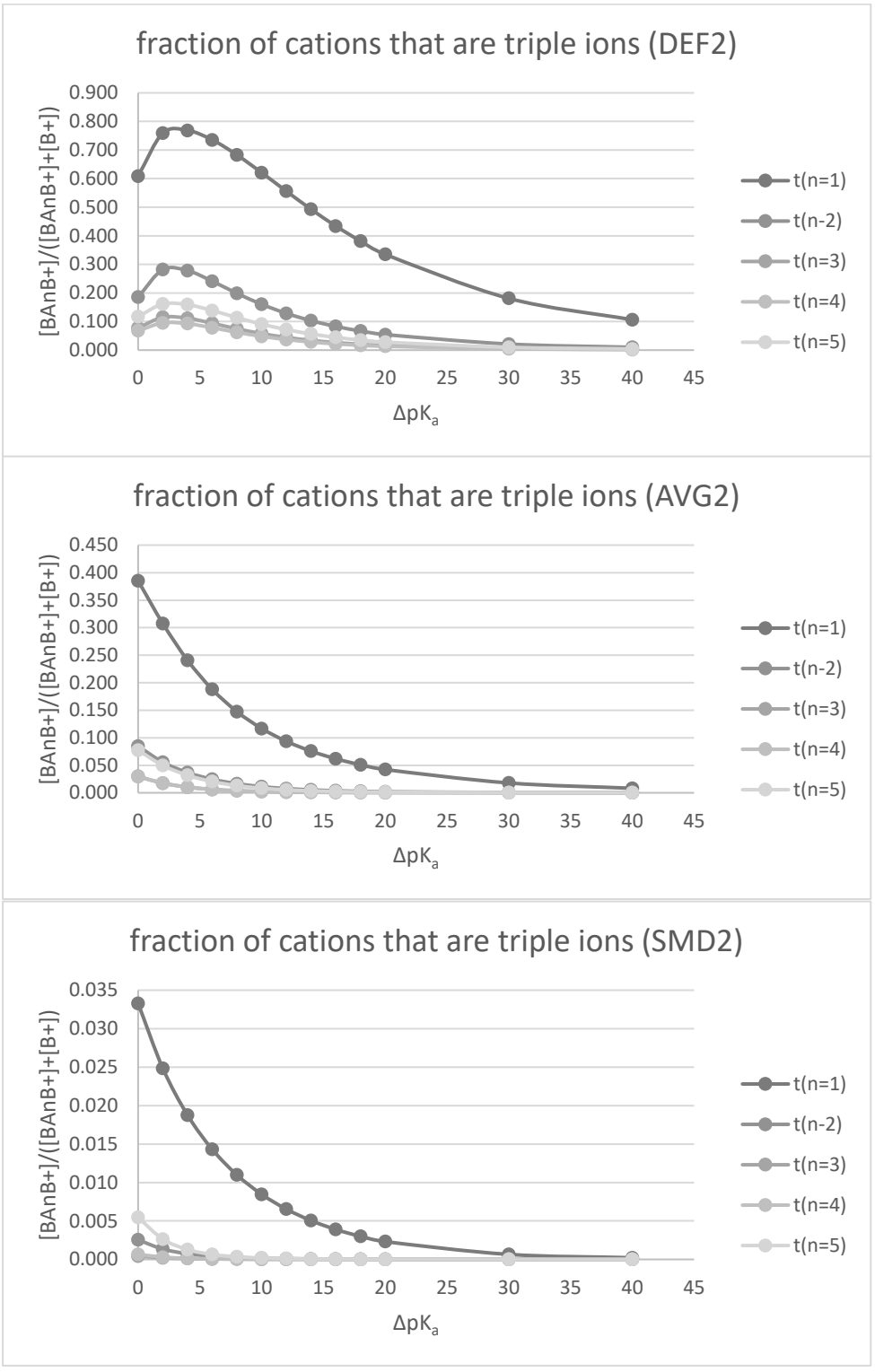

Figure 3. Fraction of cations that are triple ions; the results are generally too low compared to results of previous simulations (10,11).

Conclusions

Kite theory functions for ion concentrations and ionicities were generated by fitting to *ab initio* data obtained for a wider ΔpK_a range than before. They reveal inaccuracies in the *ab initio* datasets, caused by the approximate continuum solvation models (CSMs): the results from two different CSMs were shown, to quantitatively demonstrate this uncertainty. Future work will aim at adding some experimental data into the least-squares fitting procedures, to generate more accurate predictive functions.

Acknowledgements

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