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Limited Ionicity in Protic Ionic Liquids: Ionization Gibbs Energies in Organic Acid/Trialkylamine Mixtures

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The nature of the ions present in mixtures of trialkylamines (B) with carboxylic acids (HA) is discussed. New ab initio molecular dynamics (AIMD) simulations of mixtures of triethylamine (TEA) with acids here reveal the same cation type, the large complex $[B(HA)_nHB]^+$, as seen earlier with pyridine (PYR). Since this indicates that the ionization equilibrium reaction 2 $B(HA)_n \rightleftarrows B(HA)_nHB^+ + A(HA)_{n-1}^-$ is perhaps more general than for pyridine systems, a new analysis derives ΔG for this equilibrium reaction from experimental conductivities, viscosities, and densities, as a function of x_B (mole fraction of B in the acid/base mixture). The results show that large Walden constant values, which might be indicative of Grotthuss H^+ conductivity mechanisms, are not needed except for formic-acid-rich mixtures.

Introduction

Protic ionic liquids (PILs) are a subset of ionic liquids formed by certain mixtures of a Bronsted acid with a Bronsted base, generating ionic species through proton transfer (1-4). The ionicity of PILs is not always as high as anticipated, often calling into question their inclusion into the category of ionic liquids, and the reasons for such limited conductivity is an active research topic.

In the classic cases of carboxylic acids with amines, not only are conductivities low, but they show maxima in conductivity at acid mole fractions near $x_B = 0.17$ (1:5 base:acid) (5-9), rather than the more commonly studied 1:1 mixtures. A second maximum of varying location is also occasionally seen (5,8,9). Additionally interesting is that this conductivity maximum location ($x_B \approx 0.2$) is often close to, or even coincident with, the viscosity maximum location ($x_B \approx 0.2$-0.3), which at first may seem counterintuitive. Table 1 provides motivating data.

We are in pursuit of a theory that can explain these phenomena, qualitatively and semiquantitatively, with an ultimate goal of predicting the conductivity of a given mixture at any mixing ratio. We had begun ("2018 theory") with a system (pyridine + acetic acid) in which the conductivity and viscosity maxima are coincident, at $x_B = 0.17$ (10). In this paper we begin the extension to *non-coincident* systems. We present here an examination of the thermodynamics and plausible Walden constants of five triethylamine systems (TEA + carboxylic acids) and one tributylamine system (TBA + propionic acid).

TABLE I. Mole fractions of property extrema in amine/acid mixtures: VE = volume excess, η = viscosity, [ions] = total ion concentration, σ = specific (ionic) conductivity.

Mixture [a]	**$x_B(VE_{min})$**	**$x_B(\eta_{max})$**	**$x_B([ions]_{max})$** [b]	**$x_B(\sigma_{max})$**
TEA/a1	≥ 0.40	≥ 0.40	0.19 ± 0.01	0.10 ± 0.01
TEA/a2	0.35 ± 0.02	0.28	0.19 ± 0.01	0.13 ± 0.02
TEA/a3	0.35 ± 0.02	0.28	0.20 ± 0.01	0.16 ± 0.01
TEA/a4	0.34 ± 0.02	0.25	0.23 ± 0.01	0.18 ± 0.02
TEA/a5	0.33 ± 0.02	0.25	0.24 ± 0.01	0.20 ± 0.02
PYR/a2	0.19 ± 0.03	0.17	0.17 ± 0.01	0.17

[a] a1-a5 refer to acids formic-pentanoic; TEA = triethylamine, data from Huyskens (7); PYR = pyridine, data from Venkatesan (11).

[b] The location of the maximum of the product $\eta\sigma$; see Eq. [17].

Huyskens and co-workers had developed a very similar theory for the TEA systems already in 1980 (7). They, like us, use Walden's (Viscosity) Rule as the central relation:

$$\sigma = W\,C\,/\,\eta \qquad [1]$$

where σ and η are the specific conductivity (S cm^{-1}) and viscosity (cP) of the electrolyte, C the ion or electrolyte concentration (mol L^{-1}), and W a proportionality constant known as the Walden constant (units S cP cm^2 mol^{-1}) (12). Eq. [1], though originally empirical, can be derived from Stokes' Law (see Theory section). Huyskens et al. began their paper by agreeing with the hypothesis of Kohler et al. that an apparent preference of the mixtures for $B(HA)_3$ complexes (B = base amine, HA = carboxylic acid) explains the viscosity maximum at $x_B = 0.25$ (13). Huyskens et al. then proposed (based on some assumptions about W magnitudes in Eq. [1]) that the apparent ion concentration maximum at $x_B = 0.20$ is due to the ionization equilibrium

$$B(HA)_3 + HA \rightleftarrows BH^+ + A(HA)_3^- \qquad [2]$$

and, further, that the different conductivity magnitudes among the heavier acids could be ascribed to their dielectric constants. This proposed equilibrium was indeed a clever way to explain how a conductivity maximum could be displaced from a viscosity maximum. Their notion of a complexed anion $A(HA)_n^-$ with A = carboxylate is quite analogous with the halide cases (A = Cl- or Br-) that were detected by Angell (14) and Johnson (15) and assumed in very old studies of amines with strong mineral acids (16).

A flaw was quickly spotted. In the following year (1981), Kohler and co-workers presented ^{1}H-NMR data which placed the acidic proton at 8-12 ppm, too far downfield to indicate a free BH^+ entity, and instead indicative of a partially bridged proton, strongly hydrogen bonded (8). Kohler et al. gave a counterproposal: that the conductivity is occurring not by translating ionic aggregates but by "a flipping over of hydrogen bonds," possibly a reference to a Grotthuss H^+ mechanism. This counterproposal, however, has two problems of its own. First, Kohler et al. erringly stated that the conductivity maximum was at $x_B = 0.25$ like viscosity (which might support a Grotthuss claim), when in fact their own data shows the conductivity maxima at $x_B = 0.17$ or lower. Second, Angell (1) used Walden plots to show that these systems do not show any enhanced ion mobility afforded by a supposed Grotthuss mechanism: the conductivities are poorer than those of the most highly ionic 1:1 PILs from the strongest acid/base combinations, which, like aprotic ILs, conduct via molecular ions or ion aggregates (the so-called “vehicular” mechanism).

There is, fortunately, a resolution at hand. The ^{1}H-NMR data can be explained by our discovery, via ab initio molecular dynamics (AIMD) simulations of pyridine + acetic acid mixtures, that the cationic species at equilibrium in that system are not free BH^+ but larger $[B(HA)_nHB]^+$ cationic aggregates (n = 0, 1, 2, …) (10). Those simulations, of the mixtures at equilibrium, showed no evidence of H^+ hopping. There was rare hopping of “monomeric” acetic acid or pyridinium ions from complex to complex, which as we pointed out might contribute to conductivity, but the relative rarity of their hops at room temperature caused us to pursue a theory based on ordinary vehicular transport of charge, as Huyskens et al. had done (7), but with an updated ionization equilibrium:

$$B(HA)_m + B(HA)_n + \rightleftarrows [B(HA)_mHB]^+ + A(HA)_{n-1}^- \qquad [3]$$

and further mathematical development (10). We note in passing that this reaction requires two base molecules to generate two ions, unlike the Huyskens equilibrium which requires just one.

In that same 2018 paper we went on to produce an equation for conductivity as a function of viscosity, molar volume, dielectric constant, and ion size (10). Using fitted experimental data for the first two properties, linearly interpolated dielectric constants, the Fuoss equation (17) for degree of dissociation of ion pairs (from ion size and dielectric constant of the medium), and only two fitting parameters to represent the poorly known ion sizes needed for the Fuoss (ions that are pairing) and Walden (big ions that are translating) equations, the conductivity equation successfully reproduced the experimental conductivity curve in the pyridine/ethanoic acid system. The resulting fit gave reasonable effective conduction ion sizes of 6 Å (cations) and 11 Å (anions) for the pyridine/acetic acid system. It was noted, however, that an exploratory fit to the triethylamine/acetic acid system predicted overly large ions (10).

In this preliminary Communication, we first present results from AIMD simulations of the TEA/acid systems to examine ion speciation, supporting the continued use of Eq. [3] as the ionization reaction. Second, we derive ionization Gibbs energies for this reaction from experimental conductivities and viscosities and a selection of assumed Walden constant values W. The resulting relationship of ΔG_{ioniz} with mole fraction is discussed, and the limitations on plausible W values are used to test the assumption of vehicular (vs. Grotthuss) conductivity.

In a later full paper we intend to present an updated conductivity theory that merges the 2018 and 1980 ideas and can hopefully fit (and thus explain) the conductivities of several of these amine + organic acid systems.

Theory (Derivation of Walden's Rule)

This is improved upon our earlier presentation (10) by (i) generalizing to handle mixtures having more than two kinds of ions, and (ii) avoiding the superfluous step of converting ion velocities to ion diffusion constants. Conductivity σ is the proportionality constant relating the external electric field X to the induced electrolyte current *i*:

$$i = \sigma X \qquad [4]$$

The current, in terms of ion velocities v_j, is:

$$i = \Sigma\, q_j\, \rho_j\, v_j \qquad [5]$$

where the sum runs over all ion types *j*, and q_j and ρ_j are the ion charge and ion density (concentration). The ion velocities achieve steady ("terminal") values because the constant force F_j on the ion *j* due to the field X,

$$F_j = q_j X\,, \qquad [6]$$

accelerates the ions faster and faster until the rising viscous drag force F_j' finally matches the field force F_j, at which point acceleration stops and velocities are steady. The viscous drag force on spherical particles in a structureless medium is given by Stokes' Law:

$$F_j' = -6\pi\eta r_j v_j \qquad [7]$$

where r_j is the ion radius (Stokes radius). Thus, when the velocities are steady, $F_j' = F_j$ and equating the last two equations gives

$$v_j = q_j X/(6\pi\eta r_j) \qquad [8]$$

which inserts into Eq. [5] to give

$$\begin{aligned} i &= \Sigma\, q_j\, \rho_j\, [q_j X/(6\pi\eta r_j)] \\ i &= [\, \Sigma\, q_j^2 \rho_j/(6\pi\eta r_j)\,]\, X \qquad [9] \end{aligned}$$

This matches Eq. [4], revealing σ to be

$$\sigma = [1/(6\pi\eta)]\, \Sigma\, (q_j^2 \rho_j/r_j) \qquad [10]$$

A second way of writing this uses $q_j = z_j e_0$ (integer times electron charge) $\rho_j = N_{AVO}\, c_j$ (Avogadro's number times ion molarity), and $F = N_{AVO}\, e_0$:

$$\sigma = [e_0 F/(6\pi\eta)]\, \Sigma\, (z_j^2 c_j/r_j) \qquad [11]$$

A third way of writing this is

$$\sigma = (1/\eta)\, \Sigma\, W_j c_j\,, \qquad [12]$$

$$W_j = [e_0 F/(6\pi)]\, (z_j^2/r_j) \qquad [13]$$

where W_j is the *ion-specific Walden constant.* The constant factor $e_0F/(6\pi)$ is 81.9 S cP cm^2 Å mol^{-1}.

To accommodate ion pairing, we relate each ion concentration c_j to a formal electrolyte concentration $c = V_m^{-1}$ with a degree of ionization α_j:

$$c_j = \alpha_j c \qquad [14]$$

With this, a fourth way of writing the conductivity expression is

$$\sigma = (c/\eta)\ \Sigma\ \alpha_j W_j \qquad [15]$$

Furthermore, if the electrolyte is a simple 1:1 salt, $\alpha_+ = \alpha_- = \alpha$, which produces the expressions

$$\sigma = 2\alpha c W/\eta \qquad [16]$$
$$\sigma = WC/\eta \qquad [17]$$

where W is the *average* W_j and C is the *total* ion concentration:

$$W = \tfrac{1}{2}\,(W_+ + W_-) \qquad [18]$$
$$C = c_+ + c_- = 2\alpha c \qquad [19]$$

It is Eq. [17] that is Walden's Rule, often written as $\Lambda\eta = W$ where Λ is the molar or equivalent conductivity σ/C. The expression for W in Eq. [18] was erroneously missing the factor of ½ previously (10), due to confusion with an alternative formalism that takes C to be c instead of $2\alpha c$, i.e. that takes C in Walden's Rule (Eq. [17]) to be formal electrolyte concentration instead of total ion concentration. We shall keep W and C as defined in Eqs. [18] and [19].

There is an additional convention decision to make, regarding the definition of the formal electrolyte concentration c itself in these acid+base mixtures, due to the various ions formed as mole fraction x_B is varied. As before (10) we take c to be total initial concentration of acid + base (roughly 5-15 M),

$$c = V_m^{-1} = [B]_{init} + [HA]_{init} \qquad [20]$$

This is unlike Huyskens et al. (7) who chose c to be initial concentration of base only, $[B]_{init}$. The choice of convention affects the values of c and hence $\alpha_j = c_j/c$, but not the ion concentrations c_j.

Methodology

Simulations were performed as before (10) using the Vienna Ab-initio Simulation Package (VASP) software (19). VASP simulations assign each atom nucleus a randomized velocity and direction of motion, and moves them in steps (timestep 1 fs, as before) dictated by Newton's laws of motion, with the forces applied on each individual nucleus coming from the approximate solution of the Schrodinger equation for electronic energy. VASP performs periodic replication of a unit cell to model condensed phases. Initial Cartesian coordinates were generated using Gaussview 5.0. Unit cell side lengths were chosen to match the experimentally known density of the mixture at the given mixing ratio.

Results and Discussion

Simulations

Initially, several short 10 ps simulations (1 fs timesteps) were performed on three systems, TEA with formic (a1), acetic (a2), or propanoic (a3) acids, at selected acid-rich mixing ratios (2:18, 3:15, 4:6, 5:5), starting from neutral monomer molecules. These established that triethylamine, like pyridine, readily forms ion-pair "kites" $B(HA)_n$ of various lengths *n*, up to n=8 for TEA/a1 and n=5 for TEA/a2 or TEA/a3. Such short simulations would not be expected to achieve equilibration; indeed, none of these short simulations generated any free ions or ion complexes. The long lengths of kites, however, are noteworthy, as such lengths were not anticipated by either Huyskens et al. (7) or Kohler et al. (8).

One simulation was run for 630 ps, in hopes of observing ions to learn their nature. For this we chose the 3:15 TEA/a1 mixture, the system and mixture thought to have the highest concentration of ions. This simulation began with 10 neutral HA (HCOOH), 2 neutral B (Et_3N), and one ion-pair kite $B(HA)_5$. One of the free base molecules was protonated rather quickly. Between 100 and 200 ps the species observed were one each of $[B(HA)_7HB]^+$, $A(HA)_5^-$, B, and $(HA)_2$. The other free base was not protonated until ~ 540 ps (540000 timesteps), with a noticeable step drop in the plot of energy vs. time. At the end of the run, the species observed (Fig. 1) were one each of $[BHAHB]^+$, $A(HA)_6^-$, $B(HA)_5$, and $(HA)_2$. Hence the cations produced by the simulation were the "two-headed kites" $[B(HA)_7HB]^+$ and not the BH^+ ions assumed by Huyskens (7). This observation of the cations as two-headed kites matches what we found previously in pyridine/acetic acid simulations (10).

The insight gleaned from simulations allow us to update the past explanations of excess volume and viscosity data vs mixing ratio. Table 2 shows our summary of the expected sizes of the neutral molecules and complexes, at various mixing mole fractions, with comparison to the hypotheses put forward in 1980-81.

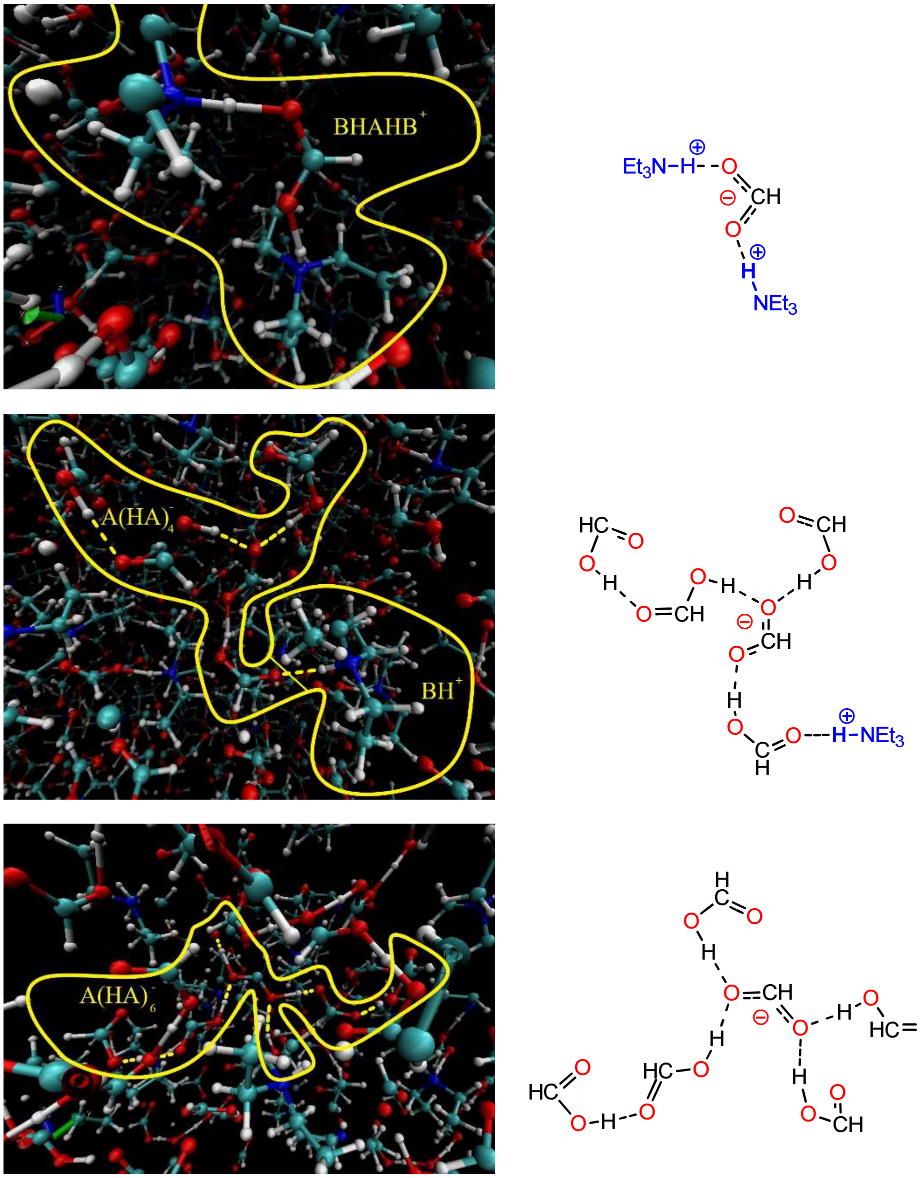

Figure 1. Snapshots of portions of the simulation cell at the final timestep of the long $(Et_3N)_3(HCOOH)_{15}$ simulation, showing (top) the BHAHB$^+$ cation, (middle) the B(HA)$_5$ ion pair "kite," and (bottom) the A(HA)$_6^-$ "free tail" anion.

TABLE II. Improvements in "minimalist" descriptions of the neutral complexes in TEA/acid mixtures (x_B = mole fraction of base, A = acid molecule HA).

x_B	ba$_3$ idea [a]	ba$_3$ + ba idea [b]	current work
0.05	$BA_3 + 8\ A_2$	$BA_3 + 8\ A_2$	$BA_{9+2y} + (5\text{-}y)\ A_2$ [c]
0.10	$BA_3 + 3\ A_2$	$BA_3 + 3\ A_2$	BA_9
0.25	$y\{BA_3\}$ + $z\{B + 1.5\ A_2\}$	$y\{BA_3\}$ + $z\{BA + A_2\}$	BA_3
0.33	$y\{BA_3 + 0.5\ B\}$ + $z\{B + A_2\}$	$y\{BA_3 + BA\}$ + $z\{BA + 0.5\ A_2\}$	BA_2
0.50	$BA_3 + 2\ B$	BA	BA
0.90	$BA_3 + 26\ B$	BA + 8 B	BA + 8 B

[a] In the spirit of Kohler et al. (8)

[b] In the spirit of Huyskens et al. (7)

[c] At very small x_B such as 0.05, the maximum kite length varies with the acid involved, e.g. y=0 for pentanoic and butanoic acid, but larger for propanoic and acetic acids.

Ionization Gibbs Energies

To simplify the mathematics, we do as before (10) and reduce the number of Eq. [3] equilibria to one at each value of x_B:

$$2\ B(HA)_n + \rightleftarrows [B(HA)_nHB]^+ + A(HA)_{n-1}^- \qquad [21]$$

$$K_{ioniz} = [B(HA)_nHB^+][A(HA)_{n-1}^-]/[B(HA)_n]^2 = (\alpha c)(\alpha c) / (x_ic - 2\alpha c)^2 \qquad [22]$$

The generation of $\Delta G_{ioniz}(x_B)$ values from experimental conductivities can be achieved if one assumes (a) that all the conductivity arises from translation of these product ions, and (b) the error made by adopting a "minimalist" model (of one Eq. [21] ionization reaction at each x_B value) is negligible. With these assumptions, the generation of $\Delta G_{ioniz}(x_B)$ values occurs via Eqs. [17-19]:

$$\alpha = \sigma_{expt}\eta_{expt} / 2c_{expt}W \qquad [23]$$

$$K_{ioniz} = \alpha^2 / (x_i - 2\alpha)^2 \qquad [24]$$

$$\Delta G_{ioniz} = -RT \ln K_{ioniz} \qquad [25]$$

where $c_{expt} = \rho_{expt}/(x_AM_A+x_BM_B)$ is the formal concentration of monomers before complexation and ionization (Eq. [20]), 2α is the degree of ionization (of the monomers, Eq. [19]), and x_i is the mole fraction of the *minority* ingredient (x_B if $x_B < 0.5$, x_A if $x_A < 0.5$). The reasoning for needing the minority x_i for kite concentration $[B(HA)_n] = x_ic - 2\alpha c$ is the following. If $x_B < 0.5$, the system consists initially of only kites $[B(HA)_n]$, whose concentration is limited by and equal to the initial base concentration, x_Bc. However, if $x_A < 0.5$, the system consists initially of minimal-length kites [BHA] and excess free base [B], and hence the kite concentration is limited by and equal to the initial acid concentration, x_Ac. Eq. [24] is Eq. [22] simplified, and Eq. [23] is Eq. [16] rearranged.

Results appear in Fig. 2. The shape of these ΔG_{ioniz} curves is driven principally by the dielectric constant $\varepsilon(x_B)$, which affects the stability of ions. While the pure acids and bases generally have low ion-destabilizing dielectric constants (except formic acid), the "kite" complexes $B(HA)_n$, especially for $n > 1$, have large dipoles, creating significantly larger dielectric constants in the range $x_B = 0.1\text{-}0.5$. Huyskens et al. (7) predicted 10-fold increases in dielectric constant at ideal mixing ratios; Orzechowski and co-workers (19) confirmed this for one system (TEA/propionic acid), their results only disagreeing with the earlier predictions on the exact dependence of ε upon x_B. The large dipoles (and their concentration) at $x_B = 0.1\text{-}0.5$ stabilizes ions, lowering ΔG_{ioniz} to be near or below zero at these mole fractions. In the limits of $x_B \rightarrow 0$ or 1, the dielectric constant falls considerably, causing ΔG_{ioniz} to rise and greatly disfavouring the existence of ions. The case involving pyridine has a different (lower) $x_B \rightarrow 1$ limit for ΔG_{ioniz} than the TEA cases because ε_{PYR} (= 13.3) is not as low as that of ε_{TEA} (= 2.4).

The case involving formic acid has a very low apparent $x_B \rightarrow 0$ limit for ΔG_{ioniz} due to the high dielectric constant of formic acid ($\varepsilon = 51$).

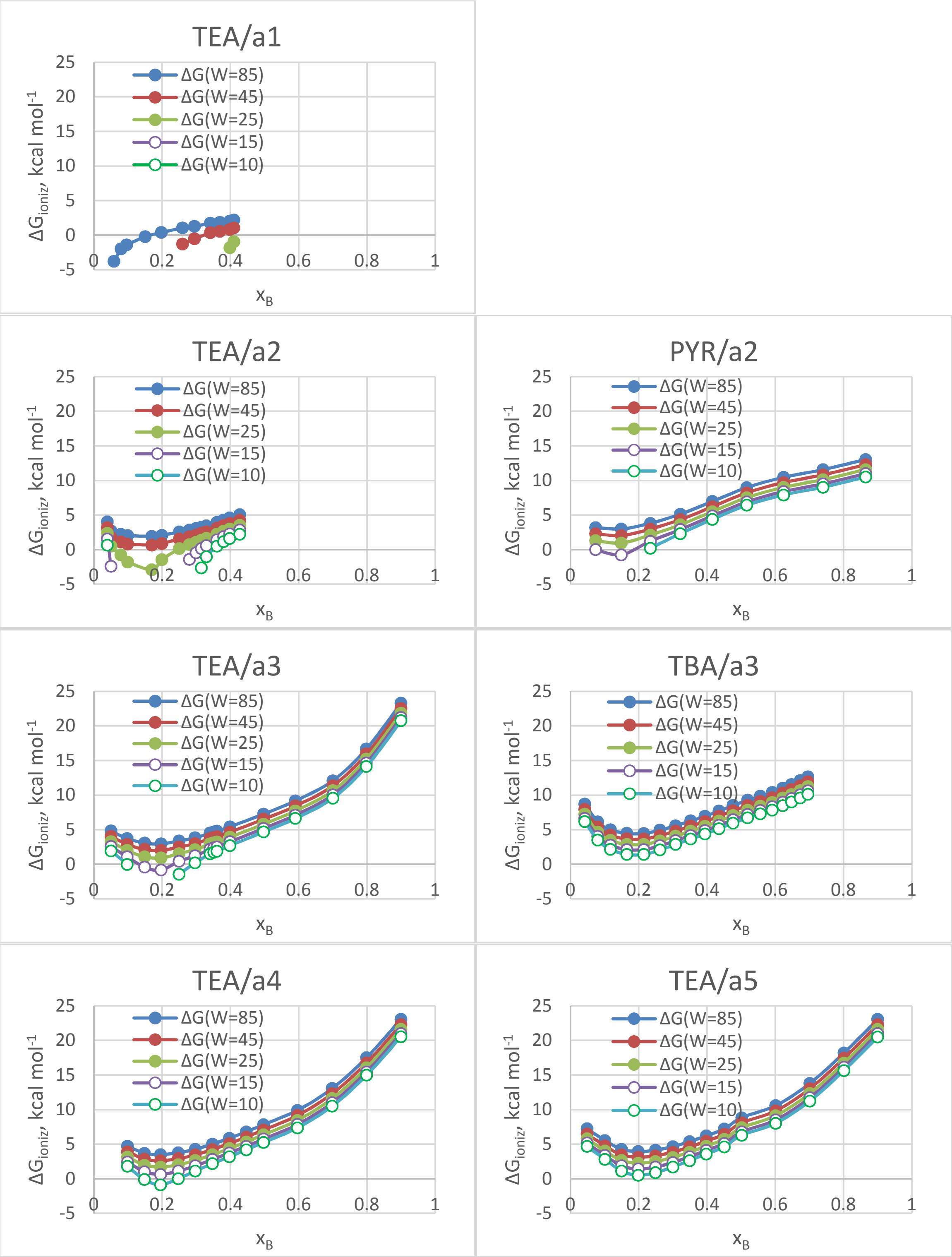

Figure 2. ΔG_{ioniz} curves from Eqs. [23-25] and the following experimental data: for TEA systems, Huyskens et al. (7); for PYR/a2, Venkatesan et al. (11); for TBA/a3, Orzechowski et al. (20) (using accurate interpolated values of their viscosities and densities).

The Walden constant (W) values tested were {10, 15, 25, 45, 85} S cP cm^2 mol^{-1}, which via Eq. [13] correspond to effective Stokes radii of {8.2, 5.5, 3.3, 1.8, 1.0} Å for the translating ions. We have chosen an extreme range of W values to demonstrate that the nature of the curves, qualitative and quantitative, depend rather little on this choice. Huyskens et al. had considered W = 31 for free BH^+ and values of 20-31 for $AHAHA^-$ anions (7). Given that our simulations do not show free BH^+, values below 30 and closer to 20 should be more realistic for the translating complexes. As x_B falls from 0.5 to 0.1, the ion complex sizes should get larger (arising from larger and larger kites), and hence the W "constant" probably decreases mildly (say from ~25 to ~15).

The more interesting question, perhaps, is if this data itself shows any particular evidence or need for unexpectedly large W values (i.e. small conducting ions) that might contradict the assumed "vehicular" conductivity mechanism involving the large translating ions of Eq. [3] and [21]. Electric fields could hypothetically induce hopping ion fragments or even relays (such as BH^+ or A^- or the classic Grotthuss H^+ mechanism). For the heavier acids, we do not think so: reasonable looking ΔG_{ioniz} curves are generated by W≈15 (TEA/a4 and TEA/a5) and W≈25 (TEA/a3 and PYR/a2). For TEA/a2, the requirement that % ionization be 100% or less requires that W be 24 or greater; W≈30 gives a reasonable curve without requiring a terribly small ion.

It is only the formic acid case (TEA/a1) where the assumptions must be questioned. In this system, W must be greater than 80 at x_B = 0.04 and 0.06 (1:20 mixing ratios); otherwise, impossibly high ion concentration (i.e. > 100% ionization) would be required to explain the high conductivities there. Huyskens et al. (7), whose incorrect equilibrium Eq. [2] would generate twice as many ions at these 1:20 mixing ratios as equilibrium Eq. [3], also had this problem for TEA/a1, needing W to be greater than about 40 in their case. At the time, they commented that the impossibly high ion concentration prediction for 1:20 TEA/a1 "is due to the inaccuracy of the Walden relation in such high polar medium." The conductivity from autoionization of formic acid is insufficient to account for the excess conductivity at 1:20 ratios. The "inaccuracy of the Walden relation" there is, possibly, the need for a particularly large W there, i.e. a Grotthuss H^+ mechanism. At such ratios, there is certainly an abundance of formic acid molecules, which are perhaps arranged into long H-bonded chains by the small amount of base present. A kite of length 13 was the result seen in our 1:15 PYR/a2 simulation (10).

Note, however, that at the most commonly used mixing ratio (x_B = 0.5), W only needs to be greater than about 23 for TEA/a1 to avoid impossible ion concentrations, and furthermore a Grotthuss-friendly H-bond network is not expected at this mixing ratio. Therefore, even with formic acid, a Grotthuss mechanism at x_B = 0.5 is unlikely.

Conclusions

AIMD simulations of mixtures of triethylamine with various carboxylic acids at several mixing ratios produce neutral "kite" structures $B(HA)_n$, with the only cations being "two-headed kites" $B(HA)_nHB^+$ and not BH^+. This is in accord with what was seen with pyridine mixtures in our previous work (10). Hence, a similar conductivity theory should apply, with a conductivity mechanism of large translating ion complexes.

A means of deriving ionization Gibbs energies from measured conductivities was presented, and curves of such values versus mole fraction of base were derived and plotted (Fig. 2). They exhibit a minimum near $x_B = 0.15$-0.20, due to an expected maximum in dielectric constant there, in turn due to the high dipole moments of the large kite structures $B(HA)_n$, $n \approx 4$. A variety of possible Walden constant values were employed to show their minor effect upon ΔG_{ioniz}. However, the limitation of no more than 100% ionization places restrictions on W values, and a problem first spotted by Huyskens et al. (7) exists in explaining the high conductivity of the TEA/formic acid mixtures at extreme 1:20 mixtures. There, very large W values would be needed in the theory, hinting that only there would there be a need to consider very small conducting ions, i.e. a Grotthuss mechanism.

Acknowledgements

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