The origin of the conductivity maximum vs. mixing ratio in pyridine/acetic acid and water/acetic acid

Nikhil P. Aravindakshan, Kyle E. Gemmell, Keith E. Johnson, and Allan L. L. East

Citation: The Journal of Chemical Physics **149**, 094505 (2018); doi: 10.1063/1.5039623 View online: https://doi.org/10.1063/1.5039623 View Table of Contents: http://aip.scitation.org/toc/jcp/149/9 Published by the American Institute of Physics





The origin of the conductivity maximum vs. mixing ratio in pyridine/acetic acid and water/acetic acid

Nikhil P. Aravindakshan, Kyle E. Gemmell, Keith E. Johnson, and Allan L. L. East^{a)} Department of Chemistry and Biochemistry, University of Regina, Regina, Saskatchewan S4S 0A2, Canada

(Received 9 May 2018; accepted 15 August 2018; published online 6 September 2018)

Explanations are provided for the first time for the historically known locations of electrical conductivity maxima versus mixing ratio (mole fraction of acid, x_A) in mixtures of (i) acetic acid with water and (ii) acetic acid with pyridine. To resolve the question for the second system, density-functionalbased molecular dynamic simulations were performed, at 1:1, 1:2, 1:3, 1:5, and 1:15 mixing ratios, to gain vital information about speciation. In a zeroth-order picture, the degree of ionization (and hence conductivity) would be maximal at $x_A = 0.5$, but these two examples see this maximum shifted to the left (water/acetic acid, $x_A^{max} = 0.06$), due to improved ion stability when the effective dielectric constant is high (i.e., water-rich mixtures), or right (pyridine/acetic acid $x_A^{max} = 0.83$), due to improved acetate stability via "self-solvation" with acetic acid molecules (i.e., acid-rich mixtures) when the dielectric constant is low. A two-parameter equation, with theoretical justification, is shown to reproduce the entire $0 < x_A < 1$ range of data for electrical conductivity for both systems. Future work will pursue the applicability of these equations to other amine/carboxylic acid mixtures; preliminary fits to a third system (trimethylamine/acetic acid) give curious parameter values. *Published by AIP Publishing*. https://doi.org/10.1063/1.5039623

I. INTRODUCTION

Protic ionic liquids (PILs) are a subset of ILs formed by mixing a liquid Bronsted acid with a liquid base, with ions generated via spontaneous proton transfer. Greaves and Drummond have written two reviews of PILs, including discussion of their physicochemical characterization and their uses.^{1,2} Angell classified ionic liquids as "poor" or "subionic" if they had lower-than-expected conductivities in a Walden plot,³ citing either partial ionization (e.g., 2-methylpyridinium acetate) or ion pairing (e.g., methoxymethyl-dimethyl-ethylammonium tetrafluoroborate) as reasons.⁴ He also noted that full ionicity generally required a sufficient combined strength of the acid A and base B, quantified as a pK_a difference of >10 between A and BH⁺,³ or a Gurney-style energy difference of ~0.7 eV.4,5 MacFarlane and Seddon in 2007 suggested requiring 99% ions for a PIL classification,⁶ though the possibility of ion pairing complicates this definition. Please also note MacFarlane's 2012 proposition that ion pairing, known to occur in aprotic ILs,^{5,7} is likely also occurring in poor PILs.⁸ It is of interest to understand better the nature of the partial ionicity (e.g., ion pairing?) in poor PILs.

Mixtures of amines with carboxylic acids are "poorer than poor"—with conductivities usually sufficiently low (\sim mS cm⁻¹) that a classification as a PIL (even a poor one) would be unwise. However, they are well-studied materials with well-tabulated data^{9–15} and hence a good testing ground for developing quantitative theories of ionicity

and conductivity. Such theories may then find applicability to higher-conducting "poor PILs" to better understand their partial ionicity. One particularly interesting phenomenon with amine/carboxylic acid mixtures is the presence of maximal conductivities at acid-rich mixing ratios (Table I), rather than 1:1 ratios which in principle should have afforded greatest ionization. Note in particular the interesting phenomenon is that $x_A(\sigma_{max}) > 0.66$ for these acids with amines, but $x_A(\sigma_{max}) < 0.17$ for these acids with H₂O. To the best of our knowledge, these maxima locations have lacked quantitative explanation for over eighty years.

Ab initio molecular dynamics (AIMD) simulations have proven useful for explaining conductivity phenomena in molten semicovalent metal halides, by providing an unbiased probe into the structure and dynamics of these liquids. For instance, they provided the discovery of a Grotthuss mechanism involving hops of halide ions^{17,18} and oxide ions¹⁹ (rather than H⁺ ions). The focus in our previous metal halide projects^{17,18} was the understanding of conductivity maxima versus temperature, a phenomenon revealed to be linked to the Grotthuss mechanism. Given those successes, it seemed promising to use AIMD simulations here, to aid in the understanding of conductivity maxima versus acid/base mixing ratio. Hence, AIMD simulations were here performed for 5 mixtures of the oldest-studied system in Table I (pyridine:acetic acid), at 1:1, 1:2, 1:3, 1:5, and 1:15 mole ratios. Based on the simulations, and the historical knowledge summarized below, a theory was composed and is presented to explain the historically known conductivity data.

For the water/acetic acid system, studies can be found of the conductivity of acetic acid in water, 20-22 and of water in

a)Author to whom correspondence should be addressed: allan.east@uregina.ca

TABLE I. Optimal mole fractions $x_A(\sigma_{max})$ for maximizing conductivity σ , for several acid/base (A/B) mixtures. Data from experiment (at 25 °C unless otherwise indicated). The pK_a values are from Ref. 13 except for the phenols which are from the work of Huyskens.¹⁶

A B		$x_A(\sigma_{max})$ $\sigma_{max} (mS cm^{-1})$		$pK_{a}\left(A\right)$	$pK_{a}\left(BH^{+}\right)$	$\Delta p K_{a}$
CF ₃ COOH	Triethylamine	0.90	10 ^{a,15}	0.52	10.75	10.23
НСООН	Triethylamine	0.90	53, ^{a,15} 48 ¹⁴	3.75	10.75	7.00
C ₂ H ₅ COOH	$(n-C_4H_9)_2NH$	0.80	1.6 ^{a, 15}	4.87	11.25 ^a	6.38
CH ₃ COOH	Triethylamine	0.90	9.6, ^{b,11} 6.0, ^{a,15} 6.4 ¹⁴	4.75	10.75	6.00
C ₃ H ₇ COOH	Triethylamine	0.80	1.1 ¹⁴	4.83	10.75	5.92
C ₄ H ₉ COOH	Triethylamine	0.80	0.63 ¹⁴	4.83 ^a	10.75	5.92
C ₂ H ₅ COOH	Triethylamine	0.80-0.85	2.8, ^{a,15} 2.6 ¹⁴	4.87	10.75	5.88
C ₂ H ₅ COOH	n-C4H9NH2	0.80	2.3 ^{a,15}	4.87	10.60	5.73
CH ₃ COOH	N-methylpyrrolidine	0.88	10 ^{b,12}	4.75	10.46	5.71
CH ₃ COOH	1-methylimidazole	0.67	9.2 ^{b,11}	4.75	6.95	2.20
2-chlorophenol	Triethylamine	0.87	0.39 ¹⁶	8.49	10.75	2.19
Phenol	Diethylamine	0.90	1.2 ¹⁶	9.98	10.84	1.04
4-methylphenol	Diethylamine	0.92	0.61 ¹⁶	10.18	10.84	0.66
4-methylphenol	Triethylamine	0.90	0.27 ¹⁶	10.18	10.75	0.57
CH ₃ COOH	Pyridine	0.83	9.2, ^{b,11} 8.3, ^{c,10} 6.7 ^{c,9}	4.75	5.25	0.50
H ₂ O	NH ₃	0.94	1.1 ^{a, 13}	14.00	9.25	-4.75
НСООН	H ₂ O	0.16	10.5 ^{a, 13}	3.75	0.00	-3.75
CH ₃ COOH	H ₂ O	0.06	1.7 ^{a, 13}	4.75	0.00	-4.75
Citric acid	H ₂ O	0.03	7.2 ^{a,13}	3.13	0.00	-3.13

^aAt 20 °C.

^bTemperature not reported.

°At 30 °C.

acetic acid,^{23,24} but only at concentrations where equations for non-ideal corrections (Debye-Hückel and Fuoss-Onsager²⁵) could be applied. These are extremely limited concentration ranges, when one considers that the two liquids are miscible in all proportions, and data (conductivity, viscosity, density) are available for the entire range of possibilities from $x_A = 0$ to 1. In 1957, Fuoss and Onsager commented²⁵ that, for concentrated electrolytes, one would probably have to abandon the idea of continually correcting the Debye-Hückel model at higher concentrations and a new theory would be needed, perhaps based on the molten salt as the zeroth-order model of such solutions. We obviated the issue of choosing a zeroth-order model by abandoning the historical desire to determine the degree of non-ideality. This liberation allowed us to change the focus from mean activity coefficients to dielectric constant, which, we shall show, solved the mystery of why $x_{\rm A}(\sigma_{\rm max}) = 0.06.$

For the pyridine/acetic acid (C₅H₅N/CH₃COOH) system, appreciable conductivities appear only for acid-rich mole ratios, in contrast to H₂O/CH₃COOH whose appreciable conductivities occur for water-rich ratios. It is also curious that σ_{max} (C₅H₅N/CH₃COOH) is less than triple that of H₂O/CH₃COOH, given the expectation that pyridine should generate considerably more ions than the mild base H₂O. This system exhibits other strange phenomena: viscosity^{10,26} and density,^{10,27} like conductivity, are all maximal at the same mixing ratio (x_A = 0.82-0.86). A crystalline form exists at this ratio but melts incongruently.²⁸ Plots of refractive index¹⁰ and pH²⁹ versus composition feature significant changes in a slope at this ratio. Mixtures of acetic acid with other organic nitrogen bases have also exhibited maxima in conductivity and

viscosity, although not always at 1:5 ratios.^{11,12} Clearly, there is potential for AIMD simulations to uncover what might be structurally special in the 1:5 mixture.

Some structural clues for the pyridine/acetic acid mixtures are known from the literature. Limbach and co-workers,^{30,31} using NMR, observed complexes of PyHAc, PyHAcHAc, and PyHAcHAcHAc in very cold (100-120 K) solutions in fluorocarbon solvents (Py = pyridine, Ac = acetate ion). They observed that the N-H bond distance decreased with increasing length of this complex and concluded that the acidity of $(HAc)_n$ must increase with *n*. Johansson and co-workers,¹² unaware of Limbach's results, hypothesized that the enhanced acidity of (HAc)_n chains was contributing to increased ion concentrations when $x_A > 0.5$ in their amine/CH₃COOH conductivity studies. Ulness and co-workers^{32,33} studied coherent anti-Stokes Raman scattering (CARS) spectra in the pyridine/pyridinium breathing mode region for mixtures of only pyridine and acetic acid. Intriguingly, they observed free pyridine and ion-paired pyridinium, but almost no free pyridinium ions.³² However, Holbrey and co-workers³⁴ performed simulations to try to fit to neutron scattering data of several pyridine/CH₃COOH mixtures, finding a distribution of (HAc)_n chains, but very few pyridinium ions of any sort (free or ion-paired), in disagreement with the work of Ulness.^{32,33} The idea that acidity might depend on the chain length could potentially be exploited in a quantitative attempt to reproduce the conductivity curve, but the uncertain existence of free pyridinium ions is a concern that AIMD simulations could help resolve.

Section II briefly reports the important results from simulations, Sec. III presents a theory, and Secs. IV and V use the theory to reproduce the entire experimental curves of conductivity vs. x_A , first for H_2O/CH_3COOH , and then for C_5H_5N/CH_3COOH . Section VI lists conclusions.

II. SIMULATION RESULTS

Five 1.1-ns simulations (time step 1 fs) were performed at 303 K, one for each of five different mixing ratios of pyridine to acetic acid (1:1, 1:2, 1:3, 1:5, and 1:15, i.e., $x_{Acid} = 0.50, 0.67, 0.75, 0.83, 0.94$). Details appear in the supplementary material. The simulations were run in a similar manner

to our previously successful metal halide simulations. However, the typical limitation of ~150 atoms (~450 electrons) in AIMD simulation cells caused some noticeable problems with these organic mixtures, in particular greater statistical uncertainties for ion-related properties (due to so few ions per cell). Examples of such problems are shown and discussed in the supplementary material. We are also somewhat wary of the necessitated omission of any possible long-range solvation-shell structures.

These caveats notwithstanding, what we observed from simulation (Fig. 1) were in agreement with experiment:



FIG. 1. A time snapshot of the contents of the simulation cells during the lowest-energy time regions. Ions appear in brackets. From the top to bottom row: 1:1, 1:2, 1:3, 1:5, and 1:15 mixtures of pyridine: acetic acid.

094505-4 Aravindakshan et al.



III. tail fragmentation IV. ionization (pyridinium exchange)

 $\begin{array}{c} BA_m + BA_n & \underset{BA_{m-1} + BA_{n+1}}{\longrightarrow} BA_{m-1} + BA_{n+1} \\ BA_n & \underset{BA_{m-2} + A_2}{\longrightarrow} BA_{m-2} + A_2 \\ BA_m + BA_n & \underset{[BA_mB]^+ + [A_n]^-}{\longrightarrow} \end{array}$

clusters of $Py(HAc)_n$ (agreeing with Limbach³⁰), clustered anions $Ac(HAc)_n^{-}$ (agreeing with Limbach³⁰), and pyridinium ions that were ion-paired but never seen to be free [agreeing with Fig. 10(a) from the work of Ulness^{32,33}]. Even the agreement with Ulness on the 1:1 mixture is remarkable: they find a nonzero but small ratio of free pyridine to bound pyridinium acetate pairs, while we found 1 free pyridine and 7 pyridine/acetic acid pairs. So, making a cautionary assumption that the clusters seen in the simulations were real, we were led to theories of ion-pairing (including dielectric effects) which ultimately was the key in developing a theory that seems to work for both pyridine/acetic acid and pyridine/water. Figure 1 is thus important enough to present here rather than in the supplementary material. The more customary presentation of atom-atom radial distribution plots and coordination numbers is placed in the supplementary material rather than here because (i) they can essentially be reproduced from Fig. 1 structures and (ii) they are less important than Fig. 1: they do not provide the essential information that Fig. 1 does on whether the H-bonded clusters are neutral or charged.

The observed speciation and the long lifetimes of the complexes gave much food for thought. In the rare moments when a pyridinium ion (BH⁺) broke free from a complex in the simulations, it quickly formed a new H-bond on femtosecond time scales, far shorter than the ps or ns time scales of the ion pairs. Therefore, we assumed that the dominant conductivity mechanism was (i) the translation of the large H-bonded ion aggregates. A minor contribution to conductivity could be from (ii) a Grotthuss-like hopping mechanism where the Grotthuss particle is not H⁺ but an entire pyridinium ion,

$$\begin{split} [BH]^{+} \cdot [A_{n}H_{n-1}]^{-} + \ [BH]^{+} \cdot [A_{m}H_{m-1}]^{-} \cdot [HB]^{+} \\ \rightarrow [BH]^{+} \cdot [A_{n}H_{n-1}]^{-} \cdot [HB]^{+} + [A_{m}H_{m-1}]^{-} \cdot [HB]^{+}. \end{split}$$

The relative contributions of (i) and (ii) could vary depending on the choice of amine and/or carboxylic acid. For pyridine/acetic acid, we have assumed (i). To develop a quantitative conductivity theory, we next needed to identify an ion-generating equilibrium, to determine the concentration of ion aggregates.

In Fig. 2, we present a "kite" model of equilibria for amine/carboxylic acid systems. These "kites," for pyridine/acetic acid, are ion pairs in the traditional sense, i.e., they are more properly written as $BH^+ \cdot Ac_n H_{n-1}^-$, except for

n = 1 where the kite is the neutral pair B·HAc. This simpler notation BA_n is less cumbersome. The model incorporates the idea^{12,30,31} that (HAc)_n chains are more acidic as they get longer, but instead of the ionization equilibrium being the *proton* transfer from (HAc)_n to base B, it is here proposed to be the *pyridinium* transfer from kite to kite (equilibrium IV, Fig. 2). Since this ionization act requires dissociation of an ion pair (a kite, BH⁺·Ac_nH_{n-1}⁻), this model pointed us to the mathematics of Fuoss for the equilibrium constant K_{ioniz} (Sec. III B).

III. THEORY: σ VERSUS x_A

A. σ versus K_{ioniz}

Walden's rule [Eq. (1)], as derived from the Stokes-Einstein and Nernst-Einstein approximations,³⁵ is

$$D_{ion} = \frac{kT}{6\pi r_{ion}\eta}$$
(Stokes - Einstein),

$$\Lambda = \frac{F^2}{RT} (\nu_+ z_+^2 D_+ + \nu_- z_-^2 D_-)$$
(Nernst - Einstein),

$$\Lambda \eta = W = \frac{e_0 F}{6\pi} \left(\frac{\nu_+ z_+^2}{r_+} + \frac{\nu_- z_-^2}{r_-} \right),$$
(1)

where {D_{ion}, v_{ion} , z_{ion} , r_{ion} } are the {diffusion coefficient, stoichiometric coefficient, integral charge magnitude, radius} of the ion, kT is the thermal energy, η is the viscosity, Λ is the molar conductivity (of fully ionized material, unlike Tödheide³⁶ and our first paper¹⁷ which defined it as per mole of possibly partially ionized material), $e_0 =$ electron charge, F is Faraday's constant, W is the Walden constant, and $e_0F/6\pi =$ 81.9 S cP cm² Å mol⁻¹. Using Eq. (1), the specific conductivity is then

$$\sigma = [ions]\Lambda = [ions](W/\eta), \tag{2}$$

where [*ions*] is the total ion concentration, calculated from ionization equilibrium constants K_{ioniz} . Using experimental values for viscosity, this Walden's rule approximation for σ was found to be sufficient to fit experimental data: the constant W was obtained via fitting, from which plausible values for r_{ion} were derived and presented.

B. K_{ioniz} versus ε and a

This step was the key advance needed to solve the mystery of conductivity maxima location, and indeed in explaining

FIG. 2. The "kite" model to explain equilibrium speciation in pyridine/acetic acid mixtures. Large and small circles are base (pyridine) and acid (acetic acid) molecules, respectively. entire conductivity curves for pyridine/water and pyridine/acetic acid: the recognition that K_{ioniz} depends upon dielectric constant ε , and (for pyridine/acetic acid) upon the ion-ion distance *a* in an associated ion pair. Fuoss³⁷ derived, for an ion-pair association constant K_A , the following equation in the so-called Gaussian cgs units:

$$K_A = \frac{4\pi}{3000} N_{AVO} a^3 e^{e_0^2/a\varepsilon kT},$$
 (3a)

where N_{AVO} = Avogadro's constant. After inverting both sides of Eq. (3a) (for ion-pair *dissociation*, i.e., ionization) and converting to SI units, Fuoss' equation becomes

$$K_{ioniz} = K_{\infty}e^{-b}, \ K_{\infty} = \left(\frac{4\pi}{3}N_{AVO}a^3\right)^{-1}, \ b = \frac{e_0^2}{4\pi\varepsilon_0 a\varepsilon kT},$$
(3b)

or

$$pK_{ioniz} = pK_{\infty} + m\varepsilon^{-1}, \ m = \frac{e_0^2}{4\pi\varepsilon_0 akT\ln 10}.$$
 (3c)

Although Fuoss' equation was derived for ion-pair dissociation in particular, it might be expected that its derived dependence upon ε [Eq. 3(c)] would also hold for the ordinary (covalent) acid-dissociation constant K_a for water/acetic acid mixtures since both processes are ion-generating ones.

Note that as ε falls, b rises, e^{-b} falls, K_{ioniz} falls, and less ionization occurs, reflecting the fact that high-dielectric solvents are better than low-dielectric solvents at stabilizing ions.

C. ϵ versus x_A

To obtain the values for K_{ioniz} via Eq. (3), a means of estimating solution dielectric constant ε at each mixing ratio was needed. The 1953 data of Critchfield *et al.*³⁸ for water/dioxane mixtures reveal that ε varies roughly linearly with mass fraction *f* (not with mole fraction *x*) (Fig. 3). Hence, ε was generally assumed to follow Eqs. (4) and (5),

$$\varepsilon = f_A \varepsilon_A^* + (1 - f_A) \varepsilon_B^*, \tag{4}$$

$$f_A = \frac{x_A M_A}{(x_A M_A + x_B M_B)},\tag{5}$$

where ε_{j} * and M_{j} are the dielectric constant and molar mass of component *j* when pure.



FIG. 3. Linearity of dielectric constant ε vs. mass fraction of one component. Data are for water/dioxane mixtures from the work of Critchfield *et al.*³⁸

TABLE II. Data³⁹ assumed for the pure components, for H_2O/CH_3COOH mixtures.

	ε	M (g mol ⁻¹)	$\begin{array}{c} \rho \\ (g \ ml^{-1}) \end{array}$	c (mol l ⁻¹)	V_{m} (ml mol ⁻¹)	η (cP)
Water	80	18.0148	0.9982	55.41	18.05	1.000
Acetic acid	6.15	60.0516	1.0477	17.45	57.32	1.221

IV. ANALYSIS OF H₂O/CH₃COOH MIXTURES

Let A = acetic acid and B = water. Table II shows the elementary data for the pure compounds.

We set out here to show that Eq. (2) can reproduce the entire conductivity curve σ vs. x_A . First, note that the functions

$$V_m = x_A V_A^* + x_B V_B^* - k_V x_A x_B,$$
 (6)

$$\rho(x_A) = \frac{x_A M_A + x_B M_B}{V_m} = \frac{x_A M_A + x_B M_B}{x_A V_A^* + x_B V_B^* - k_V x_A x_B},$$
 (7)

$$\eta(x_A) = x_A \eta_A^* + x_B \eta_B^* + k_\eta x_A x_B \tag{8}$$

reproduce experimental data for mixture densities and viscosities essentially exactly (Fig. 4). Here M_j , V_j* , and η_j* are the molar mass, molar volume, and viscosity of the pure substance j, and the mixing coefficients are $k_V = 4.85$ ml mol⁻¹ and $k_{\eta} = 6.25$ cP. Teja and co-workers have offered more sophisticated equations for the viscosity of mixtures.^{40,41}

A. Ion concentration

Let $c = V_m^{-1} = [A]_{init} + [B]_{init}$ and 2α be the degree of ionization of total initial molecules A and B i.e., here



FIG. 4. H_2O/CH_3COOH mixtures: density (top) and viscosity (bottom) vs. mole fraction of acetic acid.

TABLE III. Fitting of expt. pK_a data vs. ϵ^{-1} to generate Eq. (11), for H₂O/CH₃COOH mixtures.

f _{V,d} ^a	ε	pK _a ^a	$K_{ioniz} = K_a / [H_2O]$	ϵ^{-1}	pK _{ioniz}	pK _{ioniz} fit ^b
0	80	4.74	3.29×10^{-7}	0.0125	6.48	6.53
0.2	64.4	5.11	1.75×10^{-7}	0.0155	6.76	6.70
0.5	41	5.97	3.87×10^{-8}	0.0244	7.41	7.21
0.8	17.6	7.9	1.14×10^{-9}	0.0568	8.9	9.10

^aExpt. data;⁴² f_{V,d} = volume fraction of dioxane, $K_a = [H_3O^+][Ac^-]/[HAc]$. ^bFrom Eq. (11).

$2\alpha = ([H_3O^+] + [Ac^-])/([H_2O]_{init} + [HAc]_{init})$. Then

$$K_{ioniz} = [H_3O^+][CH_3COO^-][H_2O]^{-1}[CH_3COOH]^{-1}$$

= $(\alpha c)(\alpha c)(x_Bc - \alpha c)^{-1}(x_Ac - \alpha c)^{-1}$

$$[ions] = 2\alpha c = 2\alpha V_{\rm m}^{-1}, \tag{9}$$

$$\alpha = \frac{1 - \sqrt{1 - 4\left(1 - \{K_{ioniz}\}^{-1}\right)} x_A x_B}{2\left(1 - \{K_{ioniz}\}^{-1}\right)},$$
(10)

$$pK_{ioniz} = 5.8 + 58\varepsilon^{-1}.$$
 (11)

Equation (11) was derived (Table III) from the 1996 data of Schwarz *et al.*,⁴² who had published data on the K_a of acetic acid in various H₂O/dioxane mixtures, showing a drop in K_a $(K_{ioniz}[H_2O])$ from 10^{-5} to 10^{-8} as the volume fraction of dioxane rose from 0 to 0.8. This is the effect of declining dielectric constant ε (as they well understood⁴²). We took their volume fractions to be mass fractions f (since the densities of water and dioxane are so similar), converted the f values to ε values via Eq. (4), and then plotted $pK_{ioniz}\ vs\ \epsilon^{-1}$ [as suggested by Eq. (3c)] to derive Eq. (11). We implicitly assume that Eq. (11) holds for all mixtures of water and acetic acid, including extreme concentrations and in the complete absence of dioxane. Thus, for any mole fraction xA in the H2O/CH3COOH mixtures, total ion concentration is obtained via Eq. (9), with its α computed from Eqs. (10) \leftarrow (11) \leftarrow (4) \leftarrow (5) and its V_m computed from Eq. (6).

The degree of ionization (2α) and total ion concentration are plotted in Fig. 5, with and without the incorporation of a varying dielectric constant (ε). The effect of a varying ε lowers ion concentrations significantly in the middle and acid-rich regions of the plot (where the lowered ε reflects the lowered ability of the less-polar solvent to stabilize ions) and shifts the maxima to the left: $x_A(2\alpha_{max})$ shifts from 0.5 to 0.1 and $x_A([ions]_{max})$ from 0.25 to 0.1.

B. Conductivity

With now-established functions for viscosity [Eq. (8)] and ion concentration [Eqs. (9)–(11) and (4)–(6)], the expression for conductivity [Eq. (2)] now only lacks a value for the Walden constant W. With the choice W = 200 S cP cm² mol⁻¹, the theory is seen to reproduce the conductivity curve in its entirety [Fig. 5(c)]. This value of W seems physically reasonable; for instance, using Eq. (1), this value of W can be represented by $r_{cation} = 0.45$ Å and $r_{anion} = 5$ Å, and the particularly small value for r_{cation} reflects the advantageous Grotthuss



FIG. 5. H_2O/CH_3COOH mixtures: three plots showing the effect of ignoring (crosses) vs. incorporating (diamonds) the decline of dielectric constant as x_A rises.

mechanism by which H_3O^+ conducts electricity in aqueous solution.

The importance of this analysis should perhaps be emphasized. It is the first theoretical reproduction and explanation of not just the maximum but the *entire* conductivity curve (all possible mole fractions from 0 to 1) for a weak aqueous acid. The maximum at $x_A = 0.06$ in H₂O/CH₃COOH mixtures is due primarily to the shift of maximum ionization from $x_A = 0.5$ to $x_A = 0.1$, due to the dependence of K_a upon delectric constant. The maximum is further shifted from 0.10 to 0.06 due to the effects of reduced molar volume (V_m) and reduced viscosity (η) which occur in more water-rich mixtures. Starting with experimental data for mixture density, mixture viscosity, and K_a vs. ε , only the scaling constant W was needed to fit the entire conductivity curve.

Note that mean activity coefficients γ_{\pm} were not explicitly invoked. The data considered here (density, viscosity, and conductivity) are insufficient to determine their values. To account for them in the theory, one would (a) replace the total ion molarity ([ions]) with the total ion activity in Eqs. (2) and (9) and (b) correct for non-ideal ion mobility in the Stokes-Einstein and Nernst-Einstein approximations underlying Eq. (1). Also, note that predictive equations for γ_{\pm} (e.g., Debye-Hückel or various extensions⁴³) do not exist for the entire range of x_A values.

V. ANALYSIS OF C₅H₅N/CH₃COOH MIXTURES

Let A = HAc = acetic acid and B = pyridine. Table IV shows the elementary data for the pure compounds.

We begin with the functions

$$V_m = x_A V_A^* + x_B V_B^* - k_{V2} x_A x_B - k_{V6} x_A^5 x_B, \qquad (12)$$
$$x_A M_A + x_B M_B$$

$$\rho(x_A) = \frac{A - A - B - B}{V_m}$$
$$= \frac{x_A M_A + x_B M_B}{x_A V_A^* + x_B V_B^* - k_{V2} x_A x_B - k_{V6} x_A^5 x_B}, \quad (13)$$

$$\eta(x_A) = x_A \eta_A^* + x_B \eta_B^* + k_{\eta 2} x_A x_B + k_{\eta 6} x_A^5 x_B, \qquad (14)$$

which reproduce experimental data for mixture densities and viscosities essentially exactly (Fig. 6), with mixing coefficients $\{k_{V2}, k_{V6}\} = \{4.2, 31.8\}$ ml mol⁻¹ and $\{k_{\eta 2}, k_{\eta 6}\} = \{1.0, 34.5\}$ cP. The need for the additional $x_A^5 x_B$ mixing terms is due to complex formation (see the supplementary material).

A. Ion concentration

Let us first consider the altered nature of K_{ioniz} in changing the base from water to pyridine. It now relates to ion-pair dissociation (see the "kite" model, Fig. 2). Perhaps we can compute K_{ioniz} from first principles using the Fuoss equation [Eq. (3)]. We need values for the ion-ion distance *a* in the ion pair. Suppose this is the distance between ion centres in the ion pair; the bigger the anion (i.e., the longer the "kite"), the greater the distance *a*, and the larger the K_{ioniz} should be (i.e., easier to ionize). We took *a* to be proportional to the number *L* of acetic acid molecules in the ion pair,

$$a = \mathbf{k}_{\mathrm{L}}L, L = x_A/x_B. \tag{15}$$

Also needed for K_{ioniz} is the dielectric constant ε , taken as before from Eqs. (4) and (5). Thus the only unknown in the determination of K_{ioniz} [Eqs. (3)–(5) and (15)] at each mixing ratio is the proportionality constant k_L in Eq. (15).

To move on to obtain [ions] from K_{ioniz} , as in the H_2O/CH_3COOH case, we let $c = V_m^{-1} = [A]_{init} + [B]_{init}$ and 2α be the degree of ionization of total initial molecules A and B. Then, to reduce the number of equilibrium constants

TABLE IV. Data 10 assumed for the pure components, for pyridine/CH₃COOH mixtures.

	ε	M (g mol ⁻¹)	$\begin{array}{c} \rho \\ (g \ ml^{-1}) \end{array}$	c (mol l^{-1})	V_{m} (ml mol ⁻¹)	η (cP)
Pyridine	12.3	79.1015	0.9730	12.30	81.30	0.8354
Acetic acid	6.15	60.0516	1.0378	17.28	57.87	1.0400



FIG. 6. Pyridine/CH₃COOH mixtures: density (top) and viscosity (bottom) vs. mole fraction of acetic acid.

to be considered at each mixing ratio, we considered a single autoionization reaction,

$$K_{ioniz} = [BA_nB^+][A_n^-][BA_n]^{-2}$$

= $(\alpha c)(\alpha c)(x_Bc - 2\alpha c)^{-2},$
[ions] = $2\alpha c = 2\alpha V_m^{-1},$ (9)

$$\alpha = x_B \frac{2 - \sqrt{K_{ioniz}^{-1}}}{4 - K_{ioniz}^{-1}}.$$
 (16)

Thus, for any mole fraction x_A in the pyridine/CH₃COOH mixtures, the total ion concentration is obtained via Eq. (9), with its α computed from Eqs. (16), (15), (3b), (4), and (5) and its V_m computed from Eq. (12). These values for [ions] were then used in computing conductivities via Eq. (2). The unknown k_L in Eq. (15) was determined to be 3.3 Å (per acetic acid in the ion pair) from the fitting to expt. conductivities (see Sec. V B).

B. Conductivity

To employ Eq. (2), one might consider that the Walden constant W might require splicing into several different values since multiple sizes of cation and anion aggregates are expected. Let us simplify this with the further approximation that a single W, representing some averaged value of all W's, is sufficient. Using our derived equations for [*ions*] (from the Fuoss-equation K_{ioniz} with one fitting parameter k_L) and η [from experimental viscosities, Eq. (14)], we took W to be a 2nd fitting parameter. The two-parameter (k_L and W) fit to the experimental conductivity curve gave very reasonable

agreement with experiment [Fig. 7(c)], given the assumptions made. The resulting parameter values of $k_L = 3.3$ Å and W = 20.6 S cP cm² mol⁻¹ seem reasonable; this W value can be represented by $r_{cation} = 6.2$ Å and $r_{anion} = 11$ Å [Eq. (1)].

We can now explain why $x_A(\sigma_{max}) = 0.83$. It is certainly surprising that the conductivity maximum for pyridine/CH₃COOH mixtures is at the same location where viscosity is a maximum since Walden's rule [Eq. (1)] shows that they should be *inversely* related: high viscosity implies low mobility of molecules and ions in the mixture, and hence low conductivity. The two maxima are offset in other amine/acid mixtures, e.g., for *N*-methylpyrrolidine/CH₃COOH, $x_A(\sigma_{max}) \approx 0.83$ -0.90 but $x_A(\eta_{max}) \approx 0.67$ -0.75.¹² The mathematics here shows that the effect of high viscosity is outweighed by the more dominant maximum in the degree of ionization (see Fig. 7). The location of maximum ionization is controlled by the rate of rise of K_{ioniz} with increasing ion-pair distance



FIG. 7. Pyridine/CH₃COOH mixtures: degree of ionization, total ion concentration, and conductivity, vs. mole fraction of acetic acid.

a, whose effects are eventually overcome by the fall in kite (ion-pair) concentration at very high x_A values. It just so happens that the structural effect causing the viscosity and density maxima to shift out to $x_A = 0.83$ [increased complexation as $Ac^{-} \cdot (HAc)_n$ get longer] also causes the increase in ion concentration since these anions become more stable as they get longer.

Finally, we contrast this system with the H₂O/CH₃COOH system where $x_A(\sigma_{max}) = 0.06$. A conductivity maximum for all these acid+base systems would normally be expected near $x_A = 0.50$, to maximize ion concentration via H⁺ transfer. Strong bases of low dielectric constant (e.g., B = amines) shift this maximum to high x_A values because of the generation of acetate ions, which are most stable when complexed to excess acid molecules. Weak bases of high dielectric constant (e.g., B = H₂O) shift this maximum to low x_A values because the right-shifting effect is swamped by the left-shifting effect of a high dielectric medium to stabilize ions. In fact, all amine + carboxylic acid systems (e.g., Table I) are likely explained in these succinct ways.

VI. CONCLUSIONS

Quantum-chemical simulations of 1.1 ns of various mixtures of pyridine with acetic acid were found to be valuable for showing the ion pairs and ions to be expected in these systems. They were not very valuable for directly predicting conductivity or diffusion coefficients due to large statistical uncertainties, in turn due to so few ions and the insufficient time scale for averaging various hydrogen bonding possibilities.

The first explanations have been provided for the historical mystery of varied optimal mixing ratios for conductivity maxima in water/acetic acid and pyridine/acetic acid systems, and thus for amine/acetic acid $[x_A(\sigma_{max}) > 0.5]$ and water/weak acid $[x_A(\sigma_{max}) < 0.5]$ systems generally: (i) strong bases of low dielectric constant (e.g., amines), when paired with CH₃COOH, shift this maximum to high x_A values because of the generation of acetate ions, which are most stable when complexed to excess acid molecules; (ii) weak bases of high dielectric constant (e.g., H₂O), when paired with weak acids, shift this maximum to low x_A values because the right-shifting effect is swamped by the left-shifting effect of a high dielectric medium to stabilize ions.

A reasonably simple mathematical formalism, including dielectric constants ε and ion pair distances *a*, and avoiding determination of activity coefficients, was provided and shown to fit *entire* curves (x_A from 0 to 1) for electrical conductivity, for both systems studied. The particular breakthrough was in identifying the nature of the ionization equilibrium behind K_{ioniz} and in understanding the dependence of K_{ioniz} upon ε and *a*. Future work is planned to see how well this theory fits other mixtures of amines and carboxylic acids, and if adjustments need to be made. For example, we applied these equations to one additional system (acetic acid with trimethylamine, a stronger base than pyridine) and obtained values for k_L (7.7 Å) and W (45 cP cm² mol⁻¹) that seem curiously large. Possibly the approximation for ion-ion distance *a* [Eq. (15)], the use of a constant W, or the assumption of negligible Grotthuss

contributions to conductivity might need re-addressing as the number of examined cases increases.

SUPPLEMENTARY MATERIAL

See supplementary material for the simulation methodology, additional data from the simulations (energies, radial distribution plots, coordination numbers, diffusion coefficients, conductivity), and discussion of the $x_A^5 x_B$ terms in Eqs. (12)–(14).

ACKNOWLEDGMENTS

The work was supported by the Natural Sciences and Engineering Research Council (Discovery Grant Nos. 238871-2006, 238871-2012, and RGPIN-2017-06247) and the Canada Foundation for Innovation (Leading Edge Fund 2009, Grant No. 21625). A. Clay and C. Kuntz are thanked for exploratory T = 348 K simulations in 2008 and 2010 and comments on the manuscript.

- ¹T. L. Greaves and C. J. Drummond, Chem. Rev. **108**, 206 (2008).
- ²T. L. Greaves and C. J. Drummond, Chem. Rev. 115, 11379 (2015).
- ³M. Yoshizawa, W. Xu, and C. A. Angell, J. Am. Chem. Soc. **125**, 15411 (2003).
- ⁴C. A. Angell, N. Byrne, and J. Belieres, Acc. Chem. Res. 40, 1228 (2007).
- ⁵C. A. Angell, Y. Ansari, and Z. Zhao, Faraday Discuss. 154, 9 (2012).
- ⁶D. R. MacFarlane and K. R. Seddon, Aust. J. Chem. **60**, 3 (2007).
- ⁷K. E. Johnson, Electrochem. Soc. Interface **16**, 38 (2007).
- ⁸J. Stoimenovski, P. M. Dean, E. I. Izgorodina, and D. R. MacFarlane, Faraday Discuss. **154**, 335 (2012).
- ⁹L. E. Swearingen and R. F. Ross, J. Phys. Chem. 38, 1141 (1934).
- ¹⁰V. K. Venkatesan and C. V. Suryanarayana, J. Phys. Chem. 60, 777 (1956).
- ¹¹R. G. Treble, K. E. Johnson, and E. Tosh, Can. J. Chem. **84**, 915 (2006).
- ¹²K. M. Johansson, E. I. Izgorodina, M. Forsyth, D. R. MacFarlane, and K. R. Seddon, Phys. Chem. Chem. Phys. **10**, 2972 (2008).
- ¹³CRC Handbook of Chemistry and Physics, 96th ed., edited by W. M. Haynes (CRC Press, Boca Raton, FL, 2015).
- ¹⁴P. Huyskens, N. Felix, A. Janssens, F. Van den Broeck, and F. Kapuku, J. Phys. Chem. **84**, 1387 (1980).

- ¹⁵F. Kohler, R. Gopal, G. Goetze, H. Atrops, M. A. Demeriz, E. Liebermann, E. Wilhelm, F. Ratkovics, and B. Palagyi, J. Phys. Chem. 85, 2524 (1981).
- ¹⁶N. G. Felix and P. L. Huyskens, J. Phys. Chem. 79, 2316 (1975).
- ¹⁷A. T. Clay, C. M. Kuntz, K. E. Johnson, and A. L. L. East, J. Chem. Phys. 136, 124504 (2012).
- ¹⁸N. P. Aravindakshan, C. M. Kuntz, K. E. Gemmell, K. E. Johnson, and A. L. L. East, J. Chem. Phys. **145**, 094504 (2016).
- ¹⁹D. Corradini, F. Coudert, and R. Vuilleumier, Nat. Chem. 8, 454 (2016).
- ²⁰D. A. MacInnes and T. Shedlovsky, J. Am. Chem. Soc. 54, 1429 (1932).
- ²¹C. W. Davies, J. Am. Chem. Soc. 54, 3776 (1932).
- ²²A. Katchalsky, H. Eisenberg, and S. Lifson, J. Am. Chem. Soc. **73**, 5889 (1951).
- ²³I. M. Kolthoff and A. Willman, J. Am. Chem. Soc. 56, 1007 (1934).
- ²⁴T. B. Hoover and A. W. Hutchison, J. Am. Chem. Soc. 83, 3400 (1961).
- ²⁵R. M. Fuoss and L. Onsager, J. Phys. Chem. **61**, 668 (1957).
- ²⁶L. E. Swearingen and L. B. Heck, J. Phys. Chem. **38**, 395 (1934).
- ²⁷L. E. Swearingen and R. F. Ross, J. Phys. Chem. **39**, 821 (1935).
- ²⁸L. E. Swearingen and R. F. Ross, J. Phys. Chem. **38**, 1085 (1934).
- ²⁹V. K. Venkatesan and C. V. Suryanarayana, Nature **178**, 1345 (1956).
- ³⁰N. S. Golubev, S. N. Smirnov, V. A. Gindin, G. S. Denisov, H. Benedict, and H. Limbach, J. Am. Chem. Soc. **116**, 12055 (1994).
- ³¹S. N. Smirnov, N. S. Golubev, G. S. Denisov, H. Benedict, P. Schah-Mohammedi, and H. Limbach, J. Am. Chem. Soc. **118**, 4094 (1996).
- ³²E. R. Berg, S. A. Freeman, D. D. Green, and D. J. Ulness, J. Phys. Chem. A **110**, 13434 (2006).
- ³³E. R. Berg, D. D. Green, D. C. Moliva A., B. T. Bjerke, M. W. Gealy, and D. J. Ulness, J. Phys. Chem. A **112**, 833 (2008).
- ³⁴J. A. McCune, A. H. Turner, F. Coleman, C. M. White, S. K. Callear, T. G. A. Youngs, M. Swadzba-Kwasny, and J. D. Holbrey, Phys. Chem. Chem. Phys. **17**, 6767 (2015).
- ³⁵J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*. 1 (Plenum Press, New York, 1973).
- ³⁶K. Tödheide, Angew. Chem., Int. Ed. 19, 606 (1980).
- ³⁷R. M. Fuoss, J. Am. Chem. Soc. **80**, 5059 (1958).
- ³⁸F. E. Critchfield, J. A. Gibson, and J. L. Hall, J. Am. Chem. Soc. **75**, 1991 (1953).
- ³⁹R. C. Weast, CRC Handbook of Chemistry and Physics, 67th ed. (CRC Press, Florida, 1986).
- ⁴⁰A. S. Teja and P. Rice, Ind. Eng. Chem. Fund. **20**, 77 (1981).
- ⁴¹J. G. Bleazard, T. F. Sun, and A. S. Teja, Int. J. Thermophys. **17**, 111 (1996).
- ⁴²J. A. Schwarz, C. Contescu, V. T. Popa, A. Contescu, and Y. Lin, J. Solution Chem. 25, 877 (1996).
- ⁴³M. R. Wright, An Introduction to Aqueous Electrolyte Solutions (John Wiley & Sons Ltd., Chichester, England, 2007).