

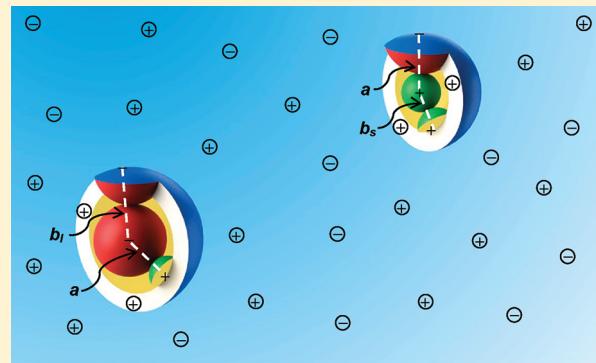
Effect of Solvent Permittivity on the Thermodynamic Behavior of HCl Solutions: Analysis Using the Smaller-Ion Shell Model of Strong Electrolytes

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ABSTRACT: The recently introduced smaller-ion shell (SiS) treatment of strong binary electrolyte solutions [Fraenkel, D. *Mol. Phys.* 2010, 108, 1435] that extends the Debye–Hückel theory to size-dissimilar ions is very effective for many electrolytes of various families up to moderate ionic concentration. The (*molal*) mean ionic activity coefficient, γ_{\pm} , as a function of the reciprocal screening length, κ , hence ionic strength, I , is given by an analytic mathematical expression that incorporates the three ion-size parameters (ISPs). Experimental γ_{\pm} data are fitted with calculated values derived from ISPs that seem to adequately represent the relevant mean effective sizes. The SiS analysis has been lately shown effective for aqueous HCl, HBr, HI, and HClO_4 at 25 °C, at which the solvent permittivity, ϵ , is 78.4 [Fraenkel, D. *J. Phys. Chem. B* 2011, 115, 557].

In this paper, the behavior of HCl in solvents ranging in ϵ between approximately 10 and 80 is analyzed and discussed. The SiS treatment is found again suitable for computing γ_{\pm} values that agree with experiment. Within the concentration range of the available experimental data, ion pairing is not indicated and, contrary to literature claims, HCl appears fully ionized even at 0.5 *m* (molal) with $\epsilon < 10$. ISPs do not seem to be affected by temperature, but co-ion ISPs increase linearly with $1/\epsilon$. The chemical nature of the solution has no observable effect on γ_{\pm} and on ISPs. The present analysis supports the view that electrolyte theories in which the solvent is considered at the McMillan–Mayer level can be successful and valuable.



1. INTRODUCTION

Electrolytes play an important role in many disciplines of science and technology, and therefore, understanding the nature of electrolyte solutions is an utmost goal. This goal can be achieved or at least advanced through using fundamental electrostatic correlations¹ that simply and straightforwardly connect between physical parameters of the ionic solution, e.g., permittivity (ϵ) and ion size, and thermodynamic excess functions, such as activity coefficients. There is thus a continuous effort to explain, through electrostatic modeling, various phenomena involving electrolytes, as exemplified by some recent studies on electrolytic effects in biological macromolecules² and on the mobility of ions in solution³ and, in particular, protons (hydronium ions) in acids⁴ and superacids.⁵ Protons play a special role in many subfields of physical chemistry, e.g., in biological systems^{6,7} and in catalysis.⁸ A fresh examination of simple electrostatic effects and their influence on the nature of protons (hence pH) in various media is the focus of the current paper. Here, I revisit the old classical study of hydrogen chloride in media of different permittivities and analyze the behavior of the acid, as electrolyte, using the recently presented smaller-ion shell (SiS) treatment of strong binary electrolyte solutions.⁹

The SiS treatment extends the Debye–Hückel (DH) theory¹⁰ for the case of ions of unequal size. Based only on ion–ion electrostatic interaction, and being within the McMillan–Mayer (MM) level of theoretical treatment,¹¹ the SiS model, like the parent

DH model, regards the electrolyte solution as a composition of an Avogadro's number (A_N) or so of "central ions" (β ions), each being surrounded by all other ions (α ions) as point charges smeared into a coherent, continuous, and isotropic charge density cloud called the ionic atmosphere. The medium in which each β ion resides together with its ionic atmosphere is simplified as a structureless continuum having a fixed permittivity ("dielectric constant"), ϵ . The change of ϵ with electrolyte concentration and the molecular nature of the solvent resulting in solvation effects are implicitly included in an "effective" ionic interaction potential.¹² The β ion has a size and a volume and it is idealized as sphere having a certain mean effective diameter; this is the ion-size parameter (ISP) of co-ions, i.e., the closest distance of approach of two ions of the same kind, as an $\alpha-\beta$ set. The distinction between counterions and co-ions is not made in the DH theory that is, thus, a subset of the more general SiS treatment: With the three ISPs being a , b_s , and b_l for the counterion, the small co-ion, and the large co-ion collision, respectively, the DH theory may be regarded simply as a reduction of the SiS treatment for the trivial case $a = b_s = b_l$.

The SiS model is illustrated in Figure 1. Depicted are the two cases of chosen (central) ions: that of a small (here, positive) ion

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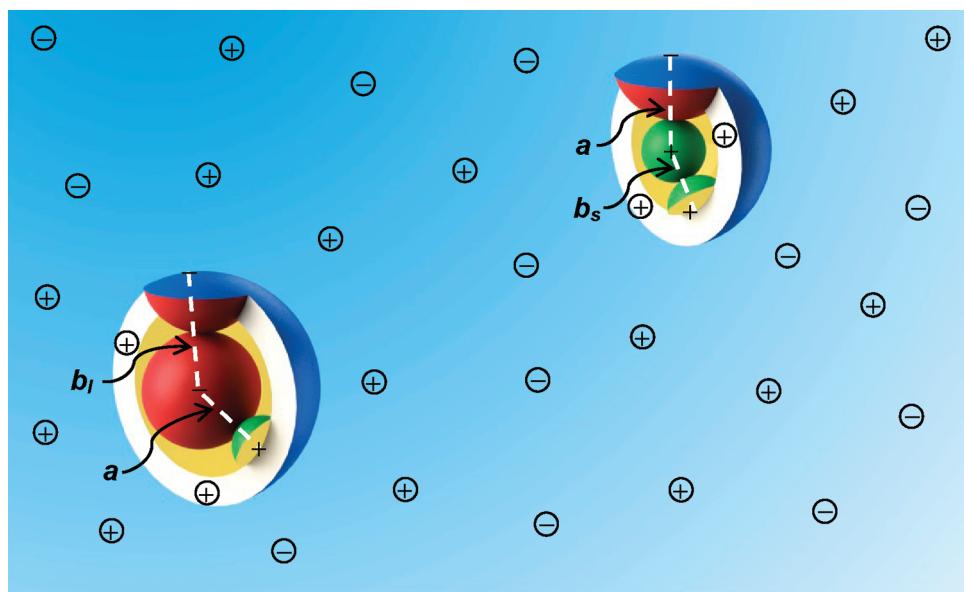


Figure 1. Smaller-ion shell model of strong electrolytes in solution (see text for explanation).

and that of a large (negative) ion. The two kinds of smaller-ion shell are clearly shown. In both, only the small (positive) ions can be accommodated, and they exist inside the shell as point charges. From the viewpoint of the central ion, all other ions, positive and negative, are point charges except for those residing on the rims of the SiS. The latter ions are “seen” by the central ion as “half ions”, having size and volume only in the spherical space confined by their SiS rim but being simultaneously “point charges” outside this space. Since each and every ion, in its turn, is a “chosen (central) ion”, the thermodynamic excess electrostatic ionic interaction potentials are calculated for each ion type, then combined linearly (after being charge-weighted), and finally summed over all (fully dissociated) electrolyte “molecules” in solution.

Being based on an “all-electrostatic” model ignoring the core potential and other nonelectrostatic factors, the SiS treatment is approximate and, from the standpoint of statistical mechanics, nonrigorous; however, it is quite accurate and physically sound with electrolyte solutions that are dilute, or moderately concentrated, or having very small average ionic size. (This is apparent because the SiS fit, with the same ISPs, is excellent even at very low concentration at which thermodynamic rigor is unnecessary.) Since, in many cases, ion-size values of binary electrolytes average to $\sim 3 \text{ \AA}$ or less,⁹ the core potential contribution may be negligible, or very small, up to a quite large concentration;^{9,13} for example, for 1–1 electrolytes, core effects may be ignored up to $\sim 1 \text{ M}$, or even higher molality. In the case of aqueous HCl, relevant to the present paper, with average ionic size of $\sim 2.4 \text{ \AA}$, the core effect may be very small at even 3 or 4 M .¹⁴ The SiS model can thus be, in general, safely applied at even $\sim 1 \text{ M}$ or sometimes higher concentration (depending on the specifics of the electrolyte system—electrolyte family and ionic sizes), therefore exceeding the DH molal range of applicability by 2–3 orders of magnitude. In comparison with the DH theory, the SiS treatment is quite accurate at least in the important concentration region of tenths of molality at which DH fits are very bad and achieved by employing ISPs that are unrealistic as ion–ion contact distances. While being more complicated than the basic DH theory, the SiS treatment is still rather simple and

fully transparent; this is in sharp contrast with modern electrolyte theories^{9,11} (MSA, HNC, MPB, etc.) that are regarded as “accurate” but are very complex and often quite vague. Unlike those, the SiS treatment provides easy-to-use analytic mathematical expressions for the deviation of electrolyte solutions from thermodynamic ideality. Such expressions do not only give a very good fit with experiment [mean ionic activity coefficient, γ_{\pm} (molal), versus concentration, or ionic strength I (molal)], but the fit is achieved with concentration-independent ISPs reflecting true ionic sizes. In many cases, the interionic collision distances are practically the sums of the respective radii of the colliding ions as naked (i.e., unsolvated) ions.

The SiS treatment has been recently proven effective in analyzing the simple 1–1 strong mineral acids HCl, HBr, HI, and HClO_4 in aqueous solution at 25 °C.¹⁴ In addition to providing good-to-excellent fit with experiment for the γ_{\pm} vs I behavior of the acids, the SiS analysis has also afforded a reliable calculation of pH at quite high acid concentrations. In the current paper, the same analysis is extended for HCl in various solvents with different ϵ 's. The effect of ϵ is thus decoupled from that of temperature (T), and the work attempts to answer two major questions: (1) Can SiS expressions successfully represent electrolyte solutions having low solvent ϵ values? (2) If so, how do the ISPs respond to the changing solvent's ϵ and what are the effects of other variables such as T and the solution's chemical nature? The results of the current analysis shed light not only on the general thermodynamic nature of HCl in solution, but also, in particular, on the strength of the acid, as reflected by pH, and its dependence on system variables (ϵ , T , solvent composition).

2. METHODS

As before,¹⁴ I again make use of the SiS expression⁹

$$\log \gamma_{\pm} = -|z_s z_l| \frac{\mathcal{A}}{\mathcal{B}} \frac{\kappa}{1 + \kappa a} \left[1 - \frac{\nu_l}{\nu} \frac{2e^{\kappa(a - b_s)} - \kappa(a - b_s) - 2}{1 + \kappa b_s} + \frac{\nu_s}{\nu} \frac{2e^{\kappa(b_l - a)} - 2\kappa(b_l - a) - 2}{1 + \kappa b_l} \right] \quad (1)$$

in which κ is the reciprocal Debye screening length, subscripts "s" and "l" denote the smaller and larger ions, respectively, z 's are ionic charges and ν 's are the ionic multiplicities (number of ions in the electrolyte molecular formula). We have $\nu = \nu_s + \nu_l$, and assume that $b_s \leq a \leq b_l$. The ISP nonadditivity factor is defined as $d/2 \equiv a - (1/2)(b_s + b_l)$. The fit between theory (SiS) and experiment is done as described previously.^{9,14} The exact values of the universal constants q (fundamental charge), k (Boltzmann constant), and A_N , used for the calculation of \mathcal{A} and \mathcal{B} ($=\kappa/I^{1/2}$)—the constants in the DH extended equation (DHEE)—are from ref 15 and so are the values of the density (σ) and permittivity (ε) of water at various temperatures. The single-ion molal activity coefficient of the proton, γ_{H^+} , when the proton is the smaller ion, is calculated using the SiS expression

$$\log \gamma_{H^+} = -\frac{\mathcal{A}}{\mathcal{B}} \frac{\kappa}{1 + \kappa a} \left\{ 1 - \frac{2[e^{\kappa(a - b_{H^+})} - 1] - \kappa(a - b_{H^+})}{1 + \kappa b_{H^+}} \right\} \quad (2)$$

where a is the closest distance between the proton and the anion (here, chloride), and b_{H^+} ($=b_s$) is the closest distance between two protons (as H_3O^+ 's); at $\varepsilon = 78.4$, this is, by convention, the mean effective diameter of the proton.

In the course of the current study, it has been found necessary to reexamine the conversion of measured electromotive forces (emf's) (or potentials, E 's) to activity coefficients and make due corrections for better-quality data, especially in the harsher cases of smaller ε values. Literature treatments¹⁶ are based on assumptions deemed here inappropriate, such as using old extensions of the DH expressions or including corrections for ion association (see below). This introduces a bias in the extrapolation of E vs m curves to 0 m (m , molal concentration) for extracting the standard potential, E° . Rather, the mechanism of extrapolation applied in the current study is based on the fundamental Nernst equation and on the "unextended" DHEE. Also, in the DHEE, the DH ion-size parameter, \bar{a} , is not chosen here arbitrarily (unlike in the literature¹⁶) but is instead estimated from a and b_s of the SiS treatment; a methodology for such an estimate, believed effective up to ~ 0.01 m , has been devised,⁹ which for 1–1 electrolytes gives $\bar{a} = a + (1/2)(a - b_s)$.

The extraction of E° was done using two methods, as follows.

Method 1: Extrapolation of E to $m = 0$. The expression $E + (2RT/\mathcal{F}) \ln m$ (where R is the gas constant, T is the absolute temperature, and \mathcal{F} is the Faraday constant) is plotted against $m^{1/2}$. We expect a straight line at very low m values and thus to extract E° as the intercept of the limiting line. Ideally, this method is correct, but E values at very low m sometimes cannot be measured, or they are not sufficiently accurate. As a result, the extrapolated lines are not exactly straight. Extrapolation can then be based on slightly curved lines such as those obtained through a polynomial regression.

Method 2: Use of DHEE. Here we incorporate the DHEE in the Nernst equation to obtain

$$E^\circ = E + \frac{2RT}{\mathcal{F}} \left(\ln m - \frac{\mathcal{A}m^{1/2} \ln 10}{1 + \mathcal{B}\bar{a}m^{1/2}} \right) \quad (3)$$

Stable, reasonably accurate E° values should be expected up to at least about 0.01 m . \mathcal{A} and \mathcal{B} for each case are the values at the given ε and T , and \bar{a} is initially estimated based on ISPs of an approximate SiS fit, with γ_\pm values as given in the literature or obtained with an assumed E° . \bar{a} is subsequently adjusted by

improved "best-fit" a and b_s obtained by adjusting E° (hence γ_\pm) until a constant E° value is reached. γ_\pm is calculated, of course, from the expression

$$\ln \gamma_\pm = \frac{\mathcal{F}}{2RT} (E^\circ - E) - \ln m \quad (4)$$

3. RESULTS AND DISCUSSION

3.1. Effect of ε and T on HCl in Water–Dioxane Solutions. When attempting to fit theory with experiment at different temperatures, we do not a priori know whether ISPs would remain constant. The fitting process could then proceed by trial and error, changing all three ISPs randomly until a satisfactory "best fit" is reached at each given temperature. If ISPs change, the trend with temperature may be unclear and, perhaps, subject to the arbitrariness introduced when all three ISPs are treated equally; then, different ISP sets may give fits of similar quality. A serious problem in fitting theory with experiment at different temperatures is the dependence of ε on T . If an ISP varies, is it because of T , ε , or perhaps both? To distinguish between these two factors, we need to change ε at *constant T*. A comprehensive study was performed by Harned and co-workers, who investigated the thermodynamic properties of HCl in water–dioxane mixtures differing considerably in ε ; for each mixture, they ran series of emf measurements of the corresponding electrochemical cell based on the silver–silver chloride electrode, at different acid concentrations and temperatures. The work, published as a group of communications and articles between 1936 and 1939, is summarized in ref 16, with the appropriate citation of the original publications (on page 457). Specifically, Harned et al. derived E values of HCl in four different mixtures containing 20, 45, 70, and 82 wt % dioxane. They measured the densities of the mixtures with and without HCl, and also the various ε values at different temperatures. From the measured E 's (and a version of smoothed E 's), they calculated the corresponding γ_\pm values. Thus, for each of the four general cases (later in this text referred to simply as 20%, 45%, 70%, and 82%) there are full sets of γ_\pm vs m data at different temperatures (in the range 0–50 °C) with the σ (Harned's notation: d_0 , water density; d , solution density) and ε (D) values provided.

Harned's water–dioxane work offers a crucial experimental test for electrolyte theories because it involves the change of ε at constant T , hence gives the net effect of ε on γ_\pm and its variation with ionic concentration. Furthermore, ε varies within a wide range, ~9–80; in contrast, when temperature is changed from say, 0 to 60 °C, the change in water permittivity is only between 88 and ~67, respectively, and most of the important range of ε that could provide critical information on the thermodynamic behavior of the electrolyte in solution and on the fit of theory with experiment, i.e., the 1–67 range, is missed. The comprehensive permittivity study of Harned and co-workers was performed only with HCl. This acid seems to be the ideal system for such a study since it is a strong electrolyte (100% dissociated) even at very high concentration in water,¹⁴ and it could be expected to remain in its fully dissociated state at rather low ε values. In the old days of electrolyte research, this seems to have not been recognized. In fact, negative apparent deviations of measured HCl's γ_\pm from the DH limiting law (DHLL) were frequently attributed to ion association; this perceived effect, sometimes deduced from conductivity studies based on a semitheoretical treatment, was introduced into the technique of

calculating γ_{\pm} from E values via the extrapolation of E to zero concentration, to extract E° . An obvious risk in such an approach is that if the assumption on which the extrapolation is based (i.e., the perceived response of the data used for the extrapolation to high dilution), is wrong, E° may be drifted away from its correct value; this may cause the calculation of $E^{\circ} - E$, hence γ_{\pm} , to err. The error may be systematic and relatively large at very low concentration, thus creating a false impression of the intrinsic thermodynamic behavior of the electrolyte.

Harned showed that while in the 20% and 45% cases γ_{\pm} approached the DHLL line "from above", as required, in the 70% and 82% cases, low-concentration γ_{\pm} data were *below* the DHLL line. Assuming ion association, Harned applied E° corrections based on the possible effect of ion association. When Janz and co-workers¹⁷ applied a "better" method for estimating the effect of ion association in the 82% case, thus arriving at even lower γ_{\pm} values than those of the original calculation (see below), Harned embraced the results. He included them in the third edition of his book¹⁶ instead of his own γ_{\pm} data, citing the Janz work¹⁸ as "in press". However, the rush to better analysis, based on a more elaborate consideration of ion association, may have been an overreaction. Here I call attention to the possibility that Harned, Janz, and co-workers may have been wrong because HCl, in fact, appears to be fully ionized in all water–dioxane mixtures of the Harned study (see below).

In the current investigation, the following assumptions have been made, which, at first glance, may look quite bold to a reader skilled in electrolyte theories. First, water–dioxane mixtures are considered at the MM level, i.e., as merely continuums with constant ϵ , which is that of the solvent (however, "H" is always H_3O^+). Second, HCl is assumed to be practically 100% dissociated even at the highest concentration studied in the 82% case, i.e., 0.5 m . I further ignore any nonelectrostatic effects (such as the core potential; see comment below) and examine the SiS model under these perhaps most demanding conditions of electrolyte solutions. The question being asked is the following: Assuming that HCl is fully ionized in the 82% dioxane mixture at even 0.5 m , could the SiS treatment provide a reasonable fit with experiment? Let us further ask the following: Which ISP values are suitable for the fit and how do they depend on ϵ and T ? The above assumptions cause a considerable undertaking since, at least for the 70% and 82% cases, one cannot use the existing recommended γ_{\pm} data; rather, one has to go back to the original E data to recalculate E° more accurately (for 100% HCl dissociation) and then, based on the improved E° value, recalculate γ_{\pm} at the various concentration points. Moreover, to further challenge the current treatment, the recalculation should also be conducted for data series measured at temperatures other than the standard 25 °C; however, it is sufficient to only choose the lowest and highest temperatures of the Harned study. Unfortunately, directly measured E data of the original Harned work were lost;¹⁹ only smoothed, calculated data are available, as given in the Harned communications of the 1930s. This somewhat compromises the quality of the calculated γ_{\pm} values, especially at very low concentration, where the $E^{\circ} - E$ difference (see eq 4) is very small, yet critical.

3.2. Relationship between ISPs and ϵ . As mentioned above, an inherent problem in fitting theory with experiment in the case of a change in T and ϵ is the loose way of choosing the ISPs; this may lead to a possible confusion arising from casual combinations of ISPs providing the "best fit" without any clear trends of the change of the particular ISPs. However, a preliminary

inspection of the data of Harned et al. has incidentally revealed a simple apparent correlation between the b 's, b_{H^+} and b_{Cl^-} , and ϵ : Over the entire range of Harned's work, the b 's appear linearly correlating with the inverse of ϵ , such that they approximately follow the empirical formulas (in angstroms)

$$b_{\text{H}^+} = 0.55 + \frac{48.0}{\epsilon} \quad (5)$$

and

$$b_{\text{Cl}^-} = 3.16 + \frac{36.4}{\epsilon} \quad (6)$$

Equations 5 and 6 provide the limiting values of b_{H^+} and b_{Cl^-} corresponding to $\epsilon^{-1} \rightarrow 0$, i.e., $b_{\text{H}^+}^0 = 0.55 \text{ \AA}$ and $b_{\text{Cl}^-}^0 = 3.16 \text{ \AA}$, respectively. This could be interpreted as the respective closest approach distances possible between two H^+ cations and between two Cl^- anions at infinite permittivity [i.e., when the medium (solvent) has infinite electric capacitance]. An ionic "size" hierarchy "switch-over" occurs at $\epsilon = 4.44$: at this value, the distance of closest approach of two protons becomes identical with that of two chloride ions, and below this value, the co-ion distance of closest approach of the proton is larger than that of the chloride. Obviously, at ϵ values substantially lower than the ϵ of water at 25 °C (i.e., 78.4), one cannot interpret distances of closest approach as genuinely reflecting ion sizes in the conventional sense. If the above equations reflect a physical reality and can be extrapolated to lower ϵ , then the co-ion closest approaches of H^+ and Cl^- as "gas ions in vacuum" (i.e., with $\epsilon = 1$) should be 48.5 and 39.5 \AA , respectively; but since the ion–ion distances of closest approach should be considerably smaller than the mean interionic distances in the solution, such large values can only be realized in very dilute solutions, $<0.001 \text{ m}$. It is more reasonable to assume, however, that eqs 5 and 6 are not valid at very low ϵ . In fact, one should expect that, at some small ϵ value (say, ~ 2 or so), b 's should start to deviate strongly from linearity with $1/\epsilon$, and increase dramatically to approach infinity at $\epsilon \rightarrow 1$. This should occur at infinite electrolyte dilution, reflecting the practical inability of free ions to exist in a medium with $\epsilon = 1$ (vacuum) in the absence of an externally exerted electric force.

With $\epsilon = 78.4$ (for water at 25 °C), one, by convention, assumes that the closest approach of the co-ions is their "collision distance" and it is equal to their effective normal (e.g., crystallographic) diameters when the ions are idealized as spheres. A closest distance of a few tens of angstroms between two ions (in fact, between one "full ion", the β ion, and one "partial ion", an α ion of the ionic atmosphere, see the Introduction) cannot be interpreted as "ion size", but rather, if not an artifact of the SiS model, as a closest distance allowed by the electric field of the solvent medium when this field is close to zero (in vacuum) and the electrostatic energy between the interacting ions cannot be effectively absorbed by the medium due to its being a very poor capacitor. In other words, an extremely small ϵ prevents any two charges from approaching each other too closely, in order to avoid a strong local electric field being induced by the ions when positioned only a short distance away from each other. If two opposite ions of equal charge magnitude (say, one with $1+$ and the other with $1-$) are placed too close to each other in a medium that cannot shield their charges effectively, those ions would pair up to form a molecular entity with a net charge of zero. For example, as relevant to the current work, if H^+ and Cl^- undergo ion pairing, an HCl molecule will form with a $\text{H}-\text{Cl}$ covalent polar bond and with no net electric charge.

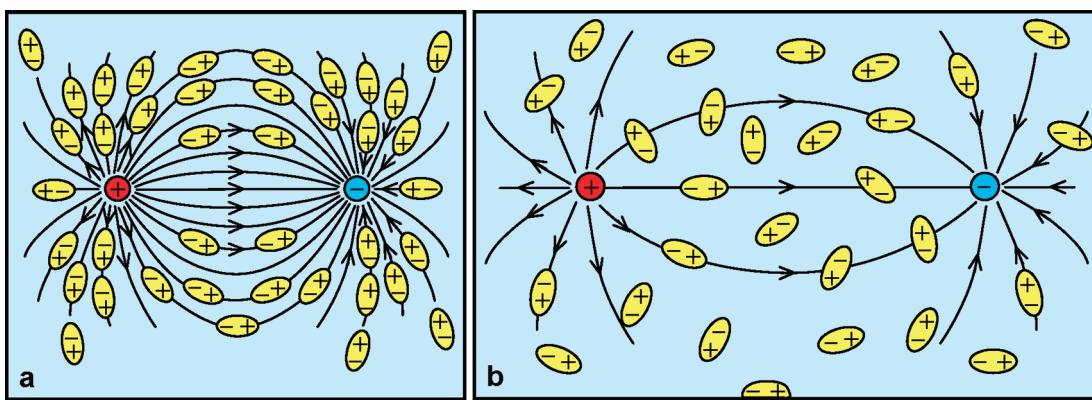


Figure 2. Electric field line diagram. Schematic presentation of two cases (after, and inspired by, Freeman, I. N. *Physics: Principles and Insights*; McGraw-Hill: New York, 1968; Chapter 14): (a) two opposite charges close to each other in a medium of high permittivity, where all solvent molecules are nicely aligned along field lines; (b) two opposite charges far from each other in a medium of low permittivity, where solvent molecules are only partially aligned along field lines, their spatial distribution close to the charges being less dense and less organized. In both cases, the medium is considered as that of molecules with permanent dipoles (e.g., water); in the case of induced dipole, the molecular shape is deformed by the electric field and molecules in (a) should be more deformed (in addition to being more aligned along field lines) than those in (b).

Even though the SiS treatment is formally within the MM modeling level, solvent molecules may be explicitly considered in attempting to rationalize the effect of ϵ on the ISPs. The decreased dipole alignment of solvent (say, water) molecules as a result of lowering ϵ may render those molecules more amenable to direct interaction with the charged ions, through solvation forces, thereby “coming in between ions” and thus causing ISPs to increase. Stated otherwise, although in high- ϵ media ions can travel and collide as naked ions, they apparently gradually undergo stronger trapping within their solvation shell when ϵ drops to very low values.

The closest approach of two oppositely charged ions in media of different permittivities is shown schematically in Figure 2. In Figure 2a, the distance of closest approach is small because the medium is strongly polarized and the dipoles of solvent molecules are effectively aligned along the lines of the electric field vectors; this “permits” (due to the high capacitance of the dielectric) a strong electric field, allowing the two ions to come close to each other, yet the two ions being close to each other aligns the dipoles. As is well-known, the electric field lines radiate away from a positive charge in all directions, and when aligned in the direction of a counter negative charge, those lines radiate into that charge, as demonstrated in Figure 2. In Figure 2b, the medium is only weakly polarizable and the dipoles are not aligned effectively. The solvent molecules now gain more degrees of freedom in realigning themselves around the ions to minimize their chemical potential through stronger interaction with the ions. While not necessarily solvating the ions in the usual sense of a clear solvent–ion structure, the electrically unaligned molecular dipoles now provide a “cushion” between mutually approaching ions, thereby limiting the distance of closest approach of any two ions to higher values that further increase with more decline in ϵ . (In fact, the approaching ions are of β - α sets only,⁹ so the electrostatic attraction and repulsion are not between two full ions but between one full ion and a “partial” rim ion of the ionic atmosphere.¹⁴) The longer distance of closest approach is thus not reflecting true ion diameters but rather the electrostatic limitation on the maximal mutual approach of the ions, as two electric charges (one full, one partial), owing to the small ϵ of the medium. I shall return to the effect of ϵ upon ionic contact distances later.

3.3. HCl in Water–Dioxane Solution: Fit between Theory and Experiment. Since the b 's of H^+ and Cl^- were found in the preliminary inspection mentioned above to not vary with temperature at each ϵ value, I have made an additional assumption, as a working approximation, that both b_{H^+} and b_{Cl^-} are not functions of T . Therefore, when T of the solution (i.e., ions in water) is changed, the b 's vary not because of the temperature per se but rather because of a change in ϵ caused by the change in T . This is a desired simplification since it allows the use of only one free ISP, the a , in fitting theory with experiment for practically *any* HCl solution. Thus, a is the *only* adjustable parameter in calculating γ_{\pm} of the HCl solution at broad ranges of concentration, temperature, and permittivity. Figure 3 presents the variation of γ_{\pm} with I ($=m$) for the four cases of water–dioxane mixtures at 25 °C. Compared are “experimental” γ_{\pm} values, i.e., values calculated from E 's using eq 4, and computed values based on eq 1, for each concentration point. The experimental values in the 20% and 45% cases are practically as in ref 16; it has been verified that no correction is necessary for the E° in those two cases, but γ_{\pm} 's were recalculated from the listed E data. The experimental data of the 70% and 82% cases, however, have been recalculated based on the E° values obtained for 100% HCl dissociation. Parameters of the fit, including E° 's (new vs old), are presented in Table 1. The E° correction is quite significant, positive and increasing in value and percentage with respect to the old E° , when going from 70 to 82 wt %. The increase is 4.3% for the 70% case, and 25%(!) for the 82% case. This is a major correction over the literature, and it results in a compelling agreement of theory with experiment (through more accurate experimental γ_{\pm} values calculated based on the new E° 's). This is demonstrated in Table 2 for the 82% case. Experimental γ_{\pm} 's were calculated from Harned's E values at various m 's in the range 0.001–0.5, using the E° values of Harned, Janz, and the current work. γ_{\pm} 's based on Harned's E° and Janz's E° , as listed in Table 2, are not always identical with the corresponding values given in the literature, but they are always very close to those values (usually differing from them only in the fourth digit after the decimal point). Janz's values are very low over the entire m scale; Harned's values are higher but still considerably lower than the new values of this work, with the difference diminishing from 0.09 at $m = 0.001$ to 0.01 at $m = 0.5$.

The theoretical γ_{\pm} values computed from eq 1, with the ISPs as listed in Table 1, are shown in Table 2 to be practically identical with (or very close to) the experimental values (derived from eq 4).

The excellent fit of theory with experiment in the 70% and 82% cases (Figure 3, Table 2) casts a serious doubt on the literature interpretation of the HCl behavior at high dioxane

concentration.^{16,17} In the present work, experimental γ_{\pm} 's are calculated with E° values that are based on the assumption of complete HCl dissociation, and a theory assuming full electrolyte dissociation computes over a broad concentration range, starting from 0 m , γ_{\pm} values that are in excellent agreement with the experimental γ_{\pm} values. Therefore, the notion of negative deviation from the limiting law and its attribution to ion association, at least in regard to simple electrolytes such as HCl, should be seriously reconsidered.

Figure 3 demonstrates that the SiS expression (eq 1) is capable of producing excellent fits in *all cases* of the water–dioxane mixtures. The fit with the two lower dioxane concentrations is very accurate at least up to m ($=I$) = 2.3. Data for the higher dioxane concentrations are limited to lower m values but the fit at the higher m 's is effective up to those m limits, i.e., ~ 1.5 for 70%

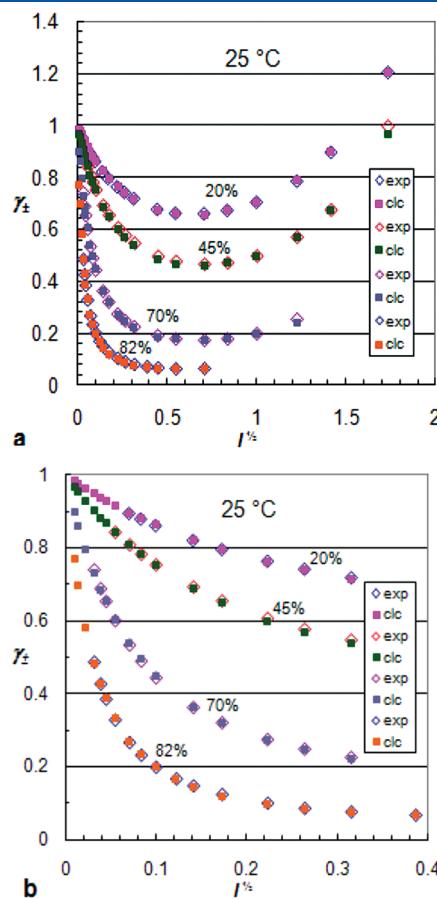


Figure 3. Experiment–theory comparison: mean ionic activity coefficient, γ_{\pm} , of HCl in water–dioxane mixtures (weight percent dioxane in the solvent mentioned in the figure) as a function of ionic strength, I , at 25 °C: (a) full I (m) range; (b) low I (m). Open diamonds, experimental values; closed squares, calculated values.

Table 2. Mean Ionic Activity Coefficients of HCl in 82% Dioxane in Water at 25 °C

m	E°	γ_{\pm} calculated from eq 4			γ_{\pm} computed		
		Harned ^a	Janz ^b	this work	Δ_1^c	from eq 1	Δ_2^d
0.0010	0.36094	0.3981	0.2692	0.4865	0.0884	0.4845	0.0020
0.0015	0.34682	0.3494	0.2363	0.4269	0.0776	0.4268	0.0001
0.002	0.33731	0.3153	0.2132	0.3853	0.0700	0.3866	-0.0013
0.003	0.32472	0.2686	0.1816	0.3282	0.0596	0.3322	-0.0040
0.005	0.30913	0.2183	0.1476	0.2667	0.0484	0.2695	-0.0028
0.007	0.29896	0.1900	0.1285	0.2322	0.0422	0.2326	-0.0004
0.010	0.28844	0.1632	0.1104	0.1995	0.0362	0.1980	0.0015
0.015	0.27650	0.1373	0.0928	0.1678	0.0305	0.1643	0.0035
0.020	0.26802	0.1215	0.0821	0.1484	0.0270	0.1440	0.0044
0.030	0.25608	0.1022	0.0691	0.1248	0.0227	0.1201	0.0047
0.050	0.24060	0.0828	0.0560	0.1012	0.0184	0.0970	0.0042
0.070	0.23099	0.0713	0.0482	0.0872	0.0158	0.0854	0.0018
0.100	0.21870	0.0634	0.0429	0.0775	0.0141	0.0759	0.0016
0.150	0.20430	0.0560	0.0378	0.0684	0.0124	0.0680	0.0004
0.200	0.19307	0.0522	0.0353	0.0638	0.0116	0.0640	-0.0002
0.300	0.17535	0.0492	0.0332	0.0601	0.0109	0.0608	-0.0007
0.500	0.14792	0.0503	0.0340	0.0615	0.0112	0.0608	0.0007
		$-0.0413^e - 0.0614^e - 0.0310^e$					

^a Harned, H. S.; Walker, F. J. *J. Am. Chem. Soc.* 1939, 61, 48. ^b Reference 17.

^c $\Delta_1 = \gamma_{\pm}(\text{this work}) - \gamma_{\pm}(\text{Harned})$. ^d $\Delta_2 = \gamma_{\pm}(\text{this work}) - \gamma_{\pm}(\text{computed, eq 1})$. ^e E° value.

Table 1. Parameters of HCl in Water–Dioxane Solutions^a

wt %	$T, ^{\circ}\text{C}$	ε	d_0	E°_{lit}	$E^{\circ}_{\text{recalc}}$	ΔE°	\mathcal{A}	\mathcal{B}	a	b_s	b_l	$d/2$	\ddot{a}	pH
20	0	69.16	1.017	0.2197	0.2197	0.0000	0.712	0.371	3.430	1.244	3.686	0.965	4.523	1.401
	25	60.79	1.014	0.2030	0.2030	0.0000	0.753	0.376	3.445	1.340	3.759	0.896	4.498	1.407
	50	53.43	1.001	0.1817	0.1817	0.0000	0.805	0.383	3.450	1.448	3.841	0.805	4.451	1.415
45	0	44.28	1.051	0.1896	0.1896	0.0000	1.406	0.469	3.460	1.634	3.982	0.652	4.373	1.486
	25	38.48	1.032	0.1635	0.1635	0.0000	1.508	0.477	3.540	1.797	4.106	0.588	4.412	1.500
	50	33.43	1.014	0.1328	0.1328	0.0000	1.636	0.487	3.635	1.986	4.249	0.518	4.460	1.517
70	0	20.37	1.062	0.1058	0.1073	0.0015	4.531	0.695	4.440	2.906	4.947	0.513	5.207	1.777
	25	17.69	1.038	0.0640	0.0668	0.0028	4.853	0.705	4.710	3.263	5.218	0.469	5.434	1.807
	50	15.37	1.015	0.0175	0.0210	0.0035	5.252	0.719	5.000	3.673	5.528	0.399	5.664	1.845
82	5	10.52	1.054	0.0026	0.0098	0.0072	11.84	0.954	6.530	5.113	6.620	0.664	7.239	2.193
	25	9.53	1.034	-0.0413	-0.0310	0.0103	12.25	0.959	6.900	5.587	6.980	0.617	7.557	2.220
	45	8.62	1.013	-0.0922	-0.0770	0.0152	12.79	0.967	7.200	6.118	7.383	0.449	7.741	2.279

^a ISPs (in Å) are of the “best fit”. E values are in volts. ε (D) and d_0 (solvent density, as g/cm³) data are from ref 16. $\Delta E^{\circ} = E^{\circ}_{\text{recalc}} - E^{\circ}_{\text{lit}}$. pH is at 0.05 m .

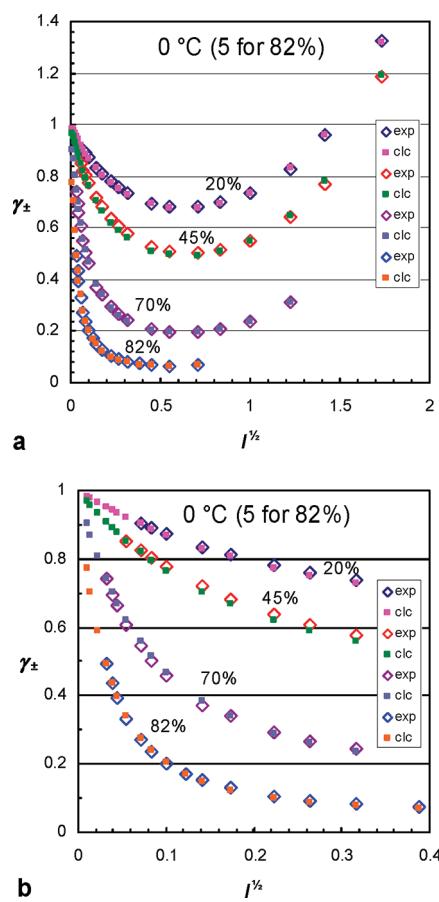


Figure 4. As Figure 3 but at low temperature.

and ~ 0.5 for 82%. The fit at lower m (Figure 3b) is revealing close to perfect agreement of the SiS treatment with all four cases, and theoretical extrapolation to lower ionic concentration, at which experimental values are unavailable, is also provided. Figure 3 shows that the SiS expression (eq 1) is effectively fitting with experiment for the entire sets of data with the four water–dioxane mixtures at 25 °C. Since in all four cases E° is the limiting E value obtained by extrapolation to $m = 0$ based on the assumption of 100% HCl dissociation, the results strongly indicate (as mentioned above) that there is no apparent ion association involved in the Harned study. It should be reemphasized that even though the SiS equation (eq 1) is a three-ISP expression, here the two co-ion ISPs are “fixed” (through eqs 5 and 6) and thus only one ISP, that of the counterion collision, remains “free” and subject to adjustment. If to an untrained reader it appears (unjustifiably!) that the SiS treatment has a considerable flexibility to adjust itself to “any” experimental behavior, that reader is encouraged to try eq 1 to only realize that this, in general, is not the case. Continued hereinafter, the current analysis will proceed using eq 1 as a single-adjustable-parameter equation (but see below on the dependence of this parameter, a , on ϵ).

Figure 4 presents results at the lowest temperature employed for each one of the four water–dioxane cases. Similarly, Figure 5 depicts the behavior at the highest temperature in each case. The fit in all four cases is good to excellent at both the lowest and highest T 's. In the 45% case, at 0 °C, the midconcentration range shows systematically a poorer fit, with the experimental data

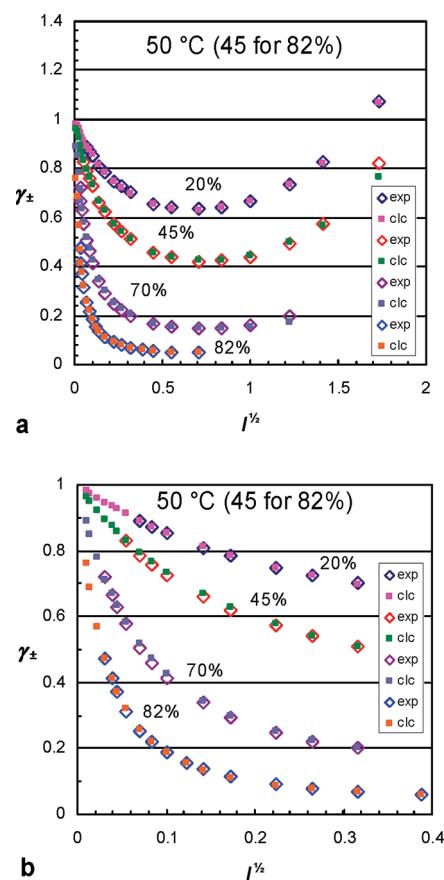


Figure 5. As Figure 3 but at high temperature.

being somewhat above the computed ones. However, such a deviation is not encountered at the higher temperatures.

Figure 6 presents calculated E° vs m plots for the 82% case at 5, 25, and 45 °C, based on method 2 (eq 3) (see Table 1 for the parameters used). Figure 6 demonstrates the effectiveness of the present method of extracting the standard potential. All three plots are practically straight lines with slope zero, as required. The E° values of the new calculation up to $\sim 0.01 m$ are stable (Figure 6), whereas Harned's values¹⁶ drift with concentration, indicating that they are not adequate. The chosen E° values for the analysis of this work (Table 1) are close to (but not exactly identical with) the values “recommended” by Figure 6 on the basis of average values derived from a least-squares regression (see intercept in equation next to each line).

As also seen in Table 1, the well-known DH parameters \mathcal{A} and \mathcal{B} are dramatically affected by the strong change in permittivity, as both increase with decrease in ϵ . This, of course, is hardly surprising since the mathematical expressions of those parameters contain $\epsilon^{3/2}$ and $\epsilon^{1/2}$, respectively, in their denominators. Table 1 also shows that acidity appears to weaken as a function of the increase in dioxane concentration and also as a function of increasing T at each dioxane concentration, as indicated by the pH calculated at 0.05 m . The increase of pH as a function of decreasing ϵ is discussed below.

In summary, with the above assumptions and the use of co-ion ISPs derived from eqs 5 and 6, the behavior of HCl in water–dioxane mixtures is fully consistent with theory (SiS treatment), thus giving no indication of any extra, nonelectrostatic effect or ion pairing. This is another triumph of the SiS

treatment in explaining the thermodynamic properties of electrolyte solutions, and it happens even under the extremely harsh conditions of very low ϵ . Furthermore, the above behavior and the fit of eq 1 with experiment add considerable weight to the argument⁹ that it is not primarily the core potential (as claimed in the literature) but rather the electrostatic repulsion due to the smaller-ion shell (see the Introduction) that is responsible for the change in course in the γ_{\pm} vs m curve, i.e., going through a minimum and then increasing, sometimes rather steeply.

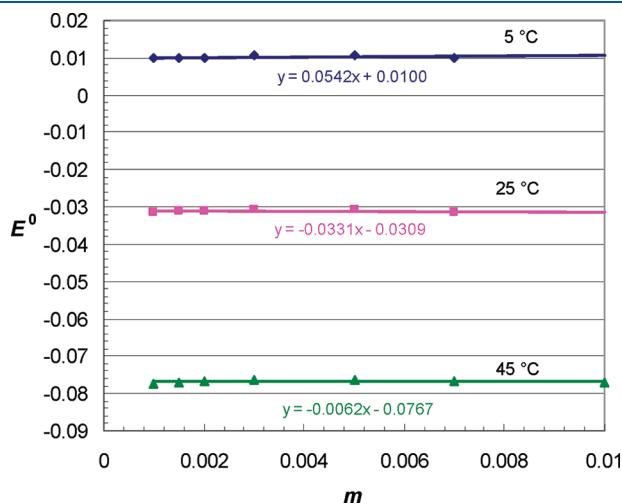


Figure 6. Calculation of E° for the case of 82% dioxane: demonstration of the effectiveness of method 2 (see section 2) in extracting stable and consistent E° values at different temperatures even at very low ϵ . Symbols are calculated E° values; lines are those of least-squares regression and represented by the corresponding y vs x equations.

As more dioxane is added, the γ_{\pm} vs m curve decreases systematically and the minimum becomes shallower; eventually, with 82% dioxane, it almost disappears. This behavior is fully consistent with the SiS model as merely an effect of ϵ . The decrease in ϵ increases \mathcal{A} that initially plays a dominant role (as in DHLL), causing a sharp decline of the curve due to increased ionic attraction. At higher concentration (when DHLL becomes inefficient), the stronger increase in $1 + \kappa a$, due to increasing \mathcal{B} and enlarging a , tends to compensate for the increasing \mathcal{A} . Also, the combination of larger b_s and larger \mathcal{B} causes the $1 + \kappa b_s$ function in the denominator of the second term on the right-hand side of eq 1 to counteract the effect of the exponent in the numerator such that at a certain very low ϵ , the repulsion effect becomes too weak and cannot overcome the extremely strong attraction effect. Thus, even though the ions apparently remain of the same size throughout the entire change in ϵ , the SiS gradually moves away from the β ion center (coordinate origin) as ϵ decreases, and the overall electrostatic repulsion effect diminishes. This is demonstrated in Figure 7, in which smaller-ion shells of H^+ and Cl^- are compared, at 25 °C, as functions of ϵ . In contrast, the core potential should not be influenced by ϵ and a lower repulsion effect arising from dispersive forces can only be reconciled with decreasing ion size (at the same concentration). It seems, however, highly implausible that the intrinsic ionic sizes of H^+ and Cl^- decrease strongly with the decrease in ϵ (see discussion above, section 3.2), thus causing a core-potential-derived repulsion to almost completely disappear.

3.4. Behavior of Aqueous HCl as a Function of T . In a further attempt of the current work, the effect of T (and ϵ) was examined by fitting eq 1 with experimental γ_{\pm} data¹⁶ of aqueous HCl in the temperature range 25–60 °C. The results are presented in Figure 8 and Table 3. As demonstrated in Figure 8 for the data at 25, 45, and 60 °C, the fit between theory and experiment is

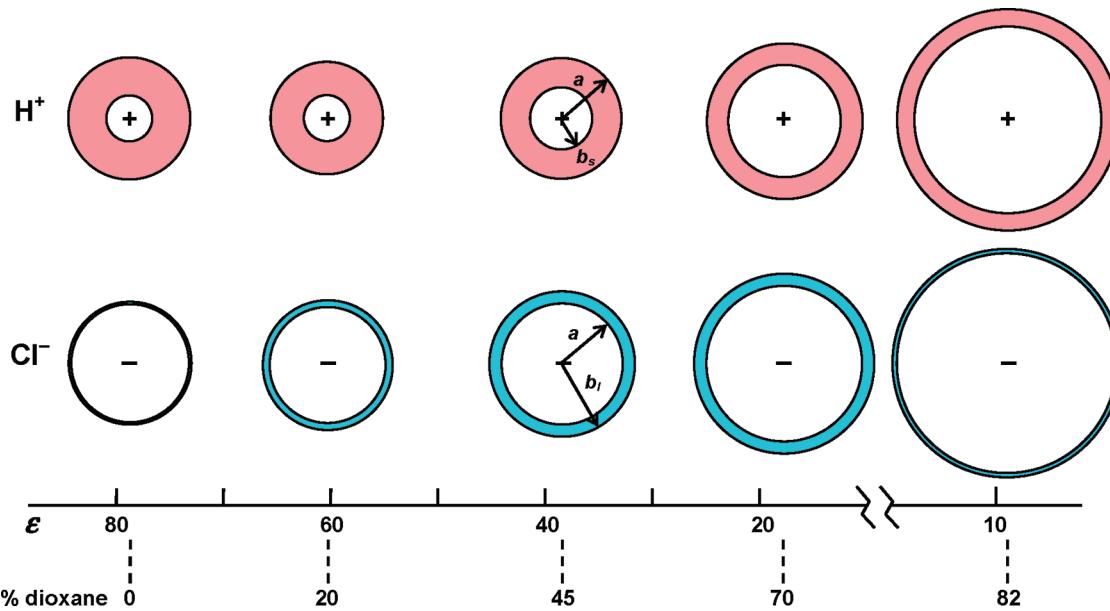


Figure 7. Change of the cross section of smaller-ion shells (SiSs) as a function of permittivity (ϵ), or of dioxane concentration (wt % in water–dioxane solvent), at 25 °C. The drawing is approximately at the appropriate scale (Table 1). For H^+ , the SiS size is about constant (meaning constant b_s and a ion–ion distances) between ~80 and ~40 on the ϵ scale; at lower ϵ , the shell moves away from the central ion (i.e., both b_s and a increase) but its width ($a - b_s$) is decreasing only moderately. For Cl^- , the shell also increases significantly below $\epsilon = 40$ (due to the increase in a and b_l) but its width (i.e., $b_l - a$) initially increases and then, below $\epsilon = 20$, decreases. The drawing, by way of comparing the two shells at each ϵ value (or wt % dioxane), shows how the combined shell effect changes with decreasing ϵ : initially, there is a strong electrostatic repulsion effect (resulting in a deep minimum in the γ_{\pm} vs $I^{1/2}$ curve, Figure 3); at lower ϵ , the repulsion effect diminishes (and the minimum becomes less pronounced).

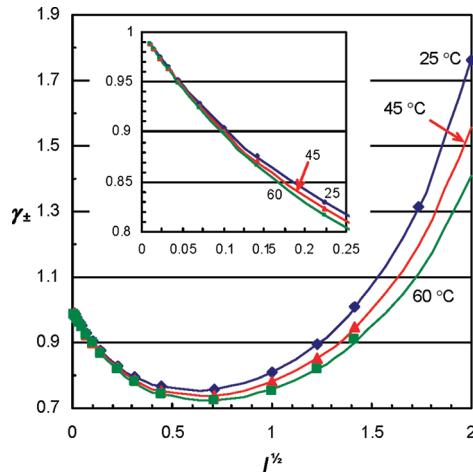


Figure 8. Effect of temperature, T , on the change of the mean ionic activity coefficient, γ_{\pm} , of aqueous HCl as a function of ionic strength, I . Symbols are experimental data (from ref 16); curves are calculated from eq 1. As T increases, γ_{\pm} shifts downward; the specific T is given next to each curve. The inset emphasizes that T changes can be recognized even at very small I .

Table 3. ISPs and Other Data of the Fit of Theory with Experiment in Aqueous HCl, at Different Temperatures^a

temp, °C	ε	m range	a	b_s	b_l	$d/2$	av % $\Delta\gamma_{\pm}$	STDV
25	78.38	10^{-4} –4.0	3.615	1.162	3.624	1.222	-0.1064	0.0010
30	76.61	10^{-4} –2.0	3.605	1.177	3.635	1.199	-0.0106	0.0008
45	71.55	10^{-4} –2.0	3.550	1.221	3.669	1.105	-0.0766	0.0010
55	68.42	10^{-4} –2.0	3.515	1.252	3.692	1.043	-0.0874	0.0017
60	66.93	10^{-4} –2.0	3.500	1.267	3.704	1.014	-0.1025	0.0026

^a ISPs are given in Å. av % $\Delta\gamma_{\pm}$ is the average percent deviation of γ_{\pm} as $(\Delta\gamma_{\pm}/\gamma_{\pm}^{\text{exp}})(100)$, where $\Delta\gamma_{\pm} = \gamma_{\pm}^{\text{calc}} - \gamma_{\pm}^{\text{exp}}$. STDV is the standard deviation.

excellent in the entire temperature range. The m range is 0.0001–4.0 at 25 °C and 0.0001–2.0 at higher T . Table 3 lists the ISPs used in each fit, for five different T values. As in the case of water–dioxane mixtures, b_{H^+} and b_{Cl^-} were calculated using eqs 5 and 6, respectively. a somewhat decreases at increased T , perhaps reflecting less anion polarization at higher temperature due to enhanced thermal electronic motion. The decrease in a is followed by a parallel decrease in $d/2$, implying closer approach to ISP additivity. The average percent error, as defined previously,¹⁴ is small, 0.1 or less in absolute values. The standard deviation is less than ~0.003.

The behavior of the single-ion activity coefficient of the proton as a function of temperature is depicted in Figure 9. The γ_{H^+} curves are, as expected, higher than the parallel γ_{\pm} curves (i.e., at the same T) and the minimum in γ_{H^+} shifts somewhat to higher concentration at higher T . γ_{H^+} is higher at lower T at constant I (or m). This implies that the pH of the solution, at constant concentration, is to some extent smaller at lower T , reflecting somewhat stronger acidity.

3.5. Effect of ε on HCl in Alcohol and Water–Alcohol Solutions. Activity coefficients of HCl in alcohol and water–alcohol solutions are available, but experimental data are somewhat limited.¹⁶ Here I show the fit of the SiS treatment with experiment for solutions of the alcohols methanol, ethanol, and

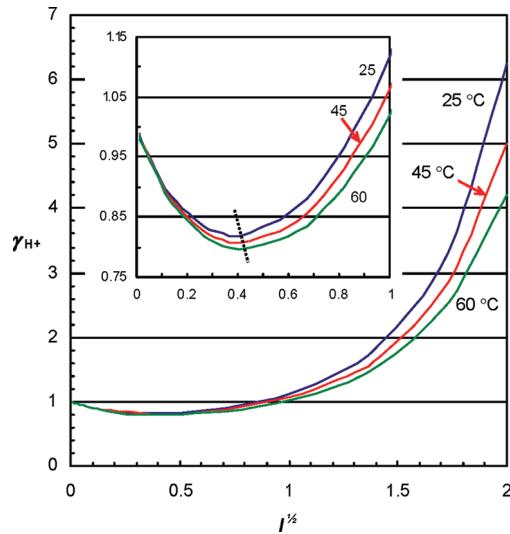


Figure 9. Effect of temperature, T , on the variation of proton activity coefficient, γ_{H^+} , with ionic strength, I , in aqueous HCl. The ion-size parameters (ISPs) of the theoretical curves (calculated using eq 2) are those derived from the fit of the SiS expression (eq 1) with experimental γ_{\pm} data (ref 16). T is mentioned next to each curve. In the inset, emphasizing the behavior at low I , the tilted dotted line passes through curve minima, to delineate the shift of the minimum with T .

2-propanol in water, and for pure methanol and ethanol, all at 25 °C. The emf cells used were again those based on the silver–silver chloride electrode. In fitting the SiS model (eq 1) to the experimental data of HCl in water–alcohol mixtures, eqs 5 and 6 were used again for calculating b_{H^+} and b_{Cl^-} , respectively, and a was again the only adjustable ISP. In the case of the pure alcohols, the cation is RH_2O^+ instead of H_3O^+ , and the mean effective cationic size (b_s) may therefore be different, apparently larger than that of H_3O^+ . Indeed, choosing b_s as 3.2 Å for 100% methanol, and as 3.7 Å for 100% ethanol, gave satisfactory fits; however, some other ISP choices are also effective. The above values seem appropriate for $(\text{CH}_3)\text{H}_2\text{O}^+$ and $(\text{CH}_3\text{CH}_2)\text{H}_2\text{O}^+$, respectively, since the alkyl substituent should definitely increase the effective ionic size of the solvated proton. By comparison, according to eq 5, b_s of H_3O^+ is 2.02 Å for the ε of pure methanol and 2.52 Å for the ε of absolute ethanol. We, of course, recall that the above values are not the “real” ionic sizes but are apparent “contact” distances in a medium of small dielectric constant in which two approaching small co-ions, when reaching their closest approach, still remain somewhat apart from each other because of the weak electric field of the solvent (see above).

Figure 10 presents the data for the water–ethanol system in the ethanol concentration range 10–100 wt %, and their fit with the SiS equation. Results in all cases are very satisfactory, and deviation of the fit from experiment in the case of low-ethanol mixtures, such as the 20% solution at $m^{1/2} \approx 0.55$, are judged to be due to measurement inaccuracies or typing errors. However, in the more demanding solutions having 72 and 100% ethanol (ε being 35 and 24, respectively), the low-concentration portion of the fit between theory and experiment appears to have a systematic disagreement. From the trend at very low acid concentration, it is indicated that the lack of fit may be due to experimental deficiencies.

In all cases, the high-concentration portion of the fit is especially pleasing, with the calculated γ_{\pm} being almost identical

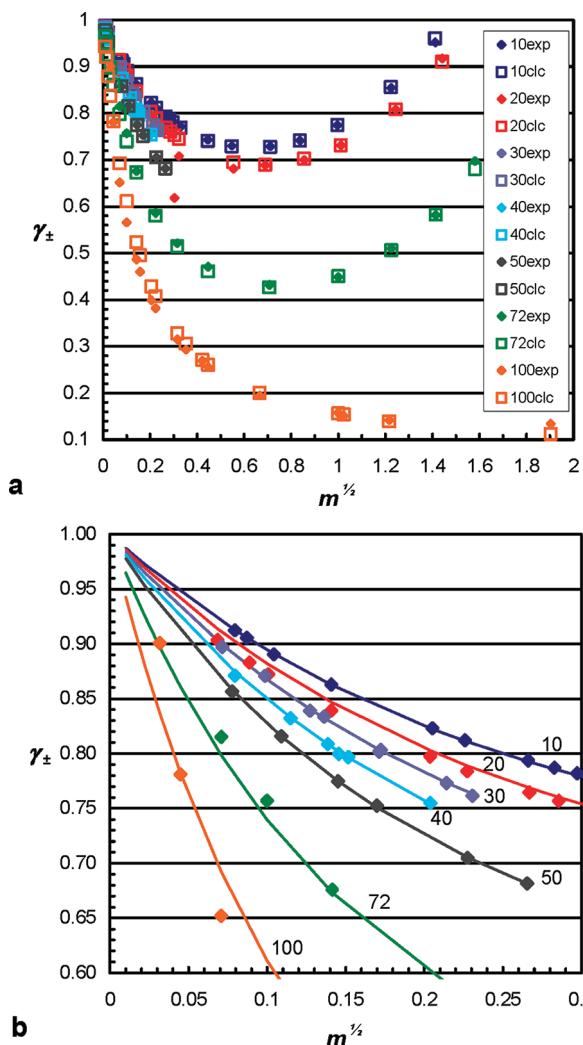


Figure 10. Fit of theory (eq 1) with experiment for γ_{\pm} vs $m^{1/2}$ of HCl in ethanol and water–ethanol solutions at 25 °C. (a) Entire m range; numbers in inset, wt % ethanol in solvent; (b) low m ; symbols are experimental data, curves are calculated (eq 1); numbers next to curves, wt % ethanol in solvent.

with experimental γ_{\pm} up to $m \approx 2$. In Figure 10b, the extrapolation of calculated γ_{\pm} to $m = 0.0001$ is emphasized through depicting continuous curves that represent the entire functional trend of calculated values. It can be concluded that the behavior of HCl in water–ethanol solutions is similar to that of HCl in water–dioxane solutions if one assumes that the only relevant factor that varies in the two types of solutions is ϵ , and b_{H^+} and b_{Cl^-} can be calculated from ϵ using the respective eqs 5 and 6. (I, of course, assume that even with the lowest water concentration of the water–ethanol mixture, i.e., in 72 wt % ethanol, H^+ appears essentially only as the hydronium ion, H_3O^+ .)

In Figure 11, the alcohol/water–alcohol analysis is extended to methanol, water–methanol, and water–2-propanol solutions. The fit with the SiS model is practically excellent, and it is so even with 100% methanol ($\epsilon = 32$). This further establishes the dominance of the ϵ factor in the thermodynamic behavior of HCl in polar solvents, while also fully supporting the assumption that, in all cases, the dissolved HCl is acting as a strong electrolyte, completely dissociated to its ions.

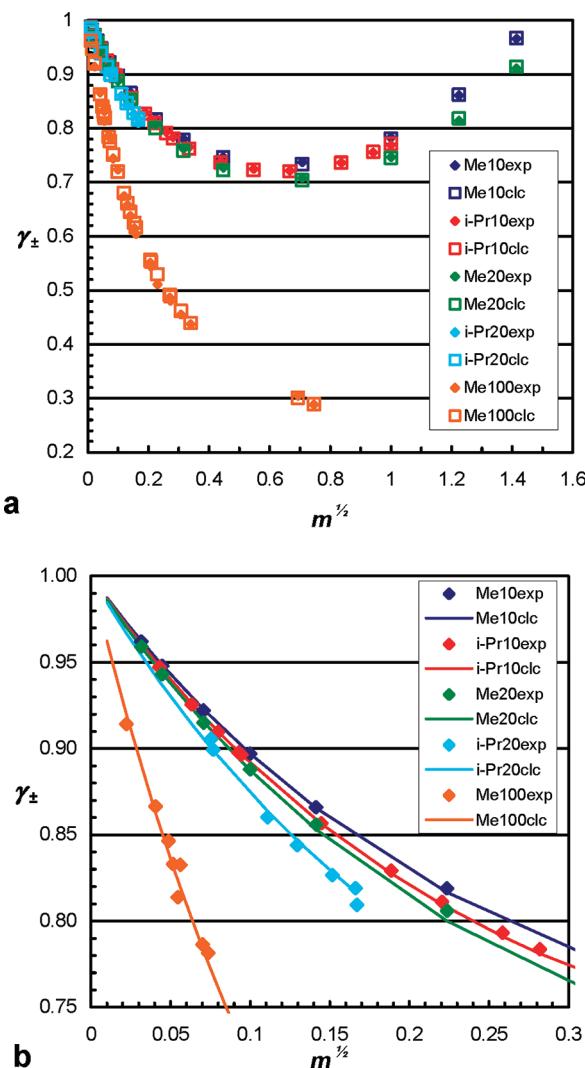


Figure 11. Fit of theory (eq 1) with experiment for γ_{\pm} vs $m^{1/2}$ of HCl in methanol, water–methanol, and water–2-propanol solutions at 25 °C. In the insets, Me denotes methanol, i-Pr denotes 2-propanol, and numbers are wt % alcohol in solvent. (a) Entire m range; (b) low m .

Table 4 summarizes parameters of the various cases of HCl in alcohol and water–alcohol solvents, all at 25 °C. In those cases for which the standard electrochemical potential was recalculated, results are listed and compared with those of the literature, if available. For the trend of a , adjusted for best fit, see below. The nonadditivity factor $d/2$ decreases with decreasing ϵ , as in the cases of water and water–dioxane mixtures, and it is especially small at very low ϵ . With the pure alcohols, $d/2$ is negative but close to zero, implying almost full ISP additivity.

3.6. $a-\epsilon$ Correlation: Could SiS Model Predictions be Extrapolated to $\epsilon < 9$? The theory–experiment fits as applied for the water, water–dioxane, and water–alcohol solvent systems are based on using eqs 5 and 6 for the calculation of the b 's and adjusting only a . For the pure alcohols, both b_s and a are adjusted. In Figure 12, the obtained a values of the various fits are presented against ϵ . In the ϵ range between ~ 30 and 80 , a is about constant around 3.5 Å in all cases, regardless of the temperature or the particular chemical composition of the solution. However, at ϵ below about 25, a starts to increase considerably with decreasing ϵ ; in the 8.5–35 range, a is

Table 4. Parameters of HCl in Alcohol and Water–Alcohol Solutions^a

alcohol	wt %	ref	ϵ	d_0	E°_{lit}	E°_{recalc}	a	$d/2$
methanol	10	20	74.05	0.9799	0.2153 ^b		3.55	1.125
	20	20	69.2	0.9644	0.2088 ^b		3.47	1.005
ethanol	100	21	32.6	0.791	-0.0103 ^b	-0.0095	3.70	-0.0383
	10	22	72.8	0.98038	0.21442	0.21434	3.54	1.105
ethanol	20	22	67.0	0.96640	0.20736	0.20670	3.44	0.955
	30	23	61.1	0.9507	0.20033	0.2004	3.45	0.904
ethanol	40	23	55.0	0.9315	0.19454	0.1944	3.55	0.928
	50	23	49.0	0.9098	0.18588	0.1860	3.65	0.934
ethanol	72	24	35(?)	0.8628		0.1480	3.65	0.589
	100	24, 25	24.35	0.789		-0.055	4.10	-0.0774
2-propanol	10	22	71.4	0.98122	0.21363	0.21354	3.54	1.094
	20	23	64.1	0.9669	0.2060	0.2060	3.40	0.887

^a a in Å, 25 °C. For b_s values in the case of 100% alcohol, see text. ^b Reference 26, p 470.

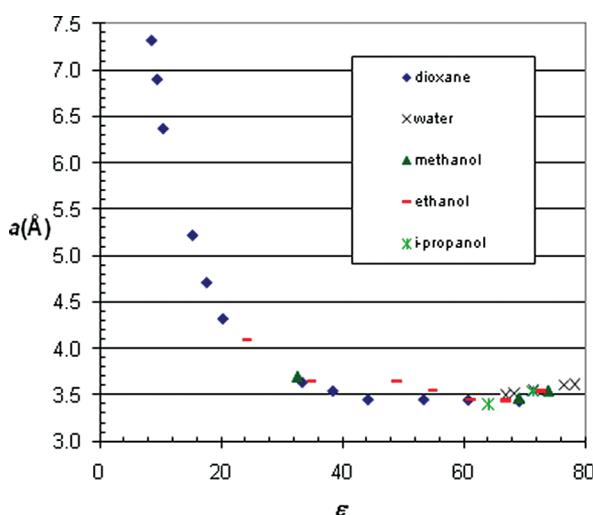


Figure 12. Relationship between counterion's ISP, a , and permittivity, ϵ , in water and in various mixtures of water and polar organic solvents (specified in inset).

approximately proportional to the inverse of ϵ , as demonstrated in Figure 13a. The dependence of a on ϵ follows the expression (in angstroms)

$$a = 2.35 + \frac{42.8}{\epsilon} \quad (7)$$

Figure 13b is presented to demonstrate that the current results may not be accidental; here, single-ISP values are plotted as a function of inverse ϵ , based on results of Fuoss et al.,²⁷ who fitted conductance data of KCl and CsI in water–dioxane solutions with an extended Debye–Hückel–Onsager equation that includes a single ISP. The “ a ” values of Fuoss et al. are thus parallel to \ddot{a} ’s of the DHEE. Even though \ddot{a} ’s are somewhat larger than a ’s (see above, section 2), the trend (Figure 13b) is similar to the one I have found in this work (Figure 13a): With ϵ below ~35 (i.e., right to the dotted vertical line), \ddot{a} —like a —appears proportional to $1/\epsilon$, with slopes and intercepts that are somewhat different than for HCl. However, at $\epsilon > 40$, the \ddot{a} values of KCl and CsI decrease monotonically instead of becoming about constant (like a of HCl). This is possibly due to the differences

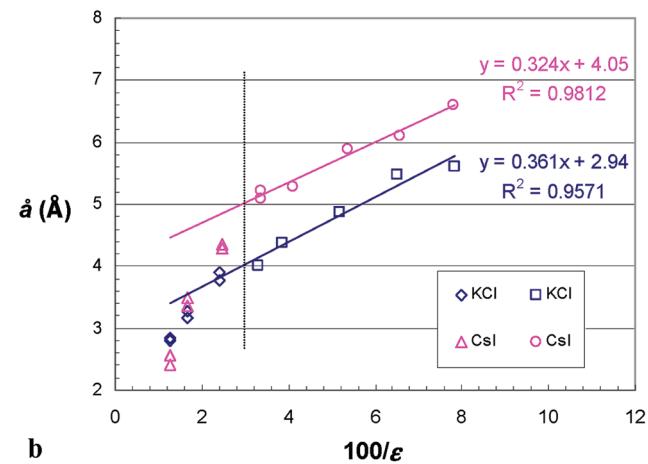
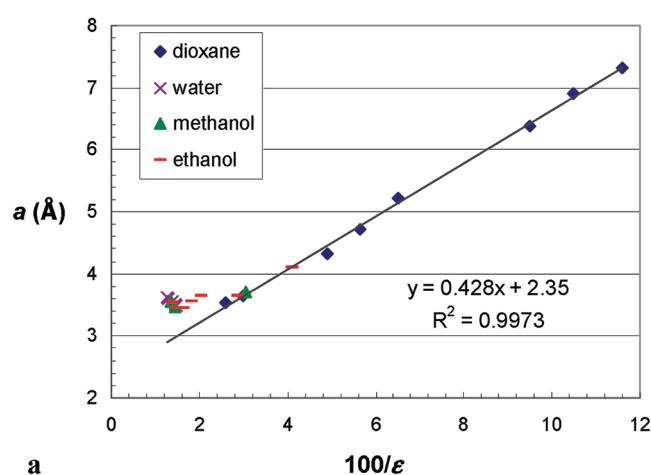


Figure 13. Pseudolinear dependence of counterion's ISP on $1/\epsilon$, for $\epsilon < \sim 40$: (a) a of this work; (b) \ddot{a} from conductance, ref 27 (see text).

between experimental data and theoretical expressions as employed by Fuoss et al. and those of the present study. For the increase in \ddot{a} as ϵ decreases, Fuoss et al. offered two possible interpretations: in one, they suggested that the local ϵ around an ion is larger than the bulk ϵ ; hence for calculating \ddot{a} one needs to

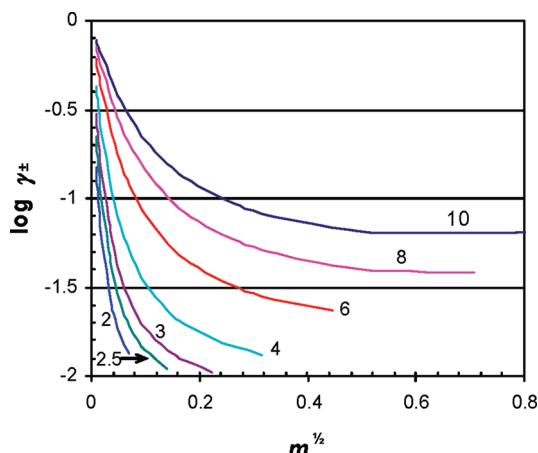


Figure 14. Computed $\log \gamma_{\pm}$ vs $m^{1/2}$ curves of HCl at 25 °C at different ϵ 's, with ISPs calculated from eqs 5–7 (see text and ref 28); extrapolation to the ϵ range 2–10 (ϵ values mentioned next to corresponding plots).

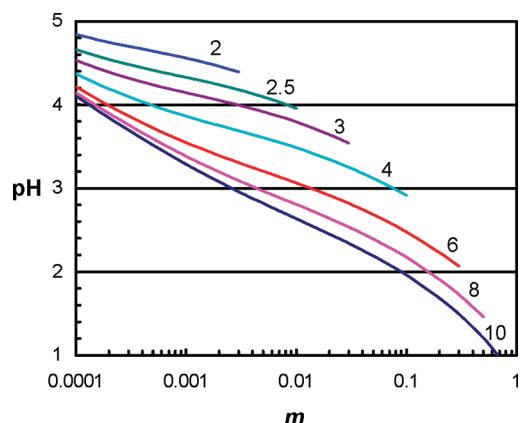


Figure 15. Computed pH vs m curves of HCl at 25 °C at different ϵ 's, with ISPs calculated from eqs 5–7 (see text and ref 28); extrapolation to the ϵ range 2–10 (ϵ values mentioned next to corresponding plots).

consider a larger ϵ value, which of course decreases \bar{a} . Alternatively, one may assume increasing ion solvation “as the fraction of non-polar component in the mixed solvent is increased.”²⁷ This, without further elaboration, is similar to the explanation provided earlier in the present text (section 3.2).

Smoothing of a based on the pseudolinear correlation of Figure 13a can be done, perhaps, up to $\epsilon = 40$, so the SiS treatment may be used to estimate γ_{\pm} values at low ϵ (<40) with all ISPs being fixed for a given ϵ value, and changing with ϵ according to eqs 5 and 6 for the b 's and eq 7 for a . In this way, $\log \gamma_{\pm}$ vs $m^{1/2}$ curves have been computed for ϵ values of 10 and below.²⁸ The results are presented in Figure 14. The concentration limit of each case is set for average ion–ion distance that is far greater than the ISPs. As expected, curves drop to lower $\log \gamma_{\pm}$ as a function of acid concentration, and the decline is steeper at lower ϵ ; apart from that, the various curves exhibit the same general contour. Below $\epsilon = 10$, no minimum is reached within the concentration limit applied. While this analysis is strictly theoretical and speculative, it nonetheless indicates that HCl should have a limit of dissolution compatible with the ISP requirements, assuming (perhaps boldly) that essentially any dissolved HCl

molecule is ionized even at ϵ considerably smaller than 10. In a solution with $\epsilon = 2$, no more than about 0.003 m of HCl could be expected to exist in the dissociated state.

Figure 15 presents pH curves corresponding to the curves of Figure 14. The pH is shown to increase with decreasing ϵ , and in each case of constant ϵ , it decreases strongly as a function of m , as should be expected. Thus, the acidity of HCl is considerably greater at higher concentration and larger ϵ . However, note that the change in pH is much less than the change in $-\log m$. This is in accord with the fact that, at very low ϵ , γ_{H^+} is decreasing in the entire concentration range of interest.²⁸ Note also the shallow S-shape of the pH curve and its diminishing with decreasing ϵ .

4. GENERAL CONCLUDING REMARKS

4.1. Implication of This Work on the Measurement of HCl Acidity. The importance of acids and bases in science and technology cannot be overemphasized, and HCl is overall perhaps the most important of all acids. It is therefore desirable to extend our understanding of the thermodynamic behavior of HCl in solution to learn more of the intrinsic physicochemical nature of the acid. In this regard, it is especially of interest to gather more information on the extent of dissociation of HCl in different media having dielectric constants (permittivities) that are considerably lower than that of water at 25 °C. HCl can also serve as a model acid for the study of acidity in general. Among other things, HCl is used in the standard measurement of pH, e.g., employing the Harned electrochemical cell (as mentioned above), and it is assumed that the activity coefficients of the proton and the chloride ion are the same at any given concentration.²⁹ The SiS treatment of strong electrolyte solutions effectively analyzes many different electrolyte solutions. It assumes that the size of colliding ions in solution is not equal for the cation and anion. For 1–1 electrolyte acids, the mean effective ionic size of the proton allowing the “best fit” of the SiS mathematical expression (e.g., eq 1) with experiment is ~1.16 Å (molal, in water at 25 °C) when the size of Cl^- is chosen as its crystallographic diameter.¹⁴ The SiS treatment provides single-ion activity coefficients; at higher ionic concentration, γ_i 's of cations (γ_+) and anions (γ_-) are very different from each other in the case of a large ion-size gap. Therefore, there is a large and increasing difference between γ_+ of H_3O^+ and γ_- of Cl^- when the acid concentration is above about 0.01 m . Consequently, pH smaller than ~2 cannot be calculated based on the above literature assumption²⁹ that $\gamma_{H^+} \approx \gamma_{Cl^-}$.¹⁴ The analysis of the present study allows calculation of pH from the single-ion activity coefficient of the proton. pH is found to increase with the decrease in ϵ , and values can be estimated even for ϵ below ~10, for which experimental data are not available. From the ISPs computed for such low ϵ 's, the limit of HCl dissolution can be estimated as a function of ϵ .

4.2. Proposed Dissociation Mechanism of HCl. In the current study, the emphasis has been on the activity coefficient (γ_{\pm}) of HCl in solvents of different permittivities and its change with concentration at different temperatures and with solvents of different chemical natures. It has been shown that ISPs increase as a function of the decrease in ϵ (eqs 5–7, Figure 7). For the b 's, there is an apparent linear relation with the inverse of ϵ , and this kind of relation also holds for a , but only below $\epsilon \approx 40$. With calculated b 's and an adjustable a , very good fits are usually obtained between experimental γ_{\pm} data and theoretical γ_{\pm}

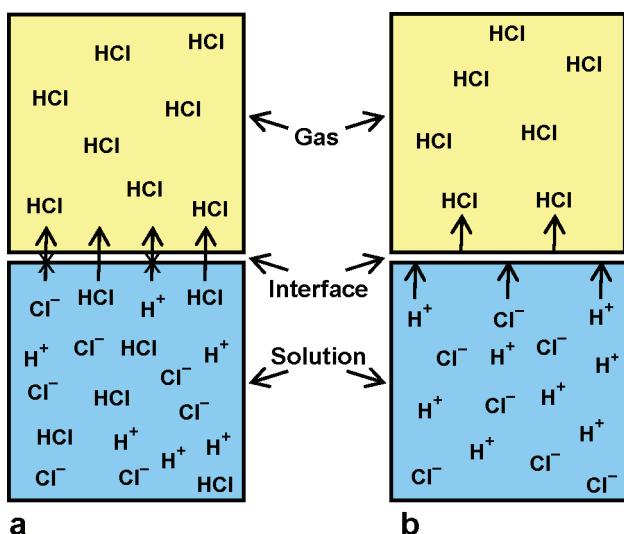


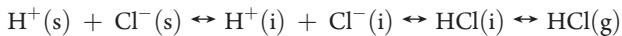
Figure 16. Distribution of HCl , H^+ , and Cl^- in different phases of polar solution, interface, and gas: (a) conventional model; (b) model proposed in this work.

values computed by the SiS expression, eq 1, under comparable conditions. This agreement of theory with experiment extends to the highest dioxane concentrations in water—82%—and to the pure alcohols methanol and ethanol. Thus, the current study strongly indicates that in polar solvents, within the relevant concentration ranges for which activity coefficients are available, HCl is practically always fully ionized, unlike what is taught by the literature.^{16,17} The decline in acid strength with decreasing ϵ is not due to ion association, causing depletion of the H^+ population in the solution, but rather is a result of the intrinsic thermodynamic behavior of the proton in solution as a function of ϵ . This is a major conclusion of the current study. It also appears that T does not influence the ISPs of HCl at any given ϵ and concentration. Furthermore, solvent composition and the chemical nature of the solvent do not play a role in the apparent thermodynamic properties of HCl in solution; the only relevant property of the solvent is its permittivity. This is fully consistent with the SiS model, upon which the current analysis is based, being within the McMillan–Mayer level of modeling, i.e., considering the medium (“solvent”) as a structureless continuum characterized only by its permittivity.

The schematic presentation in Figure 16 compares the traditional view of the $\text{HCl}-\text{H}^+-\text{Cl}^-$ equilibrium between the solution and the gas phase, with the newly proposed equilibrium according to which ion association occurs mostly (perhaps only) in the interface between the polar liquid (solution) phase and the gas phase, and *not* in the solution. Thus, while the conventional equilibrium can be described by the equation sequence



the equilibrium proposed here follows (ideally) the equation sequence



where the letters “s”, “i”, and “g” in parentheses denote the solution, interface, and gas phases, respectively. In other words, based on the results of the current study, I propose that, for polar solutions, molecular HCl can coexist with its ions H^+ and Cl^-

only in the solution–gas interface, not in the solution phase itself. The traditional view of the HCl ionization process seems to suggest that H^+ and Cl^- ions do not at all reside in the solution–gas interface; in other words, HCl is believed to dissociate not in the interface but only in the polar solution. It makes sense, however, that the reaction $[\text{solvent}] + \text{HCl} \leftrightarrow \text{H}[\text{solvent}]^+ + \text{Cl}^-$ may mostly occur on the solvent–gas interface.

5. SUMMARY OF MAIN FINDINGS

In the literature, discrepancies between experiment and theory in regard to the thermodynamic behavior of electrolyte solutions are frequently explained by assuming ion association; the existence of such a state, however, has never been proven independently. In addition, physically unrealistic ion-size parameters (ISPs) are offered as fitting factors in the theoretical expressions, and they are justified as representing ion solvation. A classical example is the activity coefficients—experimental vs theoretical—of HCl in polar solvents of varying permittivity (ϵ). In this work, I have demonstrated that ion-pair formation is an unnecessary postulate in explaining the thermodynamic behavior of HCl (e.g., as reflected by its γ_{\pm}) over a broad concentration range and within a wide span of a solvent’s ϵ . I have also attempted to shed new light on the variation of ISPs as a function of ϵ . The following have been found:

- (A) The SiS treatment of strong electrolytes (providing eq 1), which extends the simple electrostatic theory of Debye and Hückel to ions of unequal size, readily fits with experiment in the case of HCl polar solutions, using ISPs that appear to adequately reflect ion–ion closest approaches.
- (B) The above finding indicates that no substantial ion association occurs in HCl solutions even with ϵ as low as about 10; HCl should be entirely ionized at least at very low concentrations (say, below 0.01 M).
- (C) The indication in B has compelled a recalculation of the relevant standard potentials (E°) at low ϵ values (<35), by extrapolating E to concentration zero based on the DH–SiS equation and not on modified equations considering ion association.
- (D) Corrected E° values according to C have yielded corrected $E^\circ - E$ hence γ_{\pm} values (eq 4); as a result, the theory–experiment fit at low HCl concentrations (small ionic strength, I) has been considerably improved, as demonstrated in Table 2. There is therefore no need in this case to invoke “negative deviations from the limiting law”; in the absence of such deviations, there is fortunately no reason to explain them by claiming ion pairing.
- (E) In the solvent, only ϵ appears to influence the electrolytic (thermodynamic) behavior of HCl in solution; the chemical nature of the solvent has no apparent effect. The solvent is thus, as required for the consistency of the DH–SiS analysis, a “perfect” McMillan–Mayer medium.
- (F) At $\epsilon \leq 40$, all ISPs increase linearly with the inverse of ϵ , and theory is thus fittable with experiment at various ϵ values *without ISP adjustment*; above $\epsilon \approx 40$, only the cation ISPs (b’s) are linear functions of $1/\epsilon$, and the counterion’s ISP, a , is adjustable.
- (G) ISPs do not appear to be direct functions of temperature, T ; their change with T may be due only to the change of ϵ with T .

- (H) Ion association of HCl (to form the acid molecule with a covalent H—Cl bond) is proposed to take place (at least mostly) not in the polar solution but rather in the interface between solution and the gas phase above it (thereby retaining the acid in all its solutions as strong electrolyte).
- (I) The acidity of HCl strengthens (pH decreases) with increase in I and in ϵ .

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