



# Combined Theoretical and Experimental Study of Refractive Indices of Water–Acetonitrile–Salt Systems

Ni An,<sup>†,||</sup> Bilin Zhuang,<sup>‡,||</sup> Minglun Li,<sup>§</sup> Yuyuan Lu,<sup>\*,§</sup> and Zhen-Gang Wang<sup>\*,‡,§</sup>

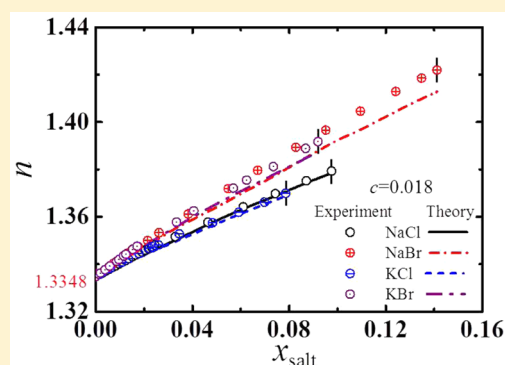
<sup>†</sup>College of Chemistry, Jilin University, Changchun 130012, People's Republic of China

<sup>‡</sup>Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

<sup>§</sup>State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

## Supporting Information

**ABSTRACT:** We propose a simple theoretical formula for describing the refractive indices in binary liquid mixtures containing salt ions. Our theory is based on the Clausius–Mossotti equation; it gives the refractive index of the mixture in terms of the refractive indices of the pure liquids and the polarizability of the ionic species, by properly accounting for the volume change upon mixing. The theoretical predictions are tested by extensive experimental measurements of the refractive indices for water–acetonitrile–salt systems for several liquid compositions, different salt species, and a range of salt concentrations. Excellent agreement is obtained in all cases, especially at low salt concentrations, with no fitting parameters. A simplified expression of the refractive index for low salt concentration is also given, which can be the theoretical basis for determination of salt concentration using refractive index measurements.



## I. INTRODUCTION

The refractive index,  $n$ , defined as the ratio of the speed of light in vacuo  $c_0$  to the speed of light in the material  $c$ , is one of the most fundamental properties of pure liquids and their solutions and has been measured and interpreted since the early 19th century.<sup>1–4</sup> This optical property can be measured for a small amount of sample in wide ranges of temperatures and pressures with high precisions<sup>5–7</sup> (typical errors are nowadays less than  $10^{-5}$ ) and contains information about intermolecular interactions;<sup>8–10</sup> it is also closely related to other electrical and thermophysical properties, such as dielectric permittivity,<sup>11,12</sup> density,<sup>13–15</sup> and surface tension.<sup>16,17</sup> Therefore, some solutions, whose properties are otherwise difficult to measure directly, can be more easily identified by knowing their  $n$  values. With many current and potential applications of solvent mixtures in analytical chemistry<sup>18–20</sup> and industrial processes,<sup>21–24</sup> such as the design of biological environments<sup>22,23</sup> and the search for greener liquid media,<sup>24</sup> the subject is receiving renewed interest both theoretically<sup>25–28</sup> and experimentally.<sup>29–35</sup>

The refractive index reflects the polarization of the molecules by the electromagnetic field of the light.<sup>36–38</sup> For liquid mixtures, a number of mixing rules for the refractive index of a mixture  $n$  in terms of the refractive indices of the pure components  $n_i$  have been proposed. The simplest is a direct volume fraction average of the refractive index of each component  $n_i$ , known as the Arago–Biot equation<sup>4</sup>

$$n = \sum_i \phi_i n_i \quad (1)$$

where the nominal volume fraction  $\phi_i = V_i / \sum_i V_i$ , with  $V_i$  denoting the volume of the  $i$ th component before mixing. Instead of the refractive index itself, the Newton equation<sup>1</sup> takes the average of  $n_i^2$

$$n^2 = \sum_i \phi_i n_i^2 \quad (2)$$

For binary solutions, two other mixing rules have been proposed for the case when one of the components, say component 2, is dilute: the Wiener equation<sup>39</sup>

$$\frac{n^2 - n_1^2}{n^2 + 2n_1^2} = \phi_2 \frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2} \quad (3)$$

and the Heller equation<sup>40</sup>

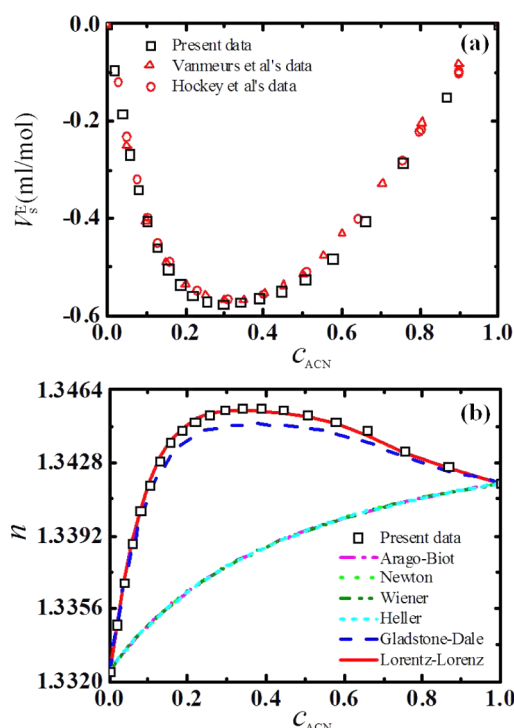
$$\frac{n - n_1}{n_1} = \frac{3}{2} \phi_2 \frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2} \quad (4)$$

All these mixing rules use the nominal volume fractions. For many solutions such as water–acetonitrile mixtures, the excess volume (the volume change per mole upon mixing) can be substantial,<sup>41</sup> as shown in Figure 1a. The excess volume reflects

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**Figure 1.** (a) Excess molar volume  $V_s^E$  as a function of the mole fraction of acetonitrile  $c_{ACN}$  in a water–acetonitrile mixture without salt. Our own experimental results (black squares) are checked against data from the literature (red triangles and circles).<sup>78,79</sup> (b) Refractive index  $n$  as a function of the mole fraction of acetonitrile  $c_{ACN}$  in a water–acetonitrile mixture without salt, where the lines are fits to the various mixing rules. The fits using eqs 1–4 are nearly indistinguishable from each other on the scale of the figure.

the physical and/or chemical interactions between components in the mixture. In fact,  $n$  and the excess molar volume  $V_s^E$  values are often reported together.<sup>42–49</sup> The Gladstone–Dale equation<sup>2,3</sup>

$$n - 1 = \sum_i \phi'_i (n_i - 1) \quad (5)$$

where  $\phi'_i = V_i/V$ , with  $V$  denoting the actual volume of the mixture, accounts for the effect of volume change upon mixing.

The most systematic mixing rule is the Lorentz–Lorenz equation,<sup>36</sup> based on an argument that led to the Clausius–Mossotti equation for the dielectric constant of polarizable molecules which assumes ideal mixing of the polarizability. The Lorentz–Lorenz equation reads

$$\frac{n^2 - 1}{n^2 + 2} = \sum_i \phi'_i \frac{n_i^2 - 1}{n_i^2 + 2} \quad (6)$$

It can be easily seen that the Gladstone–Dale equation follows from the Lorentz–Lorenz equation if the solution is dilute or the refractive indices of solute and solvent are close to each other. For the water–acetonitrile system, the Lorentz–Lorenz equation fits the data nearly perfectly, as shown in Figure 1b. The Gladstone–Dale equation also fits the data quite well. All the mixing rules mentioned above have been used to interpret experimental data for liquid mixtures to varying degrees of success<sup>30–34,50–54</sup> and their interrelationships have been discussed by Heller.<sup>13</sup>

Although the Lorentz–Lorenz equation has been widely employed to successfully interpret the refractive indices of liquid mixtures,<sup>52,53</sup> we are not aware of its generalization to liquid mixtures containing salts. In particular, water–acetonitrile–salt (WAS) mixture is an excellent extractant that is widely used in biomedical and industrial applications and has attracted much attention in recent years.<sup>23,55–62</sup> For instance, salting-out induced liquid–liquid extraction based on the WAS system has been used in quantitative analysis of fluoroquinolones in water, food and biological matrices,<sup>23</sup> benzimidazole fungicides in high salinity samples,<sup>57</sup> pesticide residues in foods,<sup>58,59</sup> and caffeine content in cocoa.<sup>60</sup> The WAS system has other attractive features, such as easy recovery and high thermal stability.<sup>61,62</sup> Characterizing and understanding the light refractive properties of the WAS system will provide useful information that can be exploited in its applications.

In this paper, we provide a simple theoretical formula for the refractive index of liquid mixtures containing salt ions by generalizing the Clausius–Mossotti equation for mixtures of neutral molecules to include the contribution of the salt ions. The theory considers the connection between the macroscopic refractive index of the mixture and the microscopic polarizabilities of the molecular and ionic species involved and takes into account the nonideality of the mixture only through the volume of mixing that can be independently measured. The theoretical predictions are tested by extensive experimental measurements of the refractive indices for water–acetonitrile–salt systems for several liquid compositions, different salt species, and a range of salt concentrations. We find excellent agreements between the measured and predicted refractive index results. Within experimental accuracy, the measured refractive indices show good linearity with the salt mole fraction  $x_{\text{salt}}$  in the mixture over a fairly wide range in salt concentration. Therefore, we also present a simplified version of our general formula to linear order in  $x_{\text{salt}}$ .

The rest of this paper is organized as follows. In Section II, we present the key concepts and mathematical details in the theoretical derivation and give a general expression for the refractive index and its corresponding linearized version in salt concentration. In Section III, we describe the materials and methods used in the experimental measurements. Results are presented and discussed in Section IV, where we provide values of the refractive indices of the WAS mixtures for three liquid compositions and four different salts as functions of the salt concentration and compare with the theoretical predictions. We conclude in Section V with some concluding remarks and outlook.

## II. THEORY

From the Maxwell equations of electromagnetism, the refractive index  $n$  of a substance is related to the substance's relative permittivity  $\epsilon$  and relative permeability  $\mu$  at optical frequencies through  $n = \sqrt{\epsilon\mu}$ .<sup>37,38</sup> As the mixtures in this work are nonmagnetic,  $\mu$  is very close to 1, and therefore  $\epsilon = n^2$ .<sup>37,38</sup> The relative permittivity relates the polarization  $\mathbf{P}$  of the system at optical frequencies with the Maxwell field  $\mathbf{E}$  through the following relation:

$$\mathbf{P} = \epsilon_0(\epsilon - 1)\mathbf{E} \quad (7)$$

with  $\epsilon_0$  denoting the permittivity of the vacuum.

The polarization of a general system is the result of three physical mechanisms in response to an electric field: the

displacement of the center of the electronic charge on the species (solvent molecules and ions for the systems studied here), cation and anion motions in opposite directions, and orientation of the molecular permanent electric dipoles.<sup>63,64</sup> These three different polarization processes respond to electric field at different timescales. Both the translational motion of the ions and the orientational motion of permanent dipoles occur on timescales much longer than the reciprocal of the frequency of visible light. Consequently, polarization from these degrees of freedom has little response to the fast-varying electric field of the light wave in the visible spectrum.<sup>65,66</sup> Therefore, at optical frequency, we write the polarization  $\mathbf{P}$  as the density of the sum of induced dipole moments of all particles as

$$\mathbf{P} = \sum_k \rho_k \alpha_k \mathbf{E}'_k \quad (8)$$

where  $\rho_k$  denotes the number density of the  $k$ th kind of particle in the mixture, and  $\alpha_k$  is its polarizability.  $\mathbf{E}'_k$  is the average local field acting on the  $k$ th kind of particles, which is defined as the average total electric field at the position of the particle minus the field due to the particle itself. The product  $\alpha_k \mathbf{E}'_k$  gives the average induced dipole moment of the  $k$ th kind of particles.

By the same consideration that the high-frequency electromagnetic field does not contribute to the structural reorganization in the mixture, the distribution of the ions remains spherically symmetric around each moiety (ions or molecules), and thus the ionic charges do not contribute to the average local field; similarly, because of the lack of orientational organization among the permanent dipoles, the permanent dipole moments of the solvent molecules do not affect the local field at the optical frequencies. From these arguments, we obtain the simple, intuitive picture that the local field on a particle is due solely to the induced dipole moments on all other particles in the system and the applied electric field. The local field is then calculated using the well-known Lorentz equation, which approximates the local field by the field inside a virtual spherical cavity in a uniformly polarized medium<sup>37,38</sup>

$$\mathbf{E}'_k = \frac{\epsilon + 2}{3} \mathbf{E} \quad (9)$$

We note that the local field is independent of the size of the virtual cavity and the particle type.

Substituting eqs 8 and 9 into eq 7, we obtain

$$\frac{n^2 - 1}{n^2 + 2} = \frac{1}{3\epsilon_0} \sum_k \rho_k \alpha_k \quad (10)$$

which reduces to the Clausius–Mossotti equation for a one-component system. The polarizability of a liquid component can be easily calculated from the refractive index of the pure liquid by applying eq 10 to a one-component liquid system. For the ions, however, it is not clear whether the refractive index of an ionic crystal provides a reasonably accurate indication for the polarization response of the solvated ions; it is more appropriate to consider the ionic polarizability directly in our theory. To this end, we separate the liquid and the ionic contributions on the right-hand side of eq 10 as

$$\frac{n^2 - 1}{n^2 + 2} = \sum_{i \in \text{ions}} \frac{\rho_i \alpha_i}{3\epsilon_0} + \sum_{j \in \text{solvents}} \frac{\rho_j n_j^2 - 1}{\rho_j^{(0)} n_j^2 + 2} \quad (11)$$

where  $n_j$  and  $\rho_j^{(0)}$  are the refractive index and the number density for the pure  $j$ th component of the solvent.

Although the polarizabilities of ions in the gas phase and in the solid phase are readily available,<sup>67,68</sup> accurate values for the polarizabilities of the solvated ions are difficult to obtain. In particular, a range of values for anion polarizabilities in the solution phase have been reported. For example, some studies suggest that the anion polarizabilities in solution are appreciably reduced with respect to their gas-phase values,<sup>69–72</sup> whereas others argue that the anion polarizabilities are practically unchanged upon solvation.<sup>73,74</sup> However, it is generally agreed that the ion polarizability in solution is in between its values in the crystalline phase and in the gas phase, as the overlap of electronic structures and the confining potentials imposed by surrounding species in the solution phase are intermediate between the gas phase and the crystalline phase.<sup>72,75</sup> Therefore, as the simplest approximation, we approximate the polarizability  $\alpha_i$  of a solvated ion by averaging its gas-phase polarizability  $\alpha_i^{(g)}$  and crystalline-phase polarizability  $\alpha_i^{(c)}$ , that is,  $\alpha_i = (\alpha_i^{(g)} + \alpha_i^{(c)})/2$ .

For the monovalent salts considered in this work, we have  $\rho_+ = \rho_- = \rho_{\text{salt}}$ . Moreover, the sum  $\alpha_+^{(c)} + \alpha_-^{(c)}$  for the ions can be calculated from the crystalline refractive index  $n_c$  using the Clausius–Mossotti equation. As such, the expression for mixture index of refraction, eq 11, can be further simplified as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\rho_{\text{salt}} \alpha_{\text{salt}}}{3\epsilon_0} + \sum_{j \in \text{solvents}} \frac{\rho_j}{\rho_j^{(0)}} \frac{n_j^2 - 1}{n_j^2 + 2} \quad (12)$$

with  $\alpha_{\text{salt}}$  being the sum of polarizabilities of the solvated ions given by

$$\begin{aligned} \alpha_{\text{salt}} &= \frac{1}{2} (\alpha_+^{(g)} + \alpha_-^{(g)} + \alpha_+^{(c)} + \alpha_-^{(c)}) \\ &= \frac{1}{2} \left( \alpha_+^{(g)} + \alpha_-^{(g)} + \frac{3\epsilon_0 n_c^2 - 1}{\rho_c n_c^2 + 2} \right) \end{aligned} \quad (13)$$

where  $\rho_c$  and  $n_c$  are respectively the number density and the index of refraction for the crystalline phase of the salt. The quantities involved in the evaluation of  $\alpha_{\text{salt}}$  are tabulated in Table I. We note that the  $\rho_j$  and  $\rho_{\text{salt}}$  appearing in eq 12 are the actual number density of the species in the solution; thus, any volume change upon mixing is automatically included.

As the focus of our work is on the salt effects on the refractive index, and as the Lorentz–Lorenz equation has been shown to give an excellent description of the refractive index of liquid mixtures, we will take the refractive index  $n_{\text{sol}}$  of the salt-free liquid solution as known and given, and derive an

**Table I. Gas-Phase Polarizabilities of the Cations<sup>a</sup> and the Anions<sup>b</sup>, as well as the Refractive Indices<sup>c</sup> and Densities<sup>d</sup> of the Salt Crystals<sup>68e</sup>**

salt	$\alpha_+^{(g)}$ [ $\text{\AA}^3$ ]	$\alpha_-^{(g)}$ [ $\text{\AA}^3$ ]	$n_c$	$\rho_c$ [ $1/\text{nm}^3$ ]	$\alpha_{\text{salt}}$ [ $\text{\AA}^3$ ]
NaCl	0.179	3.660	1.544	22.36	3.605
NaBr	0.179	4.770	1.642	18.73	4.777
KCl	0.830	3.660	1.490	16.06	4.395
KBr	0.830	4.770	1.560	13.87	5.583

<sup>a</sup>Cations,  $\alpha_+^{(g)}$ . <sup>b</sup>Anions,  $\alpha_-^{(g)}$ . <sup>c</sup>Refractive Indices,  $n_c$ . <sup>d</sup>Densities,  $\rho_c$ . <sup>e</sup> $\alpha_{\text{salt}}$  is the approximated value of the polarizability of the salt in the solution phase calculated based on eq 13. The polarizability values are for use in cgs units. To convert to SI, use the relation  $\alpha(\text{SI})/\text{C m}^2 \text{V}^{-1} = 4\pi\epsilon_0 \times 10^{-6} \alpha(\text{cgs})/\text{cm}^3$ .

expression of the refractive index of the salt solution in terms of  $n_{\text{sol}}$ , the liquid composition and the salt concentration.

We use  $x_{\text{salt}}$ , the mole fraction of the salt in the mixture, as the concentration variable for the salt

$$x_{\text{salt}} = \frac{\rho_{\text{salt}}}{\rho_{\text{salt}} + \sum_j \rho_j} \quad (14)$$

We describe the composition of the solvent by  $c_j$ , the mole fraction of the  $j$ th liquid component in the salt-free solvent, given by

$$c_j = \frac{\rho_j}{\sum_j \rho_j} \quad (15)$$

Because the volume of a system is a more directly measurable quantity in the experiments, we work with volume quantities rather than densities. Here, we define three volume quantities for the mixture: the molar volume of each liquid component  $V_j^{(0)} = N_A/\rho_j^{(0)}$ , where  $N_A$  is the Avogadro constant, the molar volume  $V_s$  of the salt-free solvent mixture, and the actual volume  $V_{\text{ss}}$  of the salt–solvent system when salt is added to 1 mol of solvent. The density of each species in the system are related to  $V_{\text{ss}}$  through

$$\rho_j = \frac{c_j N_A}{V_{\text{ss}}} \quad \text{for } j \in \text{solvents} \quad (16)$$

$$\rho_{\text{salt}} = \frac{x_{\text{salt}}}{1 - x_{\text{salt}}} \frac{N_A}{V_{\text{ss}}} \quad (17)$$

Rewriting eq 12 in terms of volume quantities and mole fractions, we arrive at

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\alpha_{\text{salt}}}{3\epsilon_0} \frac{x_{\text{salt}}}{1 - x_{\text{salt}}} \frac{N_A}{V_{\text{ss}}} + \sum_{j \in \text{solvents}} \frac{c_j V_j^{(0)}}{V_{\text{ss}}} \frac{n_j^2 - 1}{n_j^2 + 2} \quad (18)$$

In the absence of salt, we have

$$\frac{n_{\text{sol}}^2 - 1}{n_{\text{sol}}^2 + 2} = \sum_{j \in \text{solvents}} \frac{c_j V_j^{(0)}}{V_s} \frac{n_j^2 - 1}{n_j^2 + 2} \quad (19)$$

Therefore, eq 18 can be written as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{V_s}{V_{\text{ss}}} \left( \frac{x_{\text{salt}}}{1 - x_{\text{salt}}} A \alpha_{\text{salt}} + \frac{n_{\text{sol}}^2 - 1}{n_{\text{sol}}^2 + 2} \right) \quad (20)$$

where  $A = N_A/(3\epsilon_0 V_s)$ .

Equation 20 is the key result of this work. It gives a simple expression for the refractive index of a liquid mixture with added salt in terms of the refractive index of the salt-free solution, the liquid composition, the salt concentration, and the volumes of the salt-free solution and of the final mixture.

In the limit of low salt concentrations, the volume of the solution can be written as<sup>76</sup>

$$V_{\text{ss}} = V_s [1 + \gamma' x_{\text{salt}} + \eta x_{\text{salt}}^{3/2}] \quad (21)$$

where we have ignored terms of order  $x_{\text{salt}}^2$  and higher. It can be easily seen that the combination  $\gamma' V_s$  is just the infinite dilution limit of the partial molar volume of the salt  $V_{\text{salt}}^\infty \equiv \lim_{x_{\text{salt}} \rightarrow 0} [(V_{\text{ss}} - V_s)/x_{\text{salt}}]$ . The  $x_{\text{salt}}^{3/2}$  term arises from the Debye–Hückel corrections. Although theoretically  $\eta$  should be purely a solvent

**Table II. Comparison of the Limiting Proportionality Constants Obtained from Linear Approximation<sup>a</sup> and Debye–Hückel Limiting Law Fitting<sup>b</sup> for Different Salt–Solvent Systems, Respectively<sup>c</sup>**

salt	$\gamma_{0.000}$	$\gamma_{0.018}$	$\gamma_{0.128}$	$\gamma'_{0.000}$	$\gamma'_{0.018}$	$\gamma'_{0.128}$
NaCl	1.139	1.135	0.848	0.920	0.795	0.647
NaBr	1.519	1.496	1.249	1.287	1.227	1.112
KCl	1.726	1.697	1.297	1.440	1.406	1.326
KBr	1.934	1.929	1.591	1.849	1.838	1.526

<sup>a</sup>Linear Approximation,  $\gamma$ . <sup>b</sup>Debye–Hückel Limiting Law,  $\gamma'$ . <sup>c</sup>The three different subscripts refer to the mole fraction of the acetonitrile in the solvent at  $c_{\text{ACN}} = 0$ ,  $c_{\text{ACN}} = 0.018$ , and  $c_{\text{ACN}} = 0.128$ , respectively.

property, experimentally its value has been shown to depend on the salt type,<sup>76,77</sup> so we treat it here as a fitting parameter.

Although fitting the volume data using eq 21 yields accurate values for  $V_{\text{salt}}^\infty$ —for pure water, our results agree well with reported literature values<sup>77</sup> (see Supporting Information)—the resulting expression for the refractive index with these two fitting parameters is rather cumbersome; there is no advantage to using the full expression eq 20. For low salt concentrations ( $x_{\text{salt}} < 0.04$ ), both the volume and the refractive index data exhibit very good linearity with  $x_{\text{salt}}$ . Thus, we are interested in developing the limiting linearized expression for the refractive index. To this end, we fit the volume of the salt–solvent system using the simpler linear relationship

$$V_{\text{ss}} = V_s (1 + \gamma x_{\text{salt}}) \quad (22)$$

Because of the finite range of the salt concentration and experimental errors, the value of  $\gamma$  fitted from measurements can be different from  $\gamma'$ .

Substituting eq 22 into eq 20 and expanding the resulting expression to linear order in  $x_{\text{salt}}$ , we obtain the following simplified expression for low salt concentration:

$$n = n_{\text{sol}} + K x_{\text{salt}} \quad (23)$$

with the slope  $K$  given by

$$K = \frac{n_{\text{sol}}^2 + 2}{6n_{\text{sol}}} [(n_{\text{sol}}^2 + 2)A\alpha_{\text{salt}} - (n_{\text{sol}}^2 - 1)\gamma] \quad (24)$$

We see that the rate of change of  $n$  with respect to  $x_{\text{salt}}$  depends on the salt polarizability  $\alpha_{\text{salt}}$ , the rate of change in volume  $\gamma$ , as well as the refractive index of the salt-free solution.

### III. EXPERIMENTS

**A. Chemicals.** Anhydrous acetonitrile (Aladdin, H<sub>2</sub>O: 20–30 ppm) was distilled with calcium hydride (CaH<sub>2</sub>, Sinopharm Chemical Reagent, 97%) before use. Water was obtained from deionized and double-distilled water. Sodium chloride (NaCl, Vetec, 99.0%), sodium bromide (NaBr, Vetec, 98.0%), potassium chloride (KCl, Vetec, Sigma, 99.0%), and potassium bromide (KBr, Vetec, 99.0%) were of analytical grade and were not purified further. All mixtures were prepared by weighing the masses, with uncertainty  $\pm 0.0001$  g due to evaporation.

**B. Measurements.** The densities of the mixtures were measured with a precision of 0.001 g/cm<sup>3</sup> using an DAH-OMETER digital densitometer at a fixed temperature of 25 °C. The densitometer was carefully calibrated periodically with double-distilled water at 25 °C. The sample was kept in a heated water bath at 25 °C (Thermo HAAKE SC150-ASB circulating water bath with the digital temperature control unit



to maintain the required temperature within  $\pm 0.1$  °C) before being taken out for density measurement, which was made in an air-conditioned room at  $25 \pm 0.5$  °C. The measurement time was less than 1 min. The densities of the water–acetonitrile mixture at mole fractions  $c_{\text{ACN}} = 0, 0.018, 0.128$ , and 1 are, respectively, 0.997 g/mL, 0.991 g/mL, 0.950 g/mL, and 0.786 g/mL; their corresponding  $V_s$  are 18.074 mL/mol, 18.594 mL/mol, 22.065 mL/mol, and 52.899 mL/mol. The volume of the solutions as a function of the salt concentration is given in Figure 2. All measurements were made at atmospheric pressure.

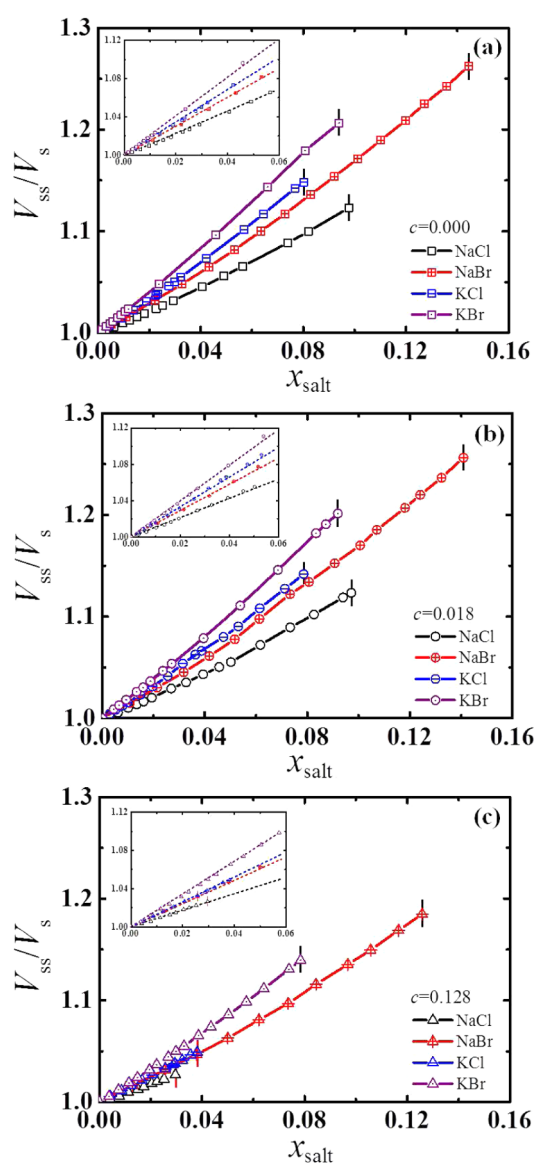
The refractive indices  $n$  of the studied solutions were measured at a fixed temperature of 25 °C and ambient pressure using a thermostatic digital Inmark IR120plus refractometer at the wavelength of the D-line of sodium, 589.3 nm. The precision of the measurements is estimated to be  $\pm 0.0001$ . The

refractive index measurements were performed after the liquid mixtures and salt solutions reached thermodynamic equilibrium at 25 °C in the refractometer cell. The temperature was controlled by circulating water into the refractometer through the same water heat bath. The data reported were results of averaging over three independent samples.

#### IV. RESULTS AND DISCUSSION

We first measure the molar excess volume of the water–acetonitrile mixtures at zero salt concentration,  $V_s^E = V_s - \sum_j c_j V_j^{(0)}$ . The data are shown in Figure 1a, and the corresponding refractive index,  $n$ , is shown in Figure 1b. Also shown for comparison in Figure 1a are data taken from the literature.<sup>78,79</sup> In all cases, the agreement with previous literature data is excellent. The water–acetonitrile mixture shows a negative deviation ( $V_s^E < 0$ ) for all mole fractions, going through a minimum at  $c_{\text{ACN}} = 0.31$ . Such a large negative excess volume indicates that the water–acetonitrile system deviates significantly from an ideal mixture, most probably due to effects of complex interactions in the mixture, such as hydrogen bonds. As shown in Figure 1b, there is remarkable agreement between the experimentally measured refractive indices and the theoretical values calculated by Lorentz–Lorenz equation, suggesting that the essential physics in the refractive index of this mixture has been well captured by the assumptions leading to the equation. Specifically, as Lorentz–Lorenz equation assumes no change in the molecular polarizability upon mixing, the excellent agreement suggests that the interactions between solvent molecules indeed cause no appreciable changes to the molecular polarizabilities of the solvents. The Gladstone–Dale equation also fits the data reasonably well because the refractive indices between water and acetonitrile are not very different. All the other mixing rules in eqs 1–4 fit the data rather poorly except very close to the pure component compositions. We also note a strong (anti)correlation between  $V_s^E$  and the excess refractive index  $n^E = n - \sum_j c_j n_j$ ,<sup>7,80</sup> such relationship has been found in earlier experiments<sup>7,25,32,80</sup> and can be understood from the density dependence in the refractive index (see eq 10).

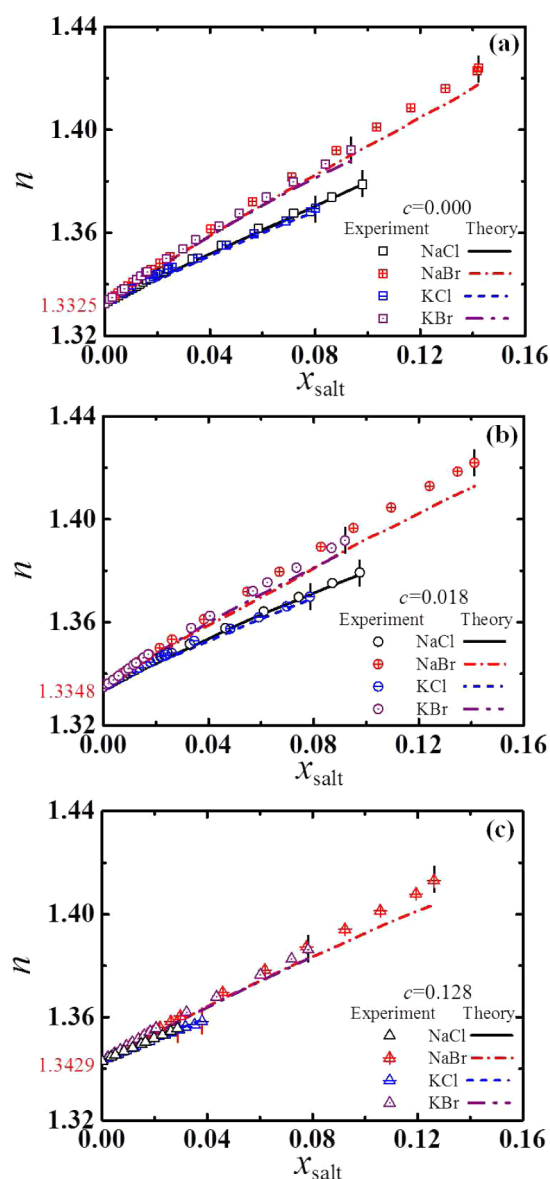
To study the effects of salt on the refractive index using eq 20, we first examine the volume change to the liquid solution upon addition of salt. Figure 2a,b,c shows  $V_{ss}/V_s$  for the three liquid compositions  $c_{\text{ACN}} = 0, 0.018$ , and 0.128 for the four different salts studied in this work. For each liquid composition, the volume expansion is the most for KBr and is the least for NaCl. This can be easily understood by the fact that the size of  $\text{K}^+$  is larger than that of  $\text{Na}^+$  and the size of  $\text{Br}^-$  is larger than that of  $\text{Cl}^-$ . However, we note that the order does not exactly follow that for the polarizability of the salts in Table I. Comparing between the different liquid compositions, we see that the volume change in pure water is the largest and decreases with increasing acetonitrile content. Another observation is that for a given anion, the difference in the volume change between different cations decreases with increasing  $c_{\text{ACN}}$ , whereas for a given cation, the difference in the volume change between different anions increases with increasing  $c_{\text{ACN}}$ . All these trends reflect the complex interactions between the ions and the different liquid components in the solution. For low salt concentration,  $V_{ss}/V_s$  shows good linearity with  $x_{\text{salt}}$ . This is more clearly demonstrated in the insets of these figures. From the slopes of these lines, we obtain  $\gamma$  and list its values for the different salts and different liquid compositions in Table II. For reference and comparison, we



**Figure 2.** Ratio  $V_{ss}/V_s$  vs  $x_{\text{salt}}$  at (a)  $c_{\text{ACN}} = 0$ , (b)  $c_{\text{ACN}} = 0.018$ , and (c)  $c_{\text{ACN}} = 0.128$ . The insets show  $V_{ss}/V_s$  vs  $x_{\text{salt}}$  at low salt concentrations. The short black and red vertical bars indicate point of saturation and salt-induced phase separation, respectively. The numerical data for the measurements are provided in the Supporting Information.

also list the values of  $\gamma'$  obtained using the two parameter fit, eq 21.

Using the volume data given in Figure 2 and the polarizability of the ions given in Table I, we calculate the refractive index  $n$  using eq 20 and compare with the experimentally measured values in Figure 3. For the four



**Figure 3.** Refractive index  $n$  as a function of the salt concentration  $x_{\text{salt}}$  at (a)  $c_{\text{ACN}} = 0$ , (b)  $c_{\text{ACN}} = 0.018$ , and (c)  $c_{\text{ACN}} = 0.128$ . The symbols are experimental data and the lines are calculated from eq 20. The numerical data for the measurements are provided in the Supporting Information.

different salts studied, NaCl, NaBr, KCl, and KBr, the curves are seen to fall into two groups, that of the bromide salts and that of the chloride salts, with the refractive index clearly larger for the bromide salt solutions. Within each group, the identity of the cation appears to have little effect, in spite of the fact that both the polarizability and the volume change between the sodium and potassium salts for the same anions are quite different. This is likely due to cancellation between two competing effects: the more polarizable  $\text{K}^+$  ion gives a direct

contribution toward increasing the refractive index but at the same time also decreases the density of the components more in the solution, thereby indirectly decreasing the refractive index. Closer inspection shows that the NaBr solution has the largest refractive index, whereas KCl solution has the smallest, even though the most polarizable salt is KBr and the least is NaCl. Thus, both the polarizability of the ions and the volume change are equally significant factors influencing the refractive index of the salt solution.

For all the four salts and the three different liquid compositions, the theoretical curves fit the experimental data very well, especially at lower salt concentrations, validating our assumption of ideal mixing of the polarization of the species at the liquid compositions and salt concentrations studied. The slight downward trend with salt concentration is also captured by the theory, which is caused primarily by the upward trend in the volume (see Figure 2). The agreement deteriorates slightly at higher salt concentrations or acetonitrile content, but given the simplicity of the theory, the agreement is quite satisfactory. Both the experimental data and the theoretical curves in Figure 3 show good linearity with salt concentration. Therefore, it is of interest to compare the data with the predictions from the linearized expression for  $n$ , eq 23, using the values of  $\gamma$  and  $K$  given in Tables II and III. Such a comparison is shown in Figure

**Table III.** Slope,  $K$ , in Eq 23<sup>a</sup>

salt	$K_{0.000}$	$K_{0.018}$	$K_{0.128}$
NaCl	0.479	0.454	0.418
NaBr	0.632	0.604	0.506
KCl	0.461	0.438	0.410
KBr	0.680	0.640	0.542

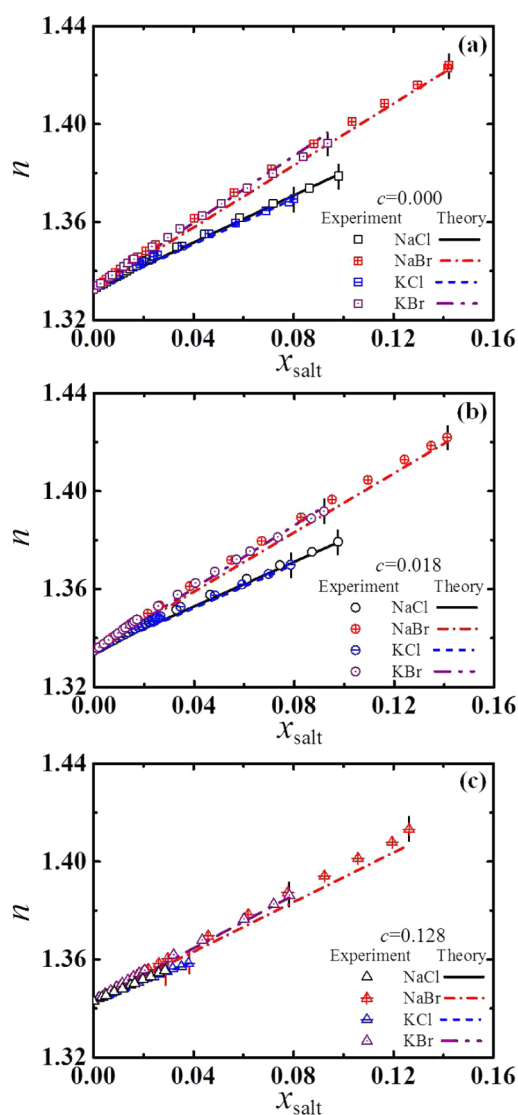
<sup>a</sup>The three different subscripts refer to the mole fraction of the acetonitrile in the solvent at  $c_{\text{ACN}} = 0$ ,  $c_{\text{ACN}} = 0.018$ , and  $c_{\text{ACN}} = 0.128$ , respectively.

4. Interestingly, the overall agreement between the theoretical predictions and the experimental data is even better using the approximate expression eq 23. This probably reflects some compensation effect: because the full expression is an approximation based on the assumption of ideal mixing of the polarizability of the components, linearization may have led to cancellation of errors in the full expression.

## V. CONCLUSION AND OVERLOOK

We have proposed a simple theory to describe the refractive index of salt solutions with mixed solvent using the knowledge of the refractive index of the pure liquids and the polarizability of the ions, as well as the volumetric data of the mixtures, which can be measured independently. The theory is tested by direct measurements of the refractive index for four halogen salts in water and acetonitrile at three different liquid compositions. Excellent agreement is observed in all cases, with the simplified expression yielding slightly better fit numerically. This agreement suggests that once the nonideality is taken into account through the excess volumes in the mixture, the contributions from the polarization of the different species in the solution are essentially additive, as assumed in the theoretical derivation.

For the four salts studied in this work, NaCl, NaBr, KCl, and KBr, our results show that the refractive index for the solutions is primarily determined by the anion, the larger anion resulting in larger refractive index. This is so in spite of the appreciable difference in the polarizability between  $\text{Na}^+$  and  $\text{K}^+$ , as well as



**Figure 4.** Refractive index  $n$  as a function of the salt concentration  $x_{\text{salt}}$  at (a)  $c_{\text{ACN}} = 0$ , (b)  $c_{\text{ACN}} = 0.018$ , and (c)  $c_{\text{ACN}} = 0.128$ . The symbols are the same experimental data as in Figure 3 and the lines are calculated from eq 23.

the difference in their contribution to the volume change. This insensitivity of the refractive index of the solution to the cation identity most probably reflects compensation between these two competing effects. It remains to be seen whether this observation has any generality beyond the salts and solvents studied here. Further experiments are clearly called for, both in order to test the applicability of the theory to other salt solution systems and in order to reveal new trends in the behavior of these systems.

Finally, we note that the theoretical formula proposed here can be used in reverse to determine the salt concentration of known salt or the polarizabilities of new salt ions, both useful applications in analytical chemistry.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.5b05433.

The Supporting Information provides calculated values of  $V_{\text{salt}}^{\infty}$  from using eq 21 and the numerical data from measurements used in Figure 2 and Figure 3. (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: [yylu@ciac.ac.cn](mailto:yylu@ciac.ac.cn).

\*E-mail: [zgw@caltech.edu](mailto:zgw@caltech.edu).

### Author Contributions

<sup>||</sup>(N.A., B.Z.) These two authors contributed equally to this work.

### Notes

The authors declare no competing financial interest.

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