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A Local-Composition Model for the Prediction of Mixture Dielectric Constants

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ABSTRACT: A local composition model is developed for mixture dielectric constants based on the nonrandom two-liquid (NRTL) model commonly used for correlating activity coefficients in vapor−liquid equilibrium (VLE) data regression. In this model the NRTL local compositions, which represent an effective local molecular structure, are the counterpart of the Kirkwood factor *g*, which in dielectric constant theory characterizes local molecular orientations and their effect on the static dielectric constant. The resultant model requires values for the pure-component dielectric constant and binary NRTL model parameters available from VLE data compilations or predicted from the universal functional activity coefficient model (UNIFAC). It is predictive in that no mixture dielectric constant data are used and there are no adjustable parameters. Predictions made on 16 binary and six ternary systems at various compositions and temperatures compare favorably with extant correlations that require experimental values to fit an adjustable parameter in the mixing rule and are significantly improved over values predicted by Oster's equation that also has no adjustable parameters.

1. INTRODUCTION

The thermodynamic nonidealities of liquid mixtures, usually expressed in terms of excess properties, arise from intermolecular interactions within the condensed phase. Permanent and induced charge separation within the molecules contributes significantly to these intermolecular interactions along with dispersion and repulsion forces. Relative values of the static dielectric constant, ε, a measure of the fluid's ability to reduce the electric force between separated charges, can be used to deduce some effects of the intermolecular interactions. For example, large values of ε suggest a propensity for molecular polarization within the liquid by molecular alignment of permanent charge distribution moments (dipole, quadrupole, etc.), which we will call orientational polarization. Large ε values may also suggest distortion of the electron distribution within the molecule in response to the local electrostatic field, which we will call electronic polarization. Because both ε and excess thermodynamic properties are directly influenced by the local structure of the fluid caused by the molecular-level interactions, it seems reasonable that localized molecular structure information obtained from thermodynamic excess properties may be useful in predicting dielectric constant.

Relating local fluid structure to ε is not a new idea. A popular early method for predicting values of ε was the Clausius−Mosotti[1] equation based on Debye's dielectric theory.[2] The Onsager equation[3] and the Kirkwood[4,5] extensions provided improvements for some polar fluids, but their overall reliability in predicting ε was poor, and the equations were not applicable in their original forms to mixtures. While the Onsager theory predicts the dielectric constant for so-called "unassociated" or "normal" liquids such as ethyl bromide or chloroform from molecular dipole moments, it fails to adequately predict values for fluids such as water, ethanol, and so forth. The Kirkwood theory includes a correlation parameter, *g*, intended to be a measure of the rotational hindering effect that the local environment has on a polar molecule because of the local intermolecular interactions that impact the orientational polarization. The extension of this concept to mixtures has been limited by the inherent complexities of orientational correlations among various polar species upon mixing.

Oster[6] assumed that the Kirkwood correlation parameter for each pure component remains unchanged upon mixing at constant temperature and pressure, and this model has been the starting point of most mixture models that have been developed.[7−10] The Oster model also assumes no volume change upon mixing, and significant errors can occur when applied to mixtures with large excess volumes. Mixing rules employed in later models generally contain an adjustable parameter to accommodate the thermodynamic mixing nonidealities associated with the complexity of the intermolecular interactions. As such, these models are correlational in nature and require mixture data to obtain the adjustable parameter in the mixing rule. Because the adjustable parameter has no physical interpretation, it is difficult to identify ways in which this parameter could be calculated so as to make these models entirely predictive. This is particularly true for multicomponent mixtures in which it is unclear whether the parameters from binary mixture data are relevant for the multicomponent mixture, and the extant experimental data on ternary and higher mixtures are too minimal to evaluate the efficacy of empirical parameters.

In an attempt to relate the common molecular underpinnings of thermodynamic excess properties and mixture dielectric constant, we propose here a mixture ε prediction method based on the concept of local compositions which has proven effective in development of excess thermodynamic properties. Effective local compositions obtained from readily available binary mixture excess properties are used to provide the specific molecular interaction information from which the mixture ε is predicted.

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The use of thermodynamic local compositions is expected to primarily account for orientational polarization; although because they are empirically obtained from VLE data, some effects of electronic polarization may be included.

2. THEORETICAL BACKGROUND

The Kirkwood equation relates the dielectric constant of a pure fluid to the molar polarization p per unit volume

$$p = \frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} \qquad (1)$$

The relationship of p to charge distribution within the molecule is usually given in terms of the Onsager equation written as

$$p = \rho \frac{4\pi N_A}{3}\left(\alpha + \frac{\mu^2}{3kT}\right) \qquad (2)$$

where N_A is Avogadro's number, T is temperature, k is Boltzmann's constant, ρ is the molar density, α is the electronic polarizability, and μ is the dipole moment. In the Osager theory, electronic and orientational polarization are explicit in the two terms of eq 2. Orientational polarization is accounted for by the propensity of the permanent dipole to align with the field and electronic polarization in which the electron distribution within the molecule adjusts to the electrostatic field is accounted for through the α term.

The Onsager equation is derived under the assumption of a random molecular environment and does not account for molecular interactions that induce order in the neighboring molecules as would occur with highly polar molecules that might associate or have orientationally specific interactions. Kirkwood introduced a correlation factor g to account for short-range intermolecular forces that would hinder rotation to obtain

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} = \rho \frac{4\pi N_A}{3}\left(\alpha + \frac{\mu^2 g}{3kT}\right) \qquad (3)$$

There has been little success in calculating g from first principles, and so it is usually treated as an adjustable parameter when correlating experimental data. The Kirkwood correlation factor is usually defined as

$$g = 1 + Z\langle \cos \gamma \rangle \qquad (4)$$

where Z is the number of nearest neighbors and $\langle \cos \gamma \rangle$ is the mean cosine of the angles between the dipole moments of the neighboring molecules. Experimental ε have been used then to obtain molecular structure information through regression of g.[11] For example, values of g close to 1 suggest little hindrance to molecular rotation, hence a random arrangement of the molecular-level dipoles since $\langle \cos \gamma \rangle = 0$. Values of $g < 1$ or $g > 1$ respectively indicate antiparallel and parallel statistical alignments.

For mixtures, the local structure effects due to different intermolecular interactions are expected to have a large effect on g, hence the dielectric constant. These effects can be conveniently represented in terms of excess quantities or deviations from the ideal mixture value. Generally, deviations from ideality have been defined with respect to the molar polarization per unit volume rather than the dielectric constant. The molar polarizations per unit volume are additive for the "ideal mixture"

$$p^{\text{id}} = \sum_{i=1}^{n} \phi_i p_i \qquad (5)$$

where n is the number of components and ϕ_i is the volume fraction of component i. This equation by Oster[6] assumes no volume change upon mixing the components. An excess molar polarization per unit volume can be defined as the deviation of the mixture p from the p^{id},

$$p^{\text{E}} = p - p^{\text{id}} = p - \sum_{i=1}^{n} \phi_i p_i \qquad (6)$$

The dielectric constant is then obtained from the mixture polarization by inverting eq 1. This can be conveniently written as

$$\varepsilon = \frac{1}{4}\left(1 + 9p + 3\sqrt{9p^2 + 2p + 1}\right) \qquad (7)$$

Equation 5, generally known as Oster"s rule, was suggested by Oster as a rough approximation for estimation of mixture ε values. Harvey and Prausnitz determined that a linear volume-fraction mixing rule like eq 5 did not reflect the increased or decreased degree of correlation between neighboring molecules in the mixture and proposed a quadratic mixing rule of the form

$$p = \sum_{i=1}^{n}\sum_{j=1}^{n} \varphi_i^{\dagger}\varphi_j^{\dagger} p_{ij}^{\dagger} \quad \text{with} \quad p_{ij}^{\dagger} = \frac{1}{2}(p_i^{\dagger} + p_j^{\dagger})(1 + k_{ij}) \qquad (8)$$

where k_{ij} is a binary parameter, close to zero, regressed from dielectric constant data for the $i{-}j$ binary system, and the superscript † signifies that the property is evaluated at a density corresponding to the reduced density of the mixture (using a mole fraction average of the critical volumes as the reducing factor). However, if all $k_{ij} = 0$, then eq 8 reduces to a linear mixing rule. Wang and Anderko suggested a similar quadratic mixing rule

$$p = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j (vp)_{ij} \quad \text{with} \quad (vp)_{ij} = \frac{1}{2}(v_i p_i + v_j p_j)(1 + k_{ij}) \qquad (9)$$

where v_i is the molar volume of component i. Again the mixing rule reduces to a linear form when all of the $k_{ij} = 0$. The accurate prediction of multicomponent ε values requires that the k_{ij} in the mixing rule be regressed from experimental binary data.

3. LOCAL COMPOSITION MODEL FOR ε

Like ε, excess thermodynamic properties are strongly related to the local structuring that occurs due to intermolecular interactions. The concept of local compositions has been widely used to obtain correlations for the composition dependence of excess properties. Here we develop a correlation for the excess molar polarization in terms of nonrandom local compositions which are themselves obtained from other excess properties, specifically from the excess Gibbs energy or the mixture activity coefficients.

Analogous to the nonrandom two-liquid (NRTL) model for the Gibbs energy developed by Renon and Prausnitz,[12] we consider a mixture p as an ideal mixture of n hypothetical fluids having polarizations per unit volume of $p^{(i)}$

$$p = \sum_{i=1}^{n} \varphi_i p^{(i)} \quad \text{where} \quad p^{(i)} = \sum_{j=1}^{n} \varphi_{ji} p_{ji} \qquad (10)$$

where p_{ji} are yet unidentified parameters characteristic of $j{-}i$ polarization interactions and ϕ_{ji} are local volume fractions of molecule type i around a central molecule of type j. The local

Table 1. Absolute Average Deviation (AAD) for Prediction and Correlation of Binary and Ternary Mixtures Using the NRTL Model in Comparison to Other Available Methods

system	# pts.	T/K	predicted AAD/%		correlation AAD/%		
			eqs 18 to 19	eq 5	eq 19	eq 8	eq 9
methanol + propan-2-one[17]	11	298	0.62	0.71	0.43	0.4	0.4
methanol + carbon disulfide[17]	8	298	3.27	3.73	3.21	NA	3.6
water + propan-1-ol[18]	55	293−353	2.93	6.1	1.74	3.9	1.7
water + methanol[18]	45	278−333	2.31	3.4	0.69	0.6	1.4
water + ethanol[18]	55	293−353	1.40	1.6	0.83	1.3	1.6
water + propan-2-ol[18]	55	293−353	3.68	5.8	1.55	4.4	2.5
water + propan-2-one[18]	55	293−323	2.92	3.5	0.87	1.2	2.1
water + ethan-1,2-diol[18]	50	293−373	2.14	3.0	0.29	1.0	1.1
water + 1,4-dioxane[19,20]	11	298	2.46	24.6	0.95	7.9	3.2
methanol + tetrachloromethane[20]	10	308	4.01	10.1	3.85	12.7	6.5
propan-2-one + carbon disulfide[17]	11	298	3.85	5.08	1.15	3.2	2.3
propan-2-ol + nitromethane[20]	12	308	3.90[c]	5.55	1.67[c]	2.1	1.4
propan-1-ol + nitromethane[20]	10	308	2.91	5.2	0.29	0.3	0.3
propan-1-ol + benzene[20]	10	308	14.34	18.87	2.78	NA	4.0
propan-1-ol + tetrachloromethane[20]	10	298	9.76	22.6	2.01	NA	3.6
dimethyl sulfoxide + tetrachloromethane[21]	19	298	1.90[c]	6.59	1.26[c]	NA	NA
propan-1-ol + nitromethane + water[20]	10	308	0.94	6.21	0.62[b]	1.1	1.4[a]
propan-1-ol + tetrachloromethane + water[20]	8	308	11.76[c]	38.64	4.80[b]	NA	9.0[a]
propan-2-ol + nitromethane + water[20]	10	308	2.66[c]	3.42	0.54[b]	0.8	1.3[a]
propan-2-one + methanol + carbon disulfide[17]	11	298	7.26	14.6	4.16[b]	14.2	11.7
methanol + tetrachloromethane + water[20]	8	308	6.75[c]	7.78	3.04[b]	5.0	4.5[a]
propan-1-ol + benzene + water[20]	8	308	10.35[c]	28.80	0.91[b]	NA	4.2[a]

[a] One of the three binary k_{ij} was determined from ternary mixture data. [b] One of the three binary p_{ij} was determined from ternary mixture data. [c] NRTL parameters obtained from activity coefficients predicted using UNIFAC[24] rather than experimental VLE data.

volume fractions add to one, and they are related to the local mole fractions x_{ij} by

$$\sum_{j=1}^{n} \varphi_{ji} = 1 \quad \text{and} \quad \varphi_{ji} = \frac{x_{ji} v_j}{\sum_{k=1}^{n} x_{ki} v_k} \tag{11}$$

Here v_k is the molar volume of component k at the mixture temperature and pressure. In the NRTL model, the local mole fractions deviate from bulk mole fractions, x_i, because of the difference in interaction energies, u_{ji}, between the unlike $(i \neq j)$ and like $(i = j)$ molecules within the hypothetical pure fluids. This relationship can be written as

$$\frac{x_{ji}}{x_{ii}} = \frac{x_j}{x_i} \exp\left[-\beta \frac{(u_{ji} - u_{ii})}{RT}\right] = \frac{x_j}{x_i} G_{ji} \tag{12}$$

where

$$G_{ji} = \exp\left[-\beta \frac{(u_{ji} - u_{ii})}{RT}\right] = \exp\left[-\beta \frac{A_{ji}}{RT}\right] \tag{13}$$

Here R is the gas constant, T is temperature, and A_{ji} are interaction parameters that are regressed from experimental data, generally vapor−liquid (VLE) or liquid−liquid equilibrium (LLE) data. The nonrandomness parameter β times the interaction parameter A_{ji} is a measure of the local structuring caused by the interactions. When $\beta = 0$, $G_{ji} = 1$ and the local and overall compositions are equal. The local volume fractions defined in eq 11 have the same relationship to the overall volume fractions seen in eq 12, or

$$\frac{\phi_{ji}}{\phi_{ii}} = \frac{\phi_j}{\phi_i} G_{ji} \tag{14}$$

Using the conservation of the volume fractions expressed in eq 11, we can write the individual local volume fractions that appear in eq 10 as

$$\phi_{ji} = \frac{\phi_j G_{ji}}{\sum_{k=1}^{n} \phi_k G_{ki}} \qquad \phi_{ii} = \frac{\phi_i}{\sum_{k=1}^{n} \phi_k G_{ki}} \tag{15}$$

Substitution of eqs 15 into eq 10 yields

$$p = \sum_{i=1}^{n} \varphi_i \left[\sum_{j=1}^{n} p_{ji} \phi_j G_{ji} \Big/ \left(\sum_{k=1}^{n} \phi_k G_{kj}\right)\right] \tag{16}$$

Equation 16 can be used as a general equation to correlate the polarizability of an n-component mixture by treating p_{ji} (with $p_{ji} = p_{ij}$) as one adjustable parameter for each constituent binary mixture. Use of the equation as a correlation requires at least one experimental value for each constituent binary mixture.

To obtain a nonparametric or predictive model, the p_{ji} interaction terms must be identified. It is clear that $p_{ii} = p_i$, the pure-component i polarization pure unit volume, because all volume fractions except ϕ_i are zero in the pure-component limit. There is, however, no rigorous relationship for the cross interaction p_{ji} $(j \neq i)$. We follow, however, the assumption previously made in developing NRTL models for thermal conductivity[13] and viscosity[14] to obtain a nonparametric value for p_{ji} in mixtures of nonpolar fluids. We write eq 16 for a binary mixture of components 1 and 2 and set the mixture p equal to p_{21} at the specific composition where $x_{21} = x_{12}$. The rationale for this assignment is that there are equivalent numbers of 1−2 and 2−1 interactions at the composition where $x_{21} = x_{12}$. Likewise there must be the same number of 1−1 and 2−2 interactions at this composition. This mixing rule allows direct evaluation of p_{21} from the pure component polarizations and the mixture thermodynamics contained in the G_{21} and G_{12} values. The volume fraction of component 1 at this composition, denoted with an asterisk, can be obtained from eqs 11 and 12 as

$$\phi_1^* = \frac{V_1\sqrt{G_{21}}}{V_1\sqrt{G_{21}} + V_2\sqrt{G_{12}}} \tag{17}$$

Setting $p = p_{21}$ at this composition yields for the binary mixture of components 1 and 2,

$$p_{21} = p_{12} = \frac{\sqrt{G_{21}}V_1p_1 + \sqrt{G_{12}}V_2p_2}{\sqrt{G_{21}}V_1 + \sqrt{G_{12}}V_2} \tag{18}$$

Equation 18 can be used generally for all of the binary pair interactions in a multicomponent mixture. Finally, eq 16 can be written as a predictive equation in the form

$$p = \sum_{i=1}^{n} \phi_i p_i + \sum_{i=1}^{n} \phi_i \left[\sum_{j=1}^{n} \phi_j G_{ji}(p_{ji} - p_j) \Big/ \left(\sum_{k=1}^{n} \phi_k G_{kj} \right) \right] \tag{19}$$

where the binary cross interaction p_{ji} are obtained from eq 18 and the G_{ji} are obtained from available binary mixture thermodynamic data. The second term on the right-hand-side of this equation is the excess polarization per unit volume, p^E, shown in eq 6. The expression is general in form for any number of components and includes a temperature dependence through the G_{ji} terms, as seen in eq 13, in addition to the temperature dependence of the pure polarization terms. The structural information included in the local composition model is intended to reflect the restriction on random orientation of the molecules in a polarizing field due to the interactions between the molecules much like Kirkwood's g factor in eq 3.

The procedure for computing the mixture ε at a given temperature and composition consists of six steps:

1. Use eq 1 to calculate p_i for each component from its ε_i value.
2. Obtain NRTL parameters, α, A_{12}, and A_{21} for all constituent binary mixtures.
3. Compute G_{12} and G_{21} and for each binary system at the desired mixture temperature.
4. Compute the p_{ij} for each binary i−j pair from eq 18.
5. Compute the mixture p from eq 19 at the desired compositions.
6. Use eq 7 to compute the mixture ε value.

4. DISCUSSION

There is a shortage of experimental mixture ε values available in the literature against which to test the predictive capabilities of the method. Sixteen binary systems and six ternary systems are shown in Table 1 for which there are reliable mixture experimental ε values and NRTL parameters. The NRTL parameters were obtained from equilibrium VLE data[15] at 298 K except as noted below; the ε values were measured at 1 atm and various temperatures and compositions as reported in the references cited in Table 1. Pure molar volumes were obtained from the recommended correlations in the DIPPR 801 database.[16] While most of the mixture data are available at only a single temperature, there are a few mixtures shown in the table for which data were available over a significant temperature range. For these systems, the NRTL model includes a temperature-dependent excess term in addition to that arising out of the temperature dependence of the pure-component ε values. Table 1 shows the average absolute percent deviation (AAD %) of predicted mixture ε values by the NRTL model in comparison to the predicted values from eq 5. The results are in all cases improved, often substantially, over Oster's mixing rule. Also shown in Table 1 are the results obtained if the p_{ij} in the NRTL model are fitted to binary experimental data. The results of using the NRTL model as a correlation are compared to the results reported in the literature for eqs 8 and 9 with k_{ij} fitted to the extant binary experimental data. The NRTL correlates the binary data as well or better than eqs 8 and 9 and significantly improves upon the correlation of the ternary data. The correlation for ternary systems shown in the table uses only the p_{ij} values correlated from the constituent binary mixtures except for the cases noted where a single ternary value was used to obtain the p_{ij} for the binary system for which there is no experimental data available. In several cases, the overall predicted results by the NRTL model are as good, or nearly so, as the correlated values using one adjustable parameter with eqs 8 or 9. The NRTL predictive model does have problems with several of the propan-1-ol-containing systems, though it still performs better than the other predictive methods. These same systems can be correlated well with the NRTL model suggesting that the mixing rule defined in eq 18 may be inadequate for all mixtures.

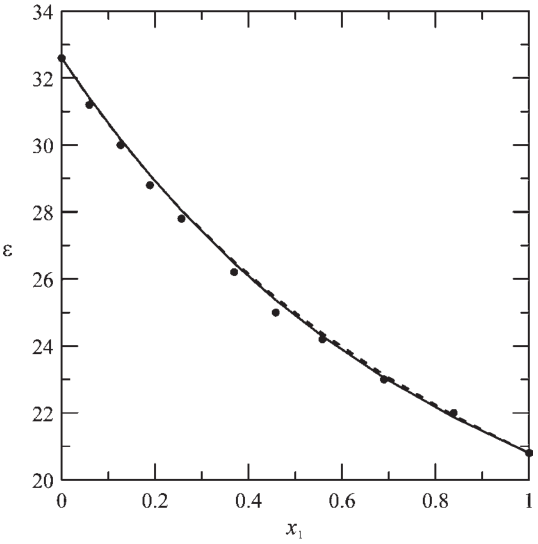

Figure 1. Comparison of experimental[17] (●) ε values to those predicted using the NRTL model (—) and Oster's rule (- - -) for mixtures of methanol (1) + propan-2-one (2) at 298 K.

Because Oster's rule assumes that volumes are additive, there is little difference between the values predicted by it and the NRTL model for mixtures with small excess volumes as illustrated in Figure 1 for methanol + propan-2-one mixtures.

Mixture dielectric constants predicted by Oster's rule tend to deviate more for mixtures with larger excess volumes such as the alcohol + water systems illustrated in Figures 2 and 3. The predicted ε values for mixtures of propan-1-ol + water at 353 K, illustrated in Figure 3, have AADs of 6.72 % and 2.82 % for Oster's rule and for the NRTL method, respectively. The local compositions in the NRTL

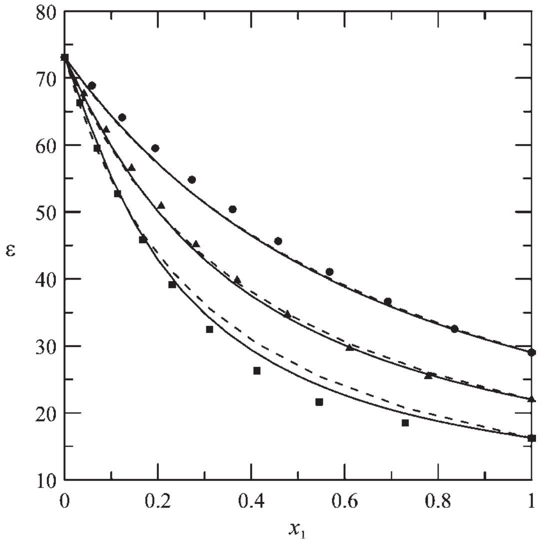

Figure 2. Experimental[18] (points) dielectric constants at 313 K for ●, methanol (1) + water (2); ▲, ethanol (2) + water (2); and ■, propan-2-ol (1) + water (2) mixtures compared to predicted values using the NRTL model (—) and Oster's rule (- - -).

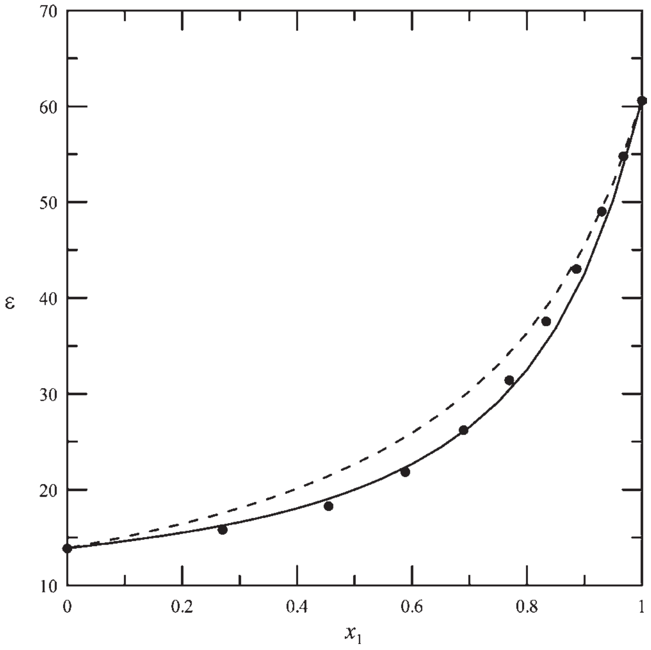

Figure 3. Comparison of experimental[18] (●) ε values to those predicted using the NRTL model (—) and Oster's rule (- - -) for mixtures of water (1) + propan-1-ol (2) at 353 K.

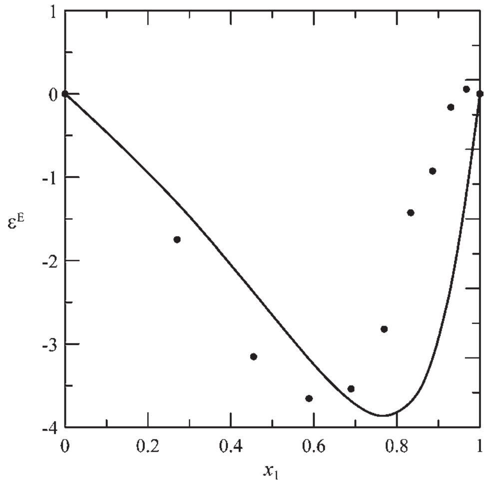

Figure 4. Experimental[18] (●) excess dielectric constant values, ε^E, compared to those predicted using the NRTL model (—) for mixtures of water (1) + propan-1-ol (2) at 353 K.

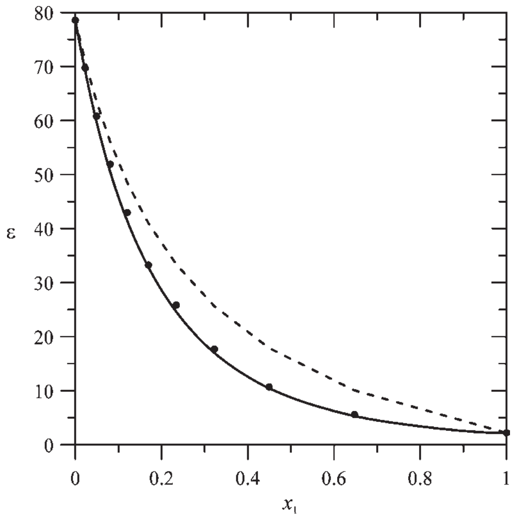

Figure 5. Comparison of experimental[20] (●) ε values to those predicted using the NRTL model (—) and Oster's rule (- - -) for mixtures of 1,4-dioxane (1) + water (2) at 298 K.

method provide a reasonable estimation of ε^E for this system as shown in Figure 4, although the minimum is shifted toward the water-rich compositions compared to the experimental values.

The difference in the efficacy of the two predictive methods is largest for the water + 1,4-dioxane system. This is likely due to the local molecular structuring that occurs due to association even though 1,4-dioxane has no dipole moment. Viscosity studies of water + 1,4-dioxane mixtures suggest that 1,4-dioxane forms a four- or five-water-molecule hydrate which also modifies the highly coordinated structure of bulk water.[22] Recent dielectric spectroscopy studies[23] suggest that microheterogeneous clustering occurs as localized water−water hydrogen bonding is strengthened in water-rich clusters surrounded by 1,4-dioxane-rich regions. This local structuring, too complex from which to formulate a Kirkwood g value, gives rise to the rather large ε^E values shown in Figures 5 and 6.

Electron polarization of nonpolar molecules by strongly polar molecules produces local structure and changes in ε that are difficult to model. Figure 7 shows that ε in nonpolar−polar mixtures typically show more nonpolar character than would be expected by either ideal behavior or the NRTL mixing rule developed in this paper, especially at compositions rich in the nonpolar component. Interestingly, the mixing rule does produce the correct S-shape behavior with composition even though the magnitude of ε^E is underestimated by the NRTL model as shown in Figure 8.

Because the NRTL method requires the binary NRTL parameters α, A_{12}, and A_{21} to model the local molecular structure, a limitation in use of the method may be the availability of these parameters. While extensive compilations of VLE data are

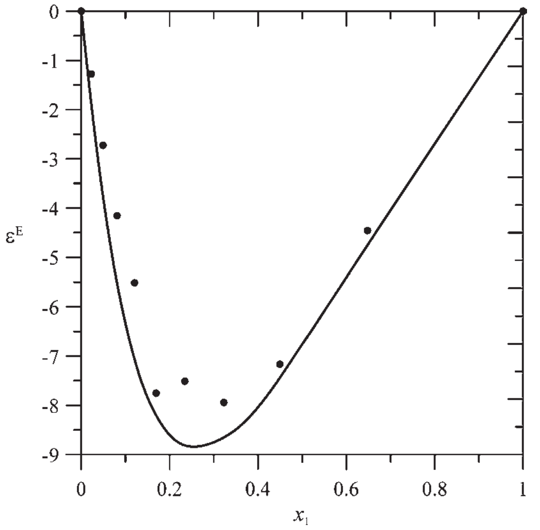

Figure 6. Experimental[20] (●) excess dielectric constants and values predicted using the NRTL model (—) for mixtures of 1,4-dioxane (1) + water (2) at 298 K.

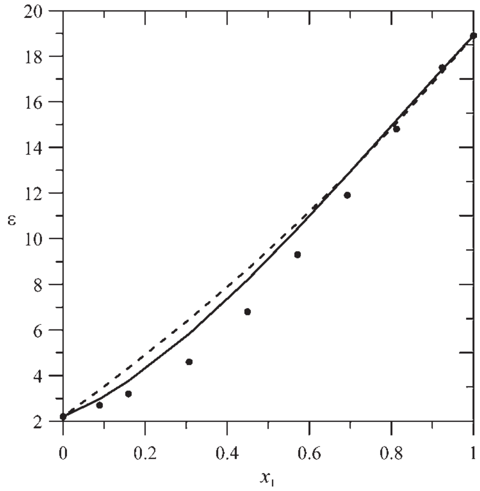

Figure 7. Comparison of experimental[18] (●) ε values to those predicted using Oster's rule (- - -) and the NRTL model (—) for mixtures of propan-1-ol (1) + benzene (2) at 308 K.

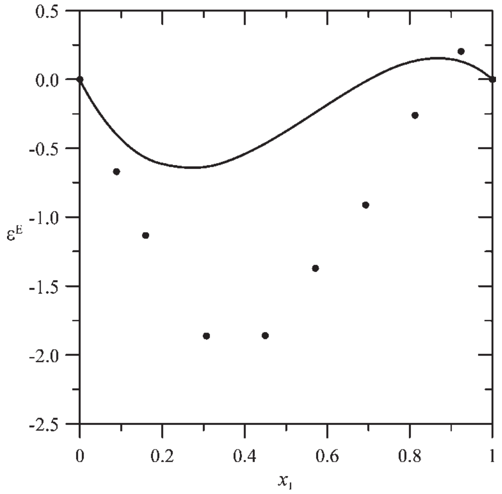

Figure 8. Excess dieclectric constant from measurements[18] (●) compared to values predicted using the NRTL model (—) for mixtures of propan-1-ol (1) + benzene (2) at 308 K.

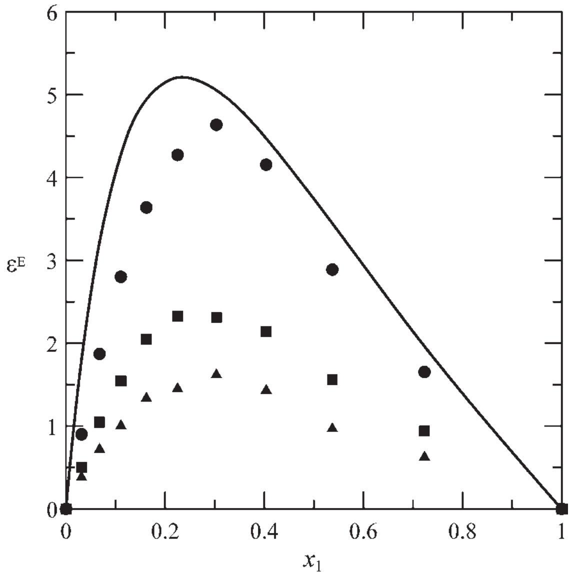

Figure 9. Comparison of experimental[18] (points) ε^E values to those predicted using the NRTL (lines) model for mixtures of ethan-1,2-diol (1) + water (2) at: ●, 293 K; ■, 333 K; and ▲, 353 K. NRTL values at 333 K and 353 K are indistinguishable from the x axis.

available, it would be naïve to assume that parameters would have been regressed for all desired binary mixtures. The universal functional activity coefficient model (UNIFAC)[24] is a prediction method for activity coefficients and excess Gibbs energy that, like the NRTL model, is based on local compositions. Because UNIFAC utilizes tabulated group contributions regressed from experimental VLE data to obtain the effective molecular interaction parameters, it can currently be applied to a wide variety of compounds although the accuracy and reliability of the predicted activity coefficients will obviously be less than activity coefficients correlated directly from experimental data. For cases where NRTL parameters are not available, we have taken the approach of using UNIFAC to predict activity coefficients as a function of composition at the desired temperature from which the NRTL parameters are regressed to use to calculate ε. With this procedure, the NRTL method can be applied to a wide range of compounds for which VLE data have not been measured. The results for dimethyl sulfoxide + tetrachloromethane, water + tetrachloromethane, and nitromethane + propan-2-ol mixtures shown in Table 1 were determined in this manner.

The temperature dependence in NRTL excess properties is known to be only approximate. Normally the temperature dependence of A_{12} and A_{21} is assumed to be either linear or inverse when VLE data are regressed over a range of temperatures. Alternatively, different values for A_{12} and A_{21} can be used at different temperatures. Similarly, one should use NRTL parameters that have been regressed from experimental VLE data at temperatures closest to the desired temperature for the most accurate predictions of ε. This can be seen in Figure 9 where NRTL values at 293 K were used to predict ε^E values at 293 K, 333 K, and 353 K for mixtures of ethan-1,2-diol + water. Although the predicted and experimental values are in very good agreement at the temperature at which the NRTL parameters

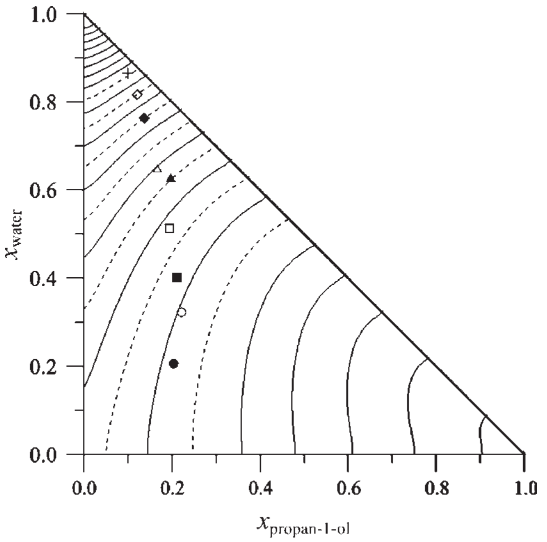

Figure 10. Constant ε contours (lines) predicted from the NRTL model for ternary mixtures of propan-1-ol (1) + water (2) + nitrobenzene at 308 K compared to extant experimental data[20] (●, ε = 30.7; ○, ε = 31.8; ■, ε = 33.1; □, ε = 35.6; ▲, ε = 38.3; △, ε = 40.2; ♦, ε = 46.0; ◊, ε = 49.4; +, ε = 53.5). The contour lines range from the lower right, ε = 20, to the top left, ε = 70, in increments of 2. For ease of comparison to experimental points, dashed contours are shown for ε values of 30, 34, 38, 42, 46, 50, and 54 from lower right to upper left.

were obtained, these same parameters incorrectly predict almost no ε^E at higher temperatures where the model reduces to Oster's rule.

The NRTL model exhibits the largest deviations from the experimental data for those ternary systems in Table 1 that have a partially miscible constituent binary system. LLE requires a large positive excess Gibbs energy, and it is known that NRTL parameters regressed from VLE data generally do not predict the LLE tie lines accurately. While this may explain the larger deviations, there is not enough experimental data on similar systems and at compositions approaching the two-phase coexistence curves to adequately test this hypothesis. On the other hand, the local-composition model predicts the available data for completely miscible ternary mixtures, shown in Table 1, quite well. An example is shown in Figure 10 where contour lines from the NRTL-predicted ε surface are shown in comparison to the extant experimental data.[20]

5. CONCLUSION

A method for prediction of liquid mixture static dielectric constant has been developed. The method requires values for the pure-component dielectric constant and information and binary NRTL model parameters available from VLE data compilations or predicted from UNIFAC. A comparison of available experimental mixture ε values for 16 binary systems showed a maximum AAD of 5 % for the NRTL predicted values. For the six ternary mixtures with available experimental data, the maximum AAD was 12 %. The agreement with the experiment is better than currently available predictive methods of which we are aware and is on par with correlative methods that contain one adjustable parameter in the mixing rule.

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REFERENCES

(1) Smyth, C. P. *Dielectric Behaviour and Structure*; McGraw-Hill: New York, 1955.

(2) (a) Debye, P. *Z. Phys.* **1912**, *13*, 97.(b) *Handbuch der Radiologie (Marx)*; Akademische Verlagsgesellschaft m.b.H.: Leipzig, Germany, 1925; Vol. VI, pp 597−653. (c) *Polar Molecules*; Chemical Catalog: New York, 1929.

(3) Onsager, L. Electric Moments of Molecules in Liquids. *J. Am. Chem. Soc.* **1938**, *58*, 1486–1493.

(4) Kirkwood, J. G. The Dielectric Polarization of Polar Liquids. *J. Chem. Phys.* **1939**, *7*, 911.

(5) Kirkwood, J. G. The Local Field in Dielectrics. *Ann. N.Y. Acad. Sci.* **1940**, *40*, 315; The influence of hindered molecular rotation on the dielectric polarisation of polar liquids. *Trans. Faraday Soc.* **1946**, *42A*, 7.

(6) Oster, G. The Dielectric Properties of Liquid Mixtures. *J. Am. Chem. Soc.* **1946**, *68*, 2036–2041.

(7) Harvey, A. H.; Prausnitz, J. M. Dielectric Constants of Fluid Mixtures over a Wide Range of Temperature and Density. *J. Solution Chem.* **1987**, *16*, 857–869.

(8) Buckingham, A. D. The Dielectric Constant of a Liquid. *Aust. J. Chem.* **1953**, *6*, 93–103.

(9) Buckingham, A. D. The Calculation of True Dipole Moments from Solutions in Polar Solvents. *Aust. J. Chem.* **1953**, *6*, 323–331.

(10) Wang, P.; Anderko, A. Computation of Dielectric Constants of Solvent Mixtures and Electrolyte Solutions. *Fluid Phase Equilib.* **2001**, *186*, 103–122.

(11) Prestbo, E. W.; McHale, J. L. Static Dielectric Constants and Kirkwood Correlation Factors of Dimethyl Sulfoxide/Carbon Tetrachloride Solutions. *J. Chem. Eng. Data* **1984**, *29*, 387–389.

(12) Renon, H.; Prausnitz, J. M. Estimation of Parameters for the NRTL Equation for Excess Gibbs Energies of Strongly Nonideal Liquid Mixtures. *Ind. Eng. Chem. Process Des. Dev.* **1969**, *8*, 413.

(13) Rowley, R. L. A Local Composition Model for Multicomponent Liquid Mixture Thermal Conductivities. *Chem. Eng. Sci.* **1982**, *37*, 897–904.

(14) Wei, I. C.; Rowley, R. L. A Local Composition Model for Multicomponent Liquid Mixture Shear Viscosity. *Chem. Eng. Sci.* **1985**, *40*, 401–408.

(15) Gmehling, J.; Onken, W.; Arlt, W. *Vapor-Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series; DECHEMA: Frankfurt, Germany, 1982.

(16) Rowley, R. L.; Wilding, W. V.; Oscarson, J. L.; Giles, N. F. *DIPPR Data Compilation of Pure Chemical Properties, Design Institute for Physical Properties*; AIChE: New York, 2010.

(17) Campbell, A. N.; Kartzmark, E. M. Thermodynamic and other properties of methanol + acetone, carbon disulphide + acetone, carbon disulphide + methanol, and carbon disulphide + methanol + acetone. *J. Chem. Thermodyn.* **1973**, *5*, 163–172.

(18) Åkerlöf, G. Dielectric Constants of Some Organic Solvent-Water Mixtures at Various Temperatures. *J. Am. Chem. Soc.* **1932**, *54*, 4125–4139.

(19) Sigvartsen, T.; Songstad, J.; Gestblom, B.; Noreland, E. Dielectric properties of solutions of tetra-iso-pentylammonium nitrate in dioxane-water mixtures. *J. Solution Chem.* **1991**, *20*, 565–5582.

(20) Suryanarayana, C. V.; Somasundaram, K. M. Dielectric Behaviour at the Miscibility Point in Some Ternary Systems. *Acta Chim. Hung.* **1960**, *24*, 31–53.

(21) Jain, D. V. S.; Wadl, R. K.; Saini, S. B.; Puri, K. Excess dielectric constants for acrylonitrile +, carbon disulphide +, and dimethyl sulphoxide + carbon tetrachloride, and + tetrachloroethylene, at 303.15 K. *J. Chem. Thermodyn.* **1978**, *10*, 707.

(22) Geddes, J. A. The Fluidity of Dioxane-Water Mixtures. *J. Am. Chem. Soc.* **1933**, *55*, 4832–4837.

(23) Schrödle, S.; Hefter, G.; Buchner, R. Dielectric Spectroscopy of Hydrogen Bond Dynamics and Microheterogenity of Water + Dioxane Mixtures. *J. Phys. Chem. B* **2007**, *111*, 5946.

(24) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibrium Using UNIFAC*; Elsevier: Amsterdam, 1977.