Activity Coefficients of the System {yKCl + (1 − y)KH$_2$PO$_4$}(aq) at T = 298.15 K Determined by Cell Potential Measurements

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ABSTRACT: Zero-current cell potential measurements were used to determine the solution activity coefficient in a ternary system {yKCl + (1 − y) KH$_2$PO$_4$}(aq) at temperature T = 298.15 K. The cell of the type K−ISE|KCl(m_{KCl}), KH$_2$PO$_4$($m_{KH_2PO_4}$)|Ag|AgCl was used in the total ionic strength range, I_m = 0.0886−1.0046 mol kg^{-1}. In order to generate a set of parameters that can be applied in a wide range of mixed solution ionic strengths, the Pitzer, Scatchard, and Clegg−Pitzer−Brimblecombe models were used to fit all available experimental data, including cell potential and isopiestic measurements from the literature. The experimental and calculated values of thermodynamic properties for the studied system are in excellent agreement. Potential interactions and solution structure were discussed by means of the excess free energy of mixing via potential pairs, triplets, or quads for the investigated solution using the Scatchard model mixing parameters.
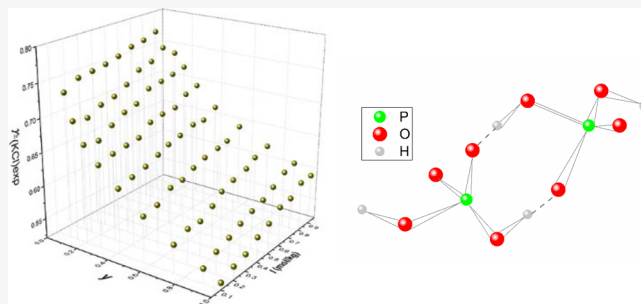
1. INTRODUCTION

Phosphorus is an essential element for all life forms on our planet. Many ground and surface waters contain phosphorus as protonated forms of the orthophosphates H$_2$PO$_4^-$ and HPO$_4^{2-}$. Natural waters have extremely low phosphate concentrations. Some wastewaters can contain phosphates in large concentrations, producing eutrophication. Soluble phosphate salts are also widely used in the chemical industry (fertilizers, toothpaste, medicines, food additives, etc.).

The aqueous solution of KCl and KH$_2$PO$_4$ is an intriguing system that requires a more detailed description of its thermodynamic properties. Our previous research included isopiestic measurement of the osmotic coefficients of several systems containing phosphate ions: K$_2$HPO$_4$(aq),[1] {yKCl + (1 − y)K$_2$HPO$_4$}(aq),[2] {yKBr + (1 − y)K$_2$HPO$_4$}(aq),[3] {yKNO$_3$ + (1 − yKH$_2$PO$_4$}(aq),[4] {yK$_2$SO$_4$ + (1 − y)K$_2$HPO$_4$}(aq),[5] {yNa$_2$HPO$_4$ + (1 − y)K$_2$HPO$_4$}(aq),[6] {yNaH$_2$PO$_4$ + (1 − y)KH$_2$PO$_4$}(aq),[7] {yK$_2$HPO$_4$ + (1 − y) KH$_2$PO$_4$}(aq),[8] {yNaH$_2$PO$_4$+ (1 − y) Na$_2$HPO$_4$}(aq).[9] Recently, we investigated the properties of the system {yKCl + (1 − y)K$_2$HPO$_4$}-(aq) at T = 298.15 K using both isopiestic and cell potential measurements.[10] It was the extension of our earlier work on this system,[2] which implies an isopiestic determination of the osmotic coefficients in the range of ionic strength, I_m = 2.37−11.25 mol kg^{-1}. In the present paper, we consider thermodynamic properties of an aqueous solution of KCl but with KH$_2$PO$_4$, at the same temperature.

Earlier, Childs et al.[11] studied the thermodynamic properties of the aqueous mixtures of Na-K-Cl-H$_2$PO$_4$, while Scharge et al.[12] investigated a more complex aqueous system of Na-K-Cl-SO$_4$-PO$_4$-HPO$_4$-H$_2$PO$_4$, and they used isopiestic measurements and solubility data to derive Pitzer's ternary interaction parameters. Despite studies on systems containing KH$_2$PO$_4$ as a mixture component, there were insufficient data on thermodynamic properties in the dilute solution range. Hence, by measuring the zero-current cell potential (cell potential) in an ionic strength range from roughly 0.01 to 1 mol kg^{-1} with different ionic strength fractions of the electrolytes, this study aimed to determine the activity coefficient of KCl in the system {yKCl + (1 − y) KH$_2$PO$_4$}(aq) at T = 298.15 K. We used three thermodynamic models to treat the activity data: Pitzer's ion interaction model,[13] Scatchard's neutral model,[14] and the Clegg−Pitzer−Brimblecombe model based on the mole fraction composition scale.[15] Since there are only a few sets of published thermodynamic model parameters that can be used to calculate the thermodynamic properties of the system {yKCl + (1 − y)KH$_2$PO$_4$}(aq) over a wider range of ionic strengths, we optimized the model parameters using all available thermodynamic data from Scharge et al.[12] and Childs et al.,[11] as well as the results of our cell potential measurements. Moreover, the proposed approach to study the contributions to the excess free energy of mixing by possible pairs, triplets, or even higher order mutliplets at the macroscopic level using appropriate Scatchard's

Table 1. Sources, Purities of Chemicals, CAS Registry Number, and the Gravimetric Analysis Results for Molality of the Stock Solutions KCl(aq) and KH₂PO₄(aq)[a]

chemicals	CAS reg. no.	supplier and grade	purity (mass fraction)[b]	stock solution molality/(mol kg⁻¹)
$KH_2PO_4(s)$	7778-77-0	Fluka, suprapure	0.99999	$1.7179_0 \pm 0.0004_9$
$KCl(s)$	7447-40-7	Merck, suprapure	0.99999	$0.1036_5 \pm 0.0001_9$

[a]Average deviations from the mean values obtained by triplicate sample analysis represent the reported standard uncertainty. Definitions of molality, in units of mol kg⁻¹, traditionally refer to moles of solute per kilogram of water. [b]These are purities based on the supplier's reported metal ion content. The assumed molar masses are as follows: 74.5513 g mol⁻¹ for KCl (cr), 136.09 g mol⁻¹ for KH₂PO₄ (cr), and 118.07 g mol⁻¹ for KPO₃ {the gravimetric weighing form for standardizing the KH₂PO₄(aq) stock solution}.

mixing parameters[16] is used for the analysis of the solution structure.
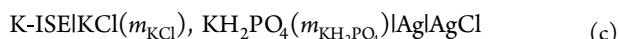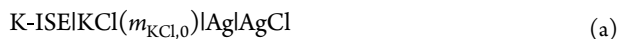
2. MATERIALS AND DESIGN

For cell potential measurements, the two primary stock solutions were prepared from anhydrous chemicals, KCl(cr) and KH₂PO₄(cr), and doubly-distilled, deionized water. By dehydrating three mass aliquots of the KCl(aq) stock solutions at temperatures, $T = 523–573$ K, as explained in our previous work,[3−8] the molality of the samples was determined in triplicate. The method suggested by Childs et al.[17] was used to assess the molality of the stock solutions KH₂PO₄(aq), in which three solution aliquots were first dried at 393.15 K, with the first residue being a hydrate KH₂PO₄·xH₂O(s). Subsequently, the phosphate residues were calcined at 773.15 K for at least 1 h, and the residues were weighed as metaphosphate salt according to the reaction:

$$KH_2PO_4 \cdot xH_2O(s) \rightarrow KPO_3(s) + (1 + x)H_2O(g)$$

Table 1 contains further information.

The arrangements of the cells for zero-current cell potential measurements are as follows:

$$\text{K-ISE}|KCl(m_{KCl,0})|Ag|AgCl \tag{a}$$

$$\text{K-ISE}|KH_2PO_4(m_{KH_2PO_4,0})|Ag|AgCl \tag{b}$$

$$\text{K-ISE}|KCl(m_{KCl}), KH_2PO_4(m_{KH_2PO_4})|Ag|AgCl \tag{c}$$

The molalities of the pure KCl(aq) and KH₂PO₄(aq) solutions are represented in (a)−(c) by $m_{KCl,0}$ and $m_{KH_2PO_4,0}$, respectively, while the molalities of KCl and KH₂PO₄ in the mixture are represented by m_{KCl} and $m_{KH_2PO_4}$, respectively. These galvanic cells contain a single liquid with no liquid junction. As previously reported,[10] a sample of the mixed solution for cell potential measurements was prepared by combining mass aliquots of the KCl(aq) and KH₂PO₄(aq) stock solutions for cell arrangement (c) or by using only appropriate pure solution aliquots for arrangements (a) and (b). The weighing was performed using a Mettler Toledo MS105DU with an accuracy of ±0.01 mg. Using buoyancy corrections, apparent masses of all solutions were converted to masses. By adding the required amounts of double-distilled, deionized water, a series of measurements were made at various concentrations of pure and mixed solutions.

After 0.5−1 h at all ionic strengths, the EMF attained a steady equilibrium value with a variation of ±0.1 mV for each run.

The Ag|AgCl electrode was made at the Faculty of Chemistry of the University of Belgrade according to Ives and Janz,[18] while the K-ion selective electrode was of the type ORION, model 93-19 (Thermo Fisher Scientific). The electrode pair demonstrated good Nernst response and selectivity during calibration. The cell

vessel holding the electrodes was maintained at a temperature of 298.15 ± 0.02 K. A magnetic stirrer was used to stir the solution in a vessel at a slow steady pace. The cell's response was measured with an Inolab pH 7110 Xylem Analytics (Germany GmbH) at a precision of ±0.1 mV.

2.1. Experimental Results. *2.1.1. K-ISE and Ag|AgCl Electrode Pair Calibration.* In our previous work,[10] cell (a) was used to calibrate the electrode pair in an ionic strength range from 0.1 to 1 mol·kg⁻¹ in order to establish the corresponding potential, E_a, from the relation $E_a = E^0 + k \ln (m_{KCl,0} \cdot \gamma_{\pm KCl,0}^2)$, where k is Nernst's slope, $m_{KCl,0}$, the molality of the solution in cell arrangement (a), and $\gamma_{\pm KCl,0}$ is the mean ionic activity coefficient of KCl in KCl(aq). Pitzer's ion-interaction model and Archer's parameters[19] were used to determine the KCl activity coefficient. Our recent work[10] has experimental data on calibration. The observed value of $k = RT/F$ (where R, F, and T stand for the gas constant, the Faraday constant, and absolute temperature, respectively) was close enough to the theoretical value and the standard electrode potential was $E^0 = 74.36$ mV.

2.1.2. Selectivity Coefficient of the Ag|AgCl Electrode for H₂PO₄⁻ (aq) Ion. The Ag|AgCl electrode can be used to detect Cl⁻(aq) ions, although the presence of H₂PO₄⁻(aq) can affect its response. If such a disturbance exists, the selectivity coefficient K^{pot} of the Ag|AgCl electrode for H₂PO₄⁻ (aq) should be evaluated.

Through combining the Nernst equation for this system, the K^{pot} can be calculated as:

$$K^{pot} = [\exp\{(E_b - E^0)/k\}]/\{(\gamma_{\pm KH_2PO_4,0}^2 m_{KH_2PO_4,0}^2)\} \tag{1}$$

where $m_{KH_2PO_4,0}$ and $\gamma_{\pm KH_2PO_4,0}$ are the stoichiometric molality and mean ionic activity coefficient of KH₂PO₄ in the KH₂PO₄(aq) solution at $T = 298.15$ K, respectively, derived using the extended Pitzer equation and the parameters of Ivanović et al.,[8] and E_b is the potential response of the cell arrangement (b). Calculations showed that the average value of K^{pot} is less than 1.0×10^{-4}.

2.1.3. Mean Ionic Activity Coefficients of KCl in the Mixed Solution {yKCl + (1 − y)KH₂PO₄}(aq). Using cell (c), the values of the mean ionic activity coefficient of KCl in the mixed solution {yKCl + (1 − y)KH₂PO₄}(aq) were determined at $T = 298.15$ K.

In the first series of experiments, the ionic strength fraction of KCl was $y = 0.1046; 0.3004; 0.5014; 0.6998;$ and 0.9001, while in the second series, it was $y = 0.2001; 0.4009; 0.6001;$ and 0.7995. The ionic strength of the studied solution and the ionic strength fraction of KCl are as follows:

$$I_m = m_{KCl} + m_{KH_2PO_4} \tag{2}$$

$$y = I_{KCl}/I_m = m_{KCl}/(m_{KCl} + m_{KH_2PO_4}) \tag{3}$$

The EMF response of the cell arrangement (c), E_m is defined as

$$E_m = E^0 + k \ln\{\gamma_{\pm KCl}^2 m_{KCl}(m_{KCl} + m_{KH_2PO_4})$$
$$+ K^{pot}\gamma_{\pm KH_2PO_4}^2 m_{KH_2PO_4}(m_{KCl} + m_{KH_2PO_4})\} \qquad (4)$$

where $\gamma_{\pm KCl}$ and $\gamma_{\pm KH_2PO_4}$ are the mean ionic activity coefficients of KCl and KH_2PO_4 respectively, in the cell (c). The relation for the activity coefficient of KCl can be expressed as follows since the value of K^{pot} is so small, that the second term in parentheses on the right-hand side of eq 4 can be ignored without considerable error:

$$\ln \gamma_{\pm KCl} = (E_m - E^0)/2k - 0.5 \ln\{m_{KCl}(m_{KCl} + m_{KH_2PO_4})\} \qquad (5)$$

Table S1 given in the Supporting information shows the cell potential, E_m, for the *arrangement* (c), stoichiometric molalities of KCl and KH_2PO_4 in the mixture $\{yKCl + (1 - y)KH_2PO_4\}$-(aq) at $T = 298.15$ K, and mean ionic activity coefficients of KCl estimated using eq 5.

2.1.4. Osmotic Coefficients of the System $\{yKCl + (1 - y)KH_2PO_4\}$(aq) at $T = 298.15$ K. Scharge et al.[12] gave values for the osmotic coefficient obtained by isopiestic measurements of the investigated system for different KCl ionic strength fractions and the ionic strength range of the mixed solution $I_m = 0.4104-1.7942$ mol kg^{-1}. Childs et al.[11] previously published the values of the osmotic coefficient for the same system in the ionic strength range, $I_m = 0.7309-2.0656$ mol kg^{-1}. The experimental data obtained in these two studies are shown in Figure 1, namely, the osmotic coefficients of the $\{yKCl + (1 - y) KH_2PO_4\}$(aq) mixed solution as a function of ionic strength at $T = 298.15$ K.

As shown in Figure 1 the values of the osmotic coefficients for KCl(aq) are higher than those for KH_2PO_4(aq) at all ionic strengths, with no overlap and values for the mixtures in a regular order with the ionic strength fraction of electrolyte in between.

The parameters of the pure electrolyte solutions as mixture components are listed in Table 2.
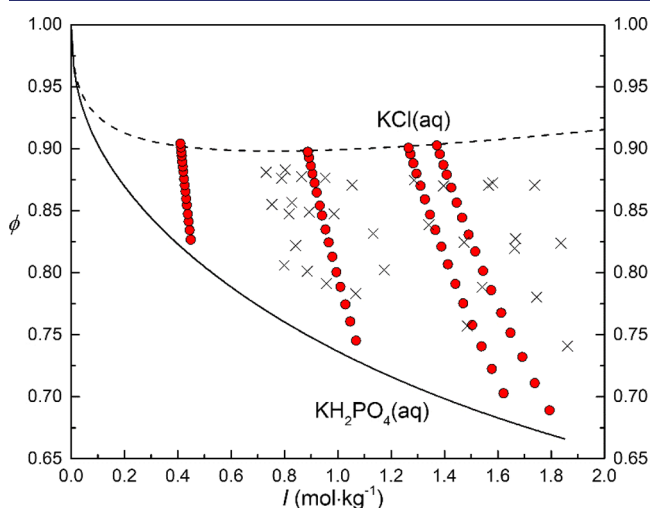

Figure 1. Osmotic coefficients of the $\{yKCl + (1 - y)KH_2PO_4\}$(aq) system at $T = 298.15$ K vs total ionic strength, experimental data from the literature: red solid circle—data from Scharge et al.,[12] black cross—data from Childs et al.,[11] curves smoothed values of the osmotic coefficients for the pure solutions KCl(aq) and KH_2PO_4(aq) obtained by extended Pitzer's model and parameters from Table 2.

Table 2. Extended Pitzer Model and the Clegg−Pitzer−Brimblecombe Model Binary Solution Parameters for KCl(aq)[15,19] and KH$_2$PO$_4$(aq)[8] at T = 298.15 K (m^θ = 1 mol kg^{-1})

extended Pitzer's model	
KCl(aq)[19]	KH$_2$PO$_4$ (aq)[8]
$\beta_{KCl}^{(0)} \cdot (m^\theta) = 0.0511414$	$\beta_{KH_2PO_4}^{(0)} \cdot (m^\theta) = -0.187619$
$\beta_{KCl}^{(1)} \cdot (m^\theta) = 0.201879$	$\beta_{KH_2PO_4}^{(1)} \cdot (m^\theta) = 0.199972$
$C_{KCl}^{(0)} \cdot (m^\theta)^2 = -0.0068023$	$C_{KH_2PO_4}^{(0)} \cdot (m^\theta)^2 = 0.0057215$
$C_{KCl}^{(1)} \cdot (m^\theta)^2 = 0.0$	$C_{KH_2PO_4}^{(1)} \cdot (m^\theta)^2 = 0.086574$
$\alpha_{KCl} \cdot (m^\theta)^{1/2} = 2.0$	$\alpha_{KH_2PO_4} \cdot (m^\theta)^{1/2} = 2.0$
$\omega_{KCl} \cdot (m^\theta)^{1/2} = 0.0$	$\omega_{KH_2PO_4} \cdot (m^\theta)^{1/2} = 1.0$
Clegg−Pitzer−Brimblecombe's model	
KCl(aq)[15]	KH$_2$PO$_4$ (aq)[8]
$\alpha_{KCl} = 13$	$\alpha_{KH_2PO_4} = 8$
$B_{KCl} = 9.091$	$B_{KH_2PO_4} = -12.2505$
$W_{w, KCl} = -3.269$	$W_{w, KH_2PO_4} = -2.3125$
$U_{w, KCl} = -2.283$	$U_{w, KH_2PO_4} = -4.8226$
$V_{w, KCl} = 0.0$	$V_{w, KH_2PO_4} = 0.0$

The parameters of the Pitzer model and the Clegg−Pitzer−Brimblecombe model for KH_2PO_4(aq) valid up to $I_m \leq 1.80547$ mol kg^{-1} were given by Ivanović et al.,[8] whereas Archer[19] reported ion-interaction parameters for KCl(aq). Dimensionless parameters appear in the Clegg−Pitzer−Brimblecombe model equations. These parameter values are valid for KCl(aq) up to $I_m \leq 7$ mol kg^{-1} and were obtained from Clegg et al.[15]

3. THERMODYNAMIC MODELS FOR THE TREATMENT OF ACTIVITY COEFFICIENT DATA

3.1. Pitzer's Model. The ionic strength of the system $\{yKCl + (1 - y)KH_2PO_4\}$(aq) is given by eq 2, while the ionic strength fraction of the electrolyte is given by eq 3. According to Pitzer's ion-interaction model,[13] the mean ionic activity coefficient of KCl in the system $\{yKCl + (1 - y)KH_2PO_4\}$(aq) is given by

$$\ln \gamma_{KCl,\pm} = F + I_m(y + 1)B_{K,Cl} + I_m(1 - y)B_{K,H_2PO_4}$$
$$+ (1 + 2y)I_m^2 C_{K,Cl}^T + 2I_m^2(1 - y)C_{K,H_2PO_4}^T$$
$$+ I_m^2(1 - y)\theta_{Cl,H_2PO_4} + (1/2)$$
$$I_m^2(1 - y^2)\psi_{K,Cl,H_2PO_4} \qquad (6)$$

and for the mean ionic activity coefficient of KH_2PO_4 as

$$\ln \gamma_{KH_2PO_4,\pm} = F + yI_m B_{K,Cl} + (2 - y)I_m B_{K,H_2PO_4}$$
$$+ 2yI_m^2 C_{K,Cl}^T + (3 - 2y)I_m^2 C_{K,H_2PO_4}^T$$
$$+ yI_m\theta_{Cl,H_2PO_4} + (1/2)(2 - y)yI_m^2\psi_{K,Cl,H_2PO_4} \qquad (7)$$

where function F is

$$F = -A^\phi\{I_m^{1/2}/(1 + bI_m^{1/2}) + (2/b)\ln(1 + bI_m^{1/2})\}$$
$$+ yI_m^2(B_{K,Cl}' + I_m C_{K,Cl}^{T'}) + I_m^2(1 - y)$$
$$(B_{K,H_2PO_4}' + I_m C_{K,H_2PO_4}^{T'}) \qquad (8)$$

and the additional functions from eqs 6 to 8 are defined as

$$B_{K,Cl} = \beta_{K,Cl}^{(0)} + \beta_{K,Cl}^{(1)} g(\alpha_{K,Cl}^{EP} I_m^{1/2}) \tag{9}$$

$$B'_{K,Cl} = (\beta_{K,Cl}^{(1)}/I_m) g'(\alpha_{K,Cl}^{EP} I_m^{1/2}) \tag{10}$$

$$C_{K,Cl}^{T} = C_{K,Cl}^{(0)} \tag{11}$$

$$C_{K,Cl}^{T'} = 0 \tag{12}$$

$$B_{K,H_2PO_4} = \beta_{K,H_2PO_4}^{(0)} + \beta_{K,H_2PO_4}^{(1)} g(\alpha_{K,H_2PO_4}^{EP} I_m^{1/2}) \tag{13}$$

$$B'_{K,H_2PO_4} = (\beta_{K,H_2PO_4}^{(1)}/I_m) g'(\alpha_{K,H_2PO_4}^{EP} I_m^{1/2}) \tag{14}$$

$$C_{K,H_2PO_4}^{T} = C_{K,H_2PO_4}^{(0)} + 4C_{K,H_2PO_4}^{(1)} h(\omega_{K,H_2PO_4} I_m^{1/2}) \tag{15}$$

$$C_{K,H_2PO_4}^{T'} = (4/I_m) C_{K,H_2PO_4}^{(1)} h'(\omega_{K,H_2PO_4} I_m^{1/2}) \tag{16}$$

$$g(x) = (2/x^2)\{1 - (1 + x)\exp(-x)\} \tag{17}$$

$$h(x) = (1/x^4)[6 - \{6 + x(6 + 3x + x^2)\exp(-x)\}] \tag{18}$$

$$g'(x) = I_m\{\partial g(x)/\partial I_m\} \quad h'(x) = I_m\{\partial h(x)/\partial I_m\} \tag{19}$$

and the relation for the osmotic coefficient of the $\{yKCl + (1 - y)KH_2PO_4\}(aq)$ solution is

$$\phi - 1 = -A^\phi I_m^{1/2}/(1 + 1.2 I_m^{1/2}) + yI_m(B_{K,Cl}^\phi + 2I_m C_{K,Cl}^{T\phi})$$
$$+ (1 - y)I_m(B_{K,H_2PO_4}^\phi + 2I_m C_{K,H_2PO_4}^{T\phi})$$
$$+ y(1 - y)I_m(\theta_{Cl,H_2PO_4} + I_m\psi_{K,Cl,H_2PO_4}) \tag{20}$$

where

$$B_{K,Cl}^\phi = \beta_{K,Cl}^{(0)} + \beta_{K,Cl}^{(1)} \exp(-\alpha_{K,Cl} I_m^{1/2}) \tag{21}$$

$$B_{K,H_2PO_4}^\phi = \beta_{K,H_2PO_4}^{(0)} + \beta_{K,H_2PO_4}^{(1)} \exp(-\alpha_{K,H_2PO_4} I_m^{1/2}) \tag{22}$$

$$C_{K,Cl}^{T\phi} = C_{K,Cl}^{(0)} \tag{23}$$

$$C_{K,H_2PO_4}^{T\phi} = C_{K,H_2PO_4}^{(0)} + C_{K,H_2PO_4}^{(1)} \exp(-\omega_{K,H_2PO_4} I_m^{1/2}) \tag{24}$$

The Debye−Hückel limiting-law slope for water is $A^\phi = 0.391475$ kg$^{1/2}$ mol$^{-1/2}$ at $T = 298.15$ K and standard pressure,[20] and the parameters $b = 1.2$ kg$^{1/2}$ mol$^{-1/2}$ and $\alpha = 2.0$ kg$^{1/2} \cdot$ mol$^{-1/2}$ are the same for KCl(aq) and KH$_2$PO$_4$(aq). While the parameters $\beta^{(0)}$, $\beta^{(1)}$, $C^{(0)}$, $C^{(1)}$ are specific for the pure solutions KCl(aq) and KH$_2$PO$_4$(aq) the mixing parameters of the model for the system $\{yKCl + (1 - y)KH_2PO_4\}(aq)$ are θ_{Cl,H_2PO_4} and ψ_{K,Cl,H_2PO_4}.

3.2. Scatchard's Model. Scatchard's neutral-electrolyte model[14] also shows the mean ionic activity coefficient of KCl in the system $\{yKCl + (1 - y)KH_2PO_4\}(aq)$ as well as the osmotic coefficients. Eqs 6 and 7 represent the contributions of the binary solution for KCl(aq) when the ionic strength fraction is $y = 1.0$ and for KH$_2$PO$_4$(aq) when $y = 0.0$, respectively.

As for the mean ionic activity coefficient of KCl in the mixed solution, the appropriate relation is as follows:

$$\ln \gamma_{\pm KCl}^* = \ln \gamma_{\pm KCl}^* + [(\phi_{KH_2PO_4}^* - 1) - (\phi_{KCl}^* - 1)]$$
$$(1 - y) + (1/2)[b_{01}I_m + (b_{02} + b_{12})I_m^2$$
$$+ (b_{03} + b_{13} + b_{23})I_m^3](1 - y)$$
$$- (1/2)[((1/2)b_{02} + (3/2)b_{12})I_m^2$$
$$+ ((2/3)b_{03} + 2b_{13} + (10/3)b_{23})I_m^3](1 - y)^2$$
$$+ (1/2)[((2/3)b_{13} + (8/3)b_{23})I_m^3](1 - y)^3 \tag{25}$$

The osmotic coefficient of the system $\{yKCl + (1 - y)KH_2PO_4\}(aq)$ according to Scatchard's model is:

$$\phi = y\phi_{KCl}^* + (1 - y)\phi_{KH_2PO_4}^* + y(1 - y)(b_{01}I_m + b_{02}I_m^2$$
$$+ b_{03}I_m^3) + y(1 - y)(2y - 1)(b_{12}I_m^2 + b_{13}I_m^3)$$
$$+ y(1 - y)(2y - 1)^2 b_{23}I_m^3 \tag{26}$$

In eqs 25 and 26, the mean ionic activity coefficients of the electrolyte KCl, $\gamma_{\pm KCl}^*$, and the osmotic coefficients of KCl(aq), ϕ_{KCl}^*, and of KH$_2$PO$_4$(aq), $\phi_{KH_2PO_4}^*$ are determined at the total ionic strength of the mixture.

The b_{kl} are empirical mixing parameters derived from experimental results. Because of the larger number of mixing parameters available in the Scatchard model, these mixing terms provide a more accurate description of the activity coefficients of electrolytes in mixtures than Pitzer's considers mixing terms. Furthermore, this model technically considers all electrolytes present as though they were completely dissociated. The binary-solution mixing approximation can frequently yield a pretty good estimate of the osmotic coefficients of ternary solutions in the case of mixtures of strong electrolytes.

In terms of the Scatchard parameters, the excess free energy of mixing for the mixed solution of, for example, A and B electrolytes is given by[16]

$$\frac{\Delta G_m^{ex}}{RT} = y(1 - y)I_m[B_{AB}^{(0)} + (2y - 1)B_{AB}^{(1)} + (2y - 1)^2 B_{AB}^{(2)}$$
$$+ ... + (2y - 1)^n B_{AB}^{(n)}] \tag{27}$$

where terms B_{AB} represent

$$B_{AB}^{(n)} = \sum_{k=n+1}^{k'} \frac{I_m^k}{k} b_{n,k} \quad \text{for } n \geq 0 \tag{28}$$

Rearranging the terms in the excess free energy of mixing via potential pairs, triplets, quads, or even higher order multiplets (HOM), we get

$$\Delta G_m^{ex}/RT = (\Delta G_m^{ex}/RT)_{pairs} + (\Delta G_m^{ex}/RT)_{triplets}$$
$$+ (\Delta G_m^{ex}/RT)_{quads} + ... + (\Delta G_m^{ex}/RT)_{HOM} \tag{29}$$

where

$$(\Delta G_m^{ex}/RT)_{pairs} = y(1 - y)I_m^2 b_{0,1} \tag{30}$$

$$(\Delta G_m^{ex}/RT)_{triplets} = y(1 - y)(1/2)I_m^3[b_{0,2} + (2y - 1)b_{1,2}] \tag{31}$$

$$(\Delta G_m^{ex}/RT)_{quads} = (1/3)y(1-y)I_m^4[b_{0,3} + (2y-1)b_{1,3}$$
$$+ (2y-1)^2 b_{2,3}] \qquad (32)$$

$$(\Delta G_m^{ex}/RT)_{HOM} = (I_m^{n+2}/n+1)y(1-y)$$
$$[b_{0.n+1} + (2y-1)b_{1.n+1} +$$
$$... + (2y-1)^n b_{n.n+1}] \qquad (33)$$

If there are only pairwise interactions in a mixed solution, then the total excess free energy is equal to $(\Delta G_m^{ex}/RT)_{pairs}$, and b_{01} is the only parameter needed to fit the data. Furthermore, triplet interactions must be present in the solution if using b_{01} alone proves insufficient to fit the data. As a result, b_{01}, $b_{02,}$ and b_{12} must all be utilized and the excess free energy of mixing will be given by two terms, namely, $(\Delta G_m^{ex}/RT)_{pairs}$ and $(\Delta G_m^{ex}/RT)_{triplets}$. Assuming that the pair and triplet parameters, as well as quadruplet terms, b_{03}, b_{13}, and b_{23}, are required to fit the data then the excess free energy of mixing is given with one more terms reflecting all the possible interactions.

3.3. Clegg−Pitzer−Brimblecombe's Model.
Clegg, Pitzer, and Brimblecombe[15] created a model on the mole-fraction composition scale as an extension of Pitzer's and Simonson's earlier work.[21]

The composition fractions, x, and solution ionic strength on a mole fraction scale, I_x, of the $\{yKCl + (1-y)KH_2PO_4\}(aq)$ system are as follows:

$$x_K = (m_{KCl} + m_{KH_2PO_4})/\{2(m_{KCl} + m_{KH_2PO_4}) + (1/M_w)\} \qquad (34)$$

$$x_{Cl} = m_{KCl}/\{2(m_{KCl} + m_{KH_2PO_4}) + (1/M_w)\} \qquad (35)$$

$$x_{HPO_4} = m_{KH_2PO_4}/\{2(m_{KCl} + m_{KH_2PO_4}) + (1/M_w)\} \qquad (36)$$

$$x_I = 2(m_{KCl} + m_{K_2HPO_4})/\{2(m_{KCl} + m_{KH_2PO_4})$$
$$+ (1/M_w)\} \qquad (37)$$

$$x_w = (1/M_w)/\{2(m_{KCl} + m_{KH_2PO_4}) + (1/M_w)\} \qquad (38)$$

$$I_x = (m_{KCl} + m_{KH_2PO_4})/\{2(m_{KCl} + m_{KH_2PO_4}) + (1/M_w)\} \qquad (39)$$

where $M_w = 0.0180153\ kg\ mol^{-1}$ is the molar mass of water at $T = 298.15\ K$.

In the mole fraction scale, the activity coefficient of KCl in the mixture $\{yKCl + (1-y)KH_2PO_4\}(aq)$ is given by

$$\ln f_{KCl} = -A_x[(2/\rho) \ln(1 + \rho I_x^{1/2}) + I_x^{1/2}\{(1-2I_x)$$
$$/(1 + \rho I_x^{1/2})\}] + (1/2)(x_K + x_{Cl})B_{KCl}g_{(KCl)}$$
$$+ (1/2)x_{H_2PO_4}B_{KH_2PO_4}g_{(KH_2PO_4)}$$
$$+ x_{H_2PO_4}x_K B_{KH_2PO_4}[g_{(KH_2PO_4)}(1/2I_x)$$
$$+ \{1 - (1/2I_x)\} \exp(-\alpha_{KH_2PO_4}I_x^{1/2})]$$
$$+ x_{Cl}x_K B_{KCl}[g_{(KCl)}(1/2I_x) + \{1 - (1/2I_x)\}$$
$$\exp(-\alpha_{KCl}I_x^{1/2})] + \{(x_W - 1)$$
$$+ E_{Cl}x_w[1 - (2/F)]\}W_{w,KCl}$$
$$- 2x_W(1/F)E_{H_2PO_4}W_{w,KH_2PO_4}$$
$$+ [2x_w(x_K + x_{Cl} - 4x_K x_{Cl})]U_{w,KCl}$$
$$+ 2x_w x_{H_2PO_4}(1 - 4x_K)U_{w,KH_2PO_4}$$
$$+ 2x_W^2[(x_K + x_{Cl} - 2x_K x_{Cl})]V_{w,KCl}$$
$$+ 2x_W^2 x_{H_2PO_4}(1 - 4x_K)V_{w,KH_2PO_4}$$
$$+ x_{H_2PO_4}(1 - 2x_{Cl})W_{K,Cl,H_2PO_4}$$
$$+ 2x_{H_2PO_4}(4x_{H_2PO_4}x_{Cl} - 4x_{Cl}^2 + 2x_{Cl} - 1)$$
$$U_{K,Cl,H_2PO_4} + 2x_w x_{H_2PO_4}(1 - 4x_{Cl})Q_{w,K,Cl,H_2PO_4} \qquad (40)$$

where

$$E_{Cl} = x_{Cl}/x_{Cl} + x_{H_2PO_4} \qquad (41)$$

$$E_{H_2PO_4} = x_{H_2PO_4}/x_{Cl} + x_{H_2PO_4} \qquad (42)$$

$$1/F = 2/(x_K + x_{Cl} + x_{H_2PO_4}) \qquad (43)$$

The relation between the mean activity coefficient of the electrolyte on the molality scale and the mean activity coefficient on the mole fraction composition scale $\gamma_{x,\pm}$ (infinite dilution reference state) is as follows:

$$\ln \gamma_\pm = \ln \gamma_{x,\pm} + \ln x_w \qquad (44)$$

Raoult's law provides the following relation for the activity coefficient of water, f_w, in the mixture:

$$\ln f_w = 2A_x I_x^{3/2}/(1 + \rho I_x^{1/2}) - x_K x_{Cl}B_{KCl} \exp(-\alpha_{KCl}^x I_x^{1/2})$$
$$- x_K x_{H_2PO_4}B_{KH_2PO_4} \exp(-\alpha_{KH_2PO_4}^x I_x^{1/2})$$
$$+ 2(1 - x_w)(1/F)[E_{Cl}W_{w,KCl} + E_{H_2PO_4}W_{w,H_2PO_4}]$$
$$+ 4(1 - 2x_w)x_K[x_{Cl}U_{w,KCl} + x_{H_2PO_4}U_{w,H_2PO_4}]$$
$$+ 4x_w x_K(2 - 3x_w)[x_{Cl}V_{w,KCl} + x_{HPO_4}V_{w,H_2PO_4}]$$
$$- 2x_{Cl}x_{H_2PO_4}W_{K,Cl,H_2PO_4} - 8x_{Cl}x_{H_2PO_4}(x_{Cl} - x_{H_2PO_4})$$
$$U_{K,Cl,H_2PO_4} + 4(1 - 2x_w)x_{Cl}x_{H_2PO_4}Q_{w,K,Cl,H_2PO_4} \qquad (45)$$

The following equation relates the molality based osmotic coefficient, ϕ, to the activity coefficient of water according to Raoult's law, f_w:

Table 3. Pitzer's, Scatchard's, and Clegg−Pitzer−Brimblecombe's Models' Optimized Parameter Values for the Set of Osmotic Coefficient Values and Mean Ionic Activity Coefficients of KCl in the System $\{y\text{KCl} + (1 − y) \text{KH}_2\text{PO}_4\}(\text{aq})$ at T = 298.15 K with a Standard Deviation of the Fit for the Osmotic Coefficients, s.d. (ϕ) and of the Mean Ionic Activity Coefficient of KCl, s.d. $(\gamma_\pm)$[a]

Pitzer's model			
$\theta_{\text{Cl, H}_2\text{PO}_4} \cdot (m^\theta)$	$\psi_{\text{K, Cl, H}_2\text{PO}_4} \cdot (m^\theta)^2$	s.d. $(\phi) \times 10^{3\,b}$	s.d. $(\gamma_\pm) \times 10^{3\,b}$
0.0805		4.7	8.1
	0.0662	5.6	3.8
0.0267	**0.0462**	**4.8**	**3.9**

Scatchard's model							
$b_{01} \times (m^\theta)$	$b_{02} \times (m^\theta)^2$	$b_{03} \times (m^\theta)^3$	$b_{12} \times (m^\theta)^2$	$b_{13} \times (m^\theta)^3$	$b_{23} \times (m^\theta)^3$	s.d. $(\phi) \times 10^{3\,b}$	s.d. $(\gamma_\pm) \times 10^{3\,b}$
9.38×10^{-2}						3.1	4.3
9.27×10^{-2}	7.755×10^{-4}					3.1	4.2
	0.1999	**-9.20×10^{-2}**				**2.8**	**3.7**
6.79×10^{-2}			1.54×10^{-2}			5.4	5.4
2.76×10^{-2}	1.487×10^{-1}	-7.02×10^{-2}				2.7	3.6
8.97×10^{-2}	3.6×10^{-3}		8.9×10^{-3}			3.0	4.1
9.57×10^{-2}		-6.673×10^{-4}	8.2×10^{-3}			2.9	4.2
			-2.15×10^{-2}	3.32×10^{-2}	0.1464	18.6	7.8
		4.39×10^{-2}		1.51×10^{-2}	1.09×10^{-2}	7.6	6.8
2.27×10^{-2}	1.6×10^{-1}	-7.73×10^{-2}	6.12×10^{-2}	-3.86×10^{-2}	9.9×10^{-3}	2.4	3.3

Clegg−Pitzer−Brimblecombe's model				
$W_{\text{K, Cl, H}_2\text{PO}_4}$	$U_{\text{K, Cl, H}_2\text{PO}_4}$	$Q_{\text{w, K, Cl, H}_2\text{PO}_4}$	s.d. $(\phi) \times 10^{3\,b}$	s.d. $(\gamma_\pm) \times 10^{3\,b}$
5.7154			13.3	12.4
	−11.3423		24.7	7.7
		2.5787	6.3	10.3
5.7097	−9.4799		13.3	12.3
−9.4685		**5.9302**	**3.0**	**4.5**
	−0.2932	2.5783	6.3	10.3
−9.7874	11.4525	6.0573	2.8	4.2

[a]Ionic strength range of the system, where the parameters are valid, according to the treated data from Table S1 and the results of Childs et al.[11] and Scharge et al.,[12] is I_m = 0.0886−1.7942 mol kg^{-1} (m^θ = 1 mol kg^{-1}). [b]s.d. (ϕ) is the standard uncertainty of the fit of the model to the experimental osmotic coefficients from the literature[11,12] and s.d. $(\gamma_\pm)$ is standard uncertainty for the experimental KCl activity coefficient data of Table S1. The boldface indicates the suggested model parameters and the associated standard uncertainty.

$$\phi = -(x_\text{w}/x_\text{I})(\ln f_\text{w} + \ln x_\text{w}) \tag{46}$$

In eqs 40 and 45, A_x is the Debye−Hückel limiting law slope on the mole-fraction scale, having a value of $A^\phi/(M_\text{w})^{1/2}$ = 2.917, and ρ is a parameter related to the distance of closest approach having an assigned value of 13.0.[15,21]

The main short-range parameters in the aforementioned equations are $W_{\text{w, KCl}}$, $W_{\text{w, KH}_2\text{PO}_4}$, $U_{\text{w, KCl}}$, $U_{\text{w, KH}_2\text{PO}_4}$, $V_{\text{w, KCl}}$, and $V_{\text{w, KH}_2\text{PO}_4}$ which indicate the contributions of pure solutions. Parameters B_{KCl} and $B_{\text{KH}_2\text{PO}_4}$ with related constants α_{KCl} and $\alpha_{\text{KH}_2\text{PO}_4}$ are for long-range forces. By fitting the model equations to data on osmotic or activity coefficients for aqueous solutions containing three ions but no neutral solutes, three mixing parameters are identified, that is, $W_{\text{K, Cl, H}_2\text{PO}_4}$, $U_{\text{K, Cl, H}_2\text{PO}_4}$, and $Q_{\text{w, K, Cl, H}_2\text{PO}_4}$.

4. DISCUSSION

4.1. Discussion and Treatment of Data Obtained from EMF and Isopiestic Measurements.
The parameter set for all three models can be determined to minimize the total weighted sum of squared deviations for the two measured properties, the mean ionic activity coefficient of KCl and the osmotic coefficients. This was achieved by using a slightly modified lsqmultinonlin MATLAB routine[22] as the fitting method for all data.

The optimal parameter values for the Pitzer, Scatchard, and Clegg−Pitzer−Brimblecombe models were estimated using experimental values for the mean ionic activity coefficient of KCl from Table S1 and isopiestic results for the osmotic coefficients of the system $\{y\text{KCl} + (1 − y)\text{KH}_2\text{PO}_4\}(\text{aq})$ at T = 298.15 K from Scharge et al.[12] and Childs et al.[11] Scharge used only Pitzer's ion-interaction model to obtain a comprehensive set of ternary interaction parameters for the system $\{y\text{KCl} + (1 − y)\text{KH}_2\text{PO}_4\}(\text{aq})$ at T = 298.15 K. Childs et al.[11] used the isopiestic technique to study five of the six possible two-salt aqueous mixtures of NaCl, KCl, NaH$_2$PO$_4$, and KH$_2$PO$_4$ at 298.15 K and calculated the excess Gibbs energies of mixing for identical ionic strength fractions of each salt for those studied systems.

Experimental data of KCl activity coefficients from Table S1 (43 experimental points) and literature data on osmotic coefficients from Scharge et al.[12] and Childs et al.[11] (60 experimental points) were used to optimize the model parameters. After reviewing the literature data, it was found that most of the osmotic coefficients from both sources were consistent, although certain values had a larger scatter and were therefore excluded from the treatment. Osmotic coefficients (25 values in total) in the range of ionic strength, I_m = 0.4118−1.2956 mol kg^{-1}, were discarded from the results of Scharge,[12] while those in the range of ionic strength, I_m = 0.7309−2.0656 mol kg^{-1} (12 values in total), were excluded from the work of Childs.[11] The optimal parameter settings of the models apply to
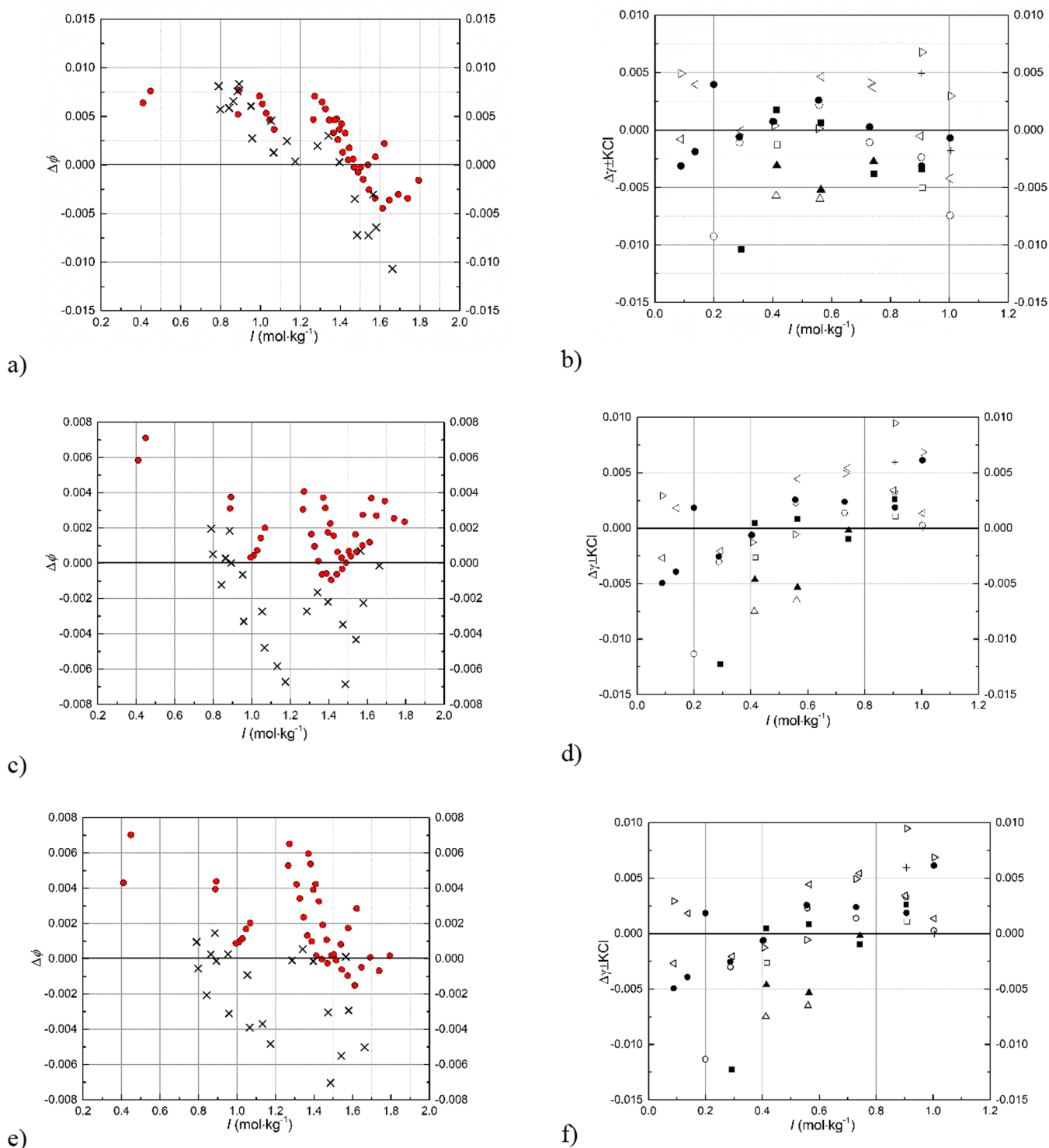
Figure 2. Differences in experimental and calculated values of osmotic (left) and mean ionic activity coefficients of KCl (right) vs ionic strength of the mixed solution $\{y\text{KCl} + (1 - y)\,\text{KH}_2\text{PO}_4\}(\text{aq})$ at $T = 298.15$ K by different approaches, using optimized parameters from Table 3 given in boldface: (a) and (b) Pitzer's model, (c) and (d) Scatchard's model, and (e) and (f) Clegg–Pitzer–Brimblecombe's model: osmotic coefficients x— experimental values from the paper of Childs et al.;[11] red solid circle — data from the paper of Scharge et al.,[12] mean ionic activity coefficients of KCl for different ionic strength fractions, y: black open triangle — $y = 0.1046$; black solid triangle — $y = 0.2001$; black open square — $y = 0.3004$; black solid square — $y = 0.4009$; black open circle — $y = 0.5014$; black solid circle — $y = 0.6001$; black open left-pointing triangle — $y = 0.6998$; black open right-pointing triangle — $y = 0.7995$; and + — $y = 0.9001$.

the ionic strength range, $I_m = 0.0886-1.7942$ mol kg^{-1}. Table 3, which also includes the standard deviation of the fit to the values of the osmotic coefficient and the mean ionic activity coefficients of KCl, for the system $\{y\text{KCl} + (1 - y)\text{KH}_2\text{PO}_4\}(\text{aq})$ at $T = $ 298.15 K, lists the optimal mixing parameters for each of the three models.

Because of the limitations imposed by Pitzer's model, we restricted our comparison to two optimized mixing parameters.

Regardless of the approach, the results of fitting the activity coefficient data of the system $\{y\text{KCl} + (1 - y)\,\text{KH}_2\text{PO}_4\}(\text{aq})$ in a studied range of ionic strength of the mixture are practically the same whether electrolytes or ions are considered as solution components, with the exception of Scatchard's model, which gives slightly better results. As we can see from Table 3, Pitzer's model could not effectively represent the activity data, and both mixing parameters gave standard deviations of s.d. $(\gamma_\pm) = 3.9 \times 10^{-3}$ for the mean ionic activity coefficients and s.d. $(\phi) = 4.8 \times 10^{-3}$ for the osmotic coefficients, despite the fact that the number of treated data was larger on the osmotic coefficient side.

With the exception of the combination of b_{12}, b_{13}, and b_{23}, every other combination of mixture parameters in Scatchard's model has a relatively small standard deviation. Even with only two mixing parameters, b_{02} and b_{03}, satisfactory results were obtained (s.d. $(\gamma_\pm) = 2.8 \times 10^{-3}$; s.d. $(\phi) = 3.7 \times 10^{-3}$), almost identical to those obtained with all six parameters (s.d. $(\gamma_\pm) = 2.4 \times 10^{-3}$; s.d. $(\phi) = 3.3 \times 10^{-3}$).

The Clegg−Pitzer−Brimblecombe model was not very successful in fitting activity coefficient data when only one or two parameters were used, except $W_{\text{K, Cl, H}_2\text{PO}_4}$ and $Q_{w,\,\text{K, Cl, H}_2\text{PO}_4}$ when the standard deviation was relatively small (s.d. $(\gamma_\pm) = 3.0 \times 10^{-3}$; s.d. $(\phi) = 4.5 \times 10^{-3}$) and as when all three mixing parameters were included (s.d. $(\gamma_\pm) = 2.8 \times 10^{-3}$; s.d. $(\phi) = 4.2 \times 10^{-3}$). With the mean ionic activity coefficient alone, this combination of two parameters ($W_{\text{K, Cl, H}_2\text{PO}_4}$ and $Q_{w,\,\text{K, Cl, H}_2\text{PO}_4}$) gave the best fitting results.

Figure 2a−f shows the deviations of all osmotic coefficients and the mean ionic activity coefficient of KCl from the calculated values using the optimal parameters from Table 3 and different thermodynamic approaches. Different symbols are used to represent each data set for the osmotic coefficients and the mean ion ionic activity coefficients. Up to the highest ionic strength, the experimental results are satisfactorily reproduced by the Pitzer, Clegg−Pitzer−Brimblecombe, and Scatchard models, and there is no region of apparent systematic variation. However, the experimental data from Table S1 dominate the fits at the low ionic strength of the mixed solution. It is also clear that the deviations of the osmotic coefficient from the experimental values are essentially randomly distributed.

The calculated mean ionic activity coefficients of KCl and KH_2PO_4 and the osmotic coefficients for the system $\{y\text{KCl} + (1 - y)\,\text{KH}_2\text{PO}_4\}(\text{aq})$ at $T = 298.15$ K, given in Tables S2−S4 in the Supplement Information, extend to $I_\text{m} = 2$ mol kg^{-1}, and are thus above the range of ionic strength of the isopiestic and cell potential data ($I_\text{m} = 1.7942$ mol kg^{-1}). With respect to the standard deviation of the fit for ϕ and $\gamma_\pm$, the estimated values should be quite reliable.

Figure 3 shows the dependence of the logarithm of the activity coefficient of KCl on the ionic strength fraction of KCl in the $\{y\text{KCl} + (1 - y)\text{KH}_2\text{PO}_4\}(\text{aq})$ system at $T = 298.15$ K at various total concentrations. The values of the mean ionic activity coefficients were calculated using the optimized Pitzer mixing parameters from Table 3. Up to an ionic strength of 1.0 mol kg^{-1}, it is obvious that the activity coefficient of KCl increases monotonically and that the relative KH_2PO_4 concentration has very little effect on KCl. However, at higher ionic strength, the relative KH_2PO_4 concentration has a greater effect on KCl, and the Harned rule is not followed.

Figure 4 shows the logarithm of the activity coefficient of KH_2PO_4 in the $\{y\text{KCl} + (1 - y)\text{KH}_2\text{PO}_4\}(\text{aq})$ system as a
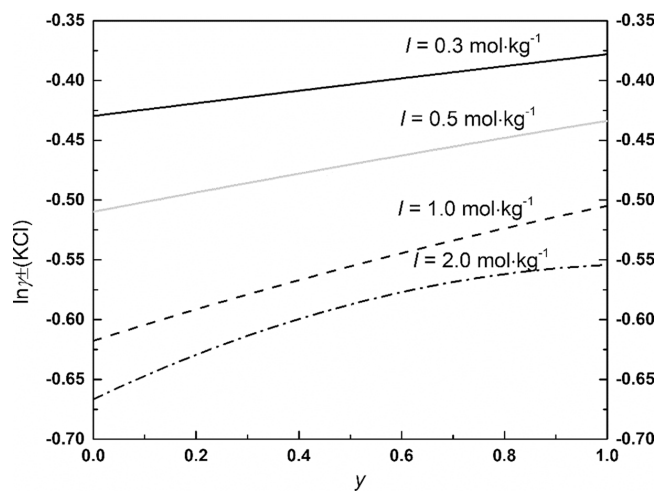

Figure 3. Logarithm of the mean ionic activity coefficient of KCl in the system $\{y\text{KCl} + (1 - y)\text{KH}_2\text{PO}_4\}(\text{aq})$ at $T = 298.15$ K as a function of the ionic strength fraction y for different total ionic strengths of the solution, calculated according to Pitzer's model and the optimized mixing parameters from Table 3.
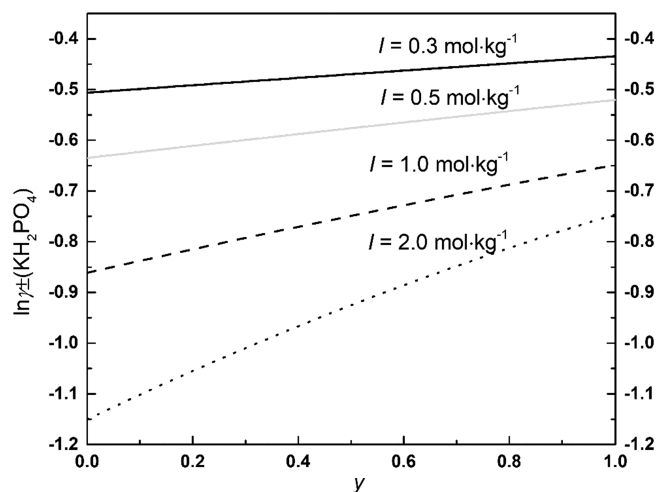

Figure 4. Logarithm of the mean ionic activity coefficient of KH_2PO_4 in the system $\{y\text{KCl} + (1 - y)\text{KH}_2\text{PO}_4\}(\text{aq})$ at $T = 298.15$ K as a function of the ionic strength fraction y for different total ionic strengths of the solution, calculated according to Pitzer's model and the optimized mixing parameters from Table 3.

function of the ionic strength fraction of KCl at various total ionic strengths. It is evident that increasing of relative concentration of KCl, as a stronger electrolyte, influences the values of the activity coefficient of KH_2PO_4, especially at higher ionic strength.

4.2. Possible Interactions in the Solution of $\{y\text{KCl} + (1 - y)\,\text{KH}_2\text{PO}_4\}(\text{aq})$. The results of Raman spectroscopy, which has been used to understand the nature of phosphate solutions,[23] revealed the presence of interactions between phosphate anions, recently termed short-range hydrogen bonding between anionic donors and acceptors or anti-electrostatic hydrogen bonding (AEHB).[24,25] Therefore, protic hydroxyanions bearing hydroxyl groups have a remarkably reliable ability to dimerize or oligomerize via hydrogen bonds, which is contrary to the expectations of Coulomb's law. According to some authors,[23] this dimerization is not a spontaneous process and causes a specific local disorder in the

solution. The dimer formation constant is in the range of 0.25 ± 0.1 M^{-1} or 0.3 ± 0.05 M^{-1} at $T = 298.15$ K.[26,23] In addition, it was discovered that a solvent or a cation can efficiently shield repulsive Coulomb interactions, which increases the stability of dimers.[24]

The lowest frequency mode in dielectric relaxation spectroscopy, on the other hand, combines ion-pair reorientation with ion-cloud relaxation and is used to study ion association in solutions of $KH_2PO_4(aq)$ and $KCl(aq)$.[27] The observed amplitude of the lowest frequency results only from ion cloud relaxation when the electrolyte is completely dissociated, as in the case of $KCl(aq)$. Relaxation in $KH_2PO_4(aq)$ is present to some extent, but at higher ionic strengths, ion pair reorientation is the main source of amplitude. The value of the overall association constant[27] in the standard state (infinite dilution) is 5.4 ± 0.4 M^{-1}.

Despite the fact that there are numerous approaches and computer simulations involving structural studies in solution,[28−30] a simple analysis is performed here based on the proposed method for analyzing the contributions to the excess free energy of mixing by possible pairs, triplets, or even higher order mutliplets at the macroscopic level[16] using appropriate Scatchard's mixing parameters (see Section 3.2). Table 3 lists the optimized parameters of the Scatchard neutral-electrolyte model of $\{yKCl + (1 − y)\, KH_2PO_4\}(aq)$ at $T = 298.15$ K for selected parameter combinations obtained by treating osmotic and mean ionic activity coefficient data.

When we focused on depicting on how the excess free energy varies within the interval of the examined solution ionic strength and ionic strength fraction of the electrolyte being $y = 0.5$, we obtained the data presented in Figure 5a, where we described the influence of the entire interactions by only pairs, or triplets, or quads. According to the standard deviations shown in Table 3, the lowest values for both osmotic and mean ionic activity coefficient values were achieved when only pairs of interactions or both, pairs and triplets were included. Despite these low standard deviations, it is clear that departures from ideality cannot be described exclusively by one form of interactions, when compared to excess free energy estimated using all six parameters obtained in treatment of data. As a result, if we depict the total departure of the solution from ideality purely by interactions of pairs or triplets or quads, we can observe that the excess free energy values are substantially greater overall, as shown in Figure 5a.

The fractions of excess free energy attributed to the various contributions of the interactions to the total free energy of the solution are shown in Figure 5b as a function of ionic strength, where the fraction of ionic strength of the electrolyte is $y = 0.5$. According to the data from this figure, in the less concentrated region, there is the possibility of the formation of solvent-involved ion pairs with an association constant much larger than the formation constant for dimers, most likely due to AEHB. Nevertheless, the structure of the solution seems to change and the shift in the nature of the interactions from pairs to triplets is evident at ionic strengths as high as 0.5 mol kg^{-1}. According to previous studies by Preston and Adams[31] and even Childs et al.,[11] the formation of polymers in this solution can be predicted at increasing concentrations. At low ionic strength, the fraction of quads is insignificant, but in highly concentrated solutions it increases to some extent. It is interesting to observe how, as the concentration of the solution increases, the fraction of triplets gradually decreases, while the influence of quads becomes more and more evident.
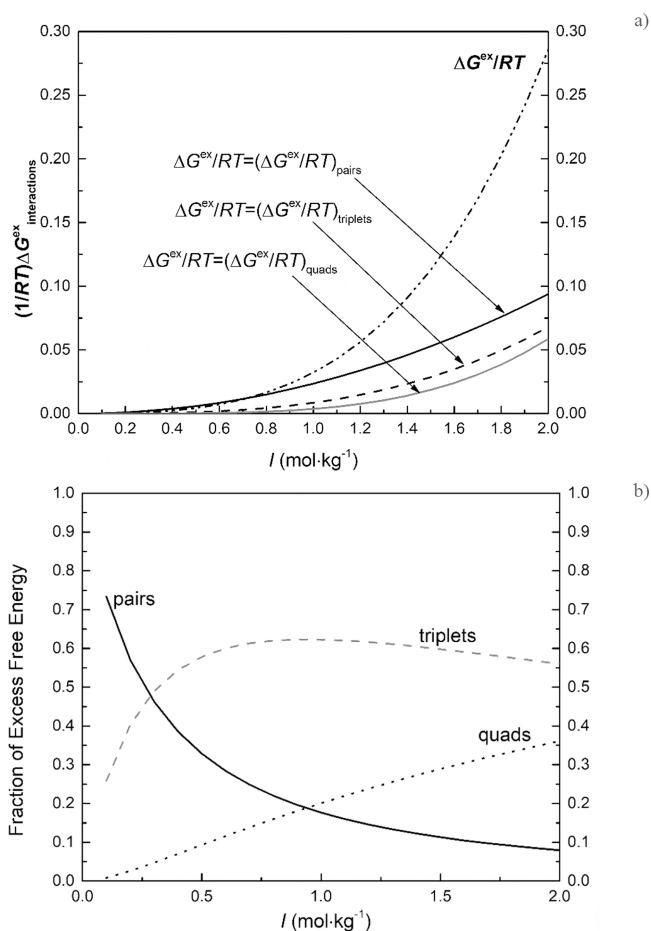

Figure 5. Excess free energy, $(\Delta G_m^{ex}/RT)_{interactions}$ of the $\{yKCl + (1 − y)KH_2PO_4\}(aq)$ system vs ionic strength at $T = 298.15$ K for the ionic strength fraction of electrolyte $y = 0.5$: (a) Excess free energy: solid curve − originating from pairs only, $(\Delta G_m^{ex}/RT) = (\Delta G_m^{ex}/RT)_{pairs}$, calculated using value b_{01} $(m^{\theta}) = 9.38 \cdot 10^{-2}$; dashed curve-originating from triplets only, $(\Delta G_m^{ex}/RT) = (\Delta G_m^{ex}/RT)_{triplets}$ calculated using value b_{02} $(m^{\theta}) = 6.79 \cdot 10^{-2}$; and $b_{12} \cdot (m^{\theta}) = 1.54 \cdot 10^{-2}$; dotted curve − originating from quads only $(\Delta G_m^{ex}/RT) = (\Delta G_m^{ex}/RT)_{quads}$ calculated using value $b_{03} \cdot (m^{\theta}) = 4.39 \cdot 10^{-2}$; $b_{13} \cdot (m^{\theta}) = 1.51 \cdot 10^{-2}$, and $b_{23} \cdot (m^{\theta}) = 1.09 \cdot 10^{-2}$; dot-dash curve-total $(\Delta G_m^{ex}/RT)$; (b) excess free energy fractions from various forms of interactions to total excess free energy of the solution against ionic strength of the $\{yKCl + (1 − y)KH_2PO_4\}(aq)$ system at $T = 298.15$ K for electrolyte ionic strength fraction $y = 0.5$: solid line—fraction of pairs, dashed line—fraction of triplets, and dotted line—fraction of quads.

Figure 6 shows the values of excess Gibbs energy of the studied solution as a function of the ionic strength fraction of the electrolyte when the total ionic strength is increased by 0.5 mol kg^{-1}. The curves show maxima that shift toward higher relative KCl concentrations with increasing total ionic strength. These high values of excess Gibbs energy are in good agreement with the results obtained in the work of Childs et al.[11]

5. CONCLUSIONS

The mean ionic activity coefficients of KCl in the system $\{yKCl + (1 − y)\, KH_2PO_4\}(aq)$ were determined with a cation-selective electrode in the ionic strength range from 0.1 to 1.0 mol kg^{-1} at temperature $T = 298.15$ K. For the mixed electrolyte solution, the models of Pitzer, Scatchard, and Clegg−Pitzer−Brimblecombe were used to treat the experimental data. Excellent agreement was found between the experimental and calculated
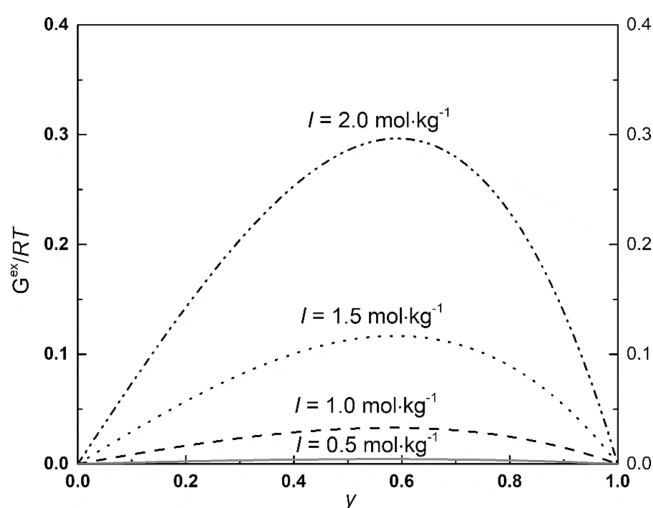
Figure 6. Excess Gibbs energy of mixing, G^{ex}/RT, obtained by the optimized Scatchard's parameters from Table 3, vs ionic strength fraction of electrolyte at a different ionic strength of the $\{yKCl + (1 - y)KH_2PO_4\}(aq)$ system at $T = 298.15$ K.

values of thermodynamic properties, with a standard deviation of fit on the order of 10^{-3}. To generate a set of parameters that can be used in a wide range of ionic strengths of the mixed solution, the model parameters were fitted to all experimental data of cell potential and isopiestic measurements from the literature. The three models are comparable in terms of reliability based on their standard uncertainties. After analyzing the possible contributions to the excess Gibbs energy of mixing by pairs, triplets, or quads using optimized Scatchard's mixing parameters obtained from the treatment of EMF and isopiestic data, one can only assume that (a) $H_2PO_4^-$ (aq) ions can associate to form dimers or even polymers; (b) deviations from ideality cannot be described exclusively by one type of interaction; (c) the shift in the type of interactions from pairs to triplets emerges around 0.5 mol kg^{-1}; and (d) the fraction of quads is negligible, but increases to some extent in highly concentrated solutions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jced.2c00704.

Experimental data on mean ionic activity coefficients of KCl in the system $\{yKCl + (1 - y)KH_2PO_4\}(aq)$ at $T = 298.15 \pm 0.01$ K; the calculated KCl and KH$_2$PO$_4$ mean ionic activity coefficients and osmotic coefficients for the $\{yKCl + (1 - y) KH_2PO_4\}(aq)$ system at $T = 298.15$ K up to $I_m = 2$ mol·kg^{-1}; model parameters for binary data; and optimized mixed parameters (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

Notes

The authors declare no competing financial interest.

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