Influence of Hydrolysis on the Osmotic Coefficients of the System $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) at Temperature 298.15 K[†]

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Isopiestic vapor pressure measurements were made for $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) solutions with $\mathrm{ZnCl_2}$ ionic strength fractions of $y = (0.2640, 0.5042, 0.7533, \text{and } 1)$ at the temperature 298.15 K, using KCl(aq) as the reference standard. To investigate the influence of hydrolysis on the osmotic coefficients of $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq), the $\mathrm{ZnCl_2}$(aq) stock solution was prepared without acidification and supression of hydrolysis. Thus obtained osmotic coefficients of the system $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) at the temperature 298.15 K were compared with the previously published results of the isopiestic measurements for the same system with $\mathrm{ZnCl_2}$(aq) stock solution that was acidified to avoid precipitation of zinc hydroxide or a hydrous oxy-chloride or hydroxy-chloride, upon dilution. This way the effects of hydrolysis on the osmotic coefficient values for the system $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) could be compared and analyzed.

Introduction

In aqueous solutions, metal ions interact with water molecules forming aqua complexes, usually tetrahedral $[\mathrm{M(H_2O)_4}]^{n+}$ or octahedral $[\mathrm{M(H_2O)_6}]^{n+}$ species. The metal ion−water interactions involve appreciable polarization of the water molecules resulting in the electron-charge clouds of the aqua ligands being attracted toward the metal ion. In turn, there is impoverishment of electron density on the hydrogen atoms, and the metal aqua ion behaves as a Brønsted-Lowry acid.[1] Therefore, dissociation of these complex ions can be expressed by

$$[\mathrm{M(H_2O)_4}]^{n+} + \mathrm{H_2O} = [\mathrm{M(H_2O)_3(OH)}]^{(n-1)+} + \mathrm{H_3O^+} \tag{1}$$

or

$$[\mathrm{M(H_2O)_6}]^{n+} + \mathrm{H_2O} = [\mathrm{M(H_2O)_5(OH)}]^{(n-1)+} + \mathrm{H_3O^+} \tag{2}$$

From that point of view, one interesting electrolyte system is aqueous $\mathrm{ZnCl_2}$ and its mixtures. Even some commercial $\mathrm{ZnCl_2}$ is pH-deficient and can undergo hydrolytic precipitation upon dilution.[2] If aqueous $\mathrm{ZnCl_2}$ solutions are not sufficiently acidic, they form a white precipitate upon dilution. This solid is either zinc hydroxide or a hydrous oxy-chloride or hydroxy-chloride. Apparently, even different allegedly high purity samples of hydrated $\mathrm{ZnCl_2}$ are showing hydrolytic precipitation. Concentrated solutions of these materials are clear, but when they were diluted to lower concentrations, copious amounts of white solid precipitate out. In general, methods[2] for the stabilization of aqueous $\mathrm{ZnCl_2}$ assume acidification of the solution with HCl(aq) until dilution of it no longer gives precipitation, involving determination of the pH of $\mathrm{ZnCl_2}$ solution samples that have the correct stoichiometric 2:1 ratio of chloride-to-zinc or modification of these methods including acidification with sufficiently concentrated HCl(aq) then heating of the solution overnight at around 335 K, rechecking for precipitation, and repeating the same procedure until dilution of a sample does not give hydrolytic precipitation even after 1 to 2 days.

On the other hand, aqueous $\mathrm{ZnCl_2}$ has been recognized to exhibit very peculiar behavior, for example: at temperature 298.15 K it acts as a strong electrolyte up to about (0.1 to 0.2) $\mathrm{mol \cdot kg^{-1}}$ but then rapidly becomes more complexed as the concentration increases.[3] This increase in complex formation does not appear gradually but above $\approx 2\ \mathrm{mol \cdot kg^{-1}}$ $\mathrm{ZnCl_2}$ has negative cationic transport numbers, which indicates the presence of negatively charged chlorozinc complexes.[4]

Aqueous $\mathrm{ZnCl_2}$ is interesting also from the point of zinc-chlorine batteries that gave good results in load leveling for electrical energy, although they are no longer extensively used.[5] In addition, thermodynamic data for $\mathrm{ZnSO_4}$(aq), $\mathrm{ZnCl_2}$(aq), and their mixtures are required for a quantitative understanding of the hydrometallurgical extraction of zinc from its ores and for predicting the voltage of several important cells and batteries under various operating conditions.

This paper gives the results of the isopiestic measurements for $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) at $T = 298.15$ K. To investigate the influence of hydrolysis on the osmotic coefficients of this system, the stock solution of $\mathrm{ZnCl_2}$(aq) was prepared without acidification of the solution with HCl(aq). This way the solutions $\mathrm{ZnCl_2} + \mathrm{H_2O}$ and $\mathrm{ZnCl_2} + \mathrm{ZnSO_4} + \mathrm{H_2O}$ exhibit hydrolysis that influenced the results for the osmotic coefficient values. To examine the effects of hydrolysis, these results were compared with the previously published osmotic coefficients[6] of $\{y\mathrm{ZnCl_2} + (1 - y)\ \mathrm{ZnSO_4}\}$(aq) solutions, prepared with the stock solution $\mathrm{ZnCl_2}$(aq) that was acidified up to the correct stoichiometric 2:1 ratio of chloride-to-zinc. The conditions of conducting the isopiestic measurements were the same in both papers: this study and the paper of Ninković et al.[6]

Experimental

The isopiestic apparatus and experimental procedure used in this work are essentially the same as previously described.[6,7]

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Table 1. Isopiestic Molalities of the Reference Solution KCl(aq), m_R, the Isopiestic Product, $\nu_R m_R \phi_R$, the Total Isopiestic Ionic Strength of the {yZnCl$_2$ + (1 − y)ZnSO$_4$}(aq) Solutions (Prepared with Nonacidified ZnCl$_2$(aq) Stock Solution), I, and the "Stoichiometric" Osmotic Coefficients (i.e., those Calculated Assuming Complete Dissociation), ϕ, of {yZnCl$_2$ + (1 − y)ZnSO$_4$}(aq) at 298.15 K Along with the Ionic Strength Fraction y of ZnCl$_2$

m_R / mol·kg^{-1}	$\nu_R m_R \phi_R$	I / mol·kg^{-1}	ϕ	I / mol·kg^{-1}	ϕ	I / mol·kg^{-1}	ϕ	I / mol·kg^{-1}	ϕ
		$y = 1.0$		$y = 0.7533$		$y = 0.5042$		$y = 0.2640$	
0.8860 ± 0.0010	1.5920	1.9818	0.8033	2.3224	0.7819	2.9060	0.7325	3.6882	0.6830
1.1025 ± 0.0020	1.9847	2.5275	0.7852	2.9204	0.7752	3.5848	0.7403	4.4663	0.7031
1.2024 ± 0.0009	2.1673	2.7843	0.7784	3.1963	0.7735	3.8916	0.7446	4.8033	0.7139
1.3327 ± 0.0004	2.4069	3.1185	0.7718	3.5506	0.7733	4.2690	0.7539	5.2274	0.7285
1.4592 ± 0.0007	2.6411	3.4509	0.7653	3.8987	0.7727	4.6473	0.7599	5.6300	0.7422
1.5238 ± 0.0004	2.7613	3.6201	0.7628	4.0750	0.7730	4.8308	0.7643	5.8275	0.7497
1.5913 ± 0.0003	2.8874	3.7929	0.7613	4.2562	0.7739	5.0295	0.7676	6.0299	0.7576
1.8577 ± 0.0004	3.3900	4.4862	0.7557	4.9826	0.7761	5.8000	0.7815	6.8194	0.7866
1.9355 ± 0.0004	3.5383	4.6851	0.7552	5.1898	0.7777	6.0069	0.7876	7.0377	0.7955
1.9982 ± 0.0003	3.6583	4.8432	0.7553	5.3559	0.7791	6.1784	0.7917	7.2131	0.8025
2.1185 ± 0.0003	3.8898	5.1456	0.7559	5.6724	0.7822	6.5126	0.7986	7.5468	0.8155
2.3936 ± 0.0002	4.4257	5.8269	0.7595	6.3773	0.7916	7.2560	0.8155		
2.5485 ± 0.0005	4.7314	6.1977	0.7634	6.7778	0.7963	7.6601	0.8259		
2.6616 ± 0.0004	4.9565	6.4623	0.7670	7.0354	0.8036	7.9410	0.8346		
2.6855 ± 0.0040	5.0043	6.4071	0.7811[a]	6.9887	0.8168[a]				
2.7116 ± 0.0010	5.0565	6.5754	0.7690	7.1547	0.8062	8.0624	0.8386		

[a] Rejected points in the evaluation of polynomial coefficients (eq 5).

Table 2. Polynomial Coefficients Obtained by Fitting the Osmotic Coefficient Values for the {yZnCl$_2$ + (1 − y)ZnSO$_4$}(aq) Solutions Prepared with Nonacidified ZnCl$_2$(aq) Stock Solution, the Ionic Strength Fraction of the ZnCl$_2$, y, and Standard Deviation of the Fit, s

	$y = 0.2640$	$y = 0.5042$	$y = 0.7533$	$y = 1.00$
p_0	0.58801	0.6785	0.82978	0.93118
p_1	0.058543	0.031139	−0.46061	−0.11231
p_2			0.010458	0.021968
p_3			−0.00045362	−0.0012082
s	0.00076	0.00170	0.00045	0.00025

Duplicate samples of each of the mixed electrolyte solutions, the KCl(aq) reference solution, and the single salt solutions ZnSO$_4$(aq) and ZnCl$_2$(aq) were equilibrated at temperature (298.15 ± 0.01) K for appropriate times that ranged between (3 and 28) days, with the longer times being required at lower molalities. The molalities of duplicate pairs of solutions at isopiestic equilibrium agreed to ± 4·10^{-3} mol·kg^{-1} or better, with the average molality being accepted for each pair of solution samples. Buoyancy corrections were made for all weightings.

The stock solution of ZnSO$_4$(aq) was prepared from ZnSO$_4$·7H$_2$O (Sigma−Aldrich suprapure grade chemicals, mass fraction 0.99999) and double-distilled, deionized water. The molality of ZnSO$_4$(aq) was determined by several methods: (1) gravimetrically by (NH$_4$)$_2$HPO$_4$ when Zn was precipitated as ZnNH$_4$PO$_4$ and then calcined at T = (1173 to 1273) K to form Zn$_2$P$_2$O$_7$,[8] (2) volumetrically, with EDTA, at pH 9 to 10, with eriochrome T as indicator, and (3) from the masses of anhydrous ZnSO$_4$ obtained after dehydration of stock solution aliquots, followed by heating the residues at T = (673 to 723) K. The average molality of ZnSO$_4$(aq) on three samples was determined in each method. The results from all of these analyses were (1.6299 ± 0.0020) mol·kg^{-1}. The assumed molar masses are 161.4526 g·mol^{-1} for ZnSO$_4$ and 304.7233 g·mol^{-1} for Zn$_2$P$_2$O$_7$.

The reference solution KCl(aq) was prepared from KCl (Sigma−Aldrich suprapure grade chemicals, mass fraction 0.9999) and double-distilled, deionized water. The molality of KCl(aq) was checked by dehydration of six samples by heating between T = (523 and 573) K. The average molality was (3.8859 ± 0.0006) mol·kg^{-1}.

The ZnCl$_2$(aq) stock solution was prepared from Sigma-Aldrich suprapure grade ZnCl$_2$ (reported mass fraction 0.99999) and double-distilled, deionized water (the ZnCl$_2$ was of the same quality and purity as the one used in the paper of Ninković et al.[6]). The concentrated stock solution was clear, not showing any amounts of white solid precipitate upon preparation. The molality of the ZnCl$_2$(aq) stock solution was determined gravimetrically as Zn$_2$P$_2$O$_7$ by the same procedure as described above for ZnSO$_4$(aq). The average ZnCl$_2$(aq) molality from these analyses is (2.9522 ± 0.0030) mol·kg^{-1}, assuming the molar mass of ZnCl$_2$ to be 136.2960 g·mol^{-1}.

The three mixed ZnCl$_2$ + ZnSO$_4$ + H$_2$O stock solutions were prepared by mixing known masses of the ZnCl$_2$(aq) and ZnSO$_4$(aq) stock solutions. The mixed solutions (except the solution with the smalest fraction of ZnCl$_2$ in the total salt mass) and the solution of ZnCl$_2$(aq) did show a small, almost undetectable, amount of white precipitate at lower molalities, when the measurements were ended.

Osmotic coefficients of the {yZnCl$_2$ + (1 − y)ZnSO$_4$}(aq) solutions at 298.15 K were calculated from the isopiestic molalities using the fundamental equation for isopiestic equilibrium

$$\phi = \nu_R m_R \phi_R / \sum_i \nu(i) m_i = \nu_R m_R \phi_R / \{0.5(1 + y)I\} \qquad (3)$$

$$y = 3m_1/I = 3m_1/(3m_1 + 4m_2) \qquad (4)$$

where $\nu(i)$ is the stoichiometric ionization number of the electrolyte i {$\nu(1) = 3$ for ZnCl$_2$ and $\nu(2) = 2$ for ZnSO$_4$}; m_i is the molality of electrolyte i; y is the ionic strength fraction of ZnCl$_2$; I is the total ionic strength of the solution; m_1 is the stoichiometric molality of ZnCl$_2$ and m_2 is the stoichiometric molality of ZnSO$_4$; and ϕ is the osmotic coefficient of the mixed electrolyte solution based on the use of stoichiometric molalities and ionization numbers. Corresponding quantities for the isopiestic reference standard KCl(aq) are denoted with a subscript R. The osmotic coefficient of each KCl(aq) reference solution at 298.15 K was calculated using the ion-interaction (Pitzer) model and parameters reported by Archer,[9] the same way the osmotic coefficients of the {yZnCl$_2$ + (1 − y)ZnSO$_4$}(aq) solutions were obtained in the paper of Ninković et al.[6] for the sake of comparison.

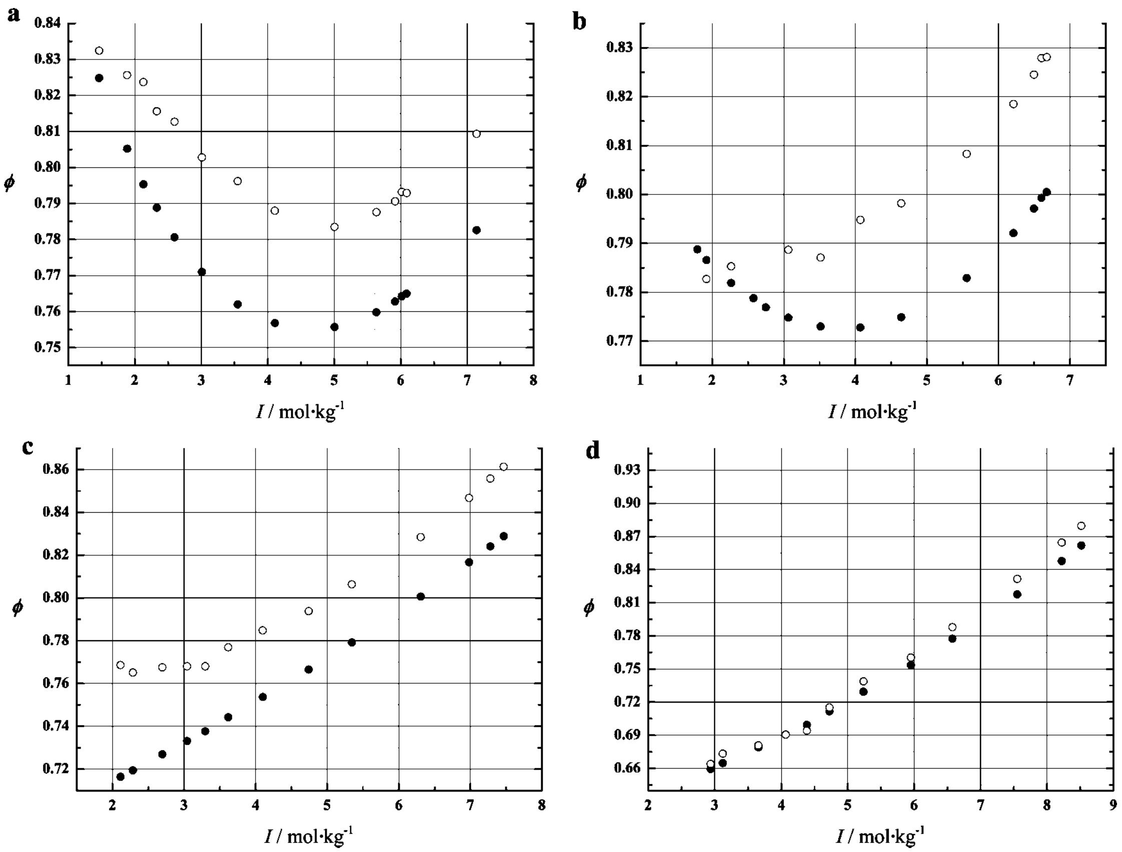

Figure 1. Osmotic coefficients of $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) at $T = 298.15$ K vs ionic strength, I, for different ionic strength fractions of $\mathrm{ZnCl_2}$: (a) $y = 1.0$; (b) $y \approx 0.75$; (c) $y \approx 0.50$; and (d) $y \approx 0.25$. ○, experimental values of the osmotic coefficients taken from the paper of Ninković et al.[6] (ϕ(NH)); ●, estimated values of the osmotic coefficients calculated by polynomial coefficients reported in Table 2 (ϕ(H)).

Table 3. Values of Isopiestic Product, $\nu_R m_R \phi_R$, Isopiestic Ionic Strengths of the $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) Solutions at $T = 298.15$ K, I, Taken from the Paper of Ninkovic′ et al.,[6] and Estimated Values of the Osmotic Coefficients of the $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) Solutions that Undergo Hydrolysis, Using Polynomial Coefficients from Table 2, ϕ(H)

$\nu_R m_R \phi_R$	ϕ(H)	$\frac{I}{\mathrm{mol \cdot kg^{-1}}}$	ϕ(H)	$\frac{I}{\mathrm{mol \cdot kg^{-1}}}$	ϕ(H)	$\frac{I}{\mathrm{mol \cdot kg^{-1}}}$	ϕ(H)	$\frac{I}{\mathrm{mol \cdot kg^{-1}}}$
	$y = 1.0$		$y \approx 0.75$		$y \approx 0.5$		$y \approx 0.25$	
1.2186	0.8248	1.4640	0.7888	1.7934	0.7164	2.1117	0.6594	2.9395
1.3125			0.7866	1.9202	0.7194	2.2848	0.6648	3.1220
1.5540	0.8052	1.8828	0.7819	2.2665	0.7269	2.6967	0.6790	3.6561
1.7539	0.7953	2.1294	0.7788	2.5765	0.7331	3.0415	0.6907	4.0683
1.9002	0.7888	2.3298	0.7769	2.7501	0.7377	3.2954	0.6993	4.3849
2.1104	0.7806	2.5968	0.7748	3.0640	0.7442	3.6179	0.7116	4.7258
2.4156	0.7710	3.0090	0.7730	3.5147	0.7537	4.0998	0.7294	5.2370
2.8253	0.7620	3.5484	0.7728	4.0708	0.7665	4.7406	0.7534	5.9518
3.2356	0.7568	4.1061	0.7749	4.6422	0.7792	5.3455	0.7774	6.5775
3.9223	0.7557	5.0061	0.7829	5.5573	0.8006	6.3068	0.8176	7.5541
4.4382	0.7598	5.6355	0.7921	6.2094	0.8167	6.9819	0.8478	8.2223
4.6770	0.7628	5.9157	0.7971	6.4961	0.8241	7.2790	0.8618	8.5160
4.7725	0.7642	6.0168	0.7993	6.6018				
4.8279	0.7650	6.0894	0.8005	6.6761	0.8288	7.4665		
5.7800	0.7826	7.1421						

Results and Discussion

The experimental results of isopiestic measurements are given in Table 1. Quantities reported are: the isopiestic molalities of the reference solution KCl(aq), m_R; the isopiestic product, $\nu_R m_R \phi_R$; the total isopiestic ionic strength of the $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) solutions; and the "stoichiometric" osmotic coefficients (i.e., those calculated assuming complete dissociation), ϕ, of $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) at 298.15 K along with the ionic strength fraction y of $\mathrm{ZnCl_2}$.

The way to treat the isopiestic results of the $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) solutions, from this study, to determine the effects of hydrolysis on the osmotic coefficients was to compare with the results of the osmotic coefficients obtained for the same system, under the same conditions except that the latter hydrolysis was suppressed by the addition of a sufficient amount of HCl(aq) in the $\mathrm{ZnCl_2}$(aq) stock solution prior to isopiestic measurements.[6]

The osmotic coefficients of the $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) solutions obtained in this study (Table 1) were fitted by the polynomials $p(x)$ where x is the isopiestic product $\nu_R m_R \phi_R$ (eq 5) by least-squares, for different ionic strength fractions of $\mathrm{ZnCl_2}$, $y = (0.2640, 0.5042, 0.7533, \text{and } 1)$.

$$\phi = p(\nu_R m_R \phi_R) = p(x) = p_0 + p_1 x + p_2 x^2 + p_3 x^3 \qquad (5)$$

The values of polynomial coefficients obtained by fitting the osmotic coefficient values for the $\{y\mathrm{ZnCl_2} + (1-y)\mathrm{ZnSO_4}\}$(aq) solutions prepared with nonacidified $ZnCl_2$(aq) stock solution, ionic strength fraction of the $ZnCl_2$ in the total ionic strength of the solutions, and standard deviation of the fit are given in Table 2.

To compare the results of the investigated system in which the hydrolysis was present with the results of the same system where the hydrolysis was suppressed, for the values of $\nu_R m_R \phi_R$ from the isopiestic measurements for $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) solutions with acidified $ZnCl_2$(aq) reported in the paper of Ninković et al.[6] (see Table 1, page 412 of this paper) using polynomial coefficients from Table 2 for approximately the same ionic strength fractions of $ZnCl_2$, $y = (0.2487, 0.5016, 0.7464, \text{and } 1.0)$, the estimation of the osmotic coefficients of the solutions that undergo hydrolysis can be obtained. The results of estimation of the osmotic coefficients, ϕ(H), calculated with polynomial coefficients from Table 2 for reported values of $\nu_R m_R \phi_R$ from the paper of Ninković et al.[6] are given in Table 3.

The comparison of the reported osmotic coefficients from the paper of Ninković et al.,[6] ϕ(NH), and estimated values from this paper, ϕ(H), for different ionic strength fractions of $ZnCl_2$, y, are given in Figure 1. From Figure 1, it is obvious that the estimated values of the osmotic coefficients of the $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) solutions that undergo hydrolysis are lower compared to the experimental results from the paper of Ninković et al.,[6] where the hydrolysis was supressed. Obviously, as the osmotic coefficient is a colligative property, the larger the particles are, due to hydrolysis, their overall presence in the solution volume is lowered and so are the osmotic coefficient values. The differences between the osmotic coefficients of acidified and nonacidified solutions gradually decrease with the ionic strength fraction of $ZnCl_2$: they are largest at $y = 1.0$ and minor at $y \approx 0.25$.

Furthermore, the major differences appeared in the ionic strength range $I = (3 \text{ to } 6)\ \mathrm{mol \cdot kg^{-1}}$, for the ionic strength fractions of $ZnCl_2$ $y = (0.75 \text{ and } 1.0)$ where hydrolysis has influenced the most. There is a question of hydration number of metal ions that decreases with the ionic strength, and this decrease, presumably, is partially due to the onset of water sharing between ions when there is insufficient water present to independently fulfill the hydration requirements of the individual ions, implying that the zinc ion does not have a stable or well-defined hydration number. Ohtaki and Radnai[10] have reviewed various diffraction methods in detail and compared these results to various types of computer simulations. In the dilute solution region of $ZnCl_2$(aq) (and presumably in its aqueous mixtures with other electrolytes), according to these authors, Zn^{2+} has six water molecules in the inner coordination sphere and therefore a hydration number of 6. However, at the ionic strength of approximately 3 $\mathrm{mol \cdot kg^{-1}}$, when the aqua complex is releasing the water molecules from the outer coordination sphere, the hydration number of Zn^{2+} in $ZnCl_2$(aq) solutions is reduced to 5.7. On the other hand, the hydration number of Zn^{2+} in $ZnSO_4$(aq) solutions according to the same authors[10] is 6 for the ionic strength range $I = (12.2 \text{ to } 13.2)\ \mathrm{mol \cdot kg^{-1}}$. The obvious influence of SO_4^{2-} ions from the $ZnSO_4$(aq) as a mixture constituent has reflected the differences between estimated and experimental osmotic coefficients even at higher ionic strengths of the solutions.

The overall influence of hydrolysis on the osmotic coefficients for the system $\{y\mathrm{ZnCl_2} + (1-y)\mathrm{ZnSO_4}\}$(aq) can be seen from Figure 2 where the ratio $[\phi(\mathrm{NH}) - \phi(\mathrm{H})]/\phi(\mathrm{NH})$ vs ionic strength fraction of $ZnCl_2$ for different total ionic strengths of the solutions is given. The smallest differences between ϕ(NH) and ϕ(H) appear for the $ZnCl_2$ ionic strength fraction of $y \approx 0.25$, and by increasing the fraction y, the differences between osmotic coefficients increase as well. The maximal differences are at $y \approx 0.5$ at the total ionic strength of the solution $I = 3\ \mathrm{mol \cdot kg^{-1}}$ and are reducing with the ionic strength increase and vice versa at $y \approx 0.75$. For the $ZnCl_2$(aq) in the ionic strength range of the solution $I = (3 \text{ to } 6)\ \mathrm{mol \cdot kg^{-1}}$, the ratio $[\phi(\mathrm{NH}) - \phi(\mathrm{H})]/\phi(\mathrm{NH})$ is approximately of the same size.

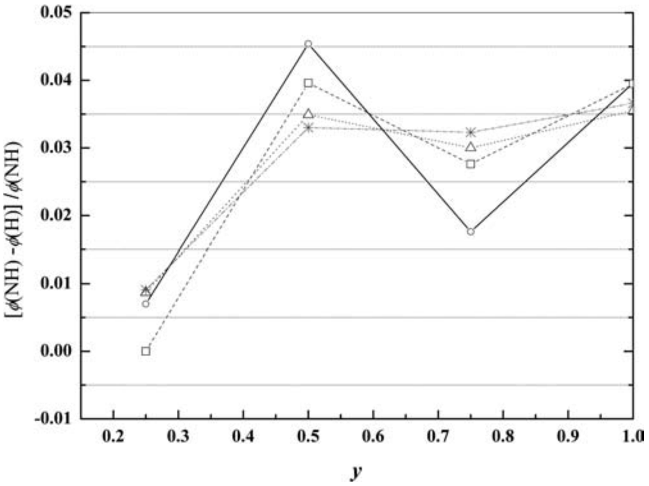

Figure 2. Ratio $[\phi(\mathrm{NH}) - \phi(\mathrm{H})]/\phi(\mathrm{NH})$ vs ionic strength fraction of $ZnCl_2$, y, for different ionic strengths of the solution $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) at $T = 298.15$ K and $I = (3.0, 4.0, 5.0, \text{and } 6.0)\ \mathrm{mol \cdot kg^{-1}}$. ϕ(NH), osmotic coefficients of the system reported by Ninković et al.;[6] ϕ(H), estimated values of the osmotic coefficients from this paper for the solutions that undergo hydrolysis; ○, $I/\mathrm{mol \cdot kg^{-1}} = 3.0$; □, $I/\mathrm{mol \cdot kg^{-1}} = 4.0$; △, $I/\mathrm{mol \cdot kg^{-1}} = 5.0$; *, $I/\mathrm{mol \cdot kg^{-1}} = 6.0$.

By comparison of the results about the influence of hydrolysis on the osmotic coefficient values for the $\{y\mathrm{ZnCl_2} + (1 - y)\mathrm{ZnSO_4}\}$(aq) solutions, it can be concluded that with the decrease of ionic strength fraction of $ZnCl_2$ in the mixed solutions the influence of hydrolysis on the osmotic coefficients is diminishing and the change in solution structure appears at an ionic strength fraction of $ZnCl_2$ $y \approx (0.5 \text{ and } 0.75)$. Apparently, the addition of the $ZnSO_4$(aq) in the system reduces the effects of hydrolysis due to the presence of large SO_4^{2-} ions. Of course, there is always a question of competing interactions among $Zn^{2+}{-}Cl^-$ and $Zn^{2+}{-}H_2O$.

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