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Thermodynamic Properties on Quaternary Aqueous Solutions of Chlorides Charge-Type 1−1*1−1*1−1, With (Na^+; K^+; Li^+; NH_4^+)

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The experimental data of quaternary aqueous solutions of chlorides charge-type 1−1*1−1*1−1 with a cation (Na^+; K^+; Li^+; NH_4^+) are determined using the hygrometric method. The quaternary systems $NH_4Cl + NaCl + KCl + H_2O$, $NH_4Cl + NaCl + LiCl + H_2O$, $NH_4Cl + KCl + LiCl + H_2O$, and $NaCl + LiCl + KCl + H_2O$ have been studied at the temperature 298.15 K. The water activities are measured at total molalities from 0.60 $mol \cdot kg^{-1}$ up to saturation for different ionic strength fractions y of NH_4Cl or NaCl, $y = 0.20$, 0.50, and 0.80, and z ratio ionic strength for other solutes, with $z = 0.20$, 0.50, and 0.80 for each y. The obtained data allow the deduction of osmotic coefficients. The ionic interaction model with our approach is developed and determined the mixing ionic parameters φ and χ for quaternary systems. From these results, the mixing ionic parameters φ and χ are used to predict the solute activity coefficients in the mixtures. The results are compared with experimental data.

Introduction

The behavior of aqueous electrolyte solutions is of interest because of their importance in areas such as chemical and process engineering, marine chemistry, environment, and atmospheric process.[1−5] Free energy values species distribution, water activity, and activity and osmotic coefficients are of fundamental importance to understanding and prediction behavior in aqueous electrolyte systems. The knowledge of the properties of these mixtures allows a good comprehension of the chemical processes governing these phenomena. Thermodynamics of aqueous electrolyte solutions continues to be an area of experimental and theoretical interest.

This paper is the continuation of the research in binary, ternary, and quaternary aqueous mixtures with a common anion or cation. We have studied binary aqueous solutions charge-type 1−1[6] and ternary alkaline chlorides 1−1*1−1[7−12] with NH_4^+, Na^+, Li^+, and K^+. The main objectives are to determine thermodynamic properties for the quaternary aqueous solutions with those of alkaline metal chlorides charge-type 1−1*1−1*1−1.

In this work, the water activities of these quaternary aqueous solutions of $NH_4Cl + NaCl + KCl + H_2O$, $NH_4Cl + NaCl + LiCl + H_2O$, $NH_4Cl + KCl + LiCl + H_2O$, and $NaCl + LiCl + KCl + H_2O$ are measured using the hygrometric method at 298.15 K. These measurements were made at total molalities from 0.6 $mol \cdot kg^{-1}$ up to saturation for different ionic strength fractions y of NH_4Cl [$y = I_{NH_4Cl}/(I_{NH_4Cl} + I_{MCl} + I_{M'Cl})$] with (M, M′ = Na, K, Li) or y of NaCl [$y = I_{NaCl}/(I_{NaCl} + I_{LiCl} + I_{KCl})$] with 0.20, 0.50, and 0.80 and for z ratios of ionic strength for other solutes at each ionic strength fraction y [$z = I_{MCl}/I_{M'Cl}$] with 0.20, 0.50, and 0.80.

The osmotic coefficients were also evaluated for these solutions from the water activities.

On the basis of the ionic interaction Pitzer model, we have developed and extended this model with our approach to the quaternary electrolyte solutions. We have introduced the newly mixing ionic parameters φ and χ for quaternary aqueous systems. Then, from the experimental data, the ionic parameters φ and χ are determined and used to predict the solute activity coefficients in the mixture. The results of these quaternary alkaline chlorides are compared. Also, the ionic interaction

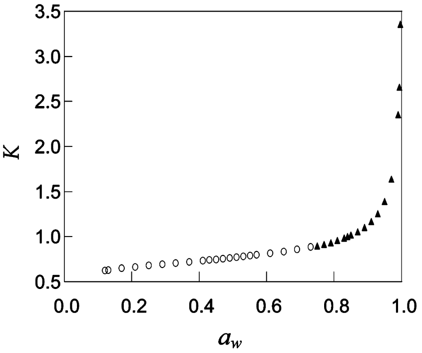

Figure 1. Variation of the ratio K of diameters of the droplets as a function of the water activity a_w for: ○, LiCl; ▲, NaCl.

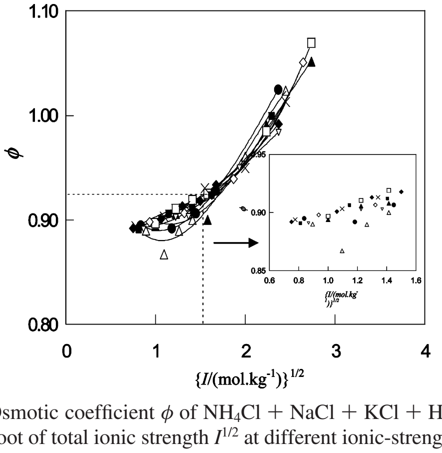

Figure 2. Osmotic coefficient ϕ of $NH_4Cl + NaCl + KCl + H_2O$, against the square root of total ionic strength $I^{1/2}$ at different ionic-strength fractions y and z of 0.20, 0.50, and 0.80. For $y = 0.20$: ▲, $z = 0.20$; □, $z = 0.50$; ◇, $z = 0.80$. $y = 0.50$: △, $z = 0.20$; ×, $z = 0.50$; ●, $z = 0.80$. $y = 0.80$: ▽, $z = 0.20$; ♦, $z = 0.50$; ■, $z = 0.80$.

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Table 1. Ratios of Growth K of the NaCl(aq) Droplets, Water Activity a_w, and Osmotic Coefficient ϕ of $NH_4Cl + NaCl + KCl + H_2O$ at Total Molalities m_t for Different Ionic-Strength Fraction y of NH_4Cl, $y = I_{NH_4Cl}/(I_{NH_4Cl} + I_{NaCl} + I_{KCl})$ with $y = 0.20$, 0.50, and 0.80, and Ratio of Ionic Strength $z = I_{NaCl}/I_{KCl}$ with $z = 0.20$, 0.50, and 0.80[a]

m_{NH_4Cl}	m_{NaCl}	m_{KCl}	m_t	K	a_w	ϕ	m_{NH_4Cl}	m_{NaCl}	m_{KCl}	m_t	K	a_w	ϕ	m_{NH_4Cl}	m_{NaCl}	m_{KCl}	m_t	K	a_w	ϕ
$y = 0.20$																				
$z = 0.20$							$z = 0.50$							$z = 0.80$						
0.27	0.18	0.30	0.75	1.740	0.9746	0.816	0.15	0.20	0.13	0.48	1.106^b	0.9848	0.816	0.27	0.48	0.20	0.95	1.162	0.9687	0.848
0.45	0.30	0.50	1.25	1.441	0.9528	0.925	0.45	0.60	0.40	1.45	1.368	0.9475	0.935	0.54	0.96	0.40	1.90	1.261	0.9309	0.979
0.72	0.48	0.80	2.00	1.192	0.9161	1.064	0.74	0.65	0.99	2.38	1.151	0.9053	1.005	0.81	1.44	0.60	2.85	1.098_8	0.8874	1.097
1.26	0.84	1.40	3.50	0.979_5	0.8265	1.210	0.90	1.20	0.80	2.90	1.074	0.8783	1.145	1.08	1.92	0.80	3.80	0.995_5	0.8374	1.217
1.62	1.08	1.80	4.50	0.900	0.7569	1.344	1.05	0.93	1.40	3.38	1.019_5	0.8511	1.157	1.35	2.40	1.00	4.75	0.928_5	0.7850	1.342
2.16	1.44	2.40	6.00	0.838^c	0.6440	1.540	1.35	1.80	1.20	4.35	0.938_5	0.7945	1.362	1.62	2.88	1.22	5.70	0.890^c	0.7280	1.469
2.52	1.68	2.80	7.00	0.800^c	0.5670	1.842	1.80	2.40	1.60	5.80	0.870^c	0.7004	1.590							
2.70	1.80	3.00	7.50	0.781^c	0.5270	2.048														
$y = 0.50$																				
$z = 0.20$							$z = 0.50$							$z = 0.80$						
0.45	0.075	0.125	0.65	1.262^b	0.9901	0.425	0.45	0.15	0.10	0.70	1.846	0.9789	0.783	0.27	0.12	0.05	0.44	1.162^b	0.9868	0.829
0.90	0.15	0.25	1.30	1.462	0.9570	0.874	0.90	0.30	0.20	1.40	1.435	0.9545	0.880	0.54	0.24	0.10	0.88	1.702	0.9731	0.816
1.80	0.30	0.50	2.60	1.150	0.9054	1.003	1.35	0.45	0.30	2.10	1.248	0.9284	0.943	1.08	0.48	0.20	1.76	1.335	0.9423	0.909
2.70	0.45	0.75	3.90	1.012_5	0.8470	1.119	2.25	0.75	0.50	3.50	1.059	0.8712	1.055	1.62	0.72	0.30	2.64	1.164	0.9091	0.977
3.60	0.60	1.00	5.20	0.932	0.7832	1.232	3.15	1.05	0.70	4.90	0.954_5	0.8084	1.162	2.16	0.96	0.40	3.52	1.065	0.8737	1.041
4.50	0.75	1.25	6.50	0.881^c	0.7163	1.339	4.50	1.50	1.00	7.00	0.876^c	0.7081	1.322	2.70	1.20	0.50	4.40	0.993_5	0.8362	1.103
														3.24	1.44	0.60	5.28	0.941_5	0.7972	1.162
														3.78	1.68	0.70	6.16	0.900_5	0.7573	1.219
														4.32	1.92	0.80	7.04	0.881^c	0.7168	1.275
$y = 0.80$																				
$z = 0.20$							$z = 0.50$							$z = 0.80$						
0.72	0.03	0.05	0.80	1.796	0.9770	0.789	0.72	0.06	0.04	0.82	1.760	0.9756	0.837	0.72	0.08	0.03	0.83	1.738	0.9745	0.865
1.44	0.06	0.10	1.60	1.398	0.9508	0.866	1.80	0.15	0.10	2.05	1.292	0.9363	0.890	1.08	0.12	0.05	1.25	1.516	0.9618	0.857
2.88	0.12	0.20	3.20	1.121	0.8962	0.948	2.88	0.24	0.16	3.28	1.115_5	0.8945	0.947	2.16	0.24	0.10	2.50	1.214	0.9216	0.911
3.60	0.15	0.25	4.00	1.051_5	0.8679	0.981	3.60	0.30	0.20	4.10	1.047_5	0.8658	0.979	3.24	0.36	0.15	3.75	1.076	0.8790	0.962
4.32	0.18	0.30	4.80	0.998	0.8390	1.011	4.68	0.39	0.26	5.33	0.973_5	0.8223	1.021	4.32	0.48	0.20	5.00	1.009_5	0.8355	1.005
5.04	0.21	0.35	5.60	0.957	0.8101	1.038	5.40	0.45	0.30	6.15	0.937_5	0.7935	1.044	5.40	0.60	0.25	6.25	0.935_5	0.7921	1.041

[a] The reference water activity is 0.84, and the reference solution is NaCl(aq). [b] Reference water activity is 0.98. [c] Reference solution is LiCl(aq).

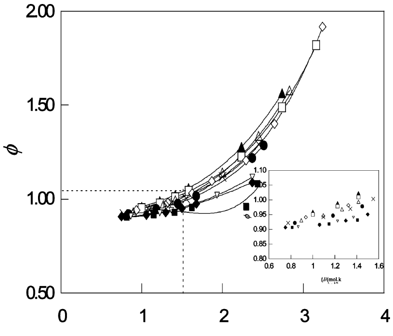

Figure 3. Osmotic coefficient ϕ of $NH_4Cl + NaCl + LiCl + H_2O$, against square root of total ionic strength $I^{1/2}$ at different ionic-strength fractions y and z of 0.20, 0.50, and 0.80. For $y = 0.20$: ▲, $z = 0.20$; □, $z = 0.50$; ◇, $z = 0.80$. $y = 0.50$: △, $z = 0.20$; ×, $z = 0.50$; ●, $z = 0.80$. y = 0.80: ▽, $z = 0.20$; ♦, $z = 0.50$; ■, $z = 0.80$.

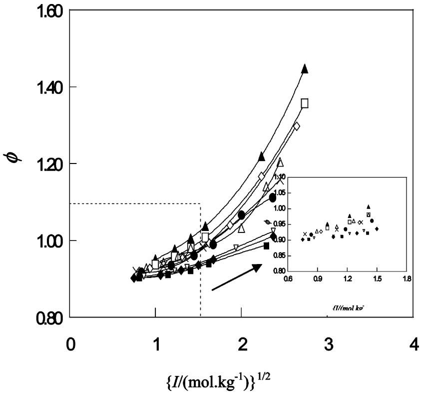

Figure 4. Osmotic coefficient ϕ of $NH_4Cl + KCl + LiCl + H_2O$ against square root of total ionic strength $I^{1/2}$ at different ionic-strength fractions y and z of 0.20, 0.50, and 0.80. For $y = 0.20$: ▲, $z = 0.20$; □, $z = 0.50$; ◇, $z = 0.80$. $y = 0.50$: △, $z = 0.20$; ×, $z = 0.50$; ●, $z = 0.80$. $y = 0.80$: ▽, $z = 0.20$; ♦, $z = 0.50$; ■, $z = 0.80$.

effects of cations in these aqueous solutions are shown. The results of these quaternary alkaline chlorides are confronted with the literature data.

Experimental Section

The water activity was determined using the hygrometric method described previously.[13,14] The apparatus consisted of a thread that was suspended over a cup. A droplet of solution was placed on the thread above the cap. The diameter of the droplet was determined with a microscope, fitted with a micrometer scale. The temperature of the hygrometer was maintained to within ± 0.02 K. The functional relation between the diameter of the droplet and water activity was determined by calibration experiments in which a suspended droplet of NaCl(aq) in the vapor phase was equilibrated with a solution of NaCl(aq) contained in the cup under the same vapor pressure. Similar calibration experiments were performed with LiCl(aq) drops and solutions. In the subsequent experiments, the solution under test was placed in the cap then equilibrated with a suspended drop of NaCl(aq) or LiCl(aq)[15−18] which served as a standard. The unknown water activity can therefore be determined from measurement of the equilibrium diameter D (a_w) at this water activity. Knowing the diameter D ($a_w = 0.84$) of this droplet at the reference water activity of 0.84, we can then calculate K and determine graphically the value of a_w (Figure 1). The values of the ratio of growth K were calculated from the equation $K = D(a_w)/D(a_{w(ref)})$ for reference NaCl(aq) and LiCl(aq). Generally, the reference water activity is 0.84. For the middle dilute solution, the reference is 0.98.

Table 2. Ratios of Growth K of the NaCl(aq) Droplets, Water Activity a_w, and Osmotic Coefficient ϕ of $NH_4Cl + NaCl + LiCl + H_2O$ at Total Molalities m_t for Different Ionic-Strength Fractions y of NH_4Cl, $y = I_{NH_4Cl}/(I_{NH_4Cl} + I_{NaCl} + I_{LiCl})$ with $y = 0.20$, 0.50, and 0.80, and Ratio of Ionic Strength $z = I_{NaCl}/I_{LiCl}$ with $z = 0.20$, 0.50, and 0.80[a]

m_{NH_4Cl}	m_{NaCl}	m_{LiCl}	m_t	K	a_w	ϕ	m_{NH_4Cl}	m_{NaCl}	m_{LiCl}	m_t	K	a_w	ϕ	m_{NH_4Cl}	m_{NaCl}	m_{LiCl}	m_t	K	a_w	ϕ
										$y = 0.20$										
			$z = 0.20$							$z = 0.50$							$z = 0.80$			
0.20	0.48	0.12	0.80	1.695	0.9727	0.960	0.20	0.20	0.40	0.80	1.700	0.9730	0.951	0.175	0.22_5	0.30	0.70	1.787	0.9765	0.941
0.30	0.72	0.18	1.20	1.475	0.9581	0.989	0.30	0.30	0.60	1.20	1.479	0.9586	0.978	0.350	0.45	0.60	1.40	1.408	0.9517	0.982
0.40	0.96	0.24	1.60	1.332	0.9427	1.023	0.40	0.40	0.80	1.60	1.336	0.9434	1.010	0.530	0.67_5	0.90	2.10	1.226	0.9247	1.034
0.50	1.20	0.30	2.00	1.238	0.9265	1.059	0.50	0.50	1.00	2.00	1.243	0.9275	1.044	0.700	0.90	1.20	2.80	1.117	0.8953	1.096
1.00	2.40	0.60	4.00	0.987	0.8313	1.278	1.50	1.50	3.00	6.00	0.887[c]	0.7249	1.488	1.400	1.80	2.40	5.60	0.907	0.7538	1.401
1.50	3.60	0.90	6.00	0.879[c]	0.7130	1.565	2.00	2.00	4.00	8.00	0.809[c]	0.5920	1.819	2.100	2.70	3.60	8.40	0.802[c]	0.5753	1.827
1.70	4.08	1.02	6.80	0.842[c]	0.6570	1.715														
										$y = 0.50$										
			$z = 0.20$							$z = 0.50$							$z = 0.80$			
0.40	0.08	0.32	0.80	1.713	0.9735	0.931	0.30	0.10	0.20	0.60	1.008[b]	0.9803	0.922	0.35	0.15	0.20	0.70	1.800	0.9777	0.922
0.60	0.12	0.48	1.20	1.492	0.9598	0.948	0.60	0.20	0.40	1.20	1.495	0.9601	0.942	0.70	0.30	0.40	1.40	1.424	0.9534	0.947
0.80	0.16	0.64	1.60	1.354	0.9457	0.968	0.90	0.30	0.60	1.80	1.308	0.9390	0.970	1.05	0.45	0.60	2.10	1.249	0.9287	0.978
1.00	0.20	0.80	2.00	1.261	0.9390	0.994	1.20	0.40	0.80	2.40	1.194	0.9169	1.003	1.40	0.60	0.80	2.80	1.139	0.9024	1.018
2.00	0.40	1.60	4.00	1.194	0.9169	1.142	3.00	1.00	2.00	6.00	0.899	0.7563	1.292	2.80	1.20	1.60	5.60	0.925	0.7816	1.221
3.00	0.60	2.40	6.00	1.022	0.8525	1.337	3.60	1.20	2.40	7.20	0.867[c]	0.6951	1.402	3.15	1.35	1.80	6.30	0.908[c]	0.7467	1.287
3.20	0.64	2.56	6.40	0.888[c]	0.7242	1.399								3.50	1.50	2.03	7.03	0.872[c]	0.7030	1.391
										$y = 0.80$										
			$z = 0.20$							$z = 0.50$							$z = 0.80$			
0.60	0.04	0.16	0.80	1.727	0.9741	0.909	0.45	0.05	0.10	0.60	1.015[b]	0.9806	0.907	0.525	0.07_5	0.10	0.70	1.810	0.9774	0.907
0.90	0.06	0.24	1.20	1.507	0.9611	0.917	0.90	0.10	0.20	1.20	1.508	0.9611	0.915	1.050	0.15	0.20	1.40	1.437	0.9547	0.919
1.20	0.08	0.32	1.60	1.383	0.9479	0.928	1.35	0.15	0.30	1.80	1.327	0.9415	0.930	1.580	0.23	0.30	2.10	1.264	0.9316	0.937
1.50	0.10	0.40	2.00	1.280	0.9344	0.941	1.80	0.20	0.40	2.40	1.211	0.9211	0.911	2.100	0.30	0.40	2.80	1.166	0.9097	0.958
3.00	0.20	0.80	4.00	0.929	0.8630	1.022	4.50	0.50	1.00	6.00	0.934	0.7902	1.089	4.200	0.60	0.80	5.60	0.975	0.8236	0.962
4.50	0.30	1.20	6.00	1.042	0.7853	1.118	5.02_5	0.30	1.37_5	6.70	0.906	0.7636	1.117	4.740	0.69	0.90	6.30	0.924	0.7810	1.089
4.92	0.32_8	1.31_2	6.56	0.903	0.7595	1.164														

[a] The reference water activity is 0.84, and the reference solution is NaCl(aq). [b] Reference water activity is 0.98. [c] Reference solution is LiCl(aq).

Table 3. Ratios of Growth K of the NaCl(aq) Droplets, Water Activity a_w, and Osmotic Coefficient ϕ of $NH_4Cl + KCl + LiCl + H_2O$ at Total Molalities m_t for Different Ionic-Strength Fractions y of NH_4Cl, $y = I_{NH_4Cl}/(I_{NH_4Cl} + I_{KCl} + I_{LiCl})$ with $y = 0.20$, 0.50, and 0.80, and Ratio of Ionic Strength $z = I_{KCl}/I_{LiCl}$ with $z = 0.20$, 0.50, and 0.80[a]

m_{NH_4Cl}	m_{KCl}	m_{LiCl}	m_t	K	a_w	ϕ	m_{NH_4Cl}	m_{KCl}	m_{LiCl}	m_t	K	a_w	ϕ	m_{NH_4Cl}	m_{KCl}	m_{LiCl}	m_t	K	a_w	ϕ
										$y = 0.20$										
			$z = 0.20$							$z = 0.50$							$z = 0.80$			
0.20	0.48	0.12	0.80	1.700	0.9730	0.951	0.20	0.20	0.40	0.80	1.707	0.9733	0.938	0.17_5	0.22_5	0.30	0.70	1.793	0.9769	0.927
0.30	0.72	0.18	1.20	1.479	0.9586	0.977	0.30	0.30	0.60	1.20	1.488	0.9594	0.958	0.35	0.45	0.60	1.40	1.419	0.9529	0.956
0.40	0.96	0.24	1.60	1.339	0.9437	1.006	0.40	0.40	0.80	1.60	1.349	0.9450	0.981	0.53	0.67_5	0.90	2.10	1.244	0.9275	0.995
0.50	1.20	0.30	2.00	1.245	0.9279	1.038	0.50	0.50	1.00	2.00	1.255	0.9299	1.008	0.70	0.90	1.20	2.80	1.133	0.9004	1.040
1.00	2.40	0.60	4.00	0.998	0.8388	1.220	1.00	1.00	2.00	4.00	1.009	0.8452	1.357	1.05	1.35	1.80	4.00	1.015	0.8484	1.141
1.30	3.12	0.78	5.20	0.918	0.7753	1.358	1.32_5	1.32_5	2.65	5.30	0.923	0.7803	1.299	1.40	1.80	2.40	5.60	0.913	0.7697	1.297
										$y = 0.50$										
			$z = 0.20$							$z = 0.50$							$z = 0.80$			
0.40	0.08	0.32	0.80	1.716	0.9736	0.928	0.30	0.10	0.20	0.60	1.006[b]	0.9803	0.919	0.35	0.15	0.20	0.70	1.797	0.9771	0.917
0.60	0.12	0.48	1.20	1.494	0.9600	0.943	0.60	0.20	0.40	1.20	1.498	0.9604	0.934	0.70	0.30	0.40	1.40	1.429	0.9539	0.935
0.80	0.16	0.64	1.60	1.357	0.9461	0.961	0.90	0.30	0.60	1.80	1.314	0.9398	0.957	1.05	0.45	0.60	2.10	1.255	0.9299	0.961
1.00	0.20	0.80	2.00	1.266	0.9318	0.980	1.20	0.40	0.80	2.40	1.200	0.9184	0.984	1.40	0.60	0.80	2.80	1.147	0.9049	0.990
2.00	0.40	1.60	4.00	1.040	0.8617	1.033	3.00	1.00	2.00	6.00	1.032	0.8577	1.158	2.80	1.20	1.60	5.60	0.944	0.7992	1.111
3.00	0.60	2.40	6.00	0.914	0.7708	1.204	3.60	1.20	2.40	7.20	0.922	0.7785	1.450							
3.10	0.62	2.48	6.20	0.903	0.7595	1.231														
										$y = 0.80$										
			$z = 0.20$							$z = 0.50$							$z = 0.80$			
0.60	0.04	0.16	0.80	1.730	0.9742	0.907	0.45	0.05	0.10	0.60	1.014[b]	0.9807	0.902	0.52_5	0.07_5	0.10	0.70	1.803	0.9775	0.903
0.90	0.06	0.24	1.20	1.510	0.9613	0.913	0.90	0.10	0.20	1.20	1.511	0.9614	0.910	1.05	0.15	0.20	1.40	1.440	0.9550	0.912
1.20	0.08	0.32	1.60	1.375	0.9483	0.921	1.35	0.15	0.30	1.80	1.328	0.9420	0.922	1.58	0.23	0.30	2.10	1.268	0.9323	0.927
1.50	0.10	0.40	2.00	1.285	0.9352	0.930	1.80	0.20	0.40	2.40	1.217	0.9223	0.936	2.10	0.30	0.40	2.80	1.165	0.9094	0.941
3.00	0.20	0.80	4.00	1.052	0.8682	0.981	2.25	0.25	0.50	3.00	0.949	0.9024	0.950	4.20	0.60	0.80	5.60	0.969	0.8194	0.987
4.29	0.28_6	1.14_4	5.72	0.955	0.8090	1.028	4.05	0.45	0.90	5.40	0.969	0.8196	1.022							

[a] The reference water activity is 0.84, and the reference solution is NaCl(aq). [b] Reference water activity is 0.98.

The solutions of NaCl, $LiCl \cdot H_2O$, NH_4Cl, and KCl, were prepared from crystalline material (extrapur-grade chemicals, mass fraction > 0.99) and deionized distilled water. The reference solutions are NaCl(aq) and LiCl(aq).

Several measurements were made of the spherical drop diameters and the mean of the results which are repeats. For one composition, five or more cups were taken, and for each cup five to six measurements were made adequately. The average diameter $(aq)_{sol}$ and diameter $(aq)_{ref}$ corresponding to each cup are used to calculate the ratio K. The average ratio K is calculated for these cups, and the ratio is represented at 4 significant digits and determined as ΔK and

Table 4. Ratios of Growth K of the NaCl(aq) Droplets, Water Activity, and Osmotic Coefficient ϕ of NaCl + LiCl + KCl + H_2O at Total Molalities m_t for Different Ionic-Strength Fractions y of NaCl, $y = I_{NaCl}/(I_{NaCl} + I_{LiCl} + I_{KCl})$ with y = 0.20, 0.50, and 0.80, and Ratio of Ionic Strength $z = I_{LiCl}/I_{KCl}$ with z = 0.20, 0.50, and 0.80[a]

m_{NaCl}	m_{KCl}	m_{LiCl}	m_t	K	a_w	ϕ	m_{NaCl}	m_{KCl}	m_{LiCl}	m_t	K	a_w	ϕ	m_{NaCl}	m_{KCl}	m_{LiCl}	m_t	K	a_w	ϕ
										$y = 0.20$										
			$z = 0.20$							$z = 0.50$							$z = 0.80$			
0.20	0.48	0.12	0.80	1.687	0.9724	0.972	0.20	0.20	0.40	0.80	1.696	0.9728	0.958	0.175	0.225	0.30	0.70	1.783	0.9765	0.943
0.30	0.72	0.18	1.20	1.464	0.9574	1.008	0.30	0.30	0.60	1.20	1.477	0.9583	0.986	0.350	0.450	0.60	1.40	1.405	0.9514	0.987
0.40	0.96	0.24	1.60	1.325	0.9414	1.048	0.40	0.40	0.80	1.60	1.334	0.9429	1.019	0.530	0.675	0.90	2.10	1.226	0.9243	1.041
0.50	1.20	0.30	2.00	1.236	0.9244	1.091	0.50	0.50	1.00	2.00	1.239	0.9268	1.055	0.700	0.900	1.20	2.80	1.117	0.8950	1.100
1.00	2.40	0.60	4.00	0.977	0.8251	1.334	1.47_5	1.47_5	2.95	5.90	0.888[b]	0.7271	1.499	1.400	1.800	2.40	5.60	0.901	0.7579	1.374
1.42_5	3.42	0.85_5	5.70	0.886[b]	0.7227	1.581														
										$y = 0.50$										
			$z = 0.20$							$z = 0.50$							$z = 0.80$			
0.40	0.08	0.32	0.80	1.693	0.9727	0.959	0.30	0.10	0.20	0.60	1.869	0.9799	0.938	0.350	0.150	0.20	0.70	1.786	0.9766	0.939
0.60	0.12	0.48	1.20	1.475	0.9581	0.989	0.60	0.20	0.40	1.20	1.480	0.9588	0.973	0.700	0.300	0.40	1.40	1.408	0.9518	0.980
0.80	0.16	0.64	1.60	1.332	0.9426	1.026	0.90	0.30	0.60	1.80	1.291	0.9362	1.017	1.050	0.450	0.60	2.10	1.230	0.9250	1.030
1.00	0.20	0.80	2.00	1.238	0.9266	1.058	1.20	0.40	0.80	2.40	1.173	0.9116	1.070	1.400	0.600	0.80	2.80	1.120	0.8960	1.088
2.00	0.40	1.60	4.00	0.989	0.8331	1.267	3.01	1.00	2.01	6.02	0.890[b]	0.7294	1.455	2.800	1.200	1.60	5.60	0.987	0.8318	1.358
3.07	0.61_4	2.45_6	6.14	0.875[b]	0.7065	1.570								3.150	1.350	1.80	6.30	0.904	0.7603	1.217
										$y = 0.80$										
			$z = 0.20$							$z = 0.50$							$z = 0.80$			
0.60	0.04	0.16	0.80	1.704	0.9732	0.944	0.45	0.05	0.10	0.60	1.001	0.9801	0.932	0.52_5	0.07_5	0.10	0.70	1.788	0.9767	0.934
0.90	0.06	0.24	1.20	1.482	0.9590	0.968	0.90	0.10	0.20	1.20	1.487	0.9593	0.962	1.05	0.15	0.20	1.40	1.413	0.9523	0.969
1.20	0.08	0.32	1.60	1.343	0.9443	0.994	1.35	0.15	0.30	1.80	1.296	0.9373	0.999	1.58	0.23	0.30	2.10	1.235	0.9261	1.015
1.50	0.10	0.40	2.00	1.250	0.9289	1.023	1.80	0.20	0.40	2.40	1.182	0.9138	1.043	2.10	0.30	0.40	2.80	1.126	0.8979	1.067
3.00	0.20	0.80	4.00	1.003	0.8417	1.196	2.25	0.25	0.50	3.00	1.040	0.8622	1.143	4.20	0.60	0.80	5.60	0.993	0.7666	1.317
4.05	0.27	1.08	5.40	0.914	0.7716	1.333	4.35	0.48	0.97	5.80	0.897	0.7530	1.358	4.74	0.69	0.90	6.30	0.909	0.8358	1.185

[a] The reference water activity is 0.84, and the reference solution is NaCl(aq). [b] Reference solution is LiCl(aq).

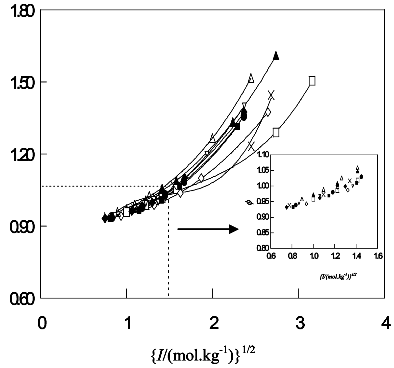

Figure 5. Osmotic coefficient ϕ of NaCl + LiCl + KCl + H_2O, against square root of total ionic strength $I^{1/2}$ at different ionic-strength fractions y and z of 0.20, 0.50, and 0.80. For y = 0.20: ▲, z = 0.20; □, z = 0.50; ◇, z = 0.80. y = 0.50: △, z = 0.20; ×, z = 0.50; ●, z = 0.80. y = 0.80: ▽, z = 0.20; ♦, z = 0.50; ■, z = 0.80.

Table 5. Pitzer Parameters for Binary Aqueous Systems[6] and Ternary Aqueous Electrolyte at 298.15 K

binary electrolyte	$\beta^{(0)}$ $(\text{kg}\cdot\text{mol}^{-1})^{-1}$	$\beta^{(1)}$ $(\text{kg}\cdot\text{mol}^{-1})^{-1}$	C^{ϕ} $(\text{kg}\cdot\text{mol}^{-1})^{-2}$
NaCl + H_2O	0.0738	0.2712	0.00167
KCl + H_2O	0.04631	0.2157	0.00003
LiCl + H_2O	0.1443	0.3191	0.00465
NH_4Cl + H_2O	0.0527	0.2011	−0.00306

ternary electrolyte	θ $(\text{kg}\cdot\text{mol}^{-1})^{-1}$	ψ $(\text{kg}\cdot\text{mol}^{-1})^{-2}$	ref
NaCl + LiCl + H_2O	0.0138	−0.0021	7
NaCl + KCl + H_2O	−0.015	0.0035	8
LiCl + KCl + H_2O	−0.0239	−0.0080	9
NH_4Cl + NaCl + H_2O	0.0159	−0.0048	10
NH_4Cl + KCl + H_2O	0.0516	−0.0085	11
NH_4Cl + LiCl + H_2O	−0.0563	0.0089	12

$\Delta K/K$ [(0.1 to 0.05) %]. For calculation of water activities, the graphs of the variation of the ratio growth of droplets were used as a function of water activity for the reference solution (NaCl or LiCl). Generally, in our study the data are given, for each cup, with four digits at low molalities and three digits at high molalities. Also, the average water activity is given and determined as a_w and $\Delta a_w/a_w$. The uncertainty in the water activity depends on the accuracy of the diameter measurements and is therefore less than ± 0.02 % for $a_w > 0.97$, ± 0.05 % for $0.97 > a_w > 0.95$, ± 0.09 % for $0.95 > a_w > 0.90$, and ± 0.2 % for $a_w < 0.90$. Also, the overall uncertainty of the osmotic coefficient is estimated to be, at most, ± 0.006.

Model

The ionic interaction Pitzer model[19−21] suggested a theory which allows the prediction of various thermodynamic properties of multicomponent electrolyte solutions, using mixing parameters calculated from the appropriate experimental data for binary, ternary, quaternary, or polyelectrolyte solutions. One of the main objectives of this paper is to suggest the best values of unknown mixing ionic parameters with our approach for the quaternary solutions to calculate the solute activity coefficient.

The ion interaction model is used to calculate thermodynamic properties of mixed-electrolyte solutions. This model requires parameters estimated from a common-ion solution to characterize binary interactions among different ions of the same sign and ternary interactions between different ions not all of the same sign in a mixed electrolyte solution. We introduce two parameters of quaternary interactions: for one it is between different cations in solution, and the other relates interaction between different cations and a common anion in solution.

The osmotic coefficient of a mixed solution of a three-salt with a common anion is given by Pitzer's model as

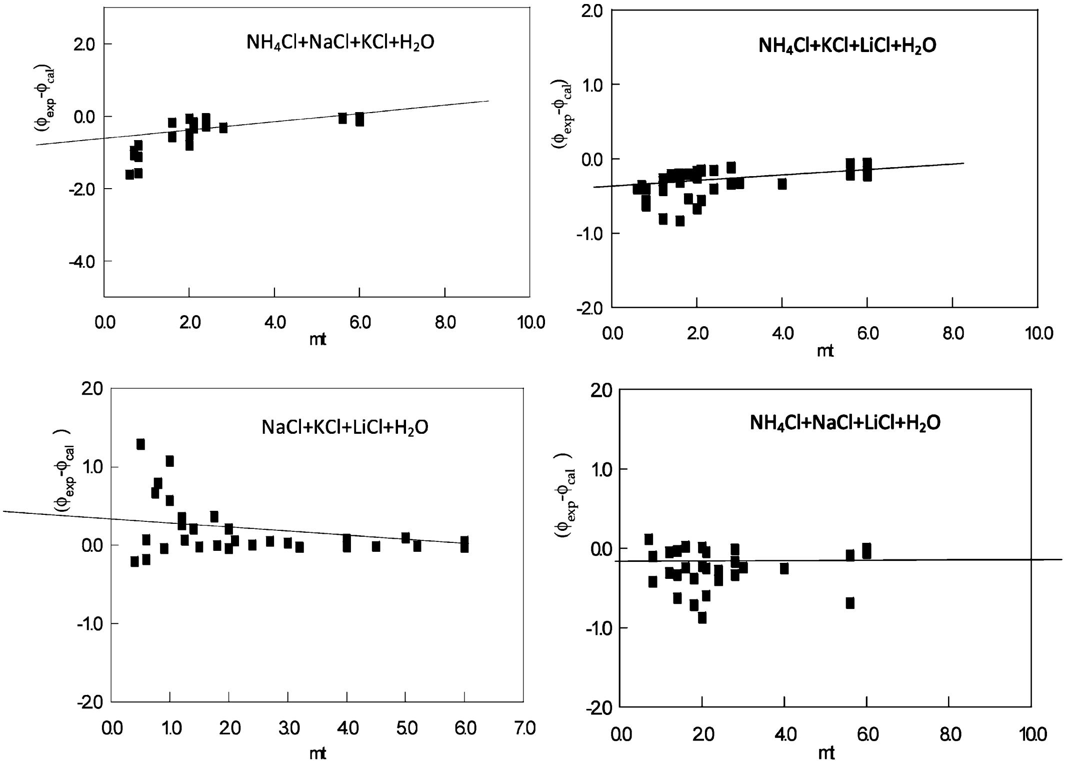

Figure 6. Plots of deviation between experimental and calculated osmotic coefficients in different quaternary systems.

Table 6. Parameters φ and χ for Quaternary Systems

quaternary systems	φ_{MNO} / $(kg \cdot mol^{-1})^{-2}$	χ_{MNOX} / $(kg \cdot mol^{-1})^{-3}$	I_{max} / $(kg \cdot mol^{-1})$	$\sigma(\phi)$
$NH_4Cl + NaCl + KCl + H_2O$	−0.5744	0.0370	0.60−6.30	0.0023
$NH_4Cl + NaCl + LiCl + H_2O$	−0.1000	0.0170	0.60−8.40	0.0004
$NH_4Cl + KCl + LiCl + H_2O$	−0.3400	0.0440	0.60−8.00	0.0001
$NaCl + KCl + LiCl + H_2O$	0.3617	−0.0470	0.60−8.40	0.0003

Table 7. Activity Coefficients γ_{NH_4Cl}, γ_{NaCl}, and γ_{KCl} in $NH_4Cl + NaCl + KCl + H_2O$ against Square Root of Total Ionic Strength $I^{1/2}$ at Different Ionic-Strength Fractions y and Ratio of Ionic Strength z of 0.20, 0.50, and 0.80

I	γ_{NH_4Cl}	γ_{NaCl}	γ_{KCl}	I	γ_{NH_4Cl}	γ_{NaCl}	γ_{KCl}	I	γ_{NH_4Cl}	γ_{NaCl}	γ_{KCl}
					$y = 0.20$						
	$z = 0.20$				$z = 0.50$				$z = 0.80$		
0.80	0.627	0.691	0.620	0.80	0.622	0.698	0.619	0.70	0.630	0.712	0.628
1.20	0.603	0.660	0.596	1.20	0.593	0.672	0.594	1.40	0.578	0.672	0.583
1.60	0.587	0.638	0.583	1.60	0.572	0.655	0.579	2.10	0.548	0.660	0.565
2.00	0.576	0.622	0.576	2.00	0.557	0.645	0.571	2.80	0.534	0.669	0.565
4.00	0.594	0.647	0.608	3.00	0.572	0.713	0.615	4.00	0.852	1.127	0.849
6.00	0.842	1.086	0.782	4.00	0.974	1.254	0.913	5.60	0.783	6.648	3.739
				6.00	3.983	4.688	2.189				
					$y = 0.50$						
	$z = 0.20$				$z = 0.50$				$z = 0.80$		
0.80	0.625	0.798	0.625	0.60	0.642	0.832	0.641	0.70	0.631	0.823	0.629
1.20	0.603	0.753	0.602	1.20	0.600	0.768	0.596	1.40	0.590	0.766	0.581
1.60	0.590	0.718	0.589	1.80	0.581	0.729	0.573	2.10	0.574	0.737	0.557
2.00	0.584	0.689	0.582	2.40	0.574	0.707	0.563	2.80	0.573	0.732	0.548
4.00	0.605	0.678	0.607	4.00	0.857	1.435	0.904	5.60	0.800	1.242	0.823
6.00	0.754	1.269	0.782	6.00	1.289	3.344	1.518	6.30	0.982	1.757	1.088
					$y = 0.80$						
	$z = 0.20$				$z = 0.50$				$z = 0.80$		
0.80	0.621	0.943	0.633	0.60	0.639	0.974	0.648	0.70	0.629	0.963	0.638
1.20	0.598	0.904	0.615	1.20	0.598	0.914	0.610	1.40	0.591	0.909	0.599
1.60	0.586	0.875	0.605	1.80	0.581	0.882	0.593	2.10	0.577	0.887	0.581
2.00	0.579	0.854	0.600	2.40	0.574	0.866	0.586	2.80	0.574	0.884	0.573
4.00	0.579	0.857	0.616	3.00	0.574	0.864	0.588	5.60	0.624	1.194	0.691
6.00	0.612	1.271	0.696	6.00	0.633	1.310	0.728	6.30	0.654	1.447	0.791

$$\phi - 1 = \left(\sum_i m_i\right)^{-1} \left\{ \begin{array}{l} 2If^{\phi} + 2\sum\sum m_c m_a \left[B^{\phi}_{ca} + \dfrac{(\sum m_z)}{(z_c z_a)^{1/2}} C^{\phi}_{ca} \right] + \\ \sum\limits_{c}\sum\limits_{c'} m_c m_{c'} [\theta_{cc'} + I\theta'_{ac'} + \sum\limits_{a} m_a \psi_{ca'a}] + \\ \sum\limits_{a}\sum\limits_{a'} m_a m_{a'} [\theta_{aa'} + I\theta'_{ca'} + \sum\limits_{c} m_c \psi_{caa'}] + \\ \sum\limits_{c}\sum\limits_{c'} m_c m_{c'} (\sum\limits_{c''} m_{c''} \psi^{\phi}_{cc'c''}) + \\ \sum\limits_{c}\sum\limits_{c'}\sum\limits_{c''} m_c m_{c'} m_{c''} (\sum\limits_{a} m_a \chi^{\phi}_{cc'c''a}) \end{array} \right\} \tag{1}$$

where I is the ionic strength of the common ion; $\theta_{cc'}$ is a binary mixing parameter involving unlike ions of the same sign; and $\psi_{ca'a}$ is a ternary mixing parameter for two unlike ions of the same sign with a third ion of the opposite sign. $\varphi^{\phi}_{cc'c''}$ is a ternary mixing parameter involving unlike ions of the same sign, and $\chi^{\phi}_{cc'c''a}$ is a quaternary mixing parameter for three unlike ions of the same sign with a fourth ion of the opposite sign.

The second virial coefficient B^{ϕ} of the subscribed ions is defined as

$$B^{\phi} = \beta^{(0)} + \beta^{(1)} \exp(-\alpha I^{1/2}) \tag{2}$$

$\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} are ion interaction parameters which are functions of temperature and pressure, where $\alpha = 2\ (\mathrm{mol \cdot kg^{-1}})^{-1/2}$.

The activity coefficients of MX in a common anion in a mixture of MX−NX−OX(aq) are given by

Table 8. Activity Coefficients γ_{NH_4Cl}, γ_{NaCl}, and γ_{LiCl} in $NH_4Cl + NaCl + LiCl + H_2O$ against the Square Root of Total Ionic Strength $I^{1/2}$ at Different Ionic-Strength Fractions y and Ratio of Ionic Strength z of 0.20, 0.50, and 0.80

I	γ_{NH_4Cl}	γ_{NaCl}	γ_{LiCl}	I	γ_{NH_4Cl}	γ_{NaCl}	γ_{LiCl}	I	γ_{NH_4Cl}	γ_{NaCl}	γ_{LiCl}
					$y = 0.20$						
	$z = 0.20$				$z = 0.50$				$z = 0.80$		
0.60	0.641	0.761	0.728	0.80	0.639	0.679	0.461	0.70	0.645	0.752	0.717
0.80	0.628	0.768	0.754	1.20	0.658	0.675	0.447	1.40	0.621	0.757	0.756
1.20	0.627	0.790	0.795	1.60	0.623	0.712	0.487	2.10	0.631	0.799	0.836
1.60	0.634	0.823	0.847	2.00	0.631	0.739	0.518	2.80	0.668	0.873	0.957
2.00	0.794	1.210	1.329	4.00	0.815	0.769	0.551	6.00	1.351	1.769	2.304
6.00	1.334	2.554	2.530	6.00	1.570	0.843	0.625	8.40	8.250	7.633	11.19
				8.00	5.252	7.085	7.557				
					$y = 0.50$						
	$z = 0.20$				$z = 0.50$				$z = 0.80$		
0.80	0.632	0.863	0.701	0.60	0.647	0.869	0.669	0.70	0.638	0.860	0.695
1.20	0.616	0.861	0.714	1.20	0.614	0.854	0.708	1.40	0.609	0.853	0.714
1.60	0.610	0.875	0.739	1.80	0.608	0.877	0.748	2.10	0.610	0.889	0.770
2.00	0.612	0.903	0.775	2.40	0.618	0.928	0.812	2.80	0.629	0.962	0.863
3.00	0.700	1.311	1.126	4.00	1.028	2.685	2.305	5.60	0.939	2.013	2.142
6.00	0.953	3.080	2.028	6.00	1.466	5.613	4.230	6.30	1.125	2.783	2.874
8.00	1.581	14.509	4.692								
					$y = 0.80$						
	$z = 0.20$				$z = 0.50$				$z = 0.80$		
0.80	0.623	0.980	0.675	0.60	0.640	0.995	0.681	0.70	0.630	0.984	0.675
1.20	0.602	0.968	0.675	1.20	0.602	0.965	0.673	1.40	0.595	0.963	0.675
1.60	0.592	0.973	0.687	1.80	0.588	0.975	0.692	2.10	0.585	0.984	0.706
2.00	0.588	0.989	0.706	2.40	0.586	1.008	0.729	2.80	0.587	1.034	0.761
4.00	0.610	1.253	0.909	3.00	0.591	1.064	0.783	5.60	0.659	1.639	1.353
6.00	0.677	2.147	1.362	6.00	0.681	1.951	1.465	6.30	0.692	1.989	1.690

Table 9. Activity Coefficients γ_{NH_4Cl}, γ_{KCl}, and γ_{LiCl} in $NH_4Cl + KCl + LiCl + H_2O$ against the Square Root of Total Ionic Strength $I^{1/2}$ at Different Ionic-Strength Fractions y and Ratio of Ionic Strength z of 0.20, 0.50, and 0.80

I	γ_{NH_4Cl}	γ_{KCl}	γ_{LiCl}	I	γ_{NH_4Cl}	γ_{KCl}	γ_{LiCl}	I	γ_{NH_4Cl}	γ_{KCl}	γ_{LiCl}
					$y = 0.20$						
	$z = 0.20$				$z = 0.50$				$z = 0.80$		
0.80	0.637	0.714	0.721	0.80	0.634	0.708	0.709	0.70	0.640	0.712	0.701
1.20	0.622	0.698	0.743	1.20	0.616	0.691	0.724	1.40	0.609	0.683	0.722
1.60	0.619	0.696	0.780	1.60	0.611	0.688	0.754	2.10	0.616	0.692	0.784
2.00	0.626	0.705	0.829	2.00	0.617	0.696	0.796	2.80	0.663	0.736	0.892
4.00	0.849	1.007	1.331	4.00	0.905	0.971	1.299	4.00	0.913	0.935	1.261
6.00	2.038	2.991	2.924	6.00	3.078	2.657	3.412	5.60	2.370	1.829	2.761
				8.00	3.796	2.019	1.762	6.30	4.612	2.887	4.503
					$y = 0.50$						
	$z = 0.20$				$z = 0.50$				$z = 0.80$		
0.80	0.630	0.820	0.696	0.60	0.646	0.838	0.692	0.7	0.636	0.825	0.683
1.20	0.614	0.797	0.706	1.20	0.611	0.795	0.691	1.4	0.605	0.789	0.688
1.60	0.608	0.791	0.728	1.80	0.605	0.792	0.723	2.1	0.607	0.800	0.733
2.00	0.610	0.799	0.762	2.40	0.618	0.823	0.784	2.8	0.635	0.859	0.825
4.00	0.735	1.242	1.154	4.00	0.763	1.197	1.180	5.6	1.302	2.728	2.909
6.00	1.215	5.485	2.542	6.00	1.509	4.508	3.437	6.3	1.863	4.966	5.243
					$y = 0.80$						
	$z = 0.20$				$z = 0.50$				$z = 0.80$		
0.80	0.623	0.952	0.673	0.60	0.640	0.974	0.677	0.70	0.630	0.962	0.670
1.20	0.602	0.928	0.671	1.20	0.601	0.929	0.665	1.40	0.594	0.924	0.662
1.60	0.596	0.921	0.681	1.80	0.588	0.924	0.680	2.10	0.585	0.931	0.687
2.00	0.588	0.928	0.700	2.40	0.586	0.947	0.715	2.80	0.589	0.976	0.742
4.00	0.617	1.239	0.917	3.00	0.593	1.003	0.770	5.60	0.703	1.950	1.623
6.00	0.711	3.141	1.514	6.00	0.735	2.662	1.785	6.30	0.764	2.762	2.312

$$\ln \gamma_{MX} = |Z_M Z_X| f^{\gamma} + \frac{2\nu_M}{\nu} m_X \left[B_{MX} + \frac{1}{2}\left|\frac{Z_X}{Z_M}\right|^{1/2} m_X C^{\phi}_{MX}\right] + \frac{2\nu_X}{\nu} m_M \left[B_{MX} + \frac{1}{2}\frac{\nu_M}{\nu}\left|\frac{Z_X}{Z_M}\right|^{1/2} m_X C^{\phi}_{MX}\right] + \frac{2\nu_X}{\nu} m_N \left[B_{NX} + \frac{1}{2} Z_X m_X C^{\phi}_{NX} + \frac{\nu_M}{\nu_X}\theta_{MN}\right] + \frac{2\nu_X}{\nu} m_O \left[B_{OX} + \frac{1}{2} Z_X m_X C^{\phi}_{OX} + \frac{\nu_M}{\nu_X}\theta_{MO}\right] + m_M m_X \left[|Z_M Z_X| B'_{MX} + \frac{\nu_M}{\nu}\left|\frac{Z_X}{Z_M}\right|^{1/2} C^{\phi}_{OX}\right] + m_N m_X \left[|Z_N Z_X| B'_{NX} + \frac{\nu_M}{\nu} Z_M C^{\phi}_{NX}\right] + m_O m_X \left[|Z_O Z_X| B'_{OX} + \frac{\nu_M}{\nu} Z_M C^{\phi}_{OX}\right] + \frac{m_M}{\nu}(\nu_M m_X + \nu_X m_M)\psi_{MNX} + \frac{m_O}{\nu}(\nu_M m_X + \nu_X m_M)\psi_{MOX} + \frac{m_N m_O}{\nu}[\nu_X \psi_{NOX} + \nu_M \varphi_{MNO}] + \frac{8}{3}\frac{m_N m_O}{\nu}(\nu_M m_X + \nu_X m_M)\chi^{\phi}_{MNOX} \quad (3)$$

f^{γ} is the long-range electrostatic term, and the coefficients B_{MX} and B'_{MX} for electrolyte 1−1 are defined as

$$B_{MX} = \beta^{(0)}_{MX} + (2\beta^{(1)}_{MX}/\alpha^2 I)[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})] \quad (4)$$

$$B'_{MX} = (2\beta^{(1)}_{MX}/\alpha^2 I^2)[-1 + (1 + \alpha I^{1/2} + 1/2\alpha^2 I)\exp(-\alpha I^{1/2})] \quad (5)$$

From the osmotic coefficients determined using the experimental water activities of the studied mixture at different ionic strength fraction, it is possible to determine that the unknown mixing ionic φ_{MNX} and χ_{MNOX} are estimated by a graphical procedure. This procedure defines the quantity $\Delta\phi$ as the difference between the experimental values ϕ_{exp} and that calculated ϕ_{calc} from eq 1. This yields

$$\frac{\sum_i m_i}{m_{MX} m_{NX} m_{OX}} \Delta\phi = \varphi_{MNX} + m_{X}\text{–}\chi^{\phi}_{MNOX} \quad (6)$$

They point out that a plot of $\Delta\varphi$ against the total molality should yield a straight line with intercept and slope equal to the three-ion φ_{MNX} and four-ion χ^{ϕ}_{MNOX} mixing parameters, respectively.

The procedure to determine quaternary mixing ionic parameters φ and χ is described by the equations of the ionic interaction model. In the first, adjustable parameters of the virial coefficients $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} describe interactions between cation c and anion a in binary system solutions. In the second, we determine the parameters θ and Ψ as characterized interactions for the ternary solutions. Finally, from these parameters, the quaternary parameters φ and χ are evaluated, and these parameters describe interactions between cation and cation−anion in the solution.

The osmotic coefficient of the systems charge-type 1−1*1−1*1−1 are defined as

$$\phi - 1 = \frac{-A_{\phi} I^{1/2}}{1 + 1.2 I^{1/2}} + yI[B^{\phi}_{MX} + IC^{\phi}_{MX}] + \frac{(1-y)}{(1+y')} zI[B^{\phi}_{NX} + IC^{\phi}_{NX}] \frac{(1-y)}{(1+y')} I[B^{\phi}_{OX} + IC^{\phi}_{OX}] + yI\frac{(1-y)}{(1+z)} z[\theta_{MN} + I\psi_{MNX}] + y\frac{(1-y)}{(1+z)} I[\theta_{MO} + I\psi_{MOX}] + z\frac{(1-y)^2}{(1+z)^2} I[\theta_{NO} + I\psi_{NOX}] + yz\frac{(1-y)^2}{(1+z)^2} I^2 \varphi_{MNO} + yz\frac{(1-y)^2}{(1+z)^2} I^3 \chi_{MNOX} \quad (7)$$

and the activity coefficients

Table 10. Activity Coefficients γ_{NaCl}, γ_{KCl}, and γ_{LiCl} in NaCl + LiCl + KCl + H_2O against the Square Root of Total Ionic Strength $I^{1/2}$ at Different Ionic-Strength Fractions *y* and Ratio of Ionic Strength *z* of 0.20, 0.50, and 0.80

I	γ_{NaCl}	γ_{KCl}	γ_{LiCl}	I	γ_{NaCl}	γ_{KCl}	γ_{LiCl}	I	γ_{NaCl}	γ_{KCl}	γ_{LiCl}
					$y = 0.20$						
	$z = 0.20$				$z = 0.50$				$z = 0.80$		
0.60	0.694	0.725	0.735	0.80	0.686	0.716	0.725	0.70	0.681	0.717	0.717
0.80	0.703	0.717	0.764	1.20	0.692	0.704	0.748	1.40	0.688	0.691	0.753
1.20	0.722	0.719	0.804	1.60	0.707	0.700	0.782	2.10	0.710	0.684	0.811
1.60	0.746	0.723	0.854	2.00	0.723	0.699	0.821	2.80	0.716	0.670	0.868
2.00	0.811	0.639	1.165	4.00	0.679	0.604	0.993	6.00	0.323	0.365	0.745
6.00	0.576	0.298	1.389	6.00	0.305	0.288	0.863	8.40	0.011	0.038	0.159
				8.00	0.038	0.049	0.409				
					$y = 0.50$						
	$z = 0.20$				$z = 0.50$				$z = 0.80$		
0.80	0.679	0.837	0.729	0.60	0.681	0.844	0.720	0.70	0.673	0.831	0.718
1.20	0.680	0.828	0.754	1.20	0.672	0.814	0.747	1.40	0.669	0.802	0.758
1.60	0.691	0.829	0.791	1.80	0.686	0.809	0.799	2.10	0.684	0.792	0.818
2.00	0.708	0.830	0.835	2.40	0.704	0.799	0.858	2.80	0.697	0.677	0.871
4.00	0.795	0.650	1.087	4.00	0.524	0.212	0.685	5.60	0.521	0.320	0.611
6.00	0.747	0.190	1.152	6.00	0.329	0.562	0.388	6.30	0.412	0.189	0.435
8.00	0.487	0.010	0.808								
					$y = 0.80$						
	$z = 0.20$				$z = 0.50$				$z = 0.80$		
0.80	0.667	0.954	0.721	0.60	0.674	0.971	0.716	0.70	0.667	0.957	0.716
1.20	0.662	0.935	0.742	1.20	0.658	0.928	0.740	1.40	0.657	0.917	0.755
1.60	0.668	0.929	0.775	1.80	0.668	0.918	0.792	2.10	0.673	0.909	0.821
2.00	0.680	0.928	0.817	2.40	0.689	0.913	0.858	2.80	0.700	0.900	0.896
4.00	0.798	0.821	1.103	3.00	0.717	0.900	0.929	4.20	0.771	0.818	1.011
6.00	0.963	0.414	1.396	4.80	0.820	0.716	1.094	5.60	0.840	0.606	0.973
				6.00	0.885	0.475	1.081	6.30	0.864	0.467	0.875

$$\begin{aligned}\ln \gamma_{\mathrm{MX}} = {} & f^{\gamma} + (1+y)I\left[B_{\mathrm{MX}} + \frac{I}{2}C^{\phi}_{\mathrm{MX}}\right] + \\ & \frac{(1-y)}{(1+z)}I\left[B_{\mathrm{NX}} + \frac{I}{2}C^{\phi}_{\mathrm{NX}} + \theta_{\mathrm{MN}}\right] \\ & \frac{(1-y)}{(1+z)}I\left[B_{\mathrm{OX}} + \frac{I}{2}C^{\phi}_{\mathrm{OX}} + \theta_{\mathrm{MO}}\right] + yI^{2}\left[B'_{\mathrm{MX}} + \frac{I}{2}C^{\phi}_{\mathrm{MX}}\right] + \\ & \frac{(1-y)}{(1+z)}zI^{2}\left[B'_{\mathrm{NX}} + \frac{I}{2}C^{\phi}_{\mathrm{NX}}\right] + \frac{(1-y)}{(1+z)}I^{2}\left[B'_{\mathrm{OX}} + \frac{I}{2}C^{\phi}_{\mathrm{OX}}\right] + \\ & \frac{1}{2}\frac{(1-y)}{(1+z)}zI^{2}(1+y)\psi_{\mathrm{MNX}} + \frac{1}{2}\frac{(1-y)}{(1+z)}I^{2}(1+y)\psi_{\mathrm{MOX}} + \\ & \frac{1}{2}\frac{(1-y)^{2}}{(1+z)^{2}}zI^{2}(\psi_{\mathrm{NOX}} + \varphi_{\mathrm{MNO}}) + \frac{4}{3}\frac{(1-y)^{2}}{(1+z)^{2}}zI^{3}(1+y)\chi_{\mathrm{MNOX}}\end{aligned} \tag{8}$$

$$\begin{aligned}\ln \gamma_{\mathrm{NX}} = {} & f^{\gamma} + I\left[B_{\mathrm{NX}} + \frac{I}{2}C^{\phi}_{\mathrm{NX}}\right] + \frac{(1-y)}{(1+z)}zI\left[B_{\mathrm{NX}} + \frac{I}{2}C^{\phi}_{\mathrm{NX}}\right] \\ & \frac{(1-y)}{(1+z)}I\left[B_{\mathrm{OX}} + \frac{I}{2}C^{\phi}_{\mathrm{OX}} + \theta_{\mathrm{NO}}\right] + yI^{2}\left[B'_{\mathrm{MX}} + \frac{I}{2}C^{\phi}_{\mathrm{MX}}\right] + \\ & \frac{(1-y)}{(1+z)}zI^{2}\left[B'_{\mathrm{NX}} + \frac{1}{2}C^{\phi}_{\mathrm{NX}}\right] + \frac{(1-y)}{(1+z)}I^{2}\left[B'_{\mathrm{OX}} + \frac{1}{2}C^{\phi}_{\mathrm{OX}}\right] + \\ & \frac{y}{2}\left(1 + \frac{(1-y)}{(1+z)}z\right)I^{2}\psi_{\mathrm{MNX}} + \frac{1}{2}\frac{(1-y)}{(1+z)}yI^{2}\psi_{\mathrm{MOX}} + \\ & \frac{1}{2}\frac{(1-y)}{(1+y)}\left(1 + \frac{(1-y)}{(1+z)}z\right)I^{2}\psi_{\mathrm{NOX}} + \frac{1}{2}\frac{(1-y)}{(1+y)}yI^{2}\varphi_{\mathrm{MNO}}) + \\ & \frac{4}{3}\frac{(1-y)}{(1+z)^{2}}(2 + z - y)yI^{3}\chi_{\mathrm{MNOX}}\end{aligned} \tag{9}$$

$$\begin{aligned}\ln \gamma_{\mathrm{OX}} = {} & f^{\gamma} + I\left[B_{\mathrm{OX}} + \frac{I}{2}C^{\phi}_{\mathrm{OX}}\right] + \frac{(1-y)}{(1+z)}I\left[B_{\mathrm{OX}} + \frac{I}{2}C^{\phi}_{\mathrm{OX}}\right] + \\ & yI\left[B_{\mathrm{MX}} + \frac{I}{2}C^{\phi}_{\mathrm{MX}}\theta_{\mathrm{OM}}\right] + \frac{(1-y)}{(1+z)}zI\left[B_{\mathrm{NX}} + \frac{I}{2}C^{\phi}_{\mathrm{NX}} + \theta_{\mathrm{OM}}\right] + \\ & yI^{2}\left[B'_{\mathrm{MX}} + \frac{1}{2}C^{\phi}_{\mathrm{MX}}\right] + \frac{(1-y)}{(1+z)}zI^{2}\left[B'_{\mathrm{NX}} + \frac{I}{2}C^{\phi}_{\mathrm{NX}}\right] + \\ & \frac{(1-y)}{(1+z)}I^{2}\left[B'_{\mathrm{OX}} + \frac{1}{2}C^{\phi}_{\mathrm{OX}}\right] + \frac{1}{2}\frac{(1-y)}{(1+z)}yzI^{2}\psi_{\mathrm{MNX}} + \\ & \frac{1}{2}\left(1 + \frac{(1-y)}{(1+z)}\right)I^{2}\psi_{\mathrm{MOX}} + \frac{1}{2}\frac{(1-y)}{(1+z)}z\left(1 + \frac{(1-y)}{(1+z)}\right)I^{2}\psi_{\mathrm{NOX}} + \\ & \frac{1}{2}yz\frac{(1-y)}{(1+z)}I^{2}\varphi_{\mathrm{MNO}} + \frac{4}{3}\frac{(1-y)}{(1+z)^{2}}(2 + z - y)yzI^{3}\chi_{\mathrm{MNOX}}\end{aligned} \tag{10}$$

Results and Discussion

Water Activity and Osmotic Coefficient. In this work, the water activities are measured for the quaternary aqueous solutions of chlorides charge-type 1−1*1−1*1−1, with a cation (NH_4^+, Na^+, K^+, Li^+), using the hygrometric method at 298.15 K. A series of measurements were made at total molalities from 0.60 mol·kg^{-1} to saturation for different ionic-strength fractions y of NH_4Cl [$y = I_{NH_4Cl}/(I_{NH_4Cl} + I_{MCl} + I_{M'Cl})$] with (M, M′ = Na^+, K^+, Li^+) for $NH_4Cl + NaCl + KCl + H_2O$, $NH_4Cl + NaCl + LiCl + H_2O$, $NH_4Cl + KCl + LiCl + H_2O$ or y of NaCl [$y = I_{NaCl}/(I_{NaCl} + I_{LiCl} + I_{KCl})$] for $NaCl + LiCl + KCl + H_2O$, with $y = 0.20$, 0.50, 0.80, and z ratio ionic strength for other solutes for each ionic fraction y, $z = I_{MCl}/I_{M'Cl}$ with 0.20, 0.50, and 0.80. Using the obtained experimental data for the water activity, we have evaluated the osmotic coefficients of the solvent for different ionic strength fractions y and ratio ionic strength z. The results are shown in Tables 1 to 4 for the quaternary systems. The osmotic coefficient of the solvent ϕ against square root of total ionic strength $I^{1/2}$ at different ionic-strength fractions y and z of 0.20, 0.50, and 0.80 are presented in Figures 2 to 5.

The corresponding values of ionic parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} of the pure electrolytes NaCl(aq), KCl(aq), LiCl(aq), and NH_4Cl(aq) and ternary aqueous systems θ and ψ were obtained from Pitzer's expressions by the fits of the experimental osmotic coefficients given in our previous works (Table 5).[6−12]

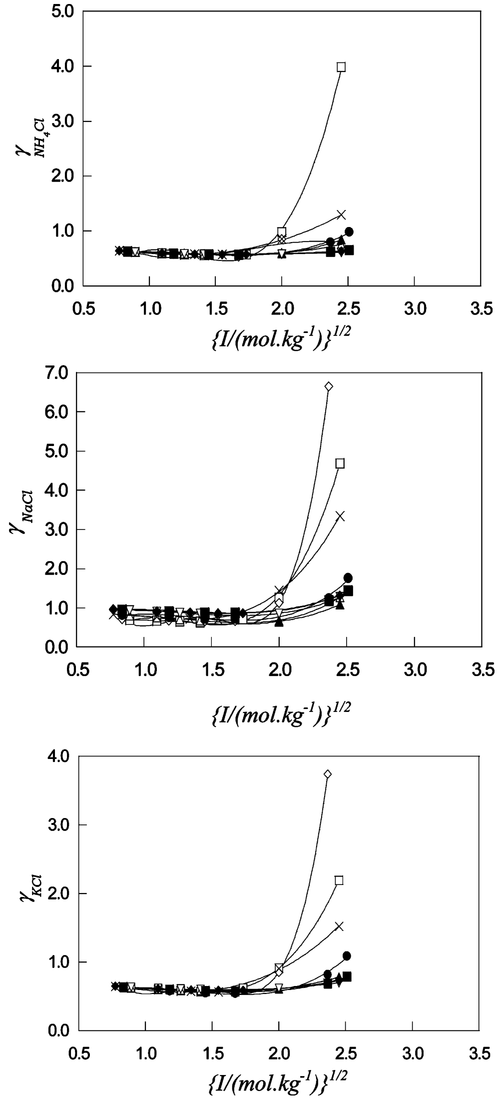

Figure 7. Activity coefficients γ_{NH_4Cl}, γ_{NaCl}, and γ_{KCl} in $NH_4Cl + NaCl + KCl + H_2O$, against square root of total ionic strength $I^{1/2}$ at different ionic-strength fractions y and z of 0.20, 0.50, and 0.80. For $y = 0.20$: ▲, $z = 0.20$; □, $z = 0.50$; ◇, $z = 0.80$. $y = 0.50$: △. $z = 0.20$; ×. $z = 0.50$; ●, $z = 0.80$. $y = 0.80$: ▽, $z = 0.20$; ◆, $z = 0.50$; ■, $z = 0.80$.

The quaternary parameters φ and χ for these aqueous solutions, $NH_4Cl + NaCl + KCl + H_2O$, $NH_4Cl + NaCl + LiCl + H_2O$, $NH_4Cl + KCl + LiCl + H_2O$, and $NaCl + LiCl + KCl + H_2O$, are evaluated by the plots of $\Delta\varphi$ (eq 6) against the total molality should yield a straight line with intercept and slope equal to the three-ion and four-ion mixing parameters, respectively (Figure 6). These parameters φ and χ are determined in Table 6. Also, the deviations between the data and model in different ranges of molality are given, and they are between 0.0001 and 0.0023. Good agreement is obtained for this ionic interaction model with our approach using the quaternary parameters φ and χ. In comparison with the literature data, we have obtained minimum deviation with our parameters φ and χ in the range of total molality 0.60 mol·kg^{-1} to saturation, and the measurements were made at a number of total ionic strengths at each of nine ionic strength ratios for each system compared to other works,[22,23] which are studied only in the range of total molality from 0.60 mol·kg^{-1} to 4.80

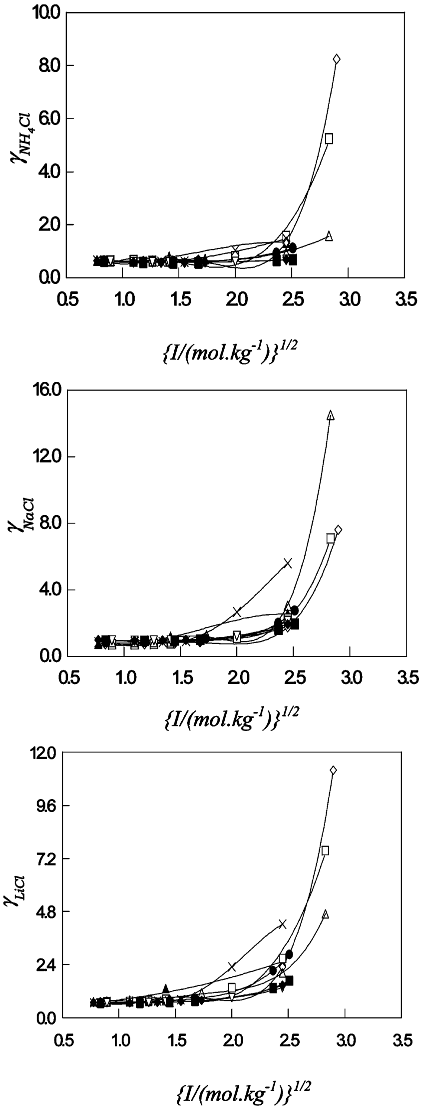

Figure 8. Activity coefficients γ_{NH_4Cl}, γ_{NaCl} and γ_{LiCl} in $NH_4Cl + NaCl + LiCl + H_2O$, against square root of total ionic strength $I^{1/2}$ at different ionic-strength fractions y and z of 0.20, 0.50, and 0.80. For $y = 0.20$: ▲, $z = 0.20$; □, $z = 0.50$; ◇, $z = 0.80$. $y = 0.50$: △, $z = 0.20$; ×, $z = 0.50$; ●, $z = 0.80$. $y = 0.80$: ▽, $z = 0.20$; ♦, $z = 0.50$; ■, $z = 0.80$.

$mol \cdot kg^{-1}$ at fixed molal ratio for the other solutes ($r = m_1/m_2 = 1$). For the $NH_4Cl + KCl + LiCl + H_2O$, the obtained parameters $\varphi = -0.3400$ and $\chi = 0.0440$ in the range 0.60 $mol \cdot kg^{-1}$ to 8.00 (saturation) with the deviation standard of $\sigma(\phi) = 0.0001$ at different ionic-strength fractions y with 0.20, 0.50, and and 0.80, and for each y, $z = 0.20$, 0.50, and 0.80. However, for the literature data for the same system,[22] the parameters $\varphi = 0.001$ and $\chi = 0.005$ with the standard deviation of 0.007, and just only in the range 0.60 $mol \cdot kg^{-1}$ to 4.80 $mol \cdot kg^{-1}$.

Activity Coefficient. The activity coefficients of NH_4Cl, NaCl, KCl, and LiCl, in the quaternary aqueous solutions, were calculated by an ion interaction model using our obtained ionic mixing parameters, and the results are listed in Tables 7 to 10. The plots of activity coefficients γ_{NH_4Cl}, γ_{NaCl}, $\gamma_{LiCl,}$ and γ_{KCl} in the mixture against the square root of the ionic strength $I^{1/2}$ are shown in Figures 7 to 10. From the theoretical point of view, it is desirable to compare and explain the behavior of various ionic solutes, sodium, potassium, lithium, and ammonium chlorides in the quaternary aqueous solutions, in wide ranges of composition.

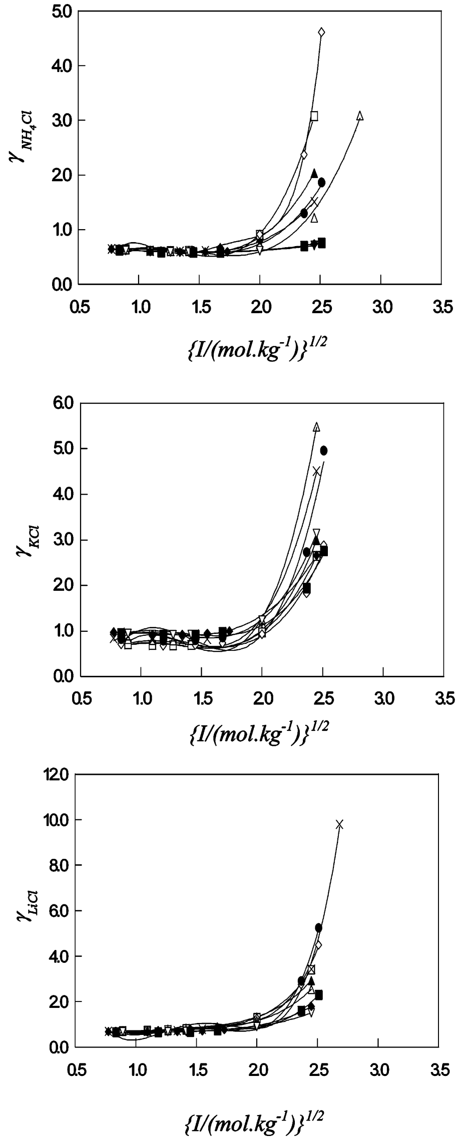

Figure 9. Activity coefficients γ_{NH_4Cl}, γ_{KCl}, and γ_{LiCl} in $NH_4Cl + KCl + LiCl + H_2O$, against square root of total ionic strength $I^{1/2}$ at different ionic-strength fractions y and z of 0.20, 0.50, and 0.80. For $y = 0.20$: ▲, $z = 0.20$; □, $z = 0.50$; ◇, $z = 0.80$. $y = 0.50$: △, $z = 0.20$; ×, $z = 0.50$; ●, $z = 0.80$. $y = 0.80$: ▽, $z = 0.20$; ♦, $z = 0.50$; ■, $z = 0.80$.

The activity coefficients in the various quaternary aqueous solutions of chlorides charge-type 1−1*1−1*1−1*, with a cation (NH_4^+, Na^+, K^+, Li^+), as a function at molality are shown in Figures 7 to 10. For the systems containing ammonium chloride, the curves show that the $\gamma_{MCl(aq)}$ are more important and decrease as a function of molality in the following order: $\{NH_4Cl + NaCl + LiCl\}(aq) > \{NH_4Cl + KCl + LiCl\}(aq) > \{NH_4Cl + NaCl + KCl\}(aq)$. Conversely for the system $\{NaCl + LiCl + KCl\}(aq)$, the activity coefficients of solute $\gamma_{MCl(aq)}$ increase with concentered solutions.

This decrease is due to the interactions in the quaternary systems containing Li^+ and NH_4^+ cations, and it is relatively less for quaternary chlorides with NH_4^+, Na^+, and K^+ cations. These interactions are responsible for an important variation of the electrolyte solutions compared to ideality. The activity coefficients in the quaternary aqueous solutions of chlorides charge-type 1−1*1−1*1−1* increase in the following order: $\gamma_{LiCl} > \gamma_{NH_4Cl} > \gamma_{NaCl} \sim \gamma_{KCl}$. Also, we can observe that the activity coefficients $\gamma_{MCl(aq)}$ present higher values at high

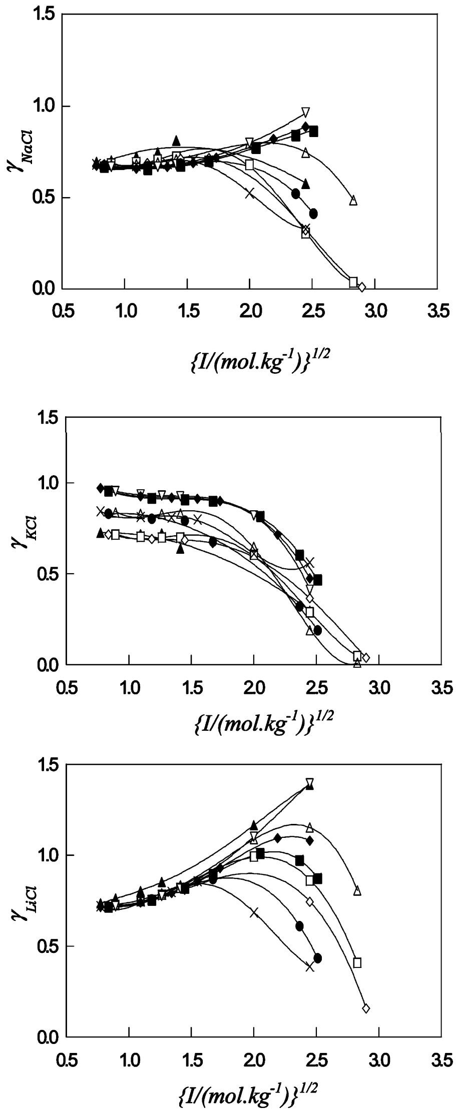

Figure 10. Activity coefficients γ_{NaCl}, γ_{KCl}, and γ_{LiCl} in NaCl + KCl + LiCl + H_2O against square root of total ionic strength $I^{1/2}$ at different ionic-strength fractions y and z of 0.20, 0.50, and 0.80. For $y = 0.20$: ▲, $z = 0.20$; □, $z = 0.50$; ◇, $z = 0.80$. $y = 0.50$: △, $z = 0.20$; ×, $z = 0.50$; ●, $z = 0.80$. $y = 0.80$: ▽, $z = 0.20$; ♦, $z = 0.50$; ■, $z = 0.80$.

concentration. The behavior of the solute activity coefficients as a function of molality can be understood by considering the ionic electrostatic interactions and ion−solvent interactions that occur in the solution.[16,24,25]

Conclusion

The water activities of quaternary aqueous solutions of chlorides type 1−1*1−1*1−1 with a cation (NH_4^+, Na^+, K^+, Li^+), NH_4Cl + NaCl + KCl + H_2O, NH_4Cl + NaCl + LiCl + H_2O, NH_4Cl + KCl + LiCl + H_2O, and NaCl + LiCl + KCl + H_2O, were measured using the hygrometric method at the temperature 298.15 K. These measurements were made at total molalities from 0.6 mol·kg^{-1} up to saturation for different ionic-strength fractions y of NH_4Cl or NaCl, $y = 0.20$, 0.50, and 0.80, and z ratio ionic strength for other solutes for each y, with $z = 0.20$, 0.50, and 0.80. The results allow the deduction of osmotic coefficients.

The activity coefficients of NH_4Cl, NaCl, KCl, and LiCl, in the quaternary systems, were calculated by the ionic interaction model with our approach, and the mixing ionic parameters φ and χ for quaternary systems were determined. The results are compared with experimental data, and good agreement is obtained. Also they are compared with the literature data, and the deviation minimum is obtained with our parameters φ and χ for all systems and in the range of molality from 0.60 mol·kg^{-1} to saturation.

The interactions in the quaternary aqueous systems are responsible for an important variation of the electrolyte solutions compared to the ideality. The activity coefficients of alkaline chlorides, charge-type 1−1*1−1*1−1 with a cation (NH_4^+, Na^+, K^+, Li^+), increase in the following order: $\gamma_{LiCl} > \gamma_{NH_4Cl} > \gamma_{NaCl} \sim \gamma_{KCl}$. Also, the activity coefficients $\gamma_{MCl(aq)}$ present higher values at high concentration. The behavior of the solute activity coefficients as a function of molality can be understood by considering the ionic electrostatic interactions and ion−solvent interactions that occur in the solution.

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