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Water Activity Measurement for Alanine + Dipotassium Oxalate + Water and the Corresponding Binary Solutions at Different Temperatures

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Water activity measurements by the isopiestic method have been carried out on the aqueous ternary system of L-alanine + dipotassium oxalate and the aqueous binary system of dipotassium oxalate over a range of temperatures at atmospheric pressure. From these measurements, values of the vapor pressure of solutions were determined. The experimental vapor−liquid equilibria data for the binary system were correlated with the Pitzer equation. The agreement between the correlations and the experimental data is good. A model based on the Pitzer formalism has been employed to correlate the experimental osmotic coefficient data for the ternary system, and the results show that this model can be satisfactorily used.

Introduction

Amino acids are the building blocks of other biomolecules such as peptides and proteins;[1] therefore, for their separation process, it is important to study their behavior in aqueous systems containing electrolytes.[2] One of the thermodynamic properties of aqueous amino acid solutions is water activity, which is an important thermodynamic property because it is closely related with the other thermodynamic properties such as vapor pressure, osmotic coefficient, activity coefficient, excess enthalpy, excess entropy, excess Gibbs energy, and excess volume.

A survey of literature[3−7] shows that although many studies have been carried out for thermodynamic properties (such as volumetric and viscometric behavior) of amino acids in aqueous electrolyte solutions, little attention has been paid to the vapor−liquid equilibrium of amino acids in aqueous systems containing electrolytes.[8−12]

Oxalate ions in aqueous solutions are of considerable significance in many chemical processes.[13] With respect to thermodynamic properties of various electrolytic solutions,[14−17] there are only few studies about the behavior of aqueous systems containing oxalate salts.[18]

In this work, vapor−liquid equilibria measurements were performed from dilute up to near saturation. The Pitzer equation was used to correlate the osmotic coefficient data.

Experimental Section

Materials. L-Alanine (IUPAC name: 2-aminopropanoic acid) with CAS Registry No. 5641-7 and dipotassium oxalate monohydrate with CAS Registry No. 6487-48-5 ($K_2C_2O_4 \cdot H_2O$) with a minimum mass fraction purity of 0.9 were obtained from Merck. Sodium chloride with CAS Registry No. 7647-14-5 with a minimum mass fraction purity 0.995 was dried in an electrical oven at about 110 °C for 24 h prior to use. The amino acid and salt were used without further purification, and double-distilled, deionized water was used. The solutions were prepared by mass using an analytical balance (Shimatzu, 321-34553, Shimatzu Co., Japan) with an uncertainty of $\pm\, 1 \cdot 10^{-7}$ kg.

Apparatus and Procedure. The isopiestic method is used to obtain the activity of water and osmotic coefficient in an aqueous binary and ternary system at $T =$ (298.15, 308.15, and 318.15) K. The isopiestic apparatus used in this work was similar to the one used by Ochs et al.[19] The apparatus used for the determination of water activity of ternary aqueous alanine + dipotassium oxalate solutions consisted of a seven-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions; one flask contained the pure alanine solution, and one flask contained the pure dipotassium oxalate solution. Two flasks contained the alanine + dipotassium oxalate solutions, and the central flask was used as a water reservoir. For th ebinary system this apparatus consisted of a five-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions; two flasks contained dipotassium oxalate solutions, and the central flask was used as a water reservoir. The typical mass of solutions used in isopiestic measurement was within (1 to 1.5)$\cdot 10^{-7}$ kg. The apparatus was held in a constant-temperature bath at least 120 h for equilibrium. The temperature was controlled to within ± 0.01 K.

After equilibrium had been reached, the manifold assembly was removed from the bath, and each flask was weighed with an analytical balance with a precision of $\pm\, 1 \cdot 10^{-7}$ kg. From the weight of each flask after equilibrium and the initial weight of salt and alanine, the mass fraction of each solution was calculated. It was assumed that the equilibrium condition was reached when the differences between the mass fractions of two standard solutions were less than 1 %. In all cases, averages of the duplicate are reported as the total isopiestic mass fraction. The water activity for the standard aqueous NaCl solutions at different concentrations and temperatures has been calculated from the correlation of Colin et al.[20] The uncertainty in the measurement of water activity was estimated to be ± 0.0002.

Results and Discussion

Isopiestic equilibrium molalities with reference standard solutions of NaCl in water as reported in Table 1 enabled the calculation of the osmotic coefficient, ϕ, of the solutions of dipotassium oxalate in water from

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Table 1. Isopiestic Equilibrium Molalities, Experimental Osmotic Coefficients, Activities, and Vapor Pressures for Dipotassium Oxalate (S) + H_2O (W) at Different Temperatures

m_{NaCl} / $mol \cdot kg^{-1}$	m_S / $mol \cdot kg^{-1}$	ϕ_{exp}	a_W	p_{exp} / kPa	m_{NaCl} / $mol \cdot kg^{-1}$	m_S / $mol \cdot kg^{-1}$	ϕ_{exp}	a_W	p_{exp} / kPa
				$T = 298.15$ K					
0.0000	0.0000	1.000	1.0000	3.175	1.4510	1.2237	0.760	0.9510	3.019
0.3391	0.2731	0.764	0.9888	3.139	1.6654	1.4027	0.770	0.9433	2.995
0.3945	0.3247	0.747	0.9870	3.134	1.7140	1.4461	0.771	0.9415	2.989
0.4487	0.3721	0.742	0.9852	3.128	1.8383	1.5534	0.775	0.9370	2.975
0.5427	0.4551	0.736	0.9821	3.118	1.9252	1.6311	0.777	0.9338	2.964
0.5842	0.4898	0.737	0.9807	3.114	2.0761	1.7629	0.782	0.9282	2.947
0.6926	0.5836	0.735	0.9771	3.102	2.1935	1.8602	0.789	0.9238	2.933
0.8531	0.7175	0.741	0.9717	3.085	2.1958	1.8655	0.787	0.9237	2.932
1.0152	0.8532	0.747	0.9661	3.067	2.3041	1.9611	0.791	0.9196	2.919
1.0429	0.8790	0.746	0.9652	3.064	2.5401	2.1661	0.801	0.9105	2.890
1.3832	1.1635	0.760	0.9534	3.027					
				$T = 308.15$ K					
0.0000	0.0000	1.000	1.0000	5.575	0.9306	0.8067	0.719	0.9691	5.403
0.2462	0.1970	0.768	0.9919	5.530	1.0247	0.8889	0.721	0.9659	5.385
0.3060	0.2519	0.745	0.9899	5.519	1.0609	0.9189	0.724	0.9647	5.378
0.3574	0.2974	0.737	0.9882	5.509	1.2559	1.0881	0.730	0.9580	5.340
0.4348	0.3637	0.734	0.9857	5.495	1.4665	1.2687	0.739	0.9506	5.299
0.5424	0.4596	0.726	0.9821	5.475	1.7784	1.5413	0.751	0.9394	5.236
0.6156	0.5269	0.720	0.9797	5.462	2.0404	1.7540	0.768	0.9298	5.183
0.6376	0.5465	0.719	0.9790	5.458	2.2463	1.9335	0.777	0.9220	5.140
0.6928	0.5956	0.719	0.9771	5.447	2.3186	1.9914	0.782	0.9193	5.124
0.8002	0.6873	0.722	0.9735	5.427	2.4634	2.1077	0.792	0.9138	5.093
0.8680	0.7481	0.721	0.9713	5.414	2.6965	2.3049	0.804	0.9047	5.043
				$T = 318.15$ K					
0.0000	0.0000	1.000	1.0000	9.508	1.2349	1.0876	0.715	0.9588	9.115
0.3276	0.2751	0.729	0.9892	9.405	1.4292	1.2614	0.720	0.9521	9.051
0.3794	0.3201	0.725	0.9875	9.389	1.4749	1.2963	0.725	0.9505	9.036
0.3805	0.3228	0.721	0.9875	9.389	1.8865	1.6433	0.749	0.9357	8.895
0.5074	0.4383	0.709	0.9833	9.349	1.9139	1.6715	0.748	0.9347	8.885
0.5653	0.4892	0.709	0.9814	9.331	1.9785	1.7197	0.754	0.9323	8.863
0.6831	0.5960	0.705	0.9775	9.294	1.9928	1.7383	0.752	0.9318	8.857
0.9009	0.7938	0.704	0.9702	9.224	2.1538	1.8691	0.763	0.9258	8.801
1.0080	0.8879	0.707	0.9666	9.190	2.5494	2.2171	0.780	0.9108	8.657

Table 2. Pitzer Model Parameters and Standard Deviations, ARD % (ϕ), for Dipotassium Oxalate (S) + H_2O (W) at Different Temperatures

T/K	$\beta^{(0)}$	$\beta^{(1)}$	C_ϕ	ARD % (ϕ)	ARD % (p)/kPa
298.15	0.14087	0.71968	−0.01449	0.279	0.0005
308.15	0.10997	0.84353	−0.00414	0.271	0.001
318.15	0.11426	0.65935	−0.00576	0.221	0.001

$$\phi = \frac{\nu^* \phi^* m^*}{\nu m_s} \qquad (1)$$

where ν^* and ν are the sum of stoichiometric numbers of anion and cation in the reference solution and the solution of dipotassium oxalate, respectively, m_S is the molality of the dipotassium oxalate solution, m^* is the molality of the reference standard in isopiestic equilibrium with this solution, and ϕ^* is the osmotic coefficient of the isopiestic reference standard, calculated at m^*. The necessary ϕ^* values at any m^* at different temperatures were calculated from the correlation given by Colin et al.[20] From the calculated osmotic coefficient data, the activity of water in dipotassium oxalate solution and the vapor pressure of this solution were determined at isopiestic equilibrium molalities, with the help of the following relations

$$\phi = -\frac{\ln a_W}{\nu m_s M_W} \qquad (2)$$

$$\ln a_W = \ln\left(\frac{p}{p^*}\right) + \frac{(B - V_W^*)(p - p^*)}{RT} \qquad (3)$$

where a_W is the activity of water, M_W is the molar mass of the water, and B is the second virial coefficient of water vapor. V_W^* is the molar volume, and p^* is the vapor pressure of pure water. The second virial coefficients of water vapor at each working temperature were calculated using the equation provided by Rard and Platford.[21] Molar volumes of liquid water were calculated using the density of water at different temperatures.[22] The vapor pressures of pure water were calculated using the equation of state of Saul and Wagner.[23] After the establishment of isopiestic equilibrium, water activities were calculated using eq 2. The results are collected in Table 1. The values of p for aqueous dipotassium oxalate calculated using eq 3 are also given in Table 1.

In this work, for the correlation of osmotic coefficient data of aqueous dipotassium oxalate solutions, we used the ion-interaction model of Pitzer.[24] The Pitzer model has the following form for a binary 1:2 electrolyte solution[24]

$$\phi - 1 = -2\left(\frac{A_\phi I^{0.5}}{1 + bI^{0.5}}\right) + \frac{3}{4} m_S B^\phi + 2\frac{2^{3/2}}{3} m_S{}^2 C^\phi \qquad (4a)$$

where

$$B^\phi = \beta^{(0)} + \beta^{(1)} \exp(-\alpha\sqrt{I}) \qquad (4b)$$

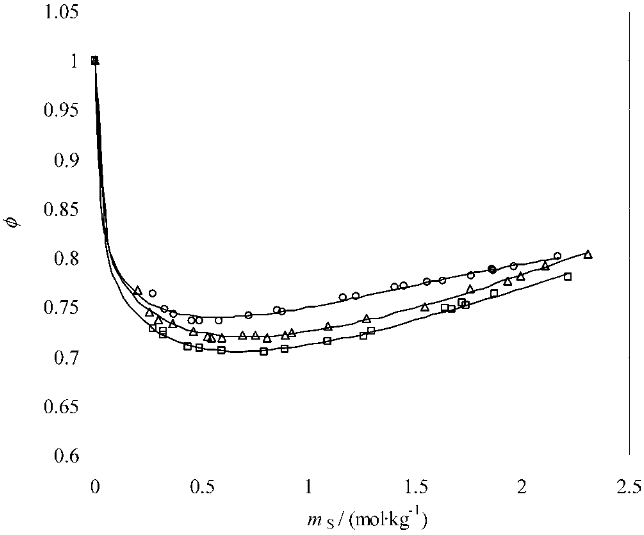

Figure 1. Experimental and calculated osmotic coefficient, ϕ, plotted against the molality of salt, m_S, for the dipotassium oxalate (S) + H_2O (W) system studied with the Pitzer model: ○, 298.15 K; △, 308.15 K; □, 318.15 K; —, Pitzer model.

Table 3. Water Activity (a_W) and Vapor Pressures (p) for Alanine (A) + Dipotassium Oxalate (S) + H_2O (W) for Different Mass Fractions, w, at T = 298.15 K

w_S	w_A	a_W	p_{exp}/kPa
0.0597	0.0000	0.9866	3.132
0.0319	0.0232		
0.0239	0.0287		
0.0000	0.0491		
0.0616	0.0000	0.9864	3.132
0.0320	0.0252		
0.0203	0.0348		
0.0000	0.0522		
0.0726	0.0000	0.9840	3.124
0.0407	0.0266		
0.0173	0.0472		
0.0000	0.0611		
0.0801	0.0000	0.9827	3.120
0.0398	0.0332		
0.0202	0.0497		
0.0000	0.0678		
0.0902	0.0000	0.9794	3.109
0.0473	0.0387		
0.0211	0.0609		
0.0000	0.0800		
0.1119	0.0000	0.9764	3.100
0.0641	0.0413		
0.0228	0.0757		
0.0000	0.0957		
0.1036	0.0000	0.9743	3.093
0.0527	0.0429		
0.0227	0.0685		
0.0000	0.0876		
0.1231	0.0000	0.9713	3.084
0.0635	0.0516		
0.0280	0.0831		
0.0000	0.1067		
0.1264	0.0000	0.9710	3.083
0.0649	0.0532		
0.0281	0.0878		
0.0000	0.1136		

$$A_\phi = \frac{1}{3}\sqrt{\frac{2\pi N_A d_0}{1000}}\left(\frac{e^2}{4\pi\varepsilon_0 DkT}\right)^{3/2} \qquad (4c)$$

Table 4. Water Activity (a_W) and Vapor Pressures (p) for Alanine (A) + Dipotassium Oxalate (S) + H_2O (W) for Different Mass Fractions, w, at T = 308.15 K

w_A	w_S	a_W	p_{exp}/kPa
0.0525	0.0000	0.9886	5.511
0.0298	0.0206		
0.0205	0.0274		
0.0000	0.0431		
0.0608	0.0000	0.9867	5.501
0.0321	0.0244		
0.0195	0.0339		
0.0000	0.0491		
0.0684	0.0000	0.9857	5.495
0.0358	0.0247		
0.0171	0.0414		
0.0000	0.0564		
0.0765	0.0000	0.9834	5.482
0.0379	0.0306		
0.0162	0.0495		
0.0000	0.0642		
0.0889	0.0000	0.9799	5.463
0.0455	0.0366		
0.0185	0.0587		
0.0000	0.0756		
0.1046	0.0000	0.9758	5.440
0.0544	0.0420		
0.0217	0.0688		
0.0000	0.0885		
0.1190	0.0000	0.9744	5.432
0.0580	0.0470		
0.0244	0.0753		
0.0000	0.0986		
0.1279	0.0000	0.9708	5.412
0.0656	0.0532		
0.0275	0.0861		
0.0000	0.1104		
0.1315	0.0000	0.9698	5.406
0.0687	0.0553		
0.0281	0.0881		
0.0000	0.1135		
0.1449	0.0000	0.9659	5.384
0.0755	0.0601		
0.0309	0.0966		
0.0000	0.1240		

In these equations $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ are Pitzer's ion-interaction parameters obtained by the fitting of experimental data; α and b are adjustable parameters. d_0, N_A, e, k, and ε_0 are the density of water, Avogadro's number, the electronic charge, Boltzmann's constant, and the permittivity of vacuum, respectively. I is the ionic strength in molality basis. For adjustable parameters the values $\alpha = 2.0\ \mathrm{kg^{1/2}\cdot mol^{-1/2}}$ and $b = 1.2\ \mathrm{kg^{1/2}\cdot mol^{-1/2}}$ were used. Table 2 summarizes the Pitzer ion-interaction parameters of dipotassium oxalate + H_2O obtained from the fitting of the experimental osmotic coefficient data to the Pitzer model. In Figure 1, the experimental and calculated osmotic coefficients from the Pitzer model are plotted against the molalities of dipotassium oxalate at different temperatures. On the basis of standard deviations reported in Table 2 and Figure 1, we conclude that the Pitzer model can be satisfactorily used for the correlation of the osmotic coefficient of dipotassium oxalate solutions from the dilute to the near-saturation region.

In this work, to describe thermodynamic properties of the ternary aqueous system containing dipotassium oxalate + L-alanine, the water activity measurements at T = (298.15, 308.15, and 318.15) K were carried out to study the vapor−liquid equilibria behavior of this system. Tables 3 to 5 report the water activities of the L-alanine + dipotassium oxalate + H_2O system at T = (298.15, 308.15, and 318.15) K, respectively. In Figure 2 parts a and b, the comparison of the experimental water activity data measured in this work with those taken from the literature[25,26] has been made for the alanine + H_2O system at (298.15 and 308.15) K, respectively. These figures show that there is a good agreement between our data and the previous

Table 5. Water Activity (a_W) and Vapor Pressures (p) for Alanine (A) + Dipotassium Oxalate (S) + H_2O (W) for Different Mass Fractions, w, at T = 318.15 K

w_A	w_S	a_W	p_{exp}/kPa
0.0556	0.0000	0.9877	9.391
0.0318	0.0222		
0.0240	0.0274		
0.0000	0.0500		
0.0588	0.0000	0.9863	9.377
0.0325	0.0250		
0.0206	0.0353		
0.0000	0.0533		
0.0683	0.0000	0.9853	9.368
0.0351	0.0259		
0.0161	0.0426		
0.0000	0.0573		
0.0882	0.0000	0.9808	9.325
0.0417	0.0358		
0.0184	0.0563		
0.0000	0.0730		
0.0947	0.0000	0.9789	9.307
0.0480	0.0390		
0.0201	0.0625		
0.0000	0.0774		
0.1075	0.0000	0.9759	9.278
0.0572	0.0461		
0.0235	0.0725		
0.0000	0.0929		
0.1204	0.0000	0.9720	9.241
0.0638	0.0519		
0.0277	0.0839		
0.0000	0.1059		
0.1317	0.0000	0.9713	9.234
0.0661	0.0534		
0.0275	0.0867		
0.0000	0.1117		
0.1343	0.0000	0.9700	9.222
0.0705	0.0574		
0.0296	0.0927		
0.0000	0.1190		
0.1461	0.0000	0.9664	9.188
0.0732	0.0596		
0.0305	0.0963		
0.0000	0.1236		
0.1543	0.0000	0.9653	9.177
0.0782	0.0634		
0.0337	0.1063		
0.0000	0.1368		

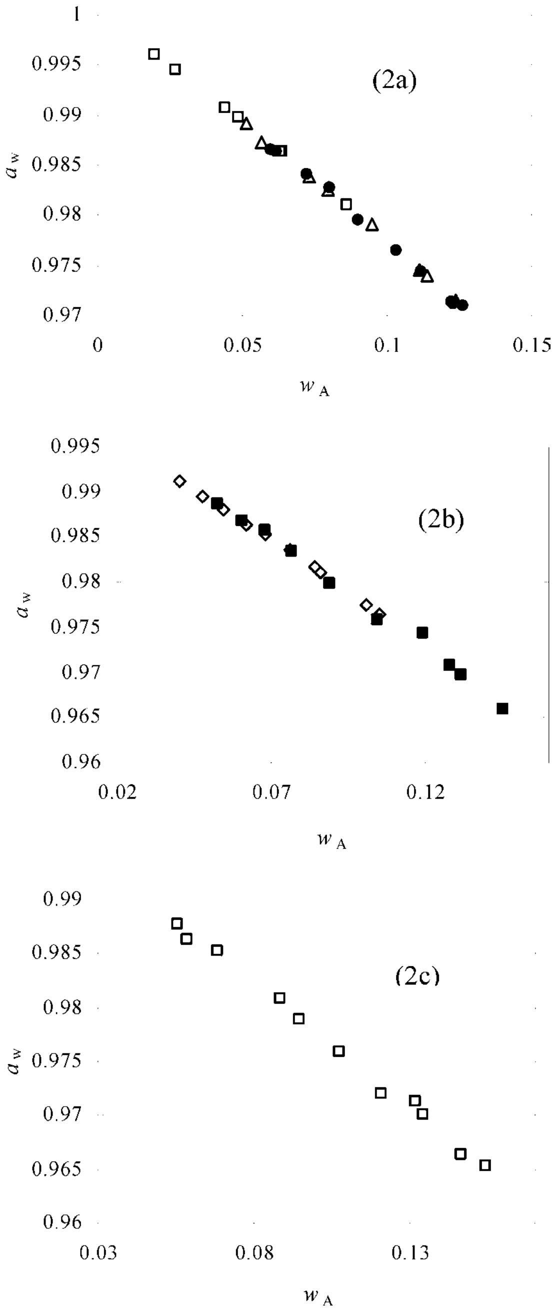

Figure 2. Comparison of measured water activity data for: (a) alanine (A) + H_2O (W) solutions at 298.15 K: ●, this work; △, ref 25; □, ref 26. (b) alanine (A) + H_2O (W) solutions at 308.15 K: ■, this work; ◇, ref 25. (c) measured water activity data for alanine (A) + H_2O (W) solutions at 318.15 K.

works.[25,26] Figure 2c shows the measured water activities of binary aqueous alanine solution at 318.15 K. The vapor pressures (p) of various aqueous solutions at each temperature were computed from the water activity measurements by using eq 3. The calculated values of p have also been given in Tables 3 to 5. The water isoactivity lines of alanine + dipotassium oxalate + H_2O system at T = (298.15, 308.15, and 318.15) K are plotted in Figures 3 to 5, respectively. As can be seen in Tables 3 to 5, in fact four points on the each line in Figures 3 to 5 have a constant water activity or chemical potential, and thus these points are in equilibrium.

In Table 6, vapor-pressure depression for the alanine + dipotassium oxalate + H_2O system along with those for corresponding binary solutions is given at T = (298.15, 308.15, and 318.15) K. This table shows that the vapor-pressure depression for ternary aqueous alanine + dipotassium oxalate system is more than the sum of those for the corresponding binary solutions. In the aqueous solutions, alanine is hydrated strongly with several water molecules. Such a binding will result in a reduction in the free water content and consequently in an increase in effective concentration of the salt. Similarly, ionic species in the aqueous dipotassium oxalate solutions are hydrated; this hydration will result in an increase in the effective concentration of the alanine. Thus, it can be expected that the vapor-pressure depression for an aqueous alanine + dipotassium oxalate system will be more than the sum of those for corresponding binary solutions.

The Pitzer formalism has been employed to model the experimental osmotic coefficient data of dipotassium oxalate in aqueous alanine solutions. According to the Pitzer formalism, the excess Gibbs free energy of a system containing a mixture of an electrolyte and a nonelectrolyte in a solvent is written in the form of a virial expansion in terms of the molalities of the solutes.[27] For a ternary system containing water, alanine, and dipotassium oxalate, we obtain the Pitzer model in the form of osmotic coefficient as

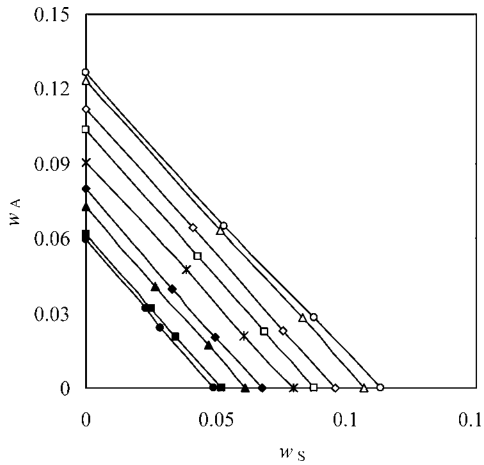

Figure 3. Plot of the mass fraction of alanine, w_A, against the mass fraction of dipotassium oxalate, w_S, for constant water activity curves of the alanine (A) + dipotassium oxalate (S) + H_2O (W) system at T = 298.15 K: ●, 0.9866; ■, 0.9864; ▲, 0.9840; ◆, 0.9827; $*$, 0.9794; □, 0.9743; ◇, 0.9764; △, 0.9713; ○, 0.9710.

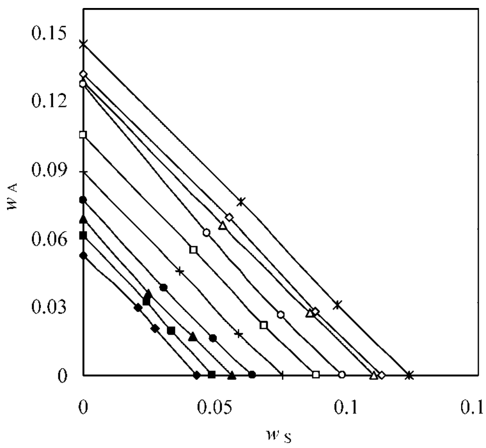

Figure 4. Plot of the mass fraction of alanine, w_A, against the mass fraction of dipotassium oxalate, w_S, for constant water activity curves of the alanine (A) + dipotassium oxalate (S) + H_2O (W) system at T = 308.15 K: ◆, 0.9886; ■, 0.9867; ▲, 0.9857; ●, 0.9834; +, 0.9799; □, 0.9758; ○, 0.9744; △, 0.9708; ◇, 0.9698; $*$, 0.9659.

$$\phi - 1 = \frac{2}{(m_A + 3m_S)}\left[-\frac{A_\phi I^{3/2}}{1 + bI^{1/2}} + 2m_S^2[\beta^{(0)} + \beta^{(1)}\exp(-\alpha I^{1/2})] + \frac{4}{\sqrt{2}}m_S^3 C^\phi + \frac{1}{2}m_A^2\lambda_{AA} + m_A^3\mu_{AAA} + 3m_A m_S\lambda_{AS} + 9m_A^2 m_S\mu_{AAS} + 2m_A m_S^2\zeta_{ASS}\right] \quad (5)$$

In this equation the parameters ζ, λ, and μ are the virial coefficients. m_A is the molality of alanine. The subscripts A and S refer to the alanine and dipotassium oxalate, respectively. To enhance the capability of this equation to correlate the experimental data of alanine both in pure water and in dipotassium oxalate solution, the following modifications to the μ_{AAA} and μ_{AAS} parameters have been introduced.[3]

$$\mu_{AAA} = \mu^0_{AAA} + \mu^1_{AAA}e^{-m_A} \quad (6)$$

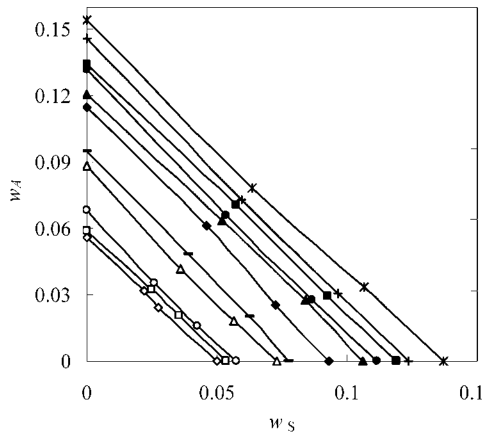

Figure 5. Plot of the mass fraction of alanine, w_A, against the mass fraction of dipotassium oxalate, w_S, for constant water activity curves of the alanine (A) + dipotassium oxalate (S) + H_2O (W) system at T = 318.15 K: ◇, 0.9877; □, 0.9863; ○, 0.9853; △, 0.9808; −, 0.9789; ◆, 0.9759; ▲, 0.9720; ●, 0.9713; ■, 0.9700; +, 0.9664; $*$, 0.9653.

Table 6. Vapor-Pressure Depression for Alanine (A) + Dipotassium Oxalate (S) + H_2O (W) Solutions along with Those for the Corresponding Binary Solutions at T = (298.15, 308.15, and 318.15) K

		$(p^0 - p)$/kPa		
w_A	w_S	alanine (A) + dipotassium oxalate (S) + H_2O (W)	alanine (A) + H_2O (W)	dipotassium oxalate (S) + H_2O (w)
		T = 298.15 K		
0.0320	0.0252	0.0922(0.0855)	0.0216	0.0210
0.0473	0.0387	0.0817(0.0782)	0.0328	0.0310
0.0641	0.0413	0.0655(0.0638)	0.0452	0.0330
0.0649	0.0532	0.0432(0.0426)	0.0455	0.0430
		T = 308.15 K		
0.0379	0.0306	0.1905(0.1402)	0.0447	0.0250
0.0544	0.0420	0.1631(0.1213)	0.0654	0.0340
0.0656	0.0532	0.1352(0.0994)	0.0793	0.0420
0.0755	0.0601	0.0927(0.0697)	0.0922	0.0480
		T = 318.15 K		
0.0351	0.0259	0.3309(0.2169)	0.0725	0.0210
0.0572	0.0461	0.2861(0.1947)	0.1211	0.0360
0.0705	0.0574	0.2299(0.1517)	0.1497	0.0450
0.0782	0.0634	0.1402(0.0935)	0.1669	0.0500

Table 7. Values of Parameters of Equation 5 Obtained from the Fitting of the Experimental Data of the Water (W) + Alanine (A) System

T/K	λ_{AA}	μ^0_{AAA}	μ^1_{AAA}	ARD %
298.15	0.6595	−0.0735	−0.6289	1.212
308.15	0.3629	−0.0386	−0.3744	1.944
318.15	0.9581	−0.1207	−0.9078	1.986

Table 8. Parameters of Equation 5 Obtained from the Fitting of the Experimental Data of the Water + Alanine + Dipotassium Oxalate Systems

T/K	λ_{AS}	μ^0_{AAS}	μ^1_{AAS}	ζ_{ASS}	ARD %
298.15	−1.274	−0.224	0.526	1.844	0.019
308.15	−1.164	−0.239	0.441	2.208	0.072
318.15	−1.203	−0.165	0.446	1.548	0.061

$$\mu_{AAS} = \mu^0_{AAS} + \mu^1_{AAS}e^{-m_S} \quad (7)$$

To evaluate the parameters of eq 5 the respective independently measured experimental data for alanine + water and potassium oxalate + water were first fitted. The relations for the properties of alanine in pure water were obtained by setting to zero the molality of dipotassium oxalate in eq 5. After setting the values of the parameters to the obtained values, eq 5 were

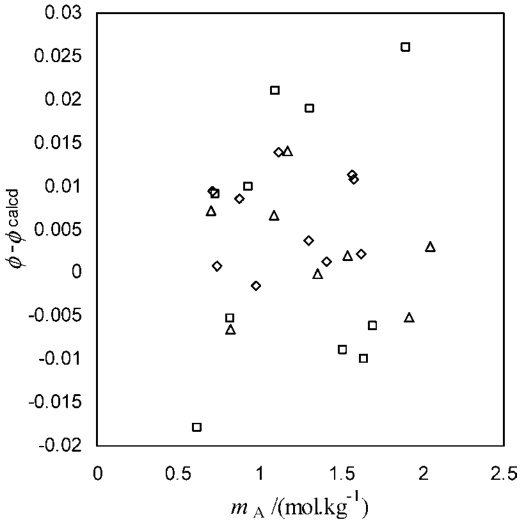

Figure 6. Plot of difference between the experimental and the calculated osmotic coefficient, ϕ, against the molality of alanine, m_A, using eq 5 for the alanine (A) + dipotassium oxalate (S) + H_2O (W) system at: ◇, T = 298.15 K; □, T = 308.15 K; △, T = 318.15 K.

applied to correlate the experimental data in the water + alanine + dipotassium oxalate ternary system. The values of the parameters of the model and corresponding deviations for water + dipotassium oxalate, water + alanine, and water + alanine + dipotassium oxalate systems are presented in Tables 2, 7, and 8, respectively. As can be seen from the small values of deviations, presented in Tables 2, 7, and 8, the Pitzer model used in this study can accurately correlate the experimental data of osmotic coefficient of dipotassium oxalate in aqueous alanine solutions over a wide range of concentration. To show the differences between the experimental and the calculated osmotic coefficient in a better manner, the values for $\phi - \phi_{calcd}$ are plotted against the molality of alanine as shown in Figure 6.

Conclusion

The accurate osmotic coefficient data measured at T = (298.15, 308.15, and 318.15) K for aqueous dipotassium oxalate solutions were fitted satisfactorily to the Pitzer model.

Vapor−liquid equilibrium data for alanine + dipotassium oxalate + water have also been determined experimentally at T = (298.15, 308.15, and 318.15) K. A model based on the Pitzer formalism has been employed to correlate the experimental osmotic coefficient data for ternary systems, and it was found that the model can be satisfactorily used to represent the vapor−liquid equilibria data for the investigated system. The results show that the vapor-pressure depression for a ternary aqueous alanine + dipotassium oxalate system is more than the sum of those for the corresponding binary solutions and increase by increasing the temperature.

Supporting Information Available:

Isopiestic equilibrium molalities, experimental osmotic coefficients, activities, and vapor pressures for the L-alanine (A) + H_2O (W) system at different temperatures in Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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