Effect of Temperature on the Volumetric Properties of the L-Alanine (1) + KCl (2) + H_2O (3) System

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The effect of temperature on the volumetric properties of the L-alanine (1) + KCl (2) + H_2O (3) system has been studied by experimentally measuring densities and speeds of sound in the temperature range 283.15 K to 313.15 K. Apparent molar expansibilities, ϕ_E, and the temperature derivative of the apparent molar compressibility, $(\partial\phi_K/\partial T)_P$, were calculated for L-alanine in aqueous KCl and for KCl in aqueous L-alanine. The positive values of expansibilities and $(\partial\phi_K/\partial T)_P$ are explained in terms of interactions between charged end groups and the ions. The derived properties are analyzed in terms of a two-parameter (λ' and λ'') model recently proposed by us. We have also attempted to examine the temperature and concentration dependence of such interaction parameters by studying the volumetric properties of the L-alanine (1) + KCl (2) + H_2O (3) system.

Introduction

Electrolytes are known to influence the stability of biologically important molecules such as proteins.[1−4] Since proteins are large complex molecules, direct study of electrolyte−protein interactions is difficult. It is therefore useful to investigate the model compounds such as amino acids that constitute the protein structures. The important tool to study the interaction between ions and amino acids is by studying the volumetric properties of amino acids in aqueous electrolyte solutions. Some reports are available in the literature on the volumetric properties of amino acids in dilute electrolytes,[5−12] suggesting the role of ion−amino acid interactions in the water-rich region. No such information is however available on how these interactions are altered in concentrated ionic solutions. Recently,[13] we have presented ion−amino acid interaction parameters with the help of a newly proposed equation for the electrolyte−amino acid and electrolyte−dipeptide systems. For complete understanding of the influence of electrolytes on amino acids, knowledge of the apparent molar expansibility in addition to volume and compressibility measurements is required. Such measurements are rare in the literature.[10−12] Some data discussing the expansibilities of only amino acids in water are available.[14,15] Thus, we herein report the temperature dependent determinations of apparent molar volume and compressibility of L-alanine in concentrated KCl, in the temperature range (283.15 to 313.15 K). We have also tried to analyze the temperature dependence of apparent molar volumes, ϕ_E, with the help of our recently proposed equation.

Experimental Section

L-Alanine (Biochemistry grade) was procured from Loba Chemicals and was used without further treatment. KCl (extra pure) was procured from Merck, and it was dried at 523 K for 3 h prior to its use. Solutions were prepared on the molality basis, using conductivity water having a specific conductivity less than 18×10^{-6} $\Omega^{-1}\cdot cm^{-1}$. The concentrations of L-alanine were 0.5 and 1 mol·kg^{-1}, while the KCl concentration varied from (1 to 4 mol·kg^{-1}).

The digital density meter (DMA 60) supplied by Anton PAAR was used to measure the densities of the solutions, ρ. The density meter was calibrated with *n*-heptane[16] and aqueous NaCl solutions.[17] The measured densities were accurate to 0.005 kg·m^{-3}, while the precision of measurement was recorded as 0.002 kg·m^{-3}.

The speeds of sound, *u*, were measured with a multifrequency ultrasonic interferometer (supplied by Mittal). The speeds of sound of aqueous NaCl at 298.15 K[18] were used for the calibration of the interferometer with an accuracy of 0.07%. The measured speeds of sound were precise to ±0.04%. Temperature was kept constant to ±0.05 K using a constant-temperature bath (supplied by Julabo).

Results and Discussion

In Table 1 are listed the experimental ρ and *u* values for the L-alanine (1) + KCl (2) + H_2O (3) system at different temperatures and concentrations of KCl. From the experimental densities and sound speeds the derived properties such as apparent molar volumes, ϕ_V, or compressibilities, ϕ_K, of L-alanine ($\phi_{V1,2,3}$ or $\phi_{K1,2,3}$) or KCl ($\phi_{V2,1,3}$ or $\phi_{K2,1,3}$) may be calculated using eqs 1a and 1b.

$$\phi_V = (\rho^\circ - \rho)/m\rho^\circ\rho + M/\rho \quad (1a)$$

$$\phi_K = (\rho^\circ\kappa_s - \rho\kappa_s^\circ)/m\rho^\circ\rho + \kappa_s M/\rho \quad (1b)$$

where ρ and κ_s denote densities and isentropic compressibilities, respectively. The superscript "°" represents the solvent properties. For calculating $\phi_{1,2,3}$ the solvent is KCl + water, and for calculating $\phi_{2,1,3}$ the solvent is L-alanine + water. *m* and *M* are the molality of the component in question and its molar mass, respectively. The densities and sound speeds of KCl (2) + water (3) (ρ° and u°) were taken from the literature,[19] and L-alanine (1) + water (3) ρ and *u* values were experimentally measured at different temperatures in our laboratory. The κ_s is calculated using the Laplace equation as $(u^2\rho)^{-1}$ with an analogous equation for κ_s°.

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Table 1. Densities and Speeds of Sound of the L-Alanine (1) + KCl (2) + H_2O (3) System at Different Temperatures

	$m_2 = 1$ mol·kg^{-1}		$m_2 = 2$ mol·kg^{-1}		$m_2 = 3$ mol·kg^{-1}		$m_2 = 4$ mol·kg^{-1}	
T/K	ρ/kg·m^{-3}	u/m·s^{-1}	ρ/kg·m^{-3}	u/m·s^{-1}	ρ/kg·m^{-3}	u/m·s^{-1}	ρ/kg·m^{-3}	u/m·s^{-1}
				$m_1 = 0.5$ mol·kg^{-1}				
283.15	1056.986	1528.5	1096.128	1569.1	1131.798	1623.1	1164.636	1654.1
288.15	1055.789	1544.5	1094.567	1592.5	1130.035	1634.2	1162.579	1664.1
298.15	1052.976	1570.1	1091.202	1611.2	1126.597	1648.1	1159.013	1675.9
308.15	1049.162	1594.2	1087.035	1624.9	1121.778	1667.9	1153.929	1681.0
313.15	1046.912	1598.1	1084.784	1636.1	1119.453	1666.2	1151.532	1686.2
				m_1=1 mol·kg^{-1}				
283.15	1067.93	1557.1	1105.031	1605.0	1139.196	1645.1	1067.93	1674.0
288.15	1066.588	1574.2	1103.486	1616.0	1137.395	1656.5	1066.588	1684.1
298.15	1063.575	1600.0	1100.028	1638.1	1133.748	1668.0	1164.957	1688.1
308.15	1059.645	1626.1	1095.695	1648.2	1129.068	1688.0	1059.645	1700.5
313.15	1057.608	1629.9	1093.556	1656.1	1126.805	1684.1	1057.608	1703.9

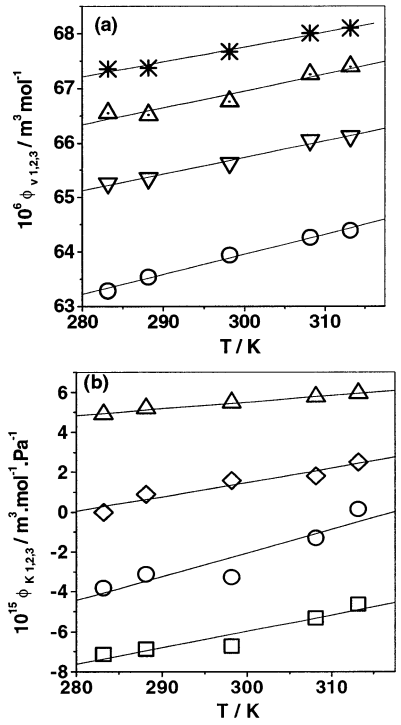

Figure 1. Plots of (a) $\phi_{V1,2,3}$ and (b) $\phi_{K1,2,3}$ versus temperature, T, in several mixtures: (a) 0.5 mol·kg^{-1} L-alanine + 3 mol·kg^{-1} KCl (△), + 4 mol·kg^{-1} KCl (∗); 1 mol·kg^{-1} L-alanine + 2 mol·kg^{-1} KCl (▽), + 1 mol·kg^{-1} KCl (○). (b) 0.5 mol·kg^{-1} L-alanine + 1 mol·kg^{-1} KCl (□), + 3 mol·kg^{-1} KCl (◇); 1 mol·kg^{-1} L-alanine + 2 mol·kg^{-1} KCl (○), + 4 mol·kg^{-1} KCl (△).

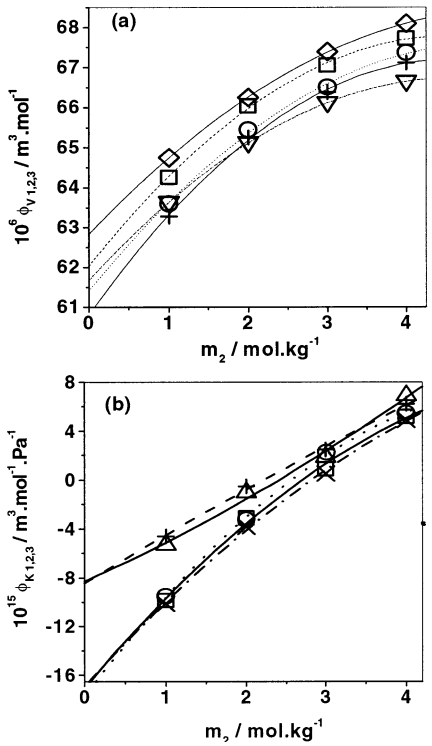

Figure 2. Plots of (a) $\phi_{V1,2,3}$ and (b) $\phi_{K1,2,3}$ versus m_2 in several mixtures: (a) 0.5 mol·kg^{-1} L-alanine at 288.15 K (○, with dotted line), 313.15 K (◇); 1 mol·kg^{-1} L-alanine at 283.15 K (+), 298.15 K (▽, with dash−dot−dash line), 308.15 K (□, with dashed line). (b) 0.5 mol·kg^{-1} L-alanine at 308.15 K (△), 313.15 K (+, with dashed line); 1 mol·kg^{-1} L-alanine at 283.15 K (×, with dash−dot−dash line), 288.15 K (□), 298.15 K (○, with dotted line).

The variation of apparent molar volume, $\phi_{V1,2,3}$, of an amino acid with temperature is shown in Figure 1a. The $\phi_{1,2,3}$ versus temperature plots show positive slopes at all the concentrations of KCl. The positive slopes shown by alanine in KCl are in accordance with the positive slopes shown by alanine in guanidinium hydrochloride[12] and KSCN.[10] The concentration of KCl does not show a drastic effect on the slopes. The average slope of the $\phi_{V1,2,3}$ versus temperature plot is 3.046×10^{-8} m^3·mol^{-1}·K^{-1}. The analogous plot for $\phi_{K1,2,3}$ is shown in Figure 1b, which also shows positive slopes.

There is an increase in the $\phi_{V1,2,3}$ from (63×10^{-6} to 68×10^{-6}) m^3·mol^{-1} due to addition of KCl and an increase in the temperature from (283.15 to 313.15 K). The change in $\phi_{V1,2,3}$ and $\phi_{K1,2,3}$ as a function of molality of KCl at different temperatures is shown in Figure 2.

At neutral pH, amino acids exist as zwitterions. The solution of amino acid in water shows an overall decrease in the volume of water. This is due to the electrostriction of water by charged end groups of amino acids. Addition of KCl will affect the hydration spheres of charged end groups. As a result of $K^+ - COO^-$ and $Cl^- - NH_3^+$ interactions, the hydrated water molecules are allowed to relax to the bulk state and cause an increase in the volume and compressibility. The increase in the temperature favors the relaxation of water molecules rather than binding of them to charged end groups, which is seen in the form of the positive slopes of $\phi_{1,2,3}$ versus temperature and $\phi_{V1,2,3}$ versus molality of KCl.

The change in hydration spheres of amino acids in the presence of ions can also be analyzed by comparing the hydration numbers of L-alanine at different temperatures and in different concentrations of KCl. The hydration number is calculated using the standard equation given by Allam and Lee:[20]

$$n_H = [1 - (\kappa_s^\circ/\kappa_s)](n_1/n_2) \qquad (2)$$

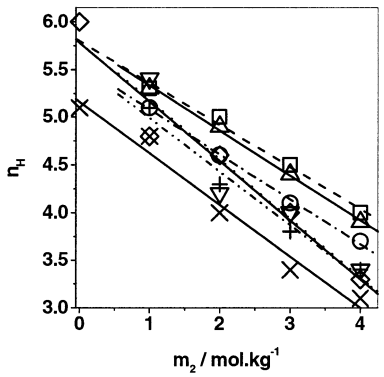

Figure 3. Hydration number, n_H, of L-alanine in L-alanine (1) + KCl (2) + H_2O (3) at 283.15 K (◇) or 313.15 K (×) and of KCl in L-alanine (1) + KCl (2) + H_2O (3) at 283.15 K (□, with dashed line), 288.15 K (△), 298.15 K (○, with dash−dot−dash line), 308.15 K (▽, with dotted line merged with solid line of (◇)), 313.15 K (+, with dash−dot−dot line).

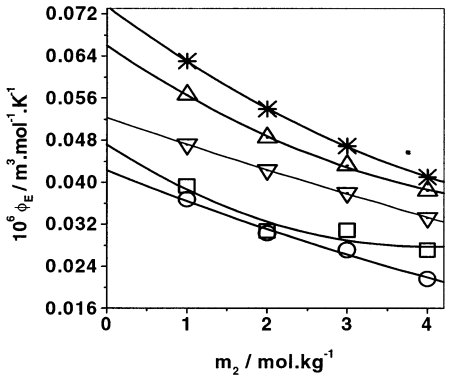

Figure 4. Plots of ϕ_E versus m_2 of 0.5 mol·kg^{-1} L-alanine (□), 1 mol·kg^{-1} L-alanine (○), KCl in H_2O (∗), 0.5 mol·kg^{-1} L-alanine (△), or 1 mol·kg^{-1} L-alanine (▽).

Table 2. Apparent Molar Expansibilities of L-Alanine and KCl in the L-Alanine (1) + KCl (2) + H_2O (3) System

m_2	$10^8\phi_{E1,2,3}$/m^3·mol^{-1}·K^{-1} at m_1/mol·kg^{-1} =		$10^8\phi_{E2,1,3}$/m^3·mol^{-1}·K^{-1} at m_1/mol·kg^{-1} =	
mol·kg^{-1}	0.5	1	0.5	1
1	3.92	3.67	5.65	4.71
2	3.07	3.03	4.84	4.23
3	3.08	2.71	4.32	3.79
4	2.71	2.16	3.84	3.32

where n_1 and n_2 are the number of moles of solvent and solute, respectively. In Figure 3 the variation of hydration numbers of L-alanine in KCl with m_2 is shown at different temperatures. The hydration numbers of 1 mol·kg^{-1} amino acid decrease from ≈5 to 3 with the increase in KCl concentration from (0 to 4) mol·kg^{-1} at 313.15 K. The hydration number of L-alanine in KCl also decreases with the increase in temperature. This decrease in n_H supports

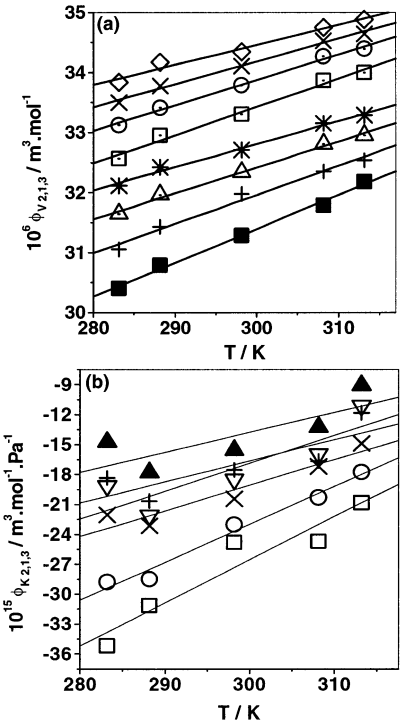

Figure 5. Plots of (a) $\phi_{V2,1,3}$ and (b) $\phi_{K1,2,3}$ versus temperature, T, in several mixtures: (a) 0.5 mol·kg^{-1} L-alanine + 1 mol kg^{-1} KCl (■), + 2 mol·kg^{-1} KCl (+), + 3 mol·kg^{-1} KCl (△), + 4 mol·kg^{-1} KCl (∗); 1 mol·kg^{-1} L-alanine + 1 mol·kg^{-1} KCl (□), + 2 mol·kg^{-1} KCl (○), + 3 mol·kg^{-1} KCl (×), + 4 mol·kg^{-1} KCl (◇). (b) 0.5 mol·kg^{-1} L-alanine + 2 mol·kg^{-1} KCl (○), + 4 mol·kg^{-1} KCl (▽); 1 mol·kg^{-1} L-alanine + 1 mol·kg^{-1} KCl (□), + 2 mol·kg^{-1} KCl (×), + 3 mol·kg^{-1} KCl (+), + 4 mol·kg^{-1} KCl (▲).

the assumption that, due to interaction of charged end groups and ions, water is relaxed in the bulk state.

The apparent molar expansibility of L-alanine, $\phi_{E1,2,3}$, in KCl may be defined as

$$\phi_{E1,2,3} = (\partial\phi_{V1,2,3}/\partial T)_P \qquad (3)$$

The values of $\phi_{E1,2,3}$ in different concentrations of KCl are listed in Table 2. In Figure 4 is illustrated the variation of $\phi_{E1,2,3}$ with respect to m_2. We have analyzed the $\phi_{E1,2,3}$ values using the model recently proposed by us.[13] The volumetric properties such as $\phi_{V1,2,3}$ and $\phi_{K1,2,3}$ can be satisfactorily estimated using a two-parameter equation. Thus, the equation for estimating $\phi_{E1,2,3}$ can be written as

$$\phi_{E1,2,3} = \phi_E^\circ{}_{1,2,3} + s_E m_1 + RT[\lambda' m_2 + \lambda'' m_2^2] \qquad (4)$$

where $\phi_E^\circ{}_{1,2,3}$ is the apparent molar expansibility of L-alanine at infinite dilution of KCl, s_E is the limiting slope for $\phi_{E1,3}$, having the value 3.15 × 10^{-8} kg·m^3·K^{-1}·mol^{-2}, R

Table 3. Values of the Interaction Parameters λ' and λ'' of Eqs 4 and 5 for the L-Alanine (1) + KCl (2) + H_2O (3) System (Values within Parentheses Are Errors in the Listed Parameters)

m_2	$10^8\phi_{E1,2,3}$	$10^{13}\lambda'$	$10^{14}\lambda''$	10^8rmsd
mol·kg^{-1}	m^3·mol^{-1}·K^{-1}	kg·mol^{-1}·K^{-1}·Pa^{-1}	kg^2·mol^{-2}·K^{-1}·Pa^{-1}	m^3·mol^{-1}·K^{-1}
0.5	3.130 (0.17)	−3.901 (0.633)	4.881 (1.250)	0.11
1	1.068 (0.08)	−2.420 (0.282)	0.928 (0.565)	0.05
m_2	$10^8\phi_{E2,1,3}$	$10^{13}\beta_{2,1}{}^{(0)E}$	$10^{14}C_{2,1}{}^{\varphi}E$	10^8rmsd
mol·kg^{-1}	m^3·mol^{-1}·K^{-1}	kg·mol^{-1}·K^{-1}·Pa^{-1}	kg^2·mol^{-2}·K^{-1}·Pa^{-1}	m^3·mol^{-1}·K^{-1}
0.5	6.29 (0.04)	−2.873 (0.008)	5.033 (0.346)	0.03
1	5.04 (0.02)	−1.810 (0.004)	1.870 (0.182)	0.01

is the universal gas constant, T is the absolute temperature, and λ' and λ'' are the amino acid−electrolyte interaction parameters indicating two- and three-body interactions terms, respectively. The λ'' term is required here, as the concentration of the electrolytes is high in this study. The values of λ' and λ'' are listed in Table 3.

Using the above equation, the $\phi_{E1,2,3}$ values can be estimated accurately. The average rmsd (root-mean-squares deviation) in the estimation of $\phi_{E1,2,3}$ is 0.1×10^{-8} kg·m^3·K^{-1}. The utility of eq 4 can be seen from Figure 4, where the line represents the estimated $\phi_{E1,2,3}$ values.

Since the temperature effect on $\phi_{1,2,3}$ in the presence of KCl was studied, it would be of interest to check the thermal expansion of KCl as modified by L-alanine. The variation of apparent molar volume, $\phi_{V2,1,3}$, and compressibility, $\phi_{K2,1,3}$, of KCl with temperature is shown in parts a and b, respectively, of Figure 5. The $\phi_{V2,1,3}$ varies from (30×10^{-6} to 35×10^{-6}) m^3·mol^{-1}. The dependence of $\phi_{V2,1,3}$ and $\phi_{K2,1,3}$ on m_2 is illustrated in parts a and b, respectively, of Figure 6. The apparent molar expansibility of KCl in the presence of L-alanine is calculated using an analogous equation to eq 3, and the values are listed in Table 2.

The apparent molar expansibility of an electrolyte, $\phi_{E2,1,3}$, in aqueous L-alanine can be obtained from a combination of the specific interaction theory of Pitzer[21] and the interaction terms (λ' and λ'') obtained in this work. The Pitzer equations employ the modified Debye−Huckel equation and a combination of virial coefficients to account for the long-range and short-range interactions, respectively. The λ' and λ'' obtained above are inserted in the Pitzer equations to give $\phi_{E2,1,3}$ (of 1:1 type electrolyte) in aqueous L-alanine as

$$\phi_{E2,1,3} = \phi_E^\circ{}_{2,1,3} + 2A_E(1/2)b \ln(1 + bI^{1/2}) + RT\{m_2\beta_{2,1}^{(0)E} + m_2{}^2C_{2,1}^{\varphi E} + \lambda' m_1 + \lambda'' m_1{}^2\} \quad (5)$$

where $\phi_E^\circ{}_{2,1,3}$ is $\phi_{E2,1,3}$ at infinite dilution of KCl and $\beta_{2,1}^{(0)E}$ and $C_{2,1}^{\varphi E}$ are the Pitzer coefficients[21] in the L-alanine−water medium (and not in pure water alone) and are specific to a given electrolyte. The values of Pitzer coefficients are listed in Table 3. The value of A_E for expansibility at 298.15 K is 1.6918×10^{-7} kg$^{0.5}$·m^3·mol$^{-1.5}$·K^{-1}. $b = 1.2$. Ionic strength, I, is defined as $I = 0.5\sum m_i z_i^2$ with z being ionic charge. The agreement between the experimental and calculated $\phi_{E2,1,3}$ values can be seen from Figure 4. The average rmsd in estimation of $\phi_{E2,1,3}$ is 0.03×10^8 m^3·mol^{-1}·K^{-1}. The temperature derivatives of $\phi_{K1,2,3}$ and $\phi_{K2,1,3}$ also show similar results, but errors incorporated in this derived property are high. So the model is not applied for $(\partial\phi_K/\partial T)_P$.

Hydration numbers are also calculated for KCl in the presence of amino acid. The effect of concentration of amino acid and temperature on the hydration number of KCl is similar to that observed for L-alanine in aqueous KCl. The hydration number of KCl in 1 mol·kg^{-1} aqueous L-alanine decreases from ≈5 to 3 when KCl concentration increases from 1 to 4 mol·kg^{-1} at 313.15 K. The change in n_H of KCl is plotted in Figure 3.

In summary, we have shown the temperature dependence of ion−amino acid interaction parameters from the volumetric properties of L-alanine + KCl + H_2O. Apparent molar expansibilities and $(\partial\phi_K/\partial T)_P$ of L-alanine in aqueous KCl and of KCl in aqueous L-alanine are calculated from the measured quantities. We have also demonstrated the use of a two-parameter equation in analyzing the apparent molar expansibilities of amino acid and electrolyte.

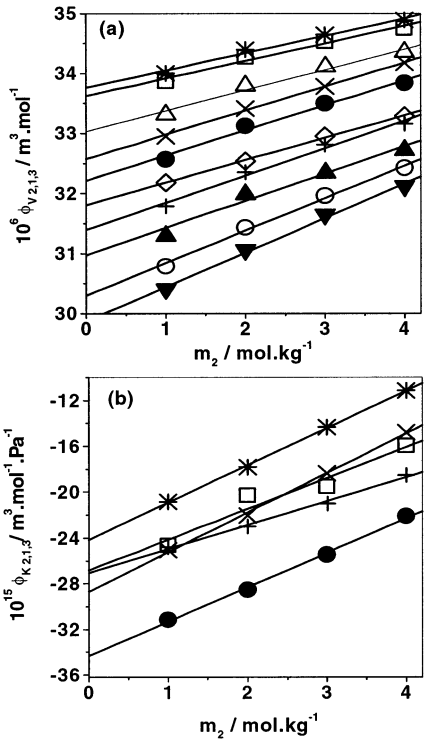

Figure 6. Plots of (a) $\phi_{V2,1,3}$ and (b) $\phi_{K1,2,3}$ versus m_2 in several mixtures: (a) 0.5 mol·kg^{-1} L-alanine at 283.15 K (▼), 288.15 K (○), 298.15 K (▲), 308.15 K (+), 313.15 K (◇); 1 mol·kg^{-1} L-alanine at 283.15 K (●), 288.15 K (×), 298.15 K (△), 308.15 K (□), 313.15 K (∗). (b) 0.5 mol·kg^{-1} L-alanine at 288.15 K (●), 298.15 K (+), 308.15 K (□), 313.15 K (∗); 1 mol·kg^{-1} L-alanine at 283.15 K (×).

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