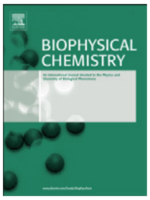
Biophysical Chemistry 135 (2008) 116–124

Contents lists available at ScienceDirect

Biophysical Chemistry

journal homepage: http://www.elsevier.com/locate/biophyschem



Effect of potassium citrate salts on the vapor–liquid equilibrium properties of aqueous solutions of alanine at different temperatures

Rahmat Sadeghi *, Baharak Goodarzi

Department of Chemistry, University of Kurdistan, Sanandaj, Iran

ARTICLE INFO

Article history:
Received 13 March 2008
Received in revised form 31 March 2008
Accepted 31 March 2008
Available online 10 April 2008

Keywords:
Water activity
Vapor–liquid equilibria
Isopiestic
Alanine
Potassium citrate

ABSTRACT

Water activity measurements by isopiestic method have been carried out on the aqueous solutions of alanine + potassium di-hydrogen citrate (KH_2Cit) and alanine + tri-potassium citrate (K_3Cit) over a range of temperatures at atmospheric pressure. From these measurements, values of the vapor pressure of solutions were determined. The effect of temperature and charge on the anion of salts on the vapor–liquid equilibrium of the investigated systems has been studied. The experimental water activities have been correlated successfully with the segment-based local composition Wilson and NRTL models. The agreement between the correlations and the experimental data is good.

1. Introduction

Separation and concentration of biochemicals are two current subjects of interest due to their high cost in comparison to the total manufacturing cost [1]. The behavior of biomolecules in mixtures is affected by many factors such as chemical structure, pH, surface charge distribution, and type of electrolyte present and its concentration. The effect of the presence of electrolytes in solutions of biochemicals is of interest in a number of separation processes, such as the reverse micellar extraction of amino acids and proteins which may not occur without the presence of an electrolyte [2,3]. In addition, amino acids are the building blocks of other biomolecules such as peptides and proteins. Thus, it is important to study their behavior in aqueous systems containing electrolytes. Although thermodynamic properties (such as volumetric and viscometric behavior) of amino acids in aqueous electrolyte solutions have been extensively studied by many research groups [4], however there ar only few studies about vapor–liquid equilibrium (VLE) of amino acids in aqueous electrolyte solutions in the literature and all of them are limited to 298.15 K and have been reported by only few research groups [5–17]. Knowledge of the vapor–liquid equilibrium of amino acids in aqueous solutions is of practical and theoretical interest to determine the thermodynamic properties of these systems and in the elucidation of solute–solute and solute–water interactions as well as in the design of industrial separation and purification processes. Furthermore regarding to the thermodynamic properties of aqueous electrolyte solutions, much less attention has been directed to organic salts which have significant biological and industrial importance. Among the organic salts, citrates are of a considerable significance in many biochemical and chemical processes and these salts are produced in large quantities and used in food, cosmetic, pharmaceutical and chemical industries [18–21].

In continuation of our previous work on the VLE properties of alanine in aqueous potassium citrate salts solutions [22], this work is devoted to obtaining the water activities of the binary KH_2Cit + water and ternary alanine + KH_2Cit + water system at (293.15 to 313.15) K. In this study, the isopiestic method [23] is used to obtain the activity of water in the investigated systems. Although there are some reports on the water activity of binary aqueous alanine solutions [24–29], however there are no any experimental data on the vapor–liquid equilibria of ternary aqueous solutions of alanine + KH_2Cit in the literature. Furthermore as far as we know there is no report on the vapor–liquid equilibrium data for binary aqueous KH_2Cit systems in the literature. In order to study the effect of type of salt on the vapor–liquid equilibria of aqueous alanine + electrolyte solutions, the isopiestic apparatus consisted of nine-leg manifold attached to round-bottom flasks was also used to obtain concentrations in ternary solutions alanine + KH_2Cit + water and alanine + K_3Cit + water which have a same water activity. Finally, the segment-based local composition Wilson [30] and NRTL [31] models were used for the correlation of the obtained experimental water activity data.

2. Experiments

2.1. Materials

Alanine (S-(+)-Alanine), potassium di-hydrogen citrate ($C_6H_7KO_7$) and sodium chloride were obtained from Merck. Tri-potassium citrate

---

* Corresponding author. Tel./fax: +98 871 6624133.
E-mail addresses: rahsadeghi@yahoo.com, rsadeghi@uok.ac.ir (R. Sadeghi).

0301-4622/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.bpc.2008.03.014

Table 1
Water activity (a_w) and vapor pressures (p) for KH_2Cit (e)+H_2O (w) system at different temperatures

T=293.15 K			T=298.15 K			T=303.15 K			T=308.15 K			T=313.15 K		
w_e	a_w	p/kPa	w_e	a_w	p/kPa	w_e	a_w	p/kPa	w_e	a_w	p/kPa	w_e	a_w	p/kPa
0.0000	1.0000	2.338	0.0000	1.0000	3.169	0.0000	1.0000	4.245	0.0000	1.0000	5.626	0.0000	1.0000	7.381
0.0430	0.9934	2.323	0.0475	0.9929	3.146	0.0413	0.9936	4.218	0.0485	0.9927	5.585	0.0451	0.9924	7.325
0.0519	0.9925	2.321	0.0607	0.9907	3.139	0.0463	0.9929	4.215	0.054	0.9923	5.583	0.0492	0.9921	7.323
0.0605	0.9914	2.318	0.0925	0.9873	3.128	0.0563	0.9916	4.209	0.0553	0.9921	5.582	0.0508	0.9917	7.320
0.0706	0.9902	2.316	0.1123	0.9852	3.122	0.0575	0.9916	4.209	0.0596	0.9916	5.579	0.0533	0.9916	7.319
0.0767	0.9895	2.314	0.1370	0.9819	3.111	0.0583	0.9916	4.209	0.0683	0.9903	5.572	0.0588	0.9912	7.316
0.0798	0.9893	2.313	0.1478	0.9806	3.107	0.0698	0.9896	4.201	0.0833	0.9885	5.562	0.0643	0.9906	7.312
0.0969	0.9869	2.308	0.1547	0.9797	3.104	0.0931	0.9868	4.189	0.0964	0.9867	5.551	0.0730	0.9894	7.303
0.1091	0.9854	2.304				0.1006	0.9856	4.184	0.1137	0.9843	5.538	0.0838	0.9878	7.291
0.1127	0.9848	2.303				0.1200	0.9834	4.175	0.1195	0.9835	5.533	0.0886	0.9875	7.289
0.1216	0.9838	2.301				0.1261	0.9821	4.169	0.1357	0.9811	5.520	0.0893	0.9873	7.287
0.1301	0.9828	2.298				0.1471	0.9797	4.159	0.1606	0.9779	5.502	0.0928	0.9868	7.284
0.1388	0.9821	2.297				0.1633	0.9772	4.148	0.1703	0.9769	5.496	0.1081	0.9850	7.270
0.1453	0.9812	2.294				0.1938	0.9738	4.134	0.1824	0.9752	5.487	0.1139	0.9844	7.266
						0.2058	0.9722	4.127				0.1157	0.9842	7.264
												0.1244	0.9829	7.255
												0.1287	0.9824	7.251
												0.1523	0.9790	7.226

($C_6H_5K_3O_7.H_2O$) was obtained from Fluka. The amino acid and salts were used without further purification, and double distilled, deionized water was used.

2.2. Method

The isopiestic apparatus used in this work was similar to the one used by Ochs et al. [23]. The apparatus used for determination of water activity of binary aqueous KH_2Cit solutions consisted of five-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions, two flasks contained the pure KH_2Cit solutions and the central flask was used as a water reservoir. The apparatus used for determination of water activity of ternary aqueous alanine+KH_2Cit solutions consisted of seven-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions, one flask contained the pure alanine solution, one flask contained the pure KH_2Cit solution, two flasks contained the alanine+KH_2Cit solutions and the central flask was used as a water reservoir. The apparatus used for determination of the effect of charge on the anion of electrolytes on the vapor–liquid equilibria of aqueous alanine+electrolyte solutions, consisted of nine-leg manifold attached to round-bottom flasks. One flask contained the standard pure NaCl solutions, one flask contained the pure alanine solution, one flask contained the pure KH_2Cit solution, one flask contained the pure K_3Cit solution, two flasks contained the alanine+KH_2Cit solutions, two flasks contained the alanine+K_3Cit solutions and the central flask was used as a water reservoir. The apparatus was held in a constant-temperature bath at least 120 h for equilibrium. During the equilibration process the manifold was removed at least once a day and the samples were agitated. After the third day the samples were not agitated, but left in the bath to approach their final equilibrium conditions. 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 $\pm 1\cdot 10^{-4}$ g. From the weight of each flask after equilibrium and the initial weight of salt and alanine, the mass fraction of each solution was calculated. The water activity for the standard aqueous NaCl solutions at different concentrations and temperatures has been calculated from the correlation of Colin et al. [32]. 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 mass fractions of two standard solutions are reported. The accuracy of the method depends upon the standard solutions, sample mixing during the equilibrium period, temperature stability, and the time allowed for the equilibrium process. The uncertainty in the measurement of solvent activity was estimated to be $\pm 2\cdot 10^{-4}$.

3. Results and discussion

3.1. Experimental results

In the present work, in order to describe thermodynamic properties of both binary aqueous KH_2Cit and ternary aqueous KH_2Cit+alanine solutions, the water activity measurements at 293.15, 298.15, 303.15, 308.15, and 313.15 K were carried out for binary KH_2Cit+H_2O and ternary KH_2Cit+alanine+H_2O solutions to study the vapor–liquid equilibria behavior of these systems. Furthermore, in order to describe the effect of type of salt on the vapor–liquid equilibrium behavior of aqueous alanine+electrolyte solutions, equilibrium compositions of ternary alanine+KH_2Cit+water and alanine+K_3Cit+water solutions have been determined at 293.15, 298.15, 303.15, 308.15, and 313.15 K. Table 1 reports the water activity data of binary KH_2Cit+H_2O system at 293.15, 298.15, 303.15, 308.15, and 313.15 K. Tables 2–6 report the water activities of alanine+KH_2Cit+H_2O system at 293.15, 298.15,

Table 2
Water activity (a_w) and vapor pressures (p) for alanine (m)+KH_2Cit (e)+H_2O (w) at T=293.15 K

w_m	w_e	a_w	p/kPa	w_m	w_e	a_w	p/kPa
0.0352	0	0.9922	2.320	0.06	0	0.9867	2.307
0.0241	0.0171			0.0391	0.033		
0.0107	0.0368			0.0176	0.0681		
0	0.053			0	0.0985		
0.0427	0	0.9907	2.317	0.0638	0	0.9856	2.305
0.0291	0.0207			0.0432	0.0323		
0.0166	0.0399			0.0218	0.0681		
0	0.0669			0	0.1033		
0.0483	0	0.9893	2.313	0.0744	0	0.9838	2.301
0.0334	0.0225			0.0503	0.0372		
0.0187	0.0458			0.0263	0.0769		
0	0.0748			0	0.1216		
0.0499	0	0.9893	2.313	0.0811	0	0.9821	2.297
0.0337	0.0257			0.0545	0.0435		
0.0136	0.0576			0.0274	0.0896		
0	0.0798			0	0.1388		
0.0594	0	0.9863	2.306	0.0857	0	0.9812	2.294
0.0411	0.0297			0.0592	0.0415		
0.0184	0.0661			0.0275	0.0962		
0	0.0984			0	0.1453		

Table 3
Water activity (a_w) and vapor pressures (p) for alanine (m)+KH_2Cit (e)+H_2O (w) at T=298.15 K

w_m	w_e	a_w	p/kPa	w_m	w_e	a_w	p/kPa
0.0421	0	0.9908	3.139	0.0714	0	0.9843	3.119
0.0291	0.0199			0.0487	0.0346		
0.0134	0.0437			0.0237	0.0751		
0	0.0649			0	0.1156		
0.0489	0	0.9895	3.135	0.0811	0	0.9814	3.110
0.0333	0.0245			0.057	0.0406		
0.0161	0.0506			0.027	0.0898		
0	0.0755			0	0.1367		
0.0535	0	0.9881	3.131	0.0909	0	0.9798	3.105
0.0316	0.034			0.0645	0.0446		
0.0164	0.0574			0.0337	0.0958		
0	0.0837			0	0.1541		
0.0558	0	0.9873	3.128	0.1069	0	0.9762	3.093
0.0356	0.0281			0.0728	0.0554		
0.0191	0.0547			0.031	0.1266		
0	0.0836			0	0.1832		
0.0649	0	0.9854	3.122				
0.0403	0.0358						
0.0198	0.0683						
0	0.0998						

Table 5
Water activity (a_w) and vapor pressures (p) for alanine (m)+KH_2Cit (e)+H_2O (w) at T=308.15 K

w_m	w_e	a_w	p/kPa	w_m	w_e	a_w	p/kPa
0.0345	0	0.9927	5.585	0.0749	0	0.9835	5.533
0.024	0.0178			0.0515	0.0369		
0.0108	0.0356			0.0237	0.0808		
0	0.0514			0	0.1179		
0.0459	0	0.9904	5.572	0.078	0	0.9832	5.532
0.0307	0.0229			0.0539	0.0358		
0.0144	0.0495			0.0261	0.0827		
0	0.0698			0	0.1242		
0.051	0	0.9882	5.560	0.084	0	0.9816	5.523
0.03	0.0306			0.0574	0.0425		
0.0192	0.0483			0.0249	0.0928		
0	0.0772			0	0.1321		
0.0608	0	0.9867	5.551	0.0987	0	0.9782	5.504
0.0453	0.0237			0.0684	0.0503		
0.02	0.063			0.0299	0.1126		
0	0.095			0	0.1614		
0.0668	0	0.9855	5.545	0.1118	0	0.9751	5.486
0.045	0.0329			0.0782	0.0513		
0.0207	0.0715			0.0426	0.1099		
0	0.1071			0	0.1869		

303.15, 308.15, and 313.15 K, respectively. Table 7 shows the different ternary aqueous KH_2Cit+alanine and K_3Cit+alanine solutions which have a constant water activity at different temperatures. Fig. 1 shows that there is a good agreement between the experimental water activity data of binary aqueous alanine solutions measured in this work and those taken from reference [29]. The vapor pressures (p) of various aqueous solutions at each temperature were computed from the water activity measurements by using the following equation:

$$p = a_w p^\circ \tag{1}$$

where p° is the vapor pressure of pure water, which was calculated using the equation of state of Saul and Wagner [33]. The uncertainties in p values obtained using method of propagation of errors and uncertainty for the experimental water activity ($\pm 2 \cdot 10^{-4}$) were found to be $\pm 5 \cdot 10^{-4}$, $\pm 6 \cdot 10^{-4}$, $\pm 8 \cdot 10^{-4}$, $\pm 1.1 \cdot 10^{-3}$ and $\pm 1.5 \cdot 10^{-3}$ respectively at 293.15, 298.15, 303.15, 308.15, and 313.15 K. Fig. 2 shows that the measured water activities of aqueous potassium di-hydrogen citrate solutions (similar to those of aqueous tri-potassium citrate solutions) are independent of temperature. As can be seen from Fig. 2, at a constant salt molality, the water activity data for K_3Cit+H_2O system are smaller than those for KH_2Cit+H_2O system. In other words, at a constant salt molality and temperature the vapor pressure depression for K_3Cit+water system is more than those for KH_2Cit+water system. This behavior can be attributed to the fact that the interactions between Cit^{3-} (produced from the dissociation of K_3Cit) and water are stronger than the interactions between H_2Cit^{1-} (produced from the dissociation of KH_2Cit) and water. In Figs. 3 and 4, the effect of temperature on the vapor pressure depression has been shown, respectively, for KH_2Cit+water and alanine+water systems. Although, temperature has very slightly effect on the water activities of alanine+water and KH_2Cit+water systems, however, as can be seen from Figs. 3 and 4, vapor pressure depression of both alanine+water and KH_2Cit+water systems increases by increasing temperature. As can be seen from Fig. 5, at a constant temperature and salt molality the vapor pressure depression follows the order K_3Cit+water>KH_2Cit+water-alanine+water, which indicate that the solute–water interactions in the electrolyte solutions are stronger than those in the amino acid solutions. In Fig. 6, comparisons of the experimental water activity data for KH_2Cit+water system measured in this work with those for

Table 4
Water activity (a_w) and vapor pressures (p) for alanine (m)+KH_2Cit (e)+H_2O (w) at T=303.15 K

w_m	w_e	a_w	p/kPa	w_m	w_e	a_w	p/kPa
0.0415	0	0.9911	4.207	0.0739	0	0.9837	4.176
0.0285	0.0199			0.0477	0.0411		
0.0168	0.0373			0.0148	0.0945		
0	0.0628			0	0.1208		
0.0554	0	0.9884	4.1960	0.0812	0	0.9822	4.169
0.0377	0.0274			0.0546	0.0429		
0.0177	0.0588			0.0274	0.0871		
0	0.0866			0	0.1326		
0.0561	0	0.9878	4.193	0.0822	0	0.9821	4.169
0.0437	0.0197			0.0594	0.0363		
0.0314	0.0388			0.0336	0.0784		
0	0.0879			0	0.1348		
0.0589	0	0.9872	4.191	0.1	0	0.9775	4.150
0.0517	0.0127			0.0692	0.0483		
0.0308	0.0442			0.032	0.1078		
0	0.0942			0	0.1574		
0.0601	0	0.987	4.190				\
0.0503	0.0157						
0.0324	0.0441						
0	0.0946						

Table 6
Water activity (a_w) and vapor pressures (p) for alanine (m)+KH_2Cit (e)+H_2O (w) at T=313.15 K

w_m	w_e	a_w	p/kPa	w_m	w_e	a_w	p/kPa
0.0459	0	0.9897	7.305	0.0818	0	0.9821	7.249
0.0312	0.0242			0.0538	0.0419		
0.014	0.0503			0.0298	0.0793		
0	0.0702			0	0.1264		
0.0486	0	0.9895	7.304	0.0965	0	0.9785	7.222
0.0322	0.0268			0.0604	0.0574		
0.015	0.0515			0.0342	0.099		
0	0.0756			0	0.154		
0.0527	0	0.9878	7.291	0.0974	0	0.9785	7.222
0.0379	0.023			0.0677	0.0474		
0.017	0.0543			0.031	0.1079		
0	0.0804			0	0.1561		
0.0605	0	0.987	7.285	0.111	0	0.9752	7.198
0.0386	0.0317			0.0764	0.0554		
0.0195	0.0617			0.0367	0.1204		
0	0.0916			0	0.1801		
0.0718	0	0.9848	7.269				
0.0459	0.0386						
0.021	0.0769						
0	0.111						

Table 7
Water activity (a_w) and vapor pressures (p) for different equilibrium compositions of alanine (m)+KH_2Cit (e)+H_2O (w) and alanine (m)+K_3Cit (e)+H_2O (w) at different temperatures

Alanine(m)+KH_2Cit(e)+H_2O(w)		Alanine (m)+K_3Cit (e)+H_2O(w)			
w_m	w_e	w_m	w_e	a_w	p/kPa
T=293.15 K					
0.0623	0	0.0623	0	0.9866	2.307
0.0412	0.0334	0.0428	0.0231		
0.0190	0.0698	0.0169	0.0551		
0	0.1003	0	0.0758		
0.0904	0	0.0904	0	0.9802	2.292
0.0621	0.0454	0.0564	0.0396		
0.0326	0.0969	0.0246	0.0794		
0	0.1546	0	0.1087		
T=298.15 K					
0.0469	0	0.0469	0	0.9902	3.138
0.0335	0.0197	0.0276	0.0228		
0.0159	0.0470	0.0120	0.0404		
0	0.0707	0	0.0556		
0.0657	0	0.0657	0	0.9857	3.123
0.0409	0.0381	0.0415	0.0293		
0.0210	0.0700	0.0170	0.0580		
0	0.1054	0	0.0788		
0.0921	0	0.0921	0	0.9794	3.103
0.0620	0.0506	0.0588	0.0416		
0.0295	0.1064	0.0272	0.0795		
0	0.1556	0	0.1118		
T=303.15 K					
0.0446	0	0.0446	0	0.9898	4.202
0.0291	0.0221	0.0271	0.0187		
0.0131	0.0467	0.0115	0.0379		
0	0.0658	0	0.0531		
0.0639	0	0.0639	0	0.9865	4.188
0.0449	0.0315	0.0409	0.0269		
0.0195	0.0692	0.0178	0.0548		
0	0.1002	0	0.0762		
0.0944	0	0.0944	0	0.9789	4.156
0.0670	0.0476	0.0594	0.0434		
0.0326	0.1026	0.0259	0.0833		
0	0.1600	0	0.1138		
T=308.15 K					
0.0480	0	0.0480	0	0.9885	5.562
0.0313	0.0238	0.0287	0.0218		
0.0144	0.0487	0.013	0.0413		
0	0.0717	0	0.0559		
0.0545	0	0.0545	0	0.9881	5.56
0.0310	0.0319	0.0312	0.0251		
0.0159	0.0554	0.0139	0.0450		
0	0.0797	0	0.0627		
0.0665	0	0.0665	0	0.9861	5.548
0.0456	0.0290	0.0411	0.0261		
0.0203	0.0698	0.0188	0.0523		
0	0.0996	0	0.0767		
T=313.15 K					
0.0390	0	0.039	0	0.9908	7.313
0.0272	0.0184	0.0247	0.0170		
0.0122	0.0413	0.0110	0.0338		
0	0.0589	0	0.0488		
0.0521	0	0.0521	0	0.9886	7.297
0.0322	0.0263	0.0311	0.0241		
0.0184	0.0470	0.0135	0.0447		
0	0.0754	0	0.0620		
0.0640	0	0.0640	0	0.9862	7.279
0.0451	0.0294	0.0420	0.0274		
0.0206	0.0664	0.0192	0.0542		
0	0.0990	0	0.0777		

K_3Cit+water [34], Na_3Cit+water [35] and H_3Cit+water [36] systems have been made at 298.15 K. This figure shows that, at a constant temperature and molality the water activity follows the order H_3Cit+water>KH_2Cit+water>Na_3Cit+water>K_3Cit+water.

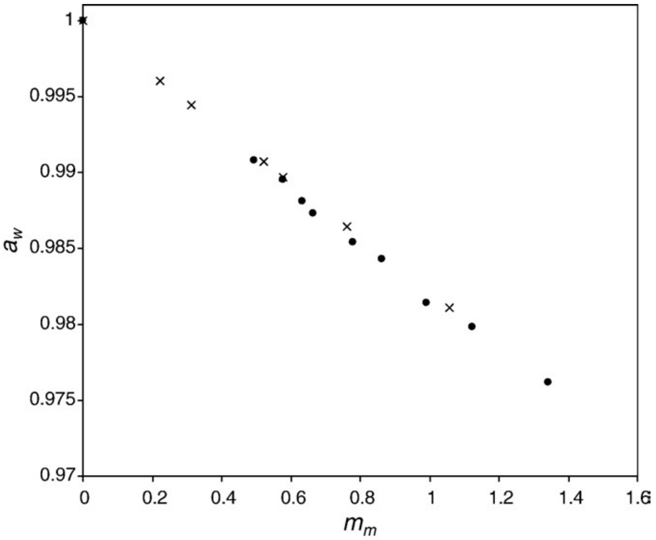


Fig. 1. Comparison of measured water activity data, a_w, for alanine+H_2O solutions at 298.15 K: ●, this work; ×, reference [29].

As an example, the lines of constant water activity or vapor pressure of alanine+KH_2Cit+H_2O system at 308.15 K are plotted in Fig. 7. As can be seen in Tables 2–7, in fact four points on each line in Fig. 7 have a constant water activity or chemical potential and thus these points are in equilibrium. In Fig. 8, comparison between the lines of constant water activity or vapor pressure for alanine+KH_2Cit+H_2O and alanine+K_3Cit+H_2O systems has been made at 298.15 K. As can be seen from this figure, the slope of the constant water activity lines increases with increasing the charge on the anion of electrolyte. Fig. 8 shows that, at the same water activity, the concentration of salt which is in equilibrium with a certain concentration of alanine decreases with increasing the charge on the anion of electrolyte. Fig. 8 also shows that, the concentration of salt in ternary systems with a same concentration of alanine and water activity, decreases with increasing the charge on the anion of electrolyte. This is because the anion with higher valence hydrates more water molecules than the anions with lower valence and therefore increasing the charge on the anion from −1 (H_2Cit^{1-}) to −3 (Cit^{3-}) lowers the salt concentrations required to achieve a certain water activity. Fig. 9 shows that, similar to the alanine+K_3Cit+H_2O system, the temperature has very slightly

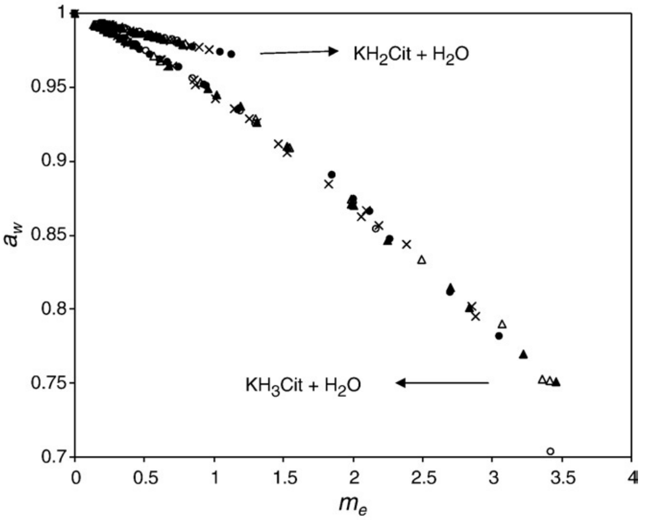


Fig. 2. Plot of water activity data, a_w, against salt molality, m_e, for KH_2Cit+H_2O and K_3Cit+H_2O [34] solutions at different temperatures: ○, T=293.15 K; △, T=298.15 K; ●, T=303.15 K; ×, T=308.15 K; ▲, T=313.15 K.

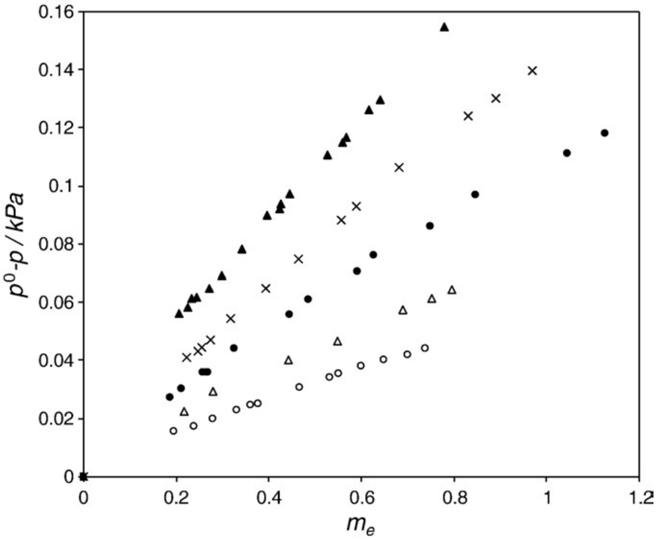


Fig. 3. Plot of vapor pressure depression data, (p^0-p)/kPa, against molality of KH_2Cit, m_e, for KH_2Cit+H_2O system at different temperatures: ○, T=293.15 K; △, T=298.15 K; ●, T=303.15 K; ×, T=308.15 K; ▲, T=313.15 K.

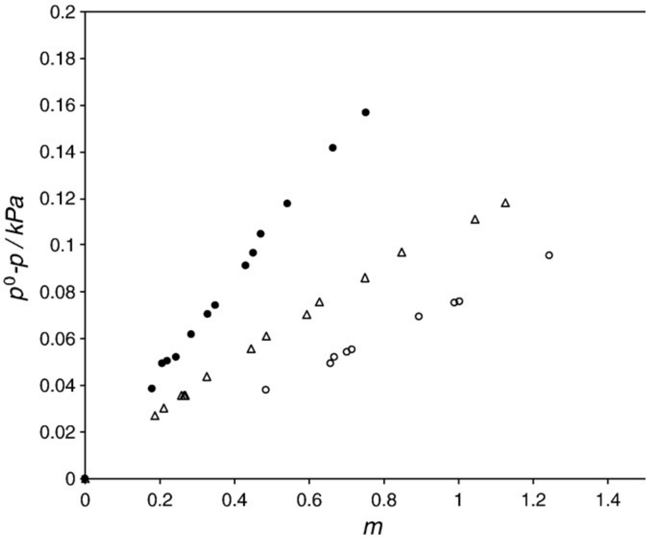


Fig. 5. Plot of vapor pressure depression data, (p^0-p)/kPa, against molality of solute, m, at T=303.15 K: ○, alanine+water; △, KH_2Cit+H_2O; ●, K_3Cit+H_2O.

effect on the lines of constant water activity or vapor pressure of alanine+KH_2Cit+H_2O system. In other words the composition of the systems in equilibrium doesn't change with varying temperature.

In Table 8, vapor pressure depression for several alanine+KH_2Cit+H_2O solutions along with those for corresponding binary solutions is given at different temperatures. This table shows that the vapor pressure depression for a ternary aqueous KH_2Cit+alanine system is almost equal to the sum of those for the corresponding binary solutions. In our previous work [22], we showed that the vapor pressure depression for a ternary aqueous K_3Cit+alanine system is more than the sum of those for the corresponding binary solutions. The amino and carboxyl groups of alanine dissociate in aqueous solutions and become respectively, negatively and positively charged or zwitterion ($^+NH_3$–(CH_3CH)–COO^-). In fact, the neutral dipolar species or zwitterions are the predominant species in the isoelectric solution of amino acids. At acidic solutions, cationic amino acid species ($^+NH_3$–(CH_3CH)–COOH) become predominant while anionic amino acid species (NH_2–(CH_3CH)–COO^-) become predominant at the basic solutions [31]. KH_2Cit is an acidic salt and therefore in the aqueous solutions of KH_2Cit, the cationic form of alanine ($^+NH_3$–(CH_3CH)–COOH) becomes predominant while neutral dipolar form of alanine ($^+NH_3$–(CH_3CH)–COO^-) is predominant in the aqueous solutions of K_3Cit. In fact, the strong attractive interactions between the alanine species and water will result in a reduction in the free water content and consequently in an increase in the effective concentration of the salt. Similarly, ionic species in the aqueous solutions are hydrated and this hydration will result in an increase in the effective concentration of the alanine. On the other hand, addition of potassium di-hydrogen citrate and tri-potassium citrate to aqueous alanine solution will coordinate the hydration spheres of the K^+ with those of the carboxylate ions and those of Cit^{3-} or H_2Cit^- with the hydration spheres of the ammonium ions. As a result of these interactions, the water molecules are allowed to relax to the bulk state and therefore these interactions will result in a decrease in the effective concentration of the alanine and salt. In the case of alanine+K_3Cit+H_2O system, the hydration of ions (because of higher valence of the

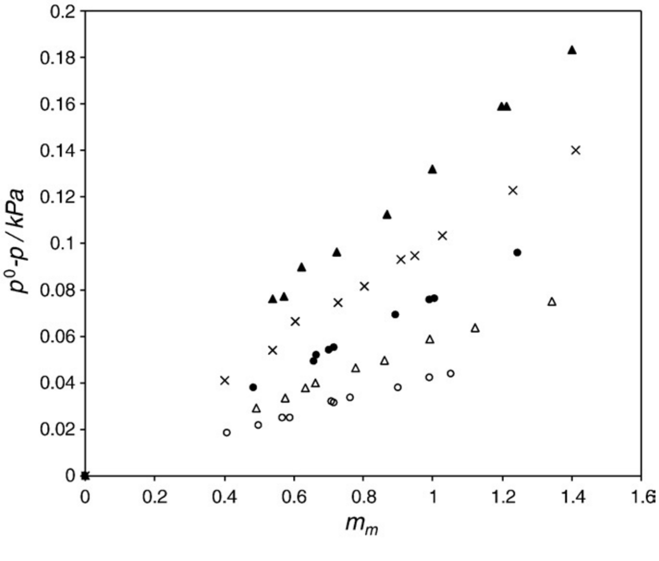


Fig. 4. Plot of vapor pressure depression data, (p^0-p)/kPa, against molality of alanine, m_m, for alanine+H_2O system at different temperatures: ○, T=293.15 K; △, T=298.15 K; ●, T=303.15 K; ×, T=308.15 K; ▲, T=313.15 K.

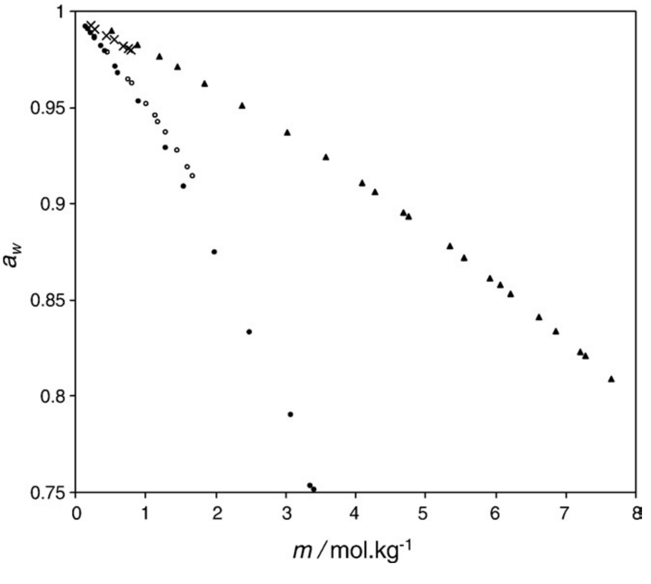


Fig. 6. Plot of water activity data, a_w, against molality of solute, m, at T=298.15 K: ▲, H_3Cit+water; ×, KH_2Cit+H_2O; ○, Na_3Cit+H_2O; ●, K_3Cit+H_2O.

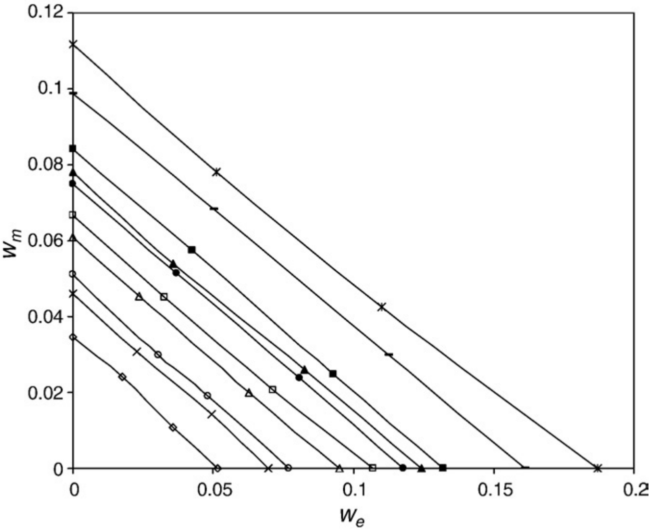


Fig. 7. Plot of mass fraction of alanine, w_m, against mass fraction of KH_2Cit, w_e, for constant water activity curves of alanine + KH_2Cit + H_2O system at T = 308.15 K: ◊, 0.9927; ×, 0.9904; ○, 0.9882; △, 0.9867; □, 0.9855; ●, 0.9835; ▲, 0.9832; ■, 0.9816; ▬, 0.9782; *, 0.9751.

anion Cit^{3-}) and zwitterions are more effective than the interactions between ions and zwitterions and therefore, the effective concentrations of the salt and alanine in a ternary aqueous alanine + K_3Cit system are larger than those in the corresponding binary solutions and therefore it can be expected that the vapor pressure depression for an aqueous alanine + K_3Cit system to be more than the sum of those for corresponding binary solutions. However, in the case of alanine + KH_2Cit + H_2O system, increasing of effective concentrations because of the hydration of ions and amino acid is offset by the interactions between H_2Cit^- and $^+NH_3$–(CH_3CH)–COOH and therefore we may conclude that, the effective concentrations of the salt and alanine in a ternary aqueous alanine + KH_2Cit system are almost similar to those in the corresponding binary solutions and therefore it can be expected that the vapor pressure depression for an aqueous alanine + KH_2Cit system to be equal to the sum of those for the corresponding binary solutions.

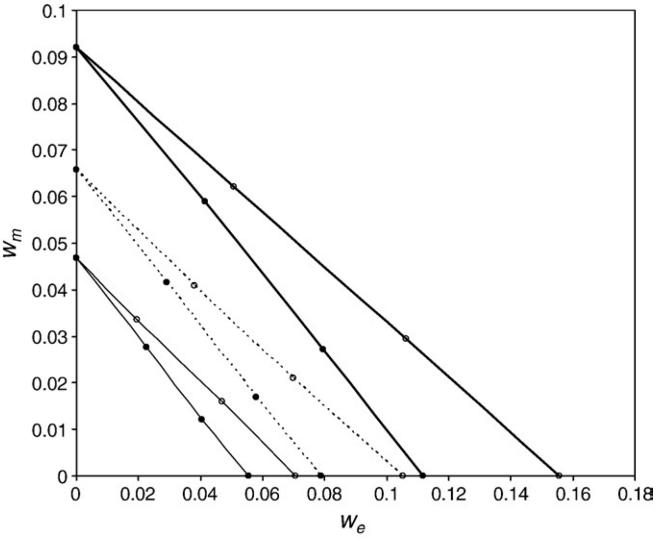


Fig. 8. Plot of mass fraction of alanine, w_m, against mass fraction of salt, w_e, for constant water activity curves of alanine + salt + H_2O system at T = 298.15 K: ○, alanine + KH_2Cit + H_2O; ●, alanine + K_3Cit + H_2O; —, a_w = 0.9902; …, a_w = 0.9857; ▬, a_w = 0.9794.

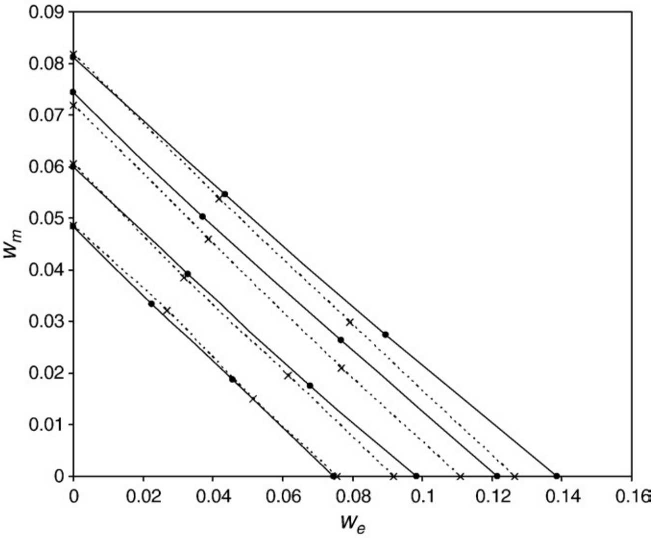


Fig. 9. Plot of mass fraction of alanine, w_m, against mass fraction of KH_2Cit, w_e, for constant water activity curves of alanine + KH_2Cit + H_2O system: ●, T = 293.15 K; ×, T = 313.15 K.

3.2. Correlation

In this work, for the correlation of solvent activity for the investigated systems the segment-based local composition Wilson [30] and NRTL [31] models developed for phase equilibrium behavior of aqueous electrolyte solutions of amino acids were considered. For a multicomponent aqueous solution containing several solvent, electrolytes and zwitterions, the Wilson model for the molar excess Gibbs energy has the following form [30]:

$$
\begin{aligned}
-\frac{g^{\mathrm{ex,Wilson}}}{CRT} = {} & \left(\sum_i x_i\right)\frac{4A_x I_x}{C\rho}\ \ln\left(1+\rho I_x^{0.5}\right) \\
& + \sum_w X_w \ln\left(\frac{\sum_{w'} X_{w'}H_{w'w} + \sum_m X_m H_{mw} + \sum_n (X_{c_n}+X_{a_n})H_{e_n w}}{\sum_{w'} X_{w'} + \sum_m X_m + \sum_n (X_{c_n}+X_{a_n})}\right) \\
& + \sum_m X_m \ln\left(\frac{\sum_w X_w H_{wm} + \sum_{m'} X_{m'}H_{m'm} + \sum_n (X_{c_n}+X_{a_n})H_{e_n m}}{\sum_w X_w + \sum_m X_m + \sum_n (X_{c_n}+X_{a_n})}\right) \\
& + \sum_n X_{c_n} \ln\left(\frac{\sum_w X_w H_{we_n} + \sum_m X_m H_{me_n} + \sum_{n'} X_{a_{n'}}H_{e_n e_n}}{\sum_w X_w + \sum_m X_m + \sum_{n'} X_{a_{n'}}}\right) \\
& + \sum_n X_{a_n} \ln\left(\frac{\sum_w X_w H_{we_n} + \sum_m X_m H_{me_n} + \sum_{n'} X_{c_{n'}}H_{e_n e_n}}{\sum_w X_w + \sum_m X_m + \sum_{n'} X_{c_{n'}}}\right)
\end{aligned}
\tag{2}
$$

where

$$A_x = \frac{1}{3}\left(\frac{2\pi N_A}{V_w}\right)^{\frac{1}{2}}\left(\frac{e^2}{4\pi\varepsilon D_w KT}\right)^{\frac{3}{2}} \tag{3}$$

$$X_i = x_i K_i \quad (K_i = Z_i \text{ for ions and } K_i = \text{unity for molecules}) \tag{4}$$

$$H_{ij} = \exp\left(-\frac{(h_{ij}-h_{jj})}{CRT}\right) = \exp\left(-\frac{E_{ij}}{CRT}\right) \tag{5}$$

$$H_{ij,kj} = \exp\left(-\frac{(h_{ij}-h_{kj})}{CRT}\right) = \exp\left(-\frac{E_{ij,kj}}{CRT}\right) \tag{6}$$

$$E_{c_n m} = E_{a_n m} = E_{e_n m}, \quad E_{c_n w} = E_{a_n w} = E_{,e_n w} \tag{7}$$

$$E_{mc_n,a_n c_n} = E_{ma_n,c_n a_n} = E_{m,e_n}, \quad E_{wc_n,a_n c_n} = E_{wa_n,c_n a_n} = E_{w,e_n} \tag{8}$$

$$E_{a_n c_{n'}} = E_{c_n a_{n'}} = E_{e_n e_{n'}} \tag{9}$$

where C is the effective coordination number in the system, which was fixed at 10, X_i is the effective mole fraction, Z is the charge

Table 8
Vapor pressure depression for several alanine (m)+KH_2Cit (e)+H_2O (w) solutions along with those for corresponding binary solutions at different temperatures

w_m	w_e	T/K	(p^0-p)/kPa		
			alanine (m)+KH_2Cit (e)+H_2O (w)	alanine (m)+H_2O (w)	K_3Cit (e)+H_2O (w)
0.0275	0.0962	293.15	0.044	0.013	0.030
0.0274	0.0896	293.15	0.042	0.013	0.028
0.0263	0.0769	293.15	0.038	0.012	0.025
0.0310	0.1266	298.15	0.075	0.020	0.053
0.0320	0.1078	303.15	0.095	0.029	0.065
0.0692	0.0483	303.15	0.095	0.064	0.031
0.0336	0.0784	303.15	0.076	0.030	0.049
0.0274	0.0871	303.15	0.076	0.024	0.053
0.0426	0.1099	308.15	0.140	0.050	0.086
0.0764	0.0554	313.15	0.183	0.121	0.064

Table 9
Values of parameters of the extended Wilson and NRTL models for alanine (m)+KH_2Cit (e)+H_2O (w) system

Wilson model					
E_{we}	E_{ew}	E_{me}	E_{em}	E_{wm}	E_{mw}
(J mol^{-1})	(J mol^{-1})	(J mol^{-1})	(J mol^{-1})	(J mol^{-1})	(J mol^{-1})
40751.8669	−17815.5345	14136.2618	0.1250	10.4216	−2401.2106
NRTL model					
a_{we}	a_{ew}	a_{me}	a_{em}	a_{wm}	a_{mw}
(J mol^{-1})	(J mol^{-1})	(J mol^{-1})	(J mol^{-1})	(J mol^{-1})	(J mol^{-1})
16193.9316	−6291.2137	3270.0202	1.0036	5897.0153	−4710.5529

number, H and E are energy parameters, ρ, N_A, K, ε and e are the closest distance parameter, Avogadro's number, Boltzmann constant, permitivity of vacuum and electronic charge, respectively. x_i is the mole fraction of component i. I_x is the ionic strength in mole fraction basis. The value of $\rho = 14.9$ has been frequently used for aqueous electrolyte solutions [37], therefore, this value was also used in this work. The V_w and D_w are the molar volume and dielectric constant of the solvent. The dielectric constants of water at 293.15, 298.15, 303.15, 308.15 and 313.15 K are 80.10, 78.30, 76.54, 74.82 and 73.15, respectively [38]. In the above relations the subscripts c, a and e stand for cation, anion and electrolyte, respectively. Also, the species w and w' can be solvent molecule, the species m and m' can be amino acid molecule, the species n and n' can be electrolyte and the species i, j and k can be cation, anion, amino acids or solvent molecule.

For a multicomponent aqueous solution containing several solvents, electrolytes and zwitterions, the modified NRTL model for the molar excess Gibbs energy has the following form [31]:

$$
\begin{aligned}
\frac{g^{\mathrm{ex,NRTL}}}{RT} = &-\left(\sum_i x_i\right)\frac{4A_xI_x}{\rho}\ln\left(1+\rho I_x^{0.5}\right)\\
&+\sum_w X_w\left(\frac{\sum_{w'} X_{w'}G_{w'w}\tau_{w'w}+\sum_m X_mG_{mw}\tau_{mw}+\sum_n (X_{c_n}+X_{a_n})G_{e_nw}\tau_{e_nw}}{\sum_{w'} X_{w'}G_{w'w}+\sum_m X_mG_{mw}+\sum_n (X_{c_n}+X_{a_n})G_{e_nw}}\right)\\
&+\sum_m X_m\left(\frac{\sum_{w} X_{w}G_{wm}\tau_{wm}+\sum_{m'} X_{m'}G_{m'm}\tau_{m'm}+\sum_n (X_{c_n}+X_{a_n})G_{e_nm}\tau_{e_nm}}{\sum_{w} X_{w}G_{wm}+\sum_{m'} X_{m'}G_{m'm}+\sum_n (X_{c_n}+X_{a_n})G_{e_nm}}\right)\\
&+\sum_n X_{c_n}\left(\frac{\sum_{w} X_{w}G_{we_n}\tau_{we_n}+\sum_{m} X_{m}G_{me_n}\tau_{me_n}+\sum_{n'} X_{a_{n'}}G_{e_ne_n}\tau_{e_ne_n}}{\sum_{w} X_{w}G_{we_n}+\sum_{m} X_{m}G_{me_n}+\sum_{n'} X_{a_{n'}}G_{e_ne_n}}\right)\\
&+\sum_n X_{a_n}\left(\frac{\sum_{w} X_{w}G_{we_n}\tau_{we_n}+\sum_{m} X_{m}G_{me_n}\tau_{me_n}+\sum_{n'} X_{c_{n'}}G_{e_ne_n}\tau_{e_ne_n}}{\sum_{w} X_{w}G_{we_n}+\sum_{m} X_{m}G_{me_n}+\sum_{n'} X_{c_{n'}}G_{e_ne_n}}\right)
\end{aligned}
\tag{10}
$$

where G and τ are energy parameters and are given by:

$$G_{ij} = \exp\left(-\alpha_{ij}\frac{(g_{ij}-g_{jj})}{RT}\right) = \exp\left(-\alpha_{ij}\tau_{ij}\right) = \exp\left(-\alpha_{ij}\frac{a_{ij}}{RT}\right) \tag{11}$$

$$
\begin{aligned}
G_{ij,kj} &= \exp\left(-\alpha_{ij,kj}\frac{(g_{ij}-g_{kj})}{RT}\right) = \exp\left(-\alpha_{ij,kj}\tau_{ij,kj}\right)\\
&= \exp\left(-\alpha_{ij,kj}\frac{a_{ij,kj}}{RT}\right)
\end{aligned}
\tag{12}
$$

$$a_{c_nm} = a_{a_nm} = a_{e_nm}, \quad a_{c_nw} = a_{a_nw} = a_{e_nw} \tag{13}$$

$$a_{mc_n,a_nc_n} = a_{ma_n,c_na_n} = a_{m,e_n}, \quad a_{wc_n,a_nc_n} = a_{wa_n,c_na_n} = a_{w,e_n} \tag{14}$$

$$a_{a_nc_{n'}} = a_{c_na_{n'}} = a_{e_ne_{n'}} \tag{15}$$

where α is the nonrandomness factor which is symmetric. The nonrandomness factor was fixed at 0.2 for binary electrolyte–molecule pairs and binary electrolyte–electrolyte pairs. It was set at 0.3 for binary molecule–molecule pairs [31].

The relation for the activity coefficient of a species i in the system can be obtained from appropriate differentiation of Eqs. (2) and (10), respectively for Wilson and NRTL models.

The model parameters were estimated by minimizing the following objective function:

$$\mathrm{OF} = \sum_{l=1}^{NP}\left(a_{\mathrm{w},l}^{\exp} - a_{\mathrm{w},l}^{\mathrm{cal}}\right)^2 \tag{16}$$

where NP is the number of experimental data points and $a_{w,l}^{\exp}$ and $a_{w,l}^{cal}$ are, respectively, the experimental and calculated values of the water activity. The evaluated parameters and corresponding deviations are given in Tables 9 and 10, respectively. That is to say, the obtained parameters are independent of temperature and in fact, one set of parameters successfully has been used to correlate all water activity data measured at five temperatures. Also, the obtained parameters have been used for the prediction of experimental water activity data of binary alanine+H_2O [29] systems and the absolute relative percentage deviations (ARD%) are also given in Table 10. As can be seen from Table 9, the energy parameters a_{ew} and E_{ew} have negative values and energy parameters a_{we} and E_{we} have positive values. This is not surprising since the interaction between the cation and the anion is stronger than the interaction between the water molecules and the ionic species which, in turn, is stronger than the interaction between two solvent molecules. The negative values of energy parameters a_{mw} and E_{mw} and positive values of the energy parameters a_{wm} and E_{wm} indicate that the interaction between the two amino acid molecules is stronger than the interaction between the water molecules and the amino acid molecules which, in turn, is stronger than the interaction between two solvent molecules. Table 9 also shows that the energy parameters a_{me} and E_{me} have positive values which indicate that the interaction

Table 10
Comparison between calculated and experimental water activity data

System	NP	T/K	ARD%	ARD%	Ref.
			Wilson	NRTL	
Alanine (m)+KH_2Cit (e)+H_2O (w)	40	293.15	0.032	0.032	This work
Alanine (m)+KH_2Cit (e)+H_2O (w)	36	298.15	0.041	0.042	This work
Alanine (m)+KH_2Cit (e)+H_2O (w)	36	303.15	0.023	0.022	This work
Alanine (m)+KH_2Cit (e)+H_2O (w)	40	308.15	0.028	0.028	This work
Alanine (m)+KH_2Cit (e)+H_2O (w)	36	313.15	0.032	0.031	This work
KH_2Cit (e)+H_2O (w)	14	293.15	0.034	0.032	This work
KH_2Cit (e)+H_2O (w)	8	298.15	0.045	0.044	This work
KH_2Cit (e)+H_2O (w)	15	303.15	0.041	0.041	This work
KH_2Cit (e)+H_2O (w)	14	308.15	0.013	0.013	This work
KH_2Cit (e)+H_2O (w)	18	313.15	0.040	0.040	This work
Alanine (m)+H_2O (w)	13	288.15	0.019	0.019	[29]
Alanine (m)+H_2O (w)	13	293.15	0.021	0.022	[29]
Alanine (m)+H_2O (w)	13	298.15	0.008	0.008	[29]
Alanine (m)+H_2O (w)	13	303.15	0.007	0.007	[29]

between the cation and the anion is stronger than the interaction between the amino acid molecules and the ionic species. Very small values of the energy parameters a_{em} and E_{em} indicate that the interaction between the ionic species and the amino acid molecules is similar to the interaction between two amino acid molecules.

4. Conclusion

Vapor–liquid equilibrium data for the aqueous solutions of alanine + potassium di-hydrogen citrate and alanine + tri-potassium citrate have been determined experimentally at 293.15, 298.15, 303.15, 308.15 and 313.15 K at atmospheric pressure. From these measurements, values of the vapor pressure of solutions were determined. The effect of temperature and charge on the anion of salts on the vapor–liquid equilibrium of the investigated systems has been studied. It was found that the measured water activities of all binary and ternary systems investigated in this work are independent of temperature and decrease by increasing the charge on the anion of electrolyte. The experimental water activities have been correlated successfully with the segment-based local composition Wilson and NRTL models. The agreement between the correlations and the experimental data is good and both models have a similar behavior in the correlation of experimental data.

Nomenclature

A_x	Pitzer–Debye–Hückel constant
a	Activity or binary parameter in the NRTL model
B	Second virial coefficient
C	Coordination number
D	Dielectric constant
E	Binary parameter in the Wilson model
e	Electronic charge
G	Binary parameter in the NRTL model
g	Gibbs energy of interaction or Gibbs energy
H	Binary parameter in the Wilson model
h	Enthalpy of interaction
I_x	Ionic strength on the mole fraction scale
K	Boltzmann constant
m	Molality
M	Molar mass (kg mol^{-1})
N_A	Avogadro's number
NP	Number of experimental data
OF	Objective function
p	Vapor pressure
R	Gas constant
T	Temperature
V	Molar volume
w	Mass fraction
x	Mole fraction
X	Effective mole fraction
Z	Charge number

Greek letters

a	Nonrandomness factor
ε	Permitivity of vacuum
ν	Stoichiometric parameter
ρ	Closest approach parameter
τ	Binary parameter in the NRTL model

Subscripts

a and c	Anion and cation
e	Salt
i, j, k	Any species, amino acid, ions and water
m, m'	Amino acid
n, n'	Electrolyte
w, w'	Solvent

Superscript

cal	Calculated value
exp	Experimental value
ex	Excess
NRTL	NRTL model
Wilson	Wilson model
°	Pure solvent

References

[1] A.M. Eyal, E. Bressler, Mini-review industrial separation of carboxylic and amino acids by liquid membranes: applicability, process considerations and potential advantages, Biotechnol. Bioeng. 41 (1993) 287–295.

[2] G. Marcozzi, N. Correa, P.L. Luisi, M. Caselli, Protein extraction by reverse micelles: a study of the factors affecting the forward and backward transfer of α-chymotrypsin and its activity, Biotechnol. Bioeng. 38 (1991) 1239–1246.

[3] M.K. Khoshkbarchi, J.H. Vera, Reverse micellar extraction and back extraction of l-lysine with three dialkyl sodium phosphinates in pentanol/isooctane mixtures, Sep. Sci. Technol. 30 (1995) 2301–2314.

[4] H. Zhao, Viscosity B-Coefficients and standard partial molar volumes of amino acids, and their roles in interpreting the protein (enzyme) stabilization, Biophys. Chemist. 122 (2006) 157–183.

[5] E.J. Cohn, J.T. Edsall, Proteins, Amino Acids and Peptides as Ions and Dipolar Ions, Hafner, New York, 1965.

[6] V.E. Bower, R.A. Robinson, Thermodynamics of the ternary system: water-glycine-potassium chloride at 25 °C from vapor pressure measurements, J. Res. Natl. Bur. Stand. 69A (1965) 131–135.

[7] E.E. Schrier, R.A. Robinson, Free energy relationships in aqueous amino acid and peptide solutions containing sodium chloride, J. Solution Chem. 3 (1974) 493–501.

[8] C.C. Briggs, T.H. Lilley, J. Rutherford, S. Woodhead, The activity of calcium chloride in aqueous solutions of some amino acids at 25 °C, J. Solution Chem. 3 (1974) 649–658.

[9] R. Rodriguez-Raposo, L.R. Fernandez-Merida, M.A. Esteso, Activity coefficients in (electrolyte + amino acid) (aq): the dependence of the ion-zwitterion interactions on the ionic strength and on the molality of the amino acid analysed in terms of Pitzers equations, J. Chem. Thermodyn. 26 (1994) 1121–1128.

[10] M.K. Khoshkbarchi, J.H. Vera, Measurement of activity coefficients of amino acids in aqueous electrolyte solutions: experimental data for the systems H_2O + NaCl + Glycine and H_2O + NaCl + DL-Alanine at 25 °C, Ind. Eng. Chem. Res. 35 (1996) 2735–2742.

[11] M. Kamali-Ardakani, H. Modarress, V. Taghikhani, M.K. Khoshkbarchi, Activity coefficients of glycine in aqueous electrolyte solutions: experimental data for (H_2O + KCl + Glycine) at T = 298.15 K and (H_2O + NaCl + Glycine) at T = 308.15 K, J. Chem. Thermodyn. 33 (2001) 821–836.

[12] M.K. Khoshkbarchi, J.H. Vera, Measurement and modeling of activities of amino acids in aqueous salt systems, AIChE J. 42 (1996) 2354–2364.

[13] M.K. Khoshkbarchi, J.H. Vera, Activity coefficients of DL-valine in aqueous solutions of KCl at 25 °C. Measurement with ion selective electrodes and modeling, J. Solution Chem. 25 (1996) 865–875.

[14] M.K. Khoshkbarchi, A.M. Soto-Campos, J.H. Vera, Interactions of DL-serine and L-serine with NaCl and KCl in aqueous solutions, J. Solution Chem. 26 (1997) 941–955.

[15] A.M. Soto-Campos, M.K. Khoshkbarchi, J.H. Vera, Interaction of DL-threonine with NaCl and $NaNO_3$ in aqueous solutions: E.M.F. measurements with ion-selective electrodes, J. Chem. Thermodyn. 29 (1997) 609–622.

[16] A.M. Soto-Campos, M.K. Khoshkbarchi, J.H. Vera, Effects of the anion and the cation of an electrolytes on the activity coefficient of DL-alanine in aqueous solutions, Fluid Phase Equilib. 142 (1998) 193–204.

[17] A. Khavaninzadeh, H. Modarress, V. Taghikhani, M.K. Khoshkbarchi, Measurements of activity coefficients of amino acids in aqueous electrolyte solutions: experimental data for the systems (H_2O + NaBr + Glycine) and (H_2O + NaBr + L-valine) at T = 298.15 K, J. Chem. Thermodyn. 35 (2003) 1553–1556.

[18] E.F. Bouchard, E.G. Meritt, 3rd ed., Kirk-Othmer Encyclopedia of Chemical Technology, vol. 6, Wiley-Interscience, New York, 1984, pp. 150–179.

[19] J.H. Van Ness, 3rd ed., Kirk-Othmer Encyclopedia of Chemical Technology, vol. 13, Wiley-Interscience, New York, 1984, pp. 80–103.

[20] S.E. Berger, 3rd ed., Kirk-Othmer Encyclopedia of Chemical Technology, vol. 13, Wiley-Interscience, New York, 1984, pp. 103–121.

[21] A.S. Kertes, C. King, Extraction chemistry of fermentation product carboxylic acids, J. Biotechnol. Bioeng. 28 (1986) 269–281.

[22] R. Sadeghi, B. Goodarzi, Measurement of water activities of alanine + tri-potassium citrate + water system at temperatures between 293.15 and 313 K — experimental and modeling, Fluid Phase Equilib, doi: 10.1016/j.fluid.2008.02.015.

[23] L.R. Ochs, M. Kabiri Badr, H. Cabezas, An improved isopiestic method to determine activities in multicomponent mixtures, AIChE J. 36 (1990) 1908–1912.

[24] R.A. Robinson, The vapor pressure of aqueous solutions of alanine, J. Biol. Chem. 199 (1952) 71–73.

[25] E.R.B. Smith, P.K. Smith, Thermodynamics properties of solutions of amino acids and related substances. II. The activity of aliphatic acids in aqueous solution at twenty-five degrees, J. Biol. Chem. 121 (1937) 607–613.

[26] E.E. Schrier, R.A. Robinson, A study of free energy relationship on some amino acid-sodium chloride-water system, J. Biol. Chem. 246 (1971) 2870–2874.

[27] H. Kuramochi, H. Noritomi, D. Hoshino, K. Nagahama, Measurements of vapor pressures of aqueous amino acid solutions and determination of activity coefficients of amino acids, J. Chem. Eng. Data 42 (1997) 470–474.
[28] L. Ninni, A.J.A. Meirelles, Water activity, pH and density of aqueous amino acids solutions, Biotechnol. Prog. 17 (2001) 703–711.
[29] C.M. Romero, M.E. Gonzalez, Osmotic and activity coefficients of glycine, DL-α-alanine and DL-α-aminobutyric acid in aqueous solutions at temperatures between 288.15 and 303.15 K, Fluid Phase Equilib. 250 (2006) 99–104.
[30] R. Sadeghi, Thermodynamic representation of phase equilibrium behavior of aqueous solutions of amino acids by the modified Wilson model, Fluid Phase Equilib. 260 (2007) 266–274.
[31] C.C. Chen, Y. Zhu, L.B. Evans, Phase partitioning of biomolecules: solubilities of amino acids, Biotechnol. Prog. 5 (1989) 111–118.
[32] E. Colin, W. Clarke, D.N. Glew, Evaluation of the thermodynamic functions for aqueous sodium chloride from equilibrium and calorimetric measurement below 154 °C, J. Phys. Chem. Ref. Data 14 (1985) 489–610.
[33] A. Saul, W.J. Wagner, International equations for the saturation properties of ordinary water substance, J. Phys. Chem. Ref. Data 16 (1987) 893–901.
[34] R. Sadeghi, F. Ziamajidi, Vapor-liquid equilibria of binary tri-potassium citrate+water and ternary polypropylene oxide 400+tri-potassium citrate+water systems from isopiestic measurements over a range of temperature, Fluid Phase Equilib. 25 (2007) 46–54.
[35] A. Schunk, G. Maurer, Activity of water in aqueous solutions of sodium citrate and in aqueous solutions of (an inorganic salt and citric acid) at 298.15 K, J. Chem. Eng. Data 49 (2004) 944–949.
[36] A. Apelblat, M. Dov, J. Wisniak, J. Zabicky, Osmotic and activity coefficients of $HO_2CCH_2C(OH)(CO_2H)CH_2CO_2H$ (citric acid) in concentrated aqueous solutions at temperatures from 298.15 K to 318.15 K, J. Chem. Thermodyn. 27 (1995) 347–353.
[37] J.M. Simonson, K.S. Pitzer, Thermodynamics of multicomponent, miscible ionic systems: the system lithium nitrate-potassium nitrate-water, J. Phys. Chem. 90 (1986) 3009–3013.
[38] R.A. Robinson, R.H. Stokes, Electrolyte Solutions, 2nd ed. Butterworths, London, 1965.