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Cryoscopic studies of α-amino acids in water

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Abstract

Freezing temperature lowering of aqueous solution of α-amino acids namely glycine, L-serine, L-proline, DL-valine, DL-alanine, L-threonine, hydroxy-L-proline, L-isoleucine and DL-methionine were determined. These values were used in the determination of osmotic coefficient, water activity, activity coefficients and number of ions formed by an electrolyte molecule. Regression analysis was further done for the above-mentioned α-amino acids in order to test the validity of ΔT_f (theo.) and ΔT_f (obs.).

Keywords: α-Amino acids; Cryoscopic; Freezing temperature lowering; Osmotic coefficient; Activity coefficient; Water activity; Regression analysis

1. Introduction

Amino acids are molecules that contain an amino group, $-NH_2$, and a carboxyl group, $-COOH$. Amino acids are the simplest biomolecules and are the building blocks of peptides and proteins. While there are many different ways to bond these two functional groups in organic compounds, the biologically significant amino acids are principally α-amino acids. An α-amino acid contains an amino group on the second carbon atom of the acid chain. The understanding of the interpretation of amino acids and electrolyte has potential applications for separation and concentration of biochemicals. Many biochemical separation processes such as induced precipitation of proteins [1,2] and reverse micellar extraction of biochemicals [3] deal directly with the interactions of biochemicals with electrolytes. In some cases, amino acids are directly produced in aqueous solutions containing electrolytes. Ghose [4] provided experimental evidence of cohesive force between the CH_2 group of long chain ions and electrostatic attraction between the Zwitter ions of long chain α-amino acids at oil/water interface. Adams [5] and Bjerrum [6] showed, a number of years ago, that amino acids in aqueous solution exist almost wholly as Zwitter ions, with large dipole moments which Wyman [7] has evaluated from the large increase in dielectric constant of their aqueous solutions.

Clementi et al. [8] presented SCF–LCAO–MO computations for 21 amino acids interacting with one molecule of water located at different positions and orientations around each amino acid. Vilcu et al. [9] made the evaluation of thermodynamic properties of binary and ternary electrolytes by a software modeling of the data from cryoscopic differential. The integral that appears in the calculus was evaluated numerically using software developed by the authors.

The main objective of the present work is to have a comprehensive view of the cryoscopic study of α-amino acids in water, for which osmotic coefficient, water activity, activity coefficient, number of ions formed by an electrolyte molecule v have been calculated and regression line analysis is performed in order to understand the correlation between ΔT_f (obs.) and ΔT_f (theo.).

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2. Experimental

All mentioned α-amino acids were purified by crystallization or reprecipitation from water, and dried at 320 K in vacuo for 3 days, stored over P_2O_5 in a dessicator and redried before use.

Demineralized water was distilled over acidified potassium dichromate and then over alkaline permanganate. The distillate with conductivity $<10^{-6}$ S cm^{-1} was cooled at room temperature. All solutions were prepared by weight and used on the same day to avoid errors due to possible fermentation of the amino acids.

Table 2
Regression analysis values of α-amino acids in water

S. no	Salt	α	β	Relation $y=\alpha+\beta x$
1	Glycine	0.0300	1.0200	$y=0.0300+1.0200x$
2	L-serine	0.0216	1.0430	$y=0.0216+1.0430x$
3	L-proline	0.0240	1.0340	$y=0.0240+1.0340x$
4	DL-valine	0.1863	1.0800	$y=0.1863+1.0800x$
5	DL-alanine	0.0109	1.3670	$y=0.0109+1.3670x$
6	L-threonine	0.0642	1.5507	$y=0.0642+1.5507x$
7	Hydroxy-L-proline	0.1898	1.0800	$y=0.1898+1.0800x$
8	L-isoleucine	0.0620	1.3378	$y=0.0620+1.3378x$
9	DL-methionine	−0.0097	1.0450	$y=-0.0097+1.0450x$

Table 1
ΔT_f (obs.), ϕ and ΔT_f (theo.) values of α-amino acids in water

S. no.	Salt	m	ΔT_f (obs.)	ϕ	ΔT_f (theo.)
1	Glycine	0.0986	0.210	1.1450	0.186
		0.1510	0.325	1.1571	0.280
		0.1932	0.400	1.1131	0.350
		0.2799	0.565	1.0852	0.510
		0.3789	0.755	1.0712	0.710
2	L-serine	0.1015	0.220	1.1653	0.186
		0.2016	0.420	1.1200	0.371
		0.3045	0.600	1.0593	0.566
		0.4016	0.755	1.0107	0.742
		0.4962	0.915	0.9914	0.902
3	L-proline	0.1030	0.220	1.1483	0.194
		0.2018	0.415	1.1056	0.372
		0.3027	0.610	1.0834	0.558
		0.4041	0.800	1.0643	0.743
		0.5023	0.975	1.0435	0.929
4	DL-valine	0.1022	0.230	1.2099	0.195
		0.2000	0.430.	1.1559	0.397
		0.2925	0.630	1.1579	0.580
		0.4008	0.840	1.1267	0.782
		0.5007	1.000	1.0737	0.969
5	DL-alanine	0.0848	0.230	1.4582	0.190
		0.1244	0.330	1.4262	0.260
		0.2082	0.545	1.4073	0.390
		0.3347	0.860	1.3814	0.620
		0.4404	0.120	1.3672	0.820
6	L-threonine	0.1015	0.225	1.1910	0.119
		0.2007	0.430	1.1518	0.234
		0.3026	0.630	1.1193	0.351
		0.4018	0.825	1.1039	0.467
		0.5024	1.000	1.0701	0.637
7	Hydroxy-L-proline	0.0879	0.215	1.3150	0.200
		0.1738	0.415	1.2837	0.380
		0.2606	0.600	1.2378	0.550
		0.3465	0.790	1.2257	0.710
		0.4387	0.970	1.1887	0.880
8	L-isoleucine	0.0514	0.110	1.1505	0.080
		0.0761	0.160	1.1303	0.100
		0.1007	0.210	1.1211	0.150
		0.2008	0.400	1.0709	0.296
		0.2505	0.494	1.0605	0.390
9	DL-methionine	0.0636	0.130	1.099	0.130
		0.0809	0.165	1.096	0.160
		0.1002	0.200	1.073	0.200
		0.1208	0.240	1.068	0.200
		0.1527	0.280	0.985	0.225

Table 3
$\ln\Upsilon$ and $-\ln a_1$ values of α-amino acids in water

S. no.	Salt	m	$\ln\Upsilon$	$-\ln a_1\times10^{-3}$
1	Glycine	0.0986	0.4250	2.0342
		0.1510	0.4713	3.1487
		0.1932	0.3393	3.8755
		0.2799	0.2556	5.4746
		0.3789	0.2136	7.3163
2	L-serine	0.1015	0.4959	2.1315
		0.2016	0.3600	4.0693
		0.3045	0.1779	5.8139
		0.4016	0.0321	7.3163
		0.4962	−0.0258	8.8676
3	L-proline	0.1030	0.4490	2.1316
		0.2018	0.3168	4.0209
		0.3027	0.2502	5.9107
		0.4041	0.1929	7.7526
		0.5023	0.1235	9.4493
4	DL-valine	0.1022	0.6297	2.2282
		0.2000	0.4677	4.1662
		0.2925	0.4737	6.1048
		0.4008	0.3801	8.1403
		0.5007	0.2311	9.6918
5	DL-alanine	0.0848	1.3746	2.2282
		0.1244	1.2786	3.1970
		0.2082	1.2219	5.2808
		0.3347	1.1442	8.3343
		0.4404	1.1016	10.8554
6	L-threonine	0.1015	0.5703	2.1797
		0.2007	0.4554	4.1663
		0.3026	0.3579	6.1047
		0.4018	0.3117	7.9949
		0.5024	0.2103	9.6918
7	Hydroxy-L-proline	0.0879	0.9350	2.0829
		0.1738	0.8481	4.0209
		0.2606	0.7134	5.8142
		0.3465	0.6771	7.6557
		0.4387	0.5661	9.4008
8	L-isoleucine	0.0514	0.4515	1.0655
		0.0761	0.3909	1.5500
		0.1007	0.3633	2.0344
		0.2008	0.2127	2.0344
		0.2505	0.1815	4.7865
9	DL-methionine	0.0636	0.2970	1.2593
		0.0809	0.2880	1.5984
		0.1002	0.2190	1.9376
		0.1208	0.2040	2.3251
		0.1527	−0.0450	2.7126