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Osmotic and Activity Coefficients of Some Amino Acids and Their Hydrochloride Salts at 298.15 K

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Osmotic and activity coefficient data are reported for lysine (Lys), arginine (Arg), lysine hydrochloride (Lys·HCl), arginine hydrochloride (Arg·HCl), and histidine hydrochloride (His·HCl). The order of the coefficients for the hydrochlorides is lysine > histidine > arginine. A comparison of the coefficients of lysine and ϵ-aminocaproic acid furnishes additional evidence that the lysine zwitterion is formed with the ϵ-amino group.

Osmotic and activity coefficients are recorded in the literature for many amino acids. Among the more interesting studies are those involving the effect of increasing the length and complexity of the aliphatic carbon chain (*1*, *2*) and the effect of increasing the dipolar distance between the functional groups (*3*). The osmotic coefficients of the amino-*n*-butyric acids are in the order $\alpha > \beta > \gamma$ for dilute solutions, while the order is exactly reversed for more concentrated solutions. The concentration at which the reversal occurs is about 2.0–2.5 *m*. Data are also reported for ϵ-aminocaproic acid (*3*). Lysine has a similar structure except that there is an additional amino group in the α position. It was felt that a comparison of the coefficients of these two amino acids might yield further evidence as to which amino group participates in the formation of the zwitterion. Data are also reported for arginine which has still more amino groups in the δ and more distant positions. Other similar amino acids histidine and norleucine were too insoluble for isopiestic studies. Data for the hydrochloride salts of lysine, arginine, and histidine are reported. These salts are similar to the monosodium and potassium salts of glutamic acid which have been previously reported (*4*) in that the complex ions all contain three ionic groups but a net charge of unity.

Method

The amino acids and hydrochloride salts were either Fisher reagent or Fisher certified grade from Fisher Scientific Co. except that the lysine was Baker grade from J. T. Baker Co. The 1,3-dimethylurea was Fisher reagent grade. All chemicals were dried in a vacuum dessicator over P_4O_{10}, and their purity was checked by titration. The pH of a 0.1 *m* solution of lysine was 9.72 (p*I* = 9.74) and of arginine was 10.73 (p*I* = 10.76). The isopiestic equilibration of the solutions was carried out in the usual manner with NaCl solutions serving as the reference except that reagent-grade 1,3-dimethylurea solutions were also included in the dilute solution range of the amino acids to facilitate extrapolations of the molality ratios to infinite dilution. Complete experimental details and the method of activity

Table I. Experimental Results for Molalities of Isopiestic Solutions at $T = 298.15$ K

NaCl	DMU[a]	Lys	NaCl	DMU[a]	Arg
0.147_9	0.285_1	0.300_2	0.103_0	0.291_6	0.299_7
0.250_0	0.483_2	0.505_6	0.201_5	0.386_1	0.400_7
0.431_2		0.828_3	0.344_4	0.676_0	0.718_0
0.715_5		1.290	0.421_4		0.889
1.053		1.798	0.500_5		1.066
1.517		2.424	0.576_7		1.237
1.947		2.970	0.705_2		1.542
2.126		3.190			
2.724		3.925			
3.109		4.380			
3.312		4.619			
4.022		5.436			
4.921		6.587			

NaCl	Lys·HCl	Arg·HCl	His·HCl
0.183_1	0.193_4	0.199_2	0.195_5
0.404_1	0.439_2	0.470_8	0.457_5
0.628_2	0.690_2	0.771_4	0.735_2
0.770	0.848	0.971	
1.013	1.117	1.328	
1.301	1.429	1.763	
1.621	1.769	2.252	
1.955	2.118	2.767	
2.278	2.458	3.272	
2.611	2.806	3.784	
2.978	3.185	4.350	
3.508	3.743	5.177	
3.618		5.333	
3.666		5.404	

[a] 1,3-Dimethylurea.

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Table II. Osmotic Coefficients at 298.15 K

molality, m	Lys	Arg	Lys·HCl	Arg·HCl	His·HCl
0.1	0.940	0.981	0.901	0.891	0.900
0.2	0.926	0.962	0.885	0.852	0.867
0.3	0.918	0.946	0.860	0.822	0.840
0.4	0.913	0.930	0.850	0.802	0.822
0.5	0.914	0.913	0.844	0.785	0.807
0.6	0.920	0.898	0.841	0.771	0.797
0.7	0.936	0.886	0.841	0.759	0.791
0.8	0.952	0.878	0.841	0.749	
0.9	0.969	0.872	0.843	0.741	
1.0	0.983	0.868	0.844	0.733	
1.2	1.011	0.859	0.852	0.721	
1.4	1.040	0.852	0.860	0.711	
1.6	1.071		0.870	0.704	
1.8	1.102		0.883	0.699	
2.0	1.132		0.896	0.695	
2.5	1.211		0.930	0.691	
3.0	1.290		0.963	0.693	
3.5	1.368		0.995	0.699	
4.0	1.442			0.708	
4.5	1.513			0.718	
5.0	1.589			0.730	
5.5	1.661				

coefficient calculations have been reported (*5*).

Results and Discussion

The primary results of the isopiestic equilibrations are presented in Table I. The osmotic and activity coefficients at rounded concentrations are given in Tables II and III. Osmotic coefficients were calculated from the relationship

$$\phi = [(\nu m)_{\text{ref}}/(\nu m)]\phi_{\text{ref}} = R\phi_{\text{ref}} \tag{1}$$

where ν is the number of ions into which the electrolyte may dissociate and m is molality. The reference was NaCl for all of the concentrated solutions, but 1,3-dimethylurea was used as a secondary reference for the dilute lysine and arginine solutions so as to obtain a more certain extrapolation to infinite dilution. The values of the coefficients in solutions of intermediate concentrations were the same when calculated from data with either reference. Activity coefficients of the hydrochlorides were calculated from the equation (*6*)

$$\ln \gamma = \ln \gamma_{\text{ref}} + \ln R + 2\int_0^{m_{\text{ref}}} (R - 1)\, \mathrm{d} \ln (m\gamma)_{\text{ref}}^{1/2} \tag{2}$$

Activity coefficients of lysine and arginine were calculated from the equation

$$\ln \gamma = (\phi - 1) + \int_0^m [(\phi - 1)/m]\, \mathrm{d}m \tag{3}$$

The osmotic coefficients of arginine are larger than those of lysine in dilute solutions with a reversal in order occurring at a concentration of about 0.5 m. The order of osmotic coefficients for the hydrochlorides is lysine > histidine > arginine at all concentrations. This is the same as for the two soluble parent amino acids in concentrated solutions.

Table III. Activity Coefficients at 298.15 K

molality, m	Lys	Arg	Lys·HCl	Arg·HCl	His·HCl
0.1	0.891	0.972	0.728	0.712	0.727
0.2	0.837	0.936	0.657	0.627	0.648
0.3	0.804	0.904	0.613	0.569	0.594
0.4	0.781	0.874	0.582	0.529	0.556
0.5	0.766	0.844	0.559	0.497	0.526
0.6	0.759	0.818	0.542	0.471	0.502
0.7	0.763	0.795	0.529	0.449	0.484
0.8	0.769	0.776	0.518	0.430	
0.9	0.779	0.760	0.509	0.414	
1.0	0.788	0.747	0.502	0.400	
1.2	0.809	0.722	0.491	0.375	
1.4	0.836	0.701	0.484	0.356	
1.6	0.869	0.684	0.480	0.340	
1.8	0.904		0.480	0.326	
2.0	0.945		0.481	0.315	
2.5	1.061		0.488	0.293	
3.0	1.202		0.499	0.277	
3.5	1.367		0.514	0.266	
4.0	1.553			0.258	
4.5	1.754			0.250	
5.0	2.017			0.247	
5.5	2.300				

A comparison of the coefficients of lysine and ϵ-aminobutyric acid (*3*) was the original impetus for this work. The coefficients of lysine are smaller in dilute solutions and larger in concentrated solutions. By analogy with the aminobutyric acid systems (*3*) and recognizing that ϵ-aminocaproic acid has only one NH_2 group, it appears that these colligative property data furnish additional evidence that the ϵ- rather than the α-amino group accepts the proton. This is in agreement with a previously proposed structure (*7*).

It has been mentioned in the introductory material that the hydrochloride salts are interesting in that, although in the zwitterionic form they contain three ionic groups (one carboxyl and two substituted ammonium groups), the net charge of the cation is unity and the salts are 1,1 electrolytes. The osmotic and activity coefficients of all of these salts are smaller than those of other chloride salts, including the tetraalkylammonium (*8*) and tetramethylguanidinium (*9*) chlorides, at the same concentrations. This leads one to believe that there is probably some association of the type that was suggested for the sodium and potassium salts of glutamic acid (*4*), i.e., through hydrogen bonding of the carboxyl oxygen and amino protons.

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