Densities, Viscosities, and Application of Transition-State Theory for Water + Potassium Thiocyanate + Amino Acid Solutions at 288.15–308.15 K†

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Precise densities ρ and viscosities η at 288.15, 298.15, and 308.15 K are reported as functions of electrolyte concentration (1, 3, and 5 m) and amino acid (up to 0.5 mol·kg^{-1}) concentrations for seven water + potassium thiocyanate + amino acid (glycine, DL-alanine, L-proline, L-threonine, β-alanine, γ-aminobutyric acid, and ϵ-aminocaproic acid) systems. The transfer volumes [$V_\phi°$(tr)($H_2O \rightarrow H_2O$+KSCN)] and the contributions to $V_\phi°$(tr) from NH_3^+,COO^- and CH_2 groups could be rationalized on the basis of electrostatic and hydrophobic interactions between various groups present in these solutions. Free energies of activation $\Delta\mu°^*_{1,2}$, for the viscous flow of aqueous potassium thiocyanate, $\Delta\mu°^*_2$, of aqueous amino acids, and $\Delta\mu°^*_3$, of water + potassium thiocyanate + amino acid solutions, were obtained by application of the transition-state theory to the B coefficient data. On the basis of the contributions of NH_3^+,COO^- and CH_2 groups to the activation free energy, $\Delta\mu°^*_i$ (i = 2, 3), comments on the relative orderness of the ground and the transition states of these solutions have been made.

Introduction

Potassium thiocyanate (KSCN) is known to interact strongly with coenzymes (*1*) and causes an effective salting-in of the nonelectrolytes (*2, 3*). The study of thermodynamic properties of aqueous solutions of amino acids in the presence of varying amounts of KSCN and their temperature dependence is therefore interesting. In continuation to our earlier work on systems of amino acids in water (*4*) and aqueous electrolytes (*5, 6*), densities, viscosities, and the thermodynamic parameters of activation of the viscous flow for seven water + potassium thiocyanate + amino acid solutions at 288.15, 298.15, and 308.15 K are reported in this paper.

Experimental Section

Glycine (Gly), DL-alanine (DL-Ala), L-proline (L-Pro), β-alanine (β-Ala), γ-aminobutyric acid (γ-Aba), and ϵ-aminocaproic acid (ϵ-Ahx) (Sigma), L-threonine (L-Thr) (Loba-chemie), and potassium thiocyanate (KSCN) (Sarabhai, A.R.) were used after drying at 373 K for 12 h and then in vacuo over phosphorous pentoxide at room temperature for a minimum of 24 h. Double-distilled water deionized by passing through two Cole-Parmer mixed-bed ion-exchange columns and of conductivity less than 6×10^{-7} S·cm^{-1} was used for preparation of solutions afresh by weight.

The densities were measured with an Anton Paar vibrating-tube digital densimeter (DMA 601/60) and viscosities with a modified suspended level Cannon-Ubbelohde viscometer. The procedural details are given elsewhere (*6*). Temperature measurements were precise to 0.01 K. The reproducibility of the density and viscosity measurements was better than 7×10^{-6} g·cm^{-3} and 4×10^{-7} kg·m^{-1}·s^{-1}, respectively.

Results and Discussion

The detailed density ρ data for solutions of glycine, DL-alanine, L-threonine, L-proline, β-alanine, γ-aminobutyric acid, and ϵ-aminocaproic acid in 1, 3, and 5 m aqueous KSCN at 288.15, 298.15, and 308.15 K are given in Table I. The apparent molar volumes were calculated as

$$V_\phi = -1000(\rho - \rho_0)/m_2\rho\rho_0 + M_2/\rho \quad (1)$$

where M_2 and m_2 are, respectively, the molar mass and molality of the amino acid in the solvent (H_2O + KSCN) of density ρ_0. The V_ϕ varied linearly with m_2 and were fitted to

$$V_\phi = V_\phi° + b_{v,m}m_2 \quad (2)$$

$$V_\phi = V_\phi° + b_{v,c}c \quad (3)$$

to yield $V_\phi°$, the limiting apparent molar volume, and $b_{v,m}$ and $b_{v,c}$, the experimental slopes, given in Table II. The amino acid molarities c were calculated as

$$c = m_2\rho_0 1000/(1000 + m_2\rho_0 V_\phi) \quad (4)$$

The variation of $V_\phi°$ with m_1, the molality of aqueous KSCN, is shown in Figure 1. The decrease in electrostriction of the solvent due to strong and localized NH_3^+–SCN^-, COO^-–K^+, and KSCN–KSCN interactions causes the observed increase in volume with KSCN concentration. The transfer volumes $V_\phi°$(tr), defined as

$$V_\phi°(\text{tr}) = V_\phi°(H_2O\text{+KSCN}) - V_\phi°(H_2O) \quad (5)$$

are positive under all conditions of the reported experiments and are given in Table III. The $V_\phi°$ data for amino acids in water were taken from the literature (*6*). The $V_\phi°$(tr) is maximum for ϵ-aminocaproic acid and minimum for DL-alanine (except at 5 m KSCN at 298.15 K) at the three temperatures and KSCN concentrations. The observed negative value for $\Delta V_\phi°$(tr) [$= V_\phi°$(tr)(DL-Ala) – $V_\phi°$(tr)(Gly)], the change in $V_\phi°$(tr) for replacement of a H by a CH_3 group, of –1.14 cm^3·mol^{-1} at 298.15 K and 3 m KSCN is in good agreement with the results from earlier studies: –0.32 for 2 m (*7*) and –1.14 for 3 m NaCl (*8*), –0.13 for 6 m urea (*9*), –0.32 for 3 m LiCl (*7*), –0.18 for 2 m NH_4Cl (*5*), and –0.25 for 2 m KCl (*7*). These negative values result from a larger decrease in volume resulting from the ion–hydrophobic group interactions in DL-alanine. The variation of $V_\phi°$(tr) with n, the number of CH_2 groups in the backbone chain of the ω-amino acid, is shown in Figure 2. Some corresponding data for

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Table I. Densities ρ for Amino Acids + Aqueous KSCN as a Function of Molality m_2 of Amino Acids in Solvent (Water + KSCN)

288.15 K		298.15 K		308.15 K		288.15 K		298.15 K		308.15 K	
$10^3 m_2$/ (mol·kg^{-1})	$10^3(\rho - 1)$/ (g·cm^{-3})	$10^3 m_2$/ (mol·kg^{-1})	$10^3(\rho - 1)$/ (g·cm^{-3})	$10^3 m_2$/ (mol·kg^{-1})	$10^3(\rho - 1)$/ (g·cm^{-3})	$10^3 m_2$/ (mol·kg^{-1})	$10^3(\rho - 1)$/ (g·cm^{-3})	$10^3 m_2$/ (mol·kg^{-1})	$10^3(\rho - 1)$/ (g·cm^{-3})	$10^3 m_2$/ (mol·kg^{-1})	$10^3(\rho - 1)$/ (g·cm^{-3})
Glycine + 1 *m* KSCN											
0	44.257	0	40.745	0	36.625	298.89	53.118	295.46	49.403	207.40	42.651
51.67	45.800	49.53	42.212	98.34	39.479	349.79	54.587	412.27	52.720	232.16	43.368
71.21	46.394	149.42	45.159	123.80	40.228	348.37	54.531	604.37	58.043	267.18	44.360
150.66	48.774	196.82	46.538	143.71	40.809					303.54	45.383
201.99	50.280	255.36	48.227	168.04	41.523						
Glycine + 3 *m* KSCN											
0	118.438	0	113.461	0	107.709	255.24	125.058	159.25	117.508	157.70	111.759
85.18	120.659	69.47	115.241	75.49	109.649	253.94	125.027	180.97	118.066	183.96	112.454
122.65	121.631	85.16	115.631	99.00	110.236	350.87	127.508	209.17	118.772	204.23	112.967
169.33	122.847	103.80	116.109	117.14	110.728	394.63	128.564	257.25	120.008	247.27	114.065
205.07	123.783	131.10	116.810	140.63	111.319			311.68	121.377	255.49	114.274
Glycine + 5 *m* KSCN											
0	177.651	0	171.713	0	165.108	400.95	186.823	160.49	175.472	220.99	170.161
107.67	180.233	43.98	172.745	63.87	166.576	451.59	187.888	189.54	176.155	253.54	170.867
186.89	182.009	64.88	173.232	91.12	167.225			230.97	177.143		
230.36	182.977	91.08	173.843	133.01	168.192			282.60	178.378		
305.12	184.673	109.86	174.277	169.75	169.014			349.69	179.974		
351.39	185.698	132.61	174.817	189.71	169.469						
DL-Alanine + 1 *m* KSCN											
0	44.171	0	40.725	0	36.517	159.18	48.292	249.44	46.993	228.29	42.238
47.68	45.419	54.39	42.119	60.32	38.046	188.19	49.016	293.18	48.104	272.52	43.351
68.84	45.962	100.30	43.280	103.54	39.123	232.29	50.149	502.24	53.122	303.07	44.094
98.69	46.738	150.00	44.543	139.37	40.039	285.06	51.465	775.95	59.468	333.00	44.807
124.82	47.413	194.75	45.658	190.67	41.308					401.11	46.443
DL-Alanine + 3 *m* KSCN											
0	118.490	0	113.381	0	107.596	216.47	122.985	238.36	118.359	236.32	112.372
53.99	119.633	49.81	114.438	74.78	109.127	270.43	124.062	286.50	119.340	304.66	113.732
76.78	120.110	74.76	114.956	120.19	110.043	321.09	125.057	329.24	120.208	308.17	113.773
104.36	120.682	113.29	115.766	139.87	110.447	407.45	126.731	361.61	120.867		
126.69	121.151	153.46	116.602	172.38	111.098	476.29	128.030	442.61	122.485		
173.41	122.112	203.37	117.631	193.76	111.528						
DL-Alanine + 3 *m* KSCN											
0	177.796	0	171.759	0	165.086	173.40	180.567	260.66	175.884	154.13	167.538
41.86	178.464	49.14	172.554	40.00	165.737	218.78	181.239	278.02	176.143	180.44	167.953
73.51	178.988	100.21	173.365	83.44	166.418	264.32	181.950			257.98	169.166
105.62	179.486	198.68	174.918	104.74	166.763	291.62	182.371			287.09	169.593
136.17	179.982	229.79	175.413	129.20	167.157						
L-Proline + 1 *m* KSCN											
0	44.289	0	40.745	0	36.459	251.38	51.395	348.55	50.368	192.23	41.794
55.79	45.879	99.01	43.532	67.99	38.379	324.25	53.411	501.07	54.372	219.67	42.538
88.97	46.819	135.73	44.561	87.16	38.901	363.93	54.475	697.28	59.348	243.17	43.172
129.05	47.969	195.28	46.193	140.03	40.352					262.24	43.682
180.32	49.403	248.35	47.654	169.85	41.180						
L-Proline + 3 *m* KSCN											
0	118.503	0	113.411	0	107.646	213.89	123.078	350.97	120.714	190.77	111.707
53.93	119.451	43.26	114.323	65.88	109.017	246.86	123.757	504.12	123.733	212.85	112.177
87.21	120.378	142.44	116.428	103.27	109.809	301.65	124.888	701.24	127.515	228.44	112.517
133.06	121.363	197.99	117.574	153.99	110.910	352.11	125.918				
184.77	122.477	241.45	118.467	177.89	111.420						
L-Proline + 5 *m* KSCN											
0	177.605	0	171.743	0	165.126	163.15	180.117	251.22	175.581	152.63	167.449
40.18	178.242	69.93	172.836	56.91	165.973	183.00	180.427	274.89	175.941	191.88	168.021
72.49	178.736	98.24	173.272	92.05	166.520	211.66	180.847	303.99	176.353	210.87	168.311
100.10	179.159	151.11	174.054	105.08	166.722	287.90	181.972			232.61	168.624
133.03	179.664	198.53	174.793	137.06	167.199						
L-Threonine + 1 *m* KSCN											
0	44.294	0	40.737	0	36.465	290.41	55.376	249.92	50.231	162.85	42.650
42.52	45.963	51.90	42.753	38.12	37.921	327.87	56.812	356.92	54.127	184.98	43.477
79.45	47.408	98.03	44.529	61.23	38.799			499.64	59.228	211.84	44.499
124.60	49.145	146.51	46.362	119.01	41.002			693.37	65.933	234.59	45.320
175.55	51.058	200.05	48.359	141.15	41.835						
L-Threonine + 3 *m* KSCN											
0	118.501	0	113.346	0	107.661	163.03	123.780	199.46	119.742	143.46	112.264
63.32	120.578	88.81	116.237	42.54	109.047	184.72	124.470	259.82	121.636	165.76	112.975
86.26	121.316	118.17	117.162	64.27	109.729	223.51	125.703	330.21	123.821	180.74	113.472
108.05	122.020	145.69	118.075	96.77	110.784	241.77	126.261			207.37	114.275
154.35	123.512	167.09	118.743	121.31	111.560						

Table I (Continued)

288.15 K		298.15 K		308.15 K		288.15 K		298.15 K		308.15 K	
10^3m_2/(mol·kg^{-1})	$10^3(\rho-1)$/(g·cm^{-3})	10^3m_2/(mol·kg^{-1})	$10^3(\rho-1)$/(g·cm^{-3})	10^3m_2/(mol·kg^{-1})	$10^3(\rho-1)$/(g·cm^{-3})	10^3m_2/(mol·kg^{-1})	$10^3(\rho-1)$/(g·cm^{-3})	10^3m_2/(mol·kg^{-1})	$10^3(\rho-1)$/(g·cm^{-3})	10^3m_2/(mol·kg^{-1})	$10^3(\rho-1)$/(g·cm^{-3})
L-Threonine + 5 *m* KSCN											
0	177.871	0	171.746	0	165.149	121.35	181.122	180.11	176.564	125.87	168.489
72.08	179.791	29.73	172.528	59.78	166.719	149.75	181.850	199.72	177.088	186.73	170.129
86.53	180.166	99.09	174.401	85.82	167.411	167.67	182.385	213.82	177.457	191.35	170.194
100.49	180.538	131.13	175.259	104.54	167.903	196.20	183.116	244.15	178.283	227.41	171.177
β-Alanine + 1 *m* KSCN											
0	44.306	0	40.706	0	36.504	269.34	51.735	215.47	46.559	187.57	41.628
74.76	46.381	52.48	42.146	67.90	38.371	344.72	53.765	245.84	47.414	202.96	42.040
108.34	47.321	88.52	43.141	93.69	39.086	377.11	54.649	299.85	48.856	233.33	42.867
152.05	48.535	132.79	44.349	127.36	40.009	434.86	56.190	365.88	50.602	264.45	43.708
186.38	49.463	171.15	45.408	147.60	40.558						
β-Alanine + 3 *m* KSCN											
0	118.607	0	113.470	0	107.701	242.81	124.083	249.74	119.083	206.14	112.357
78.07	120.394	52.10	114.662	70.01	109.289	286.24	125.023	293.83	120.044	214.99	112.576
105.17	121.007	96.49	115.661	119.59	110.424	349.76	126.436	404.97	122.553	266.56	113.716
122.61	121.382	149.05	116.834	149.41	111.102	486.74	129.416				
182.26	122.730	194.18	117.881	178.79	111.757						
β-Alanine + 5 *m* KSCN											
0	177.966	0	171.696	0	165.165	144.14	180.687	230.27	175.948	192.84	168.768
48.38	178.895	48.97	172.625	80.51	166.685	217.82	181.997	286.44	176.968	223.16	169.324
80.08	179.490	100.75	173.597	111.24	167.277	155.39	180.910	349.11	178.117	245.57	169.729
93.08	179.743	149.99	174.512	135.73	167.727					275.12	170.256
111.13	180.095	198.97	175.376	161.99	168.223						
γ-Aminobutyric Acid + 1 *m* KSCN											
0	44.292	0	40.646	0	36.620	284.78	51.723	298.39	48.279	113.58	39.547
43.52	45.451	47.84	41.887	43.19	37.728	371.03	53.868	398.93	50.720	124.62	39.829
79.01	46.399	100.14	43.237	52.97	37.981	449.85	55.769	497.31	53.103	143.22	40.314
107.52	47.157	148.98	44.501	63.43	38.248					155.47	40.613
132.88	47.813	194.55	45.656	79.10	38.651					200.48	41.760
164.86	48.656	249.57	47.062	100.44	39.213						
γ-Aminobutyric Acid + 3 *m* KSCN											
0	118.704	0	113.356	0	107.610	170.32	122.137	328.23	119.686	112.52	109.855
45.91	119.643	53.10	114.412	33.75	108.282	200.48	122.717	493.61	122.715	132.46	110.256
77.71	120.304	146.76	116.259	52.81	108.658	235.37	123.362	691.11	126.210	150.30	110.612
107.21	120.893	201.88	117.328	66.35	108.933	318.14	124.902			197.21	111.518
136.71	121.478	238.78	118.005	93.32	109.475					216.19	111.897
γ-Aminobutyric Acid + 5 *m* KSCN											
0	177.802	0	171.688	0	165.028	201.51	180.676	251.46	175.228	114.91	166.684
52.17	178.604	48.05	172.372	35.34	165.547	215.48	180.858	303.49	175.931	129.05	166.885
82.04	179.021	99.17	173.108	52.81	165.782	185.53	180.441			140.26	167.056
107.36	179.375	132.82	173.596	68.89	166.028					160.01	167.344
161.42	180.121	158.58	173.964	81.86	166.205					190.00	167.770
181.93	180.400	197.45	174.486	94.79	166.415						
ε-Aminocaproic Acid + 1 *m* KSCN											
0	44.159	0	40.750	0	36.532	197.48	48.322	252.39	46.028	83.66	38.304
51.96	45.262	50.05	41.812	29.10	37.135	245.90	49.318	355.18	48.076	108.28	38.797
69.48	45.636	102.40	42.926	44.63	37.472	299.39	50.386	497.96	50.819	123.66	39.129
93.23	46.146	142.04	43.752	59.48	37.791	405.49	52.498	704.79	54.608	138.22	39.402
148.16	47.294	198.92	44.935	71.10	38.033					147.66	39.614
ε-Aminocaproic Acid + 3 *m* KSCN											
0	118.426	0	113.144	0	107.715	157.25	120.120	171.44	115.058	105.93	108.942
38.46	118.833	50.79	113.703	31.12	108.064	189.74	120.473	202.89	115.432	118.88	109.092
65.24	119.105	80.98	114.053	39.77	108.156	251.66	121.144	277.67	116.233	125.88	109.179
79.92	119.263	117.81	114.463	81.84	108.643	277.29	121.400			182.81	109.817
125.67	119.743	138.11	114.696	93.54	108.792						
ε-Aminocaproic Acid + 5 *m* KSCN											
0	177.775	0	171.296	0	165.086	132.67	178.088	160.26	171.769	91.54	165.399
36.38	177.863	45.00	171.412	31.29	165.179	141.34	178.134	191.73	171.851	105.38	165.444
57.56	177.906	67.15	171.482	41.48	165.212	166.40	178.174	214.32	171.934	114.97	165.478
84.03	177.967	93.27	171.569	63.73	165.301	184.22	178.232	291.59	172.134	143.36	165.588
99.77	178.014	140.26	171.705	82.21	165.344					175.72	165.694

aqueous ammonium chloride (5) are also plotted. Similarity in the behaviors of the two types of systems is quite apparent. The increase in $V_\phi°$(tr) with n results from the decrease in electrostriction. For 1 *m* KSCN, the variation in $V_\phi°$(tr) with n is linear and tends to be concave upward at higher concentrations. The linear nature of $V_\phi°$(tr) – n isotherms helps estimate the $V_\phi°$(tr)(CH_2) and $V_\phi°$(tr)(NH_3^+,COO^-), the respective contributions from the CH_2 and polar NH_3^+,COO^- groups to the $V_\phi°$(tr). The $V_\phi°$(tr)(CH_2) is (0.20 ± 0.07 cm^3·mol^{-1}) fairly constant over the studied range of temperature, whereas the $V_\phi°$(tr)(NH_3^+,COO^-) decreases with the increase in temperature: 1.7, 1.2, and 0.7 cm^3 mol^{-1}

Table II. Limiting Apparent Molar Volume $V_\phi°$ and Experimental Slopes $b_{v,m}$ and $b_{v,c}$ of Equations 2 and 3 for Amino Acids in Solvent (Water + KSCN)

amino acid	$V_\phi°$/ ($cm^3 \cdot mol^{-1}$)	$b_{v,m}$/ ($cm^3 \cdot mol^{-2} \cdot kg$)	$b_{v,c}$/ ($cm^3 \cdot mol^{-2} \cdot L$)	amino acid	$V_\phi°$/ ($cm^3 \cdot mol^{-1}$)	$b_{v,m}$/ ($cm^3 \cdot mol^{-2} \cdot kg$)	$b_{v,c}$/ ($cm^3 \cdot mol^{-2} \cdot L$)
			288.15 K, 1 *m* KSCN				
glycine	44.33 (4)[a]	*b*		β-alanine	59.69 (2)	0.28 (14)	−0.27 (14)
DL-alanine	61.27 (1)	0.59 (19)	0.58 (18)	γ-aminobutyric acid	74.11 (2)	0.87 (18)	0.86 (18)
L-proline	83.99 (2)	−0.77 (20)	−0.77 (20)	ε-aminocaproic acid	105.99 (2)	−0.22 (19)	−0.23 (19)
L-threonine	77.90 (4)	0.98 (42)	0.96 (41)				
			288.15 K, 3 *m* KSCN				
glycine	46.13 (4)			β-alanine	61.33 (4)		
DL-alanine	62.61 (1)	1.02 (5)	0.95 (4)	γ-aminobutyric acid	75.53 (3)	1.94 (31)	1.78 (29)
L-proline	85.59 (2)	0.27 (19)	−0.25 (18)	ε-aminocaproic acid	108.98 (3)	−2.18 (39)	−2.03 (36)
L-threonine	80.13 (1)	0.56 (18)	0.52 (16)				
			288.15 K, 5 *m* KSCN				
glycine	46.38 (5)	1.45 (42)	1.28 (36)	β-alanine	61.62 (3)	1.79 (55)	1.55 (48)
DL-alanine	63.97 (3)	0.42 (33)	0.36 (29)	γ-aminobutyric acid	76.35 (3)	3.86 (59)	3.36 (51)
L-proline	86.36 (2)	0.64 (22)	0.56 (19)	ε-aminocaproic acid	109.75 (2)	−0.90 (43)	−0.78 (38)
L-threonine	82.08 (4)	−3.19 (87)	−2.78 (76)				
			298.15 K, 1 *m* KSCN				
glycine	44.63 (2)	0.47 (11)	0.46 (11)	β-alanine	60.12 (2)	−0.27 (22)	−0.27 (21)
DL-alanine	61.86 (2)	0.43 (7)		γ-aminobutyric acid	74.96 (5)		
L-proline	84.37 (1)	0.13 (7)	0.13 (7)	ε-aminocaproic acid	106.21 (3)	0.32 (13)	0.33 (14)
L-threonine	78.44 (2)	0.87 (10)	0.89 (9)				
			298.15 K, 3 *m* KSCN				
glycine	46.78 (1)	−0.50 (19)	−0.46 (18)	β-alanine	61.54 (5)		
DL-alanine	62.91 (1)			γ-aminobutyric acid	76.43 (2)	0.43 (9)	0.42 (8)
L-proline	86.21 (3)	−0.23 (15)	−0.22 (14)	ε-aminocaproic acid	108.88 (3)	−1.33 (41)	−1.25 (38)
L-threonine	80.50 (3)	0.48 (30)	0.45 (35)				
			298.15 K, 5 *m* KSCN				
glycine	47.07 (1)	−1.49 (13)	−1.30 (12)	β-alanine	62.17 (2)	0.61 (25)	0.54 (22)
DL-alanine	64.22 (1)	0.28 (12)	0.25 (11)	γ-aminobutyric acid	77.48 (4)		
L-proline	86.85 (4)			ε-aminocaproic acid	110.03 (3)	−0.97 (38)	−0.87 (34)
L-threonine	82.39 (4)	−3.02 (57)	−2.65 (49)				
			308.15 K, 1 *m* KSCN				
glycine	45.16 (3)			β-alanine	60.20 (4)		5.74 (26)
DL-alanine	62.29 (2)		−3.47 (17)	γ-aminobutyric acid	75.54 (2)	−1.98 (42)	−1.94 (40)
L-proline	84.71 (2)	0.64 (33)	0.64 (33)	ε-aminocaproic acid	106.81 (6)		
L-threonine	79.29 (2)	−1.05 (29)	−1.04 (28)				
			308.15 K, 3 *m* KSCN				
glycine	46.88 (2)	−1.40 (36)	−1.29 (33)	β-alanine	61.84 (2)	−0.58 (32)	−0.54 (29)
DL-alanine	63.66 (1)	0.16 (12)	0.15 (11)	γ-aminobutyric acid	76.81 (2)	−1.07 (31)	−0.99 (29)
L-proline	87.14 (1)	−4.32 (26)	−4.01 (24)	ε-aminocaproic acid	109.37 (4)	−3.65 (87)	−3.39 (80)
L-threonine	81.01 (4)						
			308.15 K, 5 *m* KSCN				
glycine	47.34 (5)			β-alanine	62.34 (2)	0.77 (27)	0.68 (24)
DL-alanine	64.51 (2)	0.48 (25)	0.43 (22)	γ-aminobutyric acid	77.71 (6)		
L-proline	87.73 (3)	−1.36 (51)	−1.21 (44)	ε-aminocaproic acid	110.42 (3)	−2.88 (68)	−2.55 (59)
L-threonine	82.91 (3)	−2.94 (58)	−2.59 (51)				

[a] Values in parentheses are 100 × standard error. [b] $V_\phi°$ are averages of the experimental V_ϕ values.

at 288.15, 298.15, and 308.15 K, respectively. A larger $V_\phi°(tr)(NH_3^+,COO^-)$ value is due to the predominance of the electrostatic interactions. The $V_\phi°(tr)(CH_2)$ obtained presently is also supported by similar results from other studies: $[V_\phi°(tr)(\beta\text{-Ala}) - V_\phi°(tr)(Gly)]$ ($cm^3 \cdot mol^{-1}$), 0.21, 1 *m* LiCl; 0.10, 2 *m* NaCl; 0.22, 1 *m* KCl (*7*); 0.40, 1 *m* NH_4Cl (*5*). This may be contrasted with the negative $V_\phi°(tr)(CH_2)$ at 298.15 K obtained for α-amino acids in 1 *m* NaCl (−0.17) (*8*), 6 *m* urea (−0.17) (*9*), and 1 *m* NH_4Cl (−0.21) (*5*). In the case of ω-amino acids, the hydrophobic hydration of the CH_2 groups is suppressed by overlap of the hydration cospheres of the polar end groups and in the presnce of KSCN strong polar–polar group interactions enhance the hydrophobic hydration, yielding positive $V_\phi°(tr)(CH_2)$.

The $V_\phi°$ results from four contributions (*10*):

$$V_\phi° = V_{vW} + V_f + V_s + V_h \quad (6)$$

where V_{vW} is the intrinsic or the van der Waals volume, V_f, the void volume, V_s, the contribution from the solute–solute-solvent interactions, and V_h, that from the hydrophobic hydration. Taking $V_{vW} + V_f$ to be the same (*8*) in aqueous KSCN as in water, the expected changes in $V_s + V_h$ should explain the observed trends in $V_\phi°$ or $V_\phi°(tr)$. The $V_s + V_h$ for amino acids in water and in aqueous salt solutions is given, respectively, by eqs 7 and 8,

$$(V_s + V_h)_W = V_{AW} + V_{WW} \quad (7)$$

$$(V_s + V_h)_{W+S} = V_{SA} + V_{SS} - V_{SW} + V_{WW} \quad (8)$$

where V_{SA}, V_{SS}, V_{SW}, and V_{WW} are, respectively, the contributions from salt–amino acid, salt–salt, salt–water, and water dipole–dipole interactions. Therefore

$$V_\phi°(tr) = V_{SA} + V_{SS} - V_{SW} - V_{AW} \quad (9)$$

The positive V_{SA} due to the predominance of the salt–polar group over salt–nonpolar group interactions, a decrease in electrostriction on addition of KSCN, i.e., decrease in V_{SW}

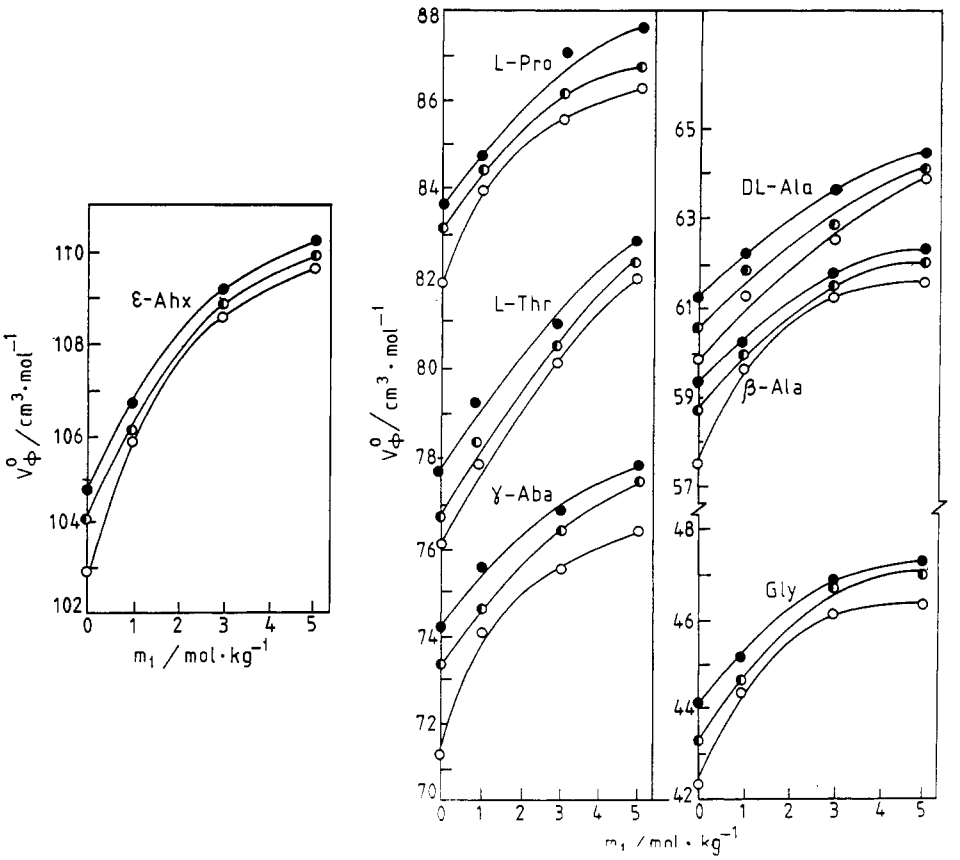

Figure 1. Variation of $V_\phi°$ with m_1, molality of KSCN, at (○) 288.15, (◐) 298.15, and (●) 308.15 K.

Table III. Limiting Apparent Molar Volumes of Transfer $V_\phi°$(tr) for Transfer of Amino Acids from Water to Water + KSCN at 288.15, 298.15, and 308.15 K

amino acid	$V_\phi°$(tr)/(cm^3·mol^{-1}) at various m_1/(mol·kg^{-1}) 1	3	5
	288.15 K		
glycine	1.98 (6)[a]	3.78 (6)	4.03 (7)
DL-alanine	1.38 (3)	2.72 (3)	4.08 (5)
L-proline	2.06 (3)	3.66 (3)	4.43 (3)
L-threonine	1.87 (5)	4.10 (5)	6.05 (5)
γ-aminobutyric acid	2.86 (5)	4.28 (6)	5.28 (6)
β-alanine	2.21 (3)	3.85 (5)	4.14 (4)
ε-aminobutyric acid	2.97 (3)	5.96 (4)	6.73 (3)
	298.15 K		
glycine	1.37 (3)	3.52 (3)	3.81 (3)
DL-alanine	1.33 (3)	2.38 (2)	3.69 (2)
L-proline	1.24 (3)	3.08 (5)	3.72 (6)
L-threonine	1.85 (4)	3.91 (5)	5.80 (6)
β-alanine	1.41 (3)	2.83 (6)	3.46 (3)
γ-aminobutyric acid	1.61 (6)	3.08 (3)	4.13 (5)
ε-aminocaproic acid	2.01 (5)	4.68 (5)	5.83 (5)
	308.15 K		
glycine	1.04 (4)	2.76 (3)	3.22 (6)
DL-alanine	1.02 (7)	2.39 (6)	3.24 (7)
L-proline	1.09 (4)	3.52 (3)	4.11 (5)
L-threonine	1.58 (3)	3.30 (5)	5.20 (4)
β-alanine	1.14 (5)	2.78 (3)	3.28 (3)
γ-aminobutyric acid	1.36 (4)	2.63 (4)	3.61 (5)
ε-aminocaproic acid	1.93 (7)	4.49 (5)	5.54 (4)

[a] Values in parentheses are 100 × standard error.

and increase in V_{SS}, and assumed constancy of the V_{WW} jointly explain the increase in $V_\phi°$ [or positive $V_\phi°$(tr)] with the increase in KSCN concentration. However, a gradual decrease in $V_{SS} - V_{SW}$ with KSCN concentration is responsible for the leveling off of the $V_\phi° - m_1$ [or $V_\phi°$(tr) $- m_1$] curves.

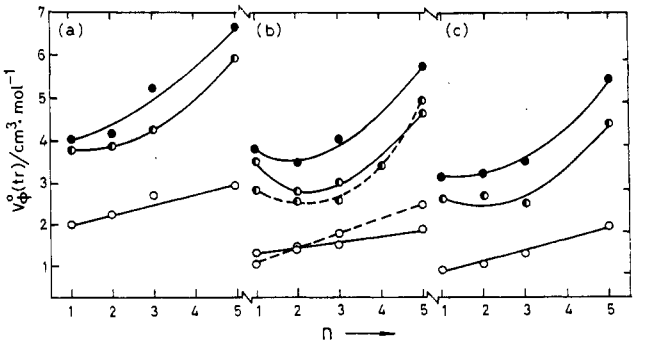

Figure 2. Variation of $V_\phi°$(tr) for ω-amino acids with n, the number of CH_2 groups in the backbone chain, at (a) 288.15, (b) 298.15, and (c) 308.15 K and (○) 1 m, (◐) 3 m, and (●) 5 m KSCN. Broken curves represent data for amino acids + aqueous ammonium chloride (ref 5).

The increase in $V_\phi°$ with temperature is contributed from the increase in V_{SA} due to the increased thermal energy of the water molecules in the electrostricted regions of NH_3^+–SCN^- and COO^-–K^+ and the decrease in the $-V_{SW}$ due to favored salt–salt interactions. The contribution from changes in $-V_{WW}$ can be taken as relatively small (*11*). The $V_\phi°$(tr) on the other hand decreases with temperature. This decrease can be rationalized by considering the temperature coefficients of various terms contributing to $V_\phi°$(tr) in eq 9.

The viscosities η of solutions of amino acids in 1, 3, and 5 m KSCN at 288.15, 298.15, and 308.15 K as a function of m_2 are collected in Table IV. The relative viscosities $\eta_r = \eta/\eta_o$, where η_o is the solvent viscosity, were regressed by a least-squares procedure and the relation

$$\eta_r = A + Bc + Dc^2 \qquad (10)$$

The best values of the parameter A were found to be unity within 10^{-4}, the standard deviation for the η_r–c fits. This was

Table IV. Viscosities η for Amino Acids + Aqueous KSCN as a Function m_2 of Amino Acids in Solvent (Water + KSCN)

288.15 K		298.15 K		308.15 K		288.15 K		298.15 K		308.15 K	
10^3m_2/ (mol·kg^{-1})	100η/ (mPa·s)	10^3m_2/ (mol·kg^{-1})	100η/ (mPa·s)	10^3m_2/ (mol·kg^{-1})	100η/ (mPa·s)	10^3m_2/ (mol·kg^{-1})	100η/ (mPa·s)	10^3m_2/ (mol·kg^{-1})	100η/ (mPa·s)	10^3m_2/ (mol·kg^{-1})	100η/ (mPa·s)
Glycine + 1 *m* KSCN											
0	107.05	0	86.86	0	69.76	211.85	110.91	336.14	91.70	205.11	72.11
42.58	107.84	40.41	87.38	44.68	70.23	257.10	111.73	391.01	92.60	238.03	72.50
108.11	109.07	98.85	88.22	89.09	70.79	289.04	112.32	278.17	90.86	269.97	72.88
146.53	109.75	157.85	88.98	143.53	71.39	321.28	112.86			299.23	73.23
180.93	110.35	216.17	89.96	179.20	71.80	350.20	113.41			326.49	73.56
Glycine + 3 *m* KSCN											
0	106.79	0	88.61	0	72.94	202.79	111.56	297.33	94.16	246.99	76.48
29.30	107.49	70.45	89.91	48.18	73.61	228.47	112.15	336.88	94.86	279.17	77.02
60.60	108.19	133.67	91.03	93.66	74.24	258.63	112.86			314.47	77.54
131.82	109.92	192.18	92.11	131.85	74.83	286.17	113.48				
166.85	110.74	242.60	93.07	213.03	76.00						
Glycine + 5 *m* KSCN											
0	114.17	0	95.99	0	79.77	156.25	118.61	303.71	102.97	205.39	83.47
31.48	115.10	48.34	97.02	55.16	80.76	188.29	119.56	359.54	104.34	240.54	84.11
56.34	115.74	103.45	98.16	93.98	81.42	212.75	120.29	489.33	107.85	275.77	84.68
96.64	116.84	144.73	99.16	138.77	82.23	240.75	121.12			319.51	85.58
126.18	117.75	234.99	101.27	175.87	82.90	267.11	121.89			350.75	86.10
DL-Alanine + 1 *m* KSCN											
0	106.67	0	86.67	0	69.71	132.17	110.72	235.27	92.28	207.47	73.38
32.08	107.67	58.50	87.93	45.98	70.48	160.64	111.55	291.55	93.68	242.49	74.05
63.87	108.57	131.33	89.74	86.57	71.21	182.02	112.24			274.16	74.64
80.46	109.13	160.75	90.43	136.36	72.11	206.84	113.03			298.46	75.10
106.16	109.93	196.57	91.35	173.51	72.78	234.84	113.97			331.42	75.72
DL-Alanine + 3 *m* KSCN											
0	106.83	0	88.73	0	72.92	201.98	113.90	255.67	95.74	173.52	76.49
54.07	108.78	56.21	90.26	38.56	73.62	237.22	115.22	336.70	98.04	198.17	77.00
95.19	110.12	99.82	91.48	80.15	74.49	274.75	116.61			226.24	77.62
134.17	111.51	143.33	92.57	116.00	75.27	305.49	117.77			253.91	78.25
169.10	112.72	221.79	94.75	146.14	75.90	331.00	118.68			281.96	78.84
DL-Alanine + 5 *m* KSCN											
0	114.31	0	95.74	0	79.73	178.20	121.60	189.17	101.96	149.62	83.39
33.70	115.57	36.05	96.91	30.19	80.44	200.32	122.50	218.54	102.89	174.99	84.00
72.10	117.11	74.37	98.18	59.34	81.16	223.71	123.51	250.39	103.97	197.07	84.59
115.63	118.95	134.88	100.11	92.16	82.01	242.78	124.34			220.50	85.21
150.76	120.42	164.60	101.09	122.41	82.71					243.06	85.79
L-Proline + 1 *m* KSCN											
0	107.42	0	86.69	0	69.82	123.86	111.73	203.27	92.29	198.61	73.93
33.00	108.41	46.96	87.99	36.73	70.57	150.64	112.65	239.25	93.29	225.52	74.46
56.12	109.28	78.79	88.79	91.37	71.72			284.76	94.66	251.01	75.01
81.21	110.15	118.57	89.92	131.48	72.50			327.32	95.84	280.88	75.68
105.01	110.96	159.82	91.06	164.93	73.18						
L-Proline + 3 *m* KSCN											
0	107.05	0	88.59	0	72.89	183.18	114.37	224.67	95.61	167.18	76.83
59.89	109.38	84.92	91.25	59.11	74.28	201.27	115.11	252.35	96.54	189.65	77.40
98.46	110.91	116.32	92.15	91.64	75.04	214.67	115.66	275.23	97.27	216.12	78.08
142.19	112.67	152.44	93.36	117.88	75.65					243.60	78.73
164.46	113.61	193.44	94.62	142.66	76.24						
L-Proline + 5 *m* KSCN											
0	114.50	0	96.05	0	79.73	138.67	120.85	163.17	101.75	137.93	83.57
24.50	115.52	32.94	97.04	25.57	80.44	176.35	122.68	222.52	104.01	167.31	84.39
51.73	116.77	63.46	98.14	60.77	81.40	192.79	123.43	250.77	105.03	187.78	85.03
75.64	117.88	96.47	99.27	89.08	82.19					210.40	85.68
117.70	119.81	129.75	100.53	113.68	82.87						
L-Threonine + 1 *m* KSCN											
0	107.28	0	86.67	0	69.73	117.72	112.18	122.98	90.56	93.76	71.97
23.89	108.18	22.05	87.35	19.04	70.16	132.03	112.80	139.41	91.12	108.68	72.33
43.71	109.04	47.01	88.12	35.08	70.57	157.17	113.86	153.42	91.60	123.06	72.71
79.59	110.55	66.17	88.72	49.81	70.91					134.61	73.00
101.31	111.48	105.55	89.97	64.49	71.29						
L-Threonine + 3 *m* KSCN											
0	107.03	0	88.69	0	72.95	125.84	112.87	95.18	92.10	76.39	75.02
24.18	108.15	22.80	89.50	18.09	73.41	144.21	113.89			92.53	75.51
67.19	110.11	44.12	90.26	33.25	73.86	160.70	114.55			107.01	75.92
86.54	111.07	62.68	90.90	48.14	74.29	173.48	115.22			127.52	76.49
105.91	111.94	76.41	91.40	62.47	74.66					149.02	77.11

Table IV (Continued)

288.15 K		298.15 K		308.15 K		288.15 K		298.15 K		308.15 K	
10^3m_2/(mol·kg^{-1})	100η/(mPa·s)	10^3m_2/(mol·kg^{-1})	100η/(mPa·s)	10^3m_2/(mol·kg^{-1})	100η/(mPa·s)	10^3m_2/(mol·kg^{-1})	100η/(mPa·s)	10^3m_2/(mol·kg^{-1})	100η/(mPa·s)	10^3m_2/(mol·kg^{-1})	100η/(mPa·s)
L-Threonine + 5 *m* KSCN											
0	114.51	0	95.91	0	79.84	69.95	118.29	60.96	98.42	56.97	81.65
17.06	115.41	17.94	96.68	15.40	80.30	113.65	120.76	87.32	99.57	68.38	82.07
37.77	116.48	33.84	97.28	29.44	80.75	126.95	121.47	97.91	99.96	91.62	82.79
53.83	117.38	47.73	97.93	42.44	81.18	138.73	122.14			105.07	83.24
β-Alanine + 1 *m* KSCN											
0	107.02	0	86.45	0	69.70	330.28	116.37	154.60	89.76	190.09	72.89
97.73	109.64	26.19	87.04	32.71	70.24			176.58	90.23	214.76	73.33
134.92	110.70	49.51	87.52	70.37	70.88			197.00	90.74	239.15	73.77
166.75	111.65	68.20	87.92	99.70	71.38			220.60	91.25	270.64	74.33
195.77	112.44	94.85	88.53	132.05	71.87					235.08	91.52
219.96	113.08	124.71	89.12	164.35	72.47						
β-Alanine + 3 *m* KSCN											
0	106.72	0	88.56	0	70.91	159.57	111.77	215.67	94.23	217.96	75.25
19.75	107.35	40.18	89.64	37.29	71.68	178.06	112.34	271.69	95.69	244.09	75.81
50.41	108.35	80.36	90.63	76.09	72.42	195.92	112.88	319.75	97.02	271.09	76.30
96.17	109.83	139.00	92.19	113.76	73.17	214.88	113.53				
138.59	111.13	176.18	93.11	148.57	73.85						
β-Alanine + 5 *m* KSCN											
0	114.09	0	95.81	0	79.99	145.08	119.64	284.39	104.66	118.69	82.88
22.37	114.94	48.53	97.24	25.75	80.61	169.95	120.62	314.24	105.64	139.46	83.34
42.11	115.72	92.07	98.58	43.22	81.01	191.69	121.53	347.27	106.85	157.98	83.77
69.05	116.69	130.45	99.75	63.01	81.52	209.62	122.18			189.59	84.52
94.48	117.70	169.84	100.94	81.50	81.95	232.28	123.09				
119.87	118.69	246.79	103.37	95.56	82.24						
γ-Aminobutyric Acid + 1 *m* KSCN											
0	107.22	0	86.51	0	69.82	151.09	113.08	139.26	90.70	146.74	73.22
19.66	107.99	29.14	87.36	292.24	70.45	178.12	114.14	164.34	91.44	167.94	73.71
41.23	108.74	71.85	88.64	53.63	70.99	202.03	115.09	180.22	91.93	184.95	74.11
91.22	110.72	93.34	89.30	81.20	71.60	220.35	115.85	199.81	92.55		
114.43	111.65	113.94	89.91	123.98	72.69						
γ-Aminobutyric Acid + 3 *m* KSCN											
0	107.93	0	88.61	0	72.97	135.89	113.02	195.90	95.55	153.23	77.14
23.45	107.93	35.44	89.86	28.10	73.70	170.61	114.60	245.15	97.35	173.46	77.70
47.44	109.04	80.95	91.44	57.67	74.52	194.98	115.81			199.49	78.44
71.49	110.08	114.67	92.59	84.41	75.25	216.93	116.81				
91.79	111.00	142.30	93.60	109.26	75.92	242.53	118.06				
113.61	111.94	165.51	94.44	133.54	76.62						
γ-Aminobutyric Acid + 5 *m* KSCN											
0	114.10	0	95.76	0	80.08	125.79	120.87	168.64	102.80	111.05	83.60
17.66	115.28	27.81	96.86	23.13	80.76	147.09	122.07	184.37	103.42	132.02	84.27
40.16	116.41	88.27	99.33	43.89	81.42	168.42	123.24			146.16	84.71
68.49	117.95	108.34	100.17	59.67	81.93	186.92	124.19			163.30	85.31
90.09	119.00	126.73	101.00	78.47	82.57					182.44	85.95
107.58	119.91	148.15	101.83	96.09	83.15						
ε-Aminocaproic Acid + 1 *m* KSCN											
0	107.23	0	88.60	0	69.90	82.37	112.24	193.45	95.77	86.40	72.96
16.62	108.24	38.92	88.46	18.20	70.58	96.94	113.14	220.13	97.11	101.62	73.55
35.13	109.35	99.61	91.28	35.96	71.19	114.10	114.27	249.19	98.58	119.64	74.14
52.23	110.38	139.83	93.20	51.95	71.76	125.86	114.97	285.66	100.46	137.24	74.85
68.71	111.33	170.96	94.69	67.46	72.34	141.01	115.88			157.39	75.58
ε-Aminocaproic Acid + 3 *m* KSCN											
0	106.78	0	88.60	0	72.94	94.26	112.91	143.42	95.97	128.49	78.08
22.96	108.16	41.86	90.69	18.59	73.63	106.41	113.69	180.07	97.92	143.04	78.68
38.14	109.18	74.12	92.30	41.55	74.52	121.15	114.73	201.87	99.19	157.71	79.30
69.18	111.24	96.97	93.50	78.25	76.00	135.50	115.63				
81.95	112.05	117.31	94.53	95.80	76.73						
ε-Aminocaproic Acid + 5 *m* KSCN											
0	114.15	0	95.68	0	80.07	64.28	118.98	152.59	105.00	77.06	83.57
12.42	115.12	24.70	97.21	20.42	80.87	77.56	120.01	175.23	106.43	91.47	84.21
24.51	116.04	51.06	98.69	34.82	81.54	87.52	120.78			103.69	84.84
37.02	116.93	91.17	101.16	47.55	82.13	99.38	121.66			121.86	85.67
51.97	118.05	129.23	103.57	62.40	82.84						

also used as a test for quality of the viscosity data. The B and D coefficients and their in-water values (*12–15*) are given in Table V. The B values are in general larger in aqueous KSCN than those in water due to the increased solute–solvent interactions in ternary solutions. The presence of the large hydrophobic part in ε-aminocaproic acid and the possible dominance of the hydrophobic group–salt interactions in the ternary solutions are expected to result in the observed lower B values as compared to those in water. The positive B values point toward the net structure promoting tendency of all the

Table V. Viscosity B and D Coefficients of Equation 10 for Amino Acids + Water and + Aqueous KSCN

T/K	m_1/ (mol·kg^{-1})	N	$100m_2$/ (mol·kg^{-1})	10^3B/ (dm^3·mol^{-1})	10^2D/ (dm^6·mol^{-2})	m_1/ (mol·kg^{-1})	N	$100m_2$/ (mol·kg^{-1})	10^3B/ (dm^3·mol^{-1})	10^2D/ (dm^6·mol^{-2})
			Glycine					DL-Alanine		
288.15	0			129[a] (1)[b]	2 (0)	0	9	3–36	259 (3)	4 (1)
	1.0001	9	4–35[g]	164 (2)		0.9996	9	3–23	261 (7)	8 (2)
	2.9991	8	3–29	189 (2)		2.9991	9	5–33	273 (5)	9 (1)
	4.9996	9	3–27	202 (4)	5 (1)[c]	4.9989	8	3–24	300 (4)	6 (1)
298.15	0			143 (2)[a]	1 (1)	0			253[d] (2)	
	0.9993	7	4–28	151 (8)	4 (2)	0.9994	6	6–29	273 (5)	2 (1)
	2.9979	6	7–34	177 (8)	4 (2)	2.9913	6	6–34	258 (7)	7 (2)
	4.9969	7	4–49	185 (3)	7 (1)	4.9948	7	4–25	284 (6)	5 (2)
308.15	0			148 (1)[a]	3 (1)	0			247[d] (2)	4 (1)
	0.9995	9	4–33	159 (4)	2 (1)	0.9995	9	4–33	241 (3)	5 (1)
	3.0000	7	4–31	173 (7)	4 (2)	2.9984	9	4–28	257 (3)	4 (1)
	4.9991	9	5–35	189 (6)	2 (1)	4.9990	9	3–24	256 (6)	6 (2)
			L-Proline					L-Threonine		
288.15	0	9	3–29	282 (5)	9 (2)	0	9	2–25	339 (6)	9(2)
	0.9990	6	3–15	314 (20)	7 (5)	0.9990	7	2–16	380 (3)	3 (1)
	2.9964	8	3–21	314 (4)	11 (1)	2.9949	8	2–17	378 (16)	12 (7)
	4.9979	7	2–19	333 (6)	10 (2)	4.9980	7	2–14	397 (9)	12 (5)
298.15	0	8	3–27	284 (5)	8 (2)	0	9	2–21	345 (7)	3 (3)
	0.9989	8	5–33	293 (6)	8 (2)	0.9994	7	2–15	322 (3)	23 (2)
	2.9974	8	4–27	295 (8)	10 (2)	2.9954	5	2–10	343 (12)	18 (9)
	4.9961	7	3–25	309 (6)	8 (2)	4.9927	6	2–10	373 (3)	
308.15	0			269[e]	13	0	8	2–19	315 (4)	7 (2)
	0.9996	8	4–28	271 (8)	8 (2)	0.9995	8	2–13	332 (10)	6 (6)
	2.9994	9	3–24	286 (5)	7 (1)	2.9990	9	2–15	341 (8)	6 (4)
	4.9967	8	2–21	284 (4)	11 (1)	4.9972	8	2–13	356 (2)	
			β-Alanine					γ-Aminobutyric Acid		
288.15	0			215 (1)[a]	3 (0)	0			322 (1)[a]	8 (0)
	0.9989	6	9–33	241 (10)	5 (3)	0.9998	8	2–22	338 (6)	8 (2)
	2.9989	8	2–21	273 (6)	−2 (2)	2.9974	10	2–24	359 (5)	12 (2)
	5.0000	10	2–23	280 (3)	5 (1)	4.9978	10	2–21	369 (6)	13 (2)
298.15	0			220 (3)[a]	4 (1)	0			314 (2)[a]	9 (1)
	0.9983	10	2–23	232 (7)	4 (2)	0.9993	8	3–20	330 (3)	5 (1)
	2.9978	7	4–32	253 (6)	6 (1)	2.9977	7	2–17	337 (7)	13 (3)
	4.9921	8	5–35	248 (6)	10 (1)	4.9919	7	2–18	355 (13)	11 (5)
308.15	0			216[f]	3[f]	0	9	3–28	299 (3)	−9 (1)
	0.9993	9	3–27	222 (5)	6 (1)	0.9999	7	3–18	314 (20)	9 (7)
	2.9993	7	4–27	252 (6)	4 (2)	2.9991	8	3–20	336 (5)	5 (2)
	4.9996	9	2–19	262 (9)		4.9962	10	2–18	343 (8)	5 (3)
			ε-Aminocaproic Acid							
288.15	0			521 (1)[a]	22 (1)					
	0.9996	9	2–14	529 (10)	20 (8)					
	2.9975	8	2–13	551 (10)	10 (6)					
	4.9980	8	1–10	543 (7)	19 (5)					
298.15	0			513 (2)[d]	16 (1)					
	0.9997	8	4–30	490 (4)	21 (1)					
	2.9935	7	4–20	479 (7)	28 (3)					
	4.9890	6	2–17	515 (15)	21 (6)					
308.15	0			499 (2)[d]	19 (1)					
	0.9997	9	2–16	468 (10)	20 (7)					
	2.9999	7	2–16	479 (5)	19 (2)					
	4.9982	8	2–12	503 (10)	10 (6)					

[a] Reference 12. [b] Values in parentheses are 1000 × standard error. [c] Values in parentheses are 100 × standard error. [d] Reference 13. [e] Reference 15 using $\eta_r = 1 = Bm_2 = Dm_2^2$. [f] Reference 14; coefficients A and B of $\eta_r = 1 = Am_2 = Bm_2^2 = Dm_2^3$. [g] Units of m_2 are mol·(kg of water = KSCN)$^{-1}$.

amino acids. Glycine and β-alanine show positive dB/dT and are reported to be structure breakers in water. The strong structure-breaking potassium thiocyanate renders its aqueous solutions too structureless for these to act as structure breakers. Furthermore, a decrease in electrostriction due to strong salt–polar group interactions also contributes to the structure making by the solute. The decrease in the B coefficient with increase in temperature and its tendency to increase with thiocyanate concentration can also be rationalized by considering the structural state of these solutions arising from the overlap of cospheres of different entities under varying conditions of temperature and electrolyte concentration.

The B coefficient of DL-alanine is, as is its $V_\phi°$, greater than that of β-alanine. However, larger $B/V_\phi°$ values for DL-alanine than for β-alanine indicate stronger solute–solvent interactions in DL-alanine systems in concurrence with the observations regarding the B coefficients of DL-alanine and β-alanine at 298.15 K in 1 and 2 m LiCl, NaCl, and KCl (7).

As in the case of water systems (12), the B values for ω-amino acids in aqueous KSCN also show a linear correlation with $V_\phi°$ values. The coefficients I and S of the regression equation

$$B = I + SV_\phi° \qquad (11)$$

are given in Table VI. A similar correlation ($B = -0.03 + 4.9\ V_\phi°$) for aqueous solutions of alkylammonium bromides [$H(CH_2)_xNH_3^+Br^-$, x = 1–6] at 298.15 K was reported by Desnoyers et al. (16). These compounds are closely related to ω-amino acids $NH_3^+(CH_2)_nCOO^-$, and it appears that the

Table VI. Parameters I and S of Equation 11 for ω-Amino Acids + Aqueous KSCN

	288.15 K		298.15 K		308.15 K	
m_1/(mol·kg^{-1})	$-I$/(dm^3·mol^{-1})	S	$-I$/(dm^3·mol^{-1})	S	$-I$/(dm^3·mol^{-1})	S
0	0.152	6.54 (0.20)[a]	0.136	6.22 (0.24)	0.121	5.84 (0.33)
1	0.107	5.99 (0.17)	0.096	5.55 (0.18)	0.075	5.09 (0.17)
3	0.078	5.77 (0.05)	0.045	4.86 (0.20)	0.050	4.88 (0.21)
5	0.049	5.42 (0.12)	0.071	5.35 (0.28)	0.047	4.99 (0.05)

[a] Values in parentheses are standard errors.

Table VII. Average Molar Volume $\bar{V}_{1,2}$ and Activation Free Energy $\Delta\mu^{\circ *}_{1,2}$ of Aqueous KSCN at Various Temperatures and Salt Concentrations

	$\bar{V}_{1,2}$/(cm^3·mol^{-1})			$\Delta\mu^{\circ *}_{1,2}$/(kJ·mol^{-1})		
T/K	1 m	3 m	5 m	1 m	3 m	5 m
288.15	18.59	19.73	20.82	9.37	9.54	9.83
298.15	18.65	19.83	20.97	9.16	9.37	9.71
308.15	18.73	19.93	21.11	9.00	9.29	9.66

difference between the slope value of 6.22 for amino acids and 4.9 for alkylammonium bromides arises solely from the replacement of COO^- by H and is too small to warrant detailed interpretation. However, a nonlinear dependence of B values on V_ϕ° has been observed for tertiary n-alkylammonium chlorides (*17*) and tertiary n-alkylammonium picrates (*18*) in benzene solutions at 298.15 K. The slope S representing the B/V_ϕ° value for the CH_2 group decreases with increase in temperature and KSCN concentration. The occurrence of the larger slope values at lower temperatures is due to the structure-enhancing nature of CH_2 groups. Decreasing S values with KSCN concentration at constant temperature indicate increasing CH_2–KSCN interaction and hence decreasing solvent structure around CH_2 groups.

On the basis of the transition-state theory for the activation free energy of viscous flow, eq 12, where the subscript 1,2 refers to the average property for the binary (water + KSCN) solvent at constant thiocyanate concentration, proposed

$$B = (\bar{V}_{1,2} - V_\phi^\circ)/1000 + \bar{V}_{1,2}(\Delta\mu^{\circ *}_3 - \Delta\mu^{\circ *}_{1,2})/1000RT \quad (12)$$

initially (*19*) for the electrolyte solutions could be applied to the solutions of amino acids. The average activation free energy of the solvent ($\Delta\mu^{\circ *}_{1,2}$) can be calculated using the Eyring (*20*) equation:

$$\eta_{1,2} = (hN/\bar{V}_{1,2}) \exp(\Delta\mu^{\circ *}_{1,2}/RT) \quad (13)$$

The solvent parameters $\bar{V}_{1,2}$ and $\Delta\mu^{\circ *}_{1,2}$ calculated from the density and viscosity of aqueous potassium thiocyanate (*21*) are given in Table VII. The $\Delta\mu^{\circ *}_3$ values thus obtained for the reported amino acids in aqueous potassium thiocyanate and the corresponding values ($\Delta\mu^{\circ *}_2$) in water are listed in Table VIII.

Due to irregular variation of $\Delta\mu^{\circ *}_3$ with electrolyte concentration, henceforth, only the averages of $\Delta\bar{X}^{\circ *}_3$ are referred to. For DL-alanine, L-proline, and L-threonine, the $\Delta\mu^{\circ *}_3$ and the corresponding $\Delta\mu^{\circ *}_2$ values do not differ significantly. The difference $\Delta\mu^{\circ *}_3 - \Delta\mu^{\circ *}_2$ is positive for glycine, decreases gradually with the increase of CH_2 groups in the backbone of ω-amino acids, and becomes negative for ε-aminocaproic acid. This shows that for glycine the ground state in aqueous potassium thiocyanate is more structured than in water, while for ε-aminocaproic acid the reverse is true. Although the hydrophobic contribution in glycine is a minimum, localized NH_3^+–SCN^- and COO^-–K^+ interactions in aqueous potassium thiocyanate increase the solvent structure. For the higher ω-amino acids, the zwitterion–salt interaction does not increase the solvent structure in aqueous potassium thiocyanate to the extent done by hydrophobic CH_2 groups in water. Thus, the ground state in water becomes more structured than in the salt solution. This can be further supported by separating the polar and nonpolar contributions of $\Delta\mu^{\circ *}_i$ (i = 2, 3).

Table VIII. Activation Free Energies $\Delta\mu^{\circ *}_2$ for Viscous Flow of Amino Acid + Water and $\Delta\mu^{\circ *}_3$ for Amino Acid + Aqueous KSCN

	$\Delta\mu^{\circ *}_2$/(kJ·mol^{-1})	$\Delta\mu^{\circ *}_3$/(kJ·mol^{-1})		
	0 m	1 m	3 m	5 m
	288.15 K			
glycine	29.7 (0)[a]	33.9 (4)	35.6 (4)	36.0 (4)
DL-alanine	49.4 (4)	48.5 (8)	47.7 (8)	49.4 (4)
L-proline	55.2 (8)	58.2 (8)	55.6 (4)	55.6 (8)
L-threonine	62.3 (8)	66.1 (4)	62.8 (21)	62.3 (8)
β-alanine	43.1 (0)	45.6 (13)	47.7 (8)	46.9 (4)
γ-aminobutyric acid	59.4 (0)	60.2 (8)	59.8 (8)	58.6 (8)
ε-aminocaproic acid	90.0 (0)	88.7 (13)	87.4 (13)	82.4 (8)
	298.15 K			
glycine	32.2 (4)	32.6 (8)	34.7 (8)	34.7 (4)
DL-alanine	49.8 (4)	51.0 (8)	46.9 (8)	48.5 (8)
L-proline	56.9 (8)	56.9 (8)	54.4 (8)	54.0 (8)
L-threonine	64.4 (8)	59.8 (4)	59.8 (8)	61.1 (4)
β-alanine	44.8 (4)	45.6 (8)	46.0 (8)	43.9 (8)
γ-aminobutyric acid	59.8 (4)	60.7 (4)	58.6 (8)	58.2 (17)
ε-aminocaproic acid	91.2 (4)	85.8 (4)	80.3 (13)	81.2 (17)
	308.15 K			
glycine	33.5 (0)	34.3 (4)	35.1 (8)	35.6 (8)
DL-alanine	49.8 (4)	47.7 (4)	48.1 (4)	46.0 (4)
L-proline	56.1 (0)	55.2 (13)	54.8 (4)	52.3 (4)
L-threonine	61.9 (4)	62.8 (13)	61.1 (13)	60.7 (4)
β-alanine	45.2 (4)	45.2 (8)	46.9 (8)	46.4 (13)
γ-aminobutyric acid	59.0 (4)	59.8 (30)	59.8 (4)	58.2 (8)
ε-aminocaproic acid	91.6 (4)	84.9 (13)	82.4 (4)	81.6 (13)

[a] Entries in parentheses are 10 × standard deviation.

As for V_ϕ° and the B coefficient of ω-amino acids (*6*), $\Delta\mu^{\circ *}_i$ (i = 2, 3) also varies linearly with n as shown in Figure 3. The regression of $\Delta\mu^{\circ *}_i$–n data using eq 14 gives $\Delta\mu^{\circ *}_i(NH_3^+,COO^-)$

$$\Delta\mu^{\circ *}_i = \Delta\mu^{\circ *}_i(NH_3^+,COO^-) + n\Delta\mu^{\circ *}_i(CH_2) \quad (14)$$

and $\Delta\mu^{\circ *}_i(CH_2)$ as the respective contributions of NH_3^+,COO^- and the CH_2 groups. Since $\Delta\mu^{\circ *}_3(NH_3^+,COO^-)$ and $\Delta\mu^{\circ *}_3(CH_2)$ are almost constant over the studied KSCN concentrations, only averages at different temperatures are given in Table IX.

As expected from the sign of $\Delta\mu^{\circ *}_3$ for ω-amino acids, the contribution of CH_2 groups to the activation free energy is higher in water than in aqueous potassium thiocyanate and for NH_3^+,COO^- groups, the water values are smaller. But as $d\Delta\mu^{\circ *}_{3,2}(NH_3^+,COO^-)$ [$d\Delta\mu^{\circ *}_{3,2}(i) = \Delta\mu^{\circ *}_3(i) - \Delta\mu^{\circ *}_2(i)$; i =

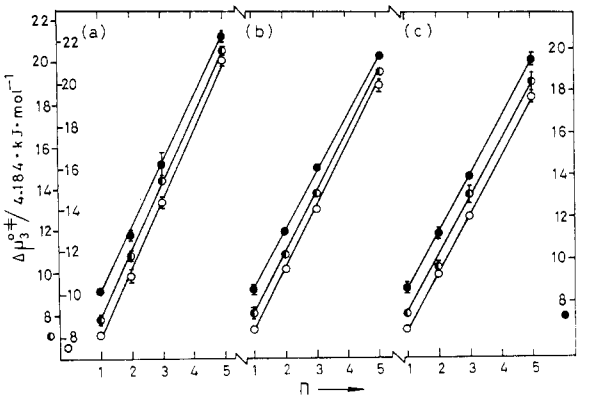

Figure 3. Variation of $\Delta\mu^{\circ\ddagger}_3$ of ω-amino acids with n, the number of CH_2 groups in the backbone chain, at (○) 288.15, (◐) 298.15, and (●) 308.15 K and (a) 1 m KSCN, (b) 3 m KSCN, and (c) 5 m KSCN.

Table IX. Contribution of CH_2 and NH_3^+,COO^- Groups to Activation Free Energy $\Delta\mu^{\circ\ddagger}_i$ (i = 2, 3) in Water and Aqueous KSCN

	$\Delta\mu^{\circ\ddagger}_i/(kJ\cdot mol^{-1})$			
	H_2O		H_2O + KSCN	
T/K	CH_2	NH_3^+,COO^-	CH_2	NH_3^+,COO^-
288.15	15.1	14.6	13.4	19.7
298.15	14.2	18.0	12.1	23.0
308.15	13.8	20.0	11.3	23.8

CH_2 or NH_3^+,COO^-] is much larger than $d\Delta\mu^{\circ\ddagger}_{3,2}(CH_2)$, the hydrophobic effects are observed only after three or four CH_2 groups.

The $\Delta\mu^{\circ\ddagger}_3(CH_2)$ decreases from 288.15 to 308.15 K while $\Delta\mu^{\circ\ddagger}_3(NH_3^+,COO^-)$ increases, giving $T\Delta\bar{S}^{\circ\ddagger}_3$ equal to 31.4 and −62.8 kJ·mol^{-1}, respectively. Similar trends are observed in aqueous solutions where the $T\Delta\bar{S}^{\circ\ddagger}_2$ values at the two extreme temperatures for CH_2 and NH_3^+,COO^- groups are 18.8 and −75.3 kJ·mol^{-1}, respectively. Unlike the parameter $\Delta\mu^{\circ\ddagger}_i$, $\Delta\bar{S}^{\circ\ddagger}_i$ and hence $\Delta\bar{H}^{\circ\ddagger}_i$ involve a contribution from both solute–solvent and solvent–solvent interactions (22). Thus, the $T\Delta\bar{S}^{\circ\ddagger}_i$ and $\Delta\bar{H}^{\circ\ddagger}_i$ contribution of CH_2 and NH_3^+,COO^- groups can only be considered as a composite of the solute–solvent–solvent bond-breaking/making effects around these groups. A larger $T\Delta\bar{S}^{\circ\ddagger}_3(CH_2)$ than $T\Delta\bar{S}^{\circ\ddagger}_2(CH_2)$ shows that even the ground state is less structured in aqueous salt solutions and the transition state is attained by considerable solvent–solvent bond breaking. For polar NH_3^+,COO^- groups, $T\Delta\bar{S}^{\circ\ddagger}_i$ values are negative and do not differ much in water and aqueous potassium thiocyanate. This shows that the flow process is accompanied by zwitterion–solvent and zwitterion–ion (KSCN) bond breaking in addition to ion–solvent and solvent–solvent bond making.

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Registry No. H_2O, 7732-18-5; KSCN, 333-20-0; glycine, 56-40-6; DL-alanine, 302-72-7; L-proline, 147-85-3; L-threonine, 72-19-5; β-alanine, 107-95-9; γ-aminobutyric acid, 56-12-2; ε-aminocaproic acid, 60-32-2.