

Volumetric Properties of Amino Acids in Aqueous *N*-Methylformamide Solutions at $T = 298.15\text{ K}^\dagger$

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Densities of glycine, L-alanine, and L-serine in aqueous solutions of *N*-methylformamide (NMF) were measured at 298.15 K. The standard partial molar volumes (V_ϕ°), standard partial molar volumes of transfer ($\Delta_{\text{tr}}V_\phi^\circ$) and hydration numbers for the amino acids were also determined. It is shown that hydrophilic–hydrophilic interactions between charged groups of amino acids and the –CONH– group of NMF are predominant in the case of glycine and L-serine. For L-alanine, however, in NMF solutions with $m < 1.5\text{ mol}\cdot\text{kg}^{-1}$, the interaction between the alanine –CH₃ group and NMF weakens the interaction between its charged group and the hydrophilic group of NMF, while for NMF solutions with $m > 1.5\text{ mol}\cdot\text{kg}^{-1}$, the hydrophilic–hydrophilic interactions increase with the increasing concentration of NMF. The results are interpreted in terms of a cosphere overlap model.

Introduction

Amino acids incorporate some of the structural features present in globular proteins. The thermodynamic properties of amino acids in mixed aqueous solutions have been extensively investigated.^{1–6} Volumetric studies on molecules of interest can provide unique insights into the molecular origins of the intramolecular and intermolecular recognition events that modulate biomolecular processes.⁷ Volumetric methods have also been widely used to study the interaction between solute and solvent.^{8–10}

Aliphatic amides have the –OCN– structure of peptide bonds and are model compounds for proteins. In order to better understand the important role that nonbonding interactions play in biological systems, we have studied the enthalpy properties of amino acids in a series of aqueous amides solutions^{11,12} and the volumetric properties of amino acids in aqueous *N,N*-dimethylacetamide (DMA) solutions.¹³ As a continuation of our thermodynamic investigations of biological-molecule model systems in our laboratory, the interactions between amino acids and *N*-methylformamide (NMF) were studied in this work.

Experimental Section

Glycine, L-alanine, and L-serine (biological reagent, purity > 99 %, Shanghai Chemical Co.) were recrystallized twice from aqueous ethanol solutions and dried under vacuum at 348 K for 6 h. NMF (GR, Japan) was stored over 4 Å molecular sieves for at least 48 h and used without further purification. All of the solutions were freshly prepared by mass on a Mettler AE200 balance. The uncertainty in the molality (m) was less than $2.0\cdot 10^{-4}\text{ mol}\cdot\text{kg}^{-1}$.

The densities of the solutions were measured with a DMA 55 digital densimeter (Anton Paar, Austria). The sensitivity of the densimeter was $\pm 1\cdot 10^{-5}\text{ g}\cdot\text{cm}^{-3}$. The overall uncertainty in the density depends on the temperature control of the water bath, the concentration, and the digital densimeter and was estimated to

be $1\cdot 10^{-4}\text{ g}\cdot\text{cm}^{-3}$. The densimeter was calibrated with twice-distilled water and dried air;¹⁴ the density of water was $0.99705\text{ g}\cdot\text{cm}^{-3}$. The temperature was kept constant using a thermostat bath (Haake, Germany) with an uncertainty of 0.02 K.

Results and Discussion

Standard Partial Molar Volume and Transfer Partial Volume. The experimentally measured densities of glycine, L-alanine, and L-serine in aqueous NMF solutions at 298.15 K are given in Tables 1 to 3. Apparent molar volumes (V_ϕ , $\text{cm}^3\cdot\text{mol}^{-1}$) of the amino acids were calculated from the solution densities (ρ , $\text{g}\cdot\text{cm}^{-3}$) using the equation

$$V_\phi = \frac{M}{\rho} - \frac{1000\cdot(\rho - \rho_0)}{m\rho\rho_0} \quad (1)$$

where M is the molar mass ($\text{g}\cdot\text{mol}^{-1}$) of amino acid, ρ_0 is the density of the aqueous NMF solution, and m is the molality ($\text{mol}\cdot\text{kg}^{-1}$) of the amino acid in the aqueous NMF solution. The calculated apparent molar volumes for the amino acids are also listed in Tables 1 to 3. The results can be linearly fitted by the equation

$$V_\phi = V_\phi^\circ + B_v m \quad (2)$$

where V_ϕ° is the infinite-dilution apparent molar volume of the amino acid in water or in NMF/water and B_v is the experimental slope indicating solute–solute interactions.¹⁵ The standard partial molar volumes for the amino acids in aqueous solutions of NMF are given in Table 4.

The partial molar volumes of transfer ($\Delta_{\text{tr}}V_\phi^\circ$) from water to aqueous NMF solutions, which were calculated using eq 3, are listed in Table 4 and illustrated in Figure 1.

$$\Delta_{\text{tr}}V_\phi^\circ = V_\phi^\circ(\text{in aqueous NMF solution}) - V_\phi^\circ(\text{in water}) \quad (3)$$

V_ϕ° for an amino acid can be viewed as¹⁶

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$$V_{\phi}^{\circ} = V_{\text{VW}} + V_{\text{void}} - V_{\text{shrinkage}} \quad (4)$$

where V_{VW} is the van der Waals volume, V_{void} is the contribution associated with the voids and empty volume, and $V_{\text{shrinkage}}$ is the shrinkage in volume due to solute–solvent interactions. It is generally assumed that V_{VW} and V_{void} remain approximately the same in water and aqueous solutions, so the values of $\Delta_{\text{tr}}V_{\phi}^{\circ}$ reflect solely the interactions between the amino acid and NMF.

There are three types of interactions between amino acids and NMF: (a) hydrophilic–hydrophilic interactions between the

head groups ($-\text{NH}_3^+$ and $-\text{COO}^-$) or hydrophilic group ($-\text{CH}_2\text{OH}$) of the amino acid and the $-\text{CONH}-$ group of NMF, which would lead to a positive $\Delta_{\text{tr}}V_{\phi}^{\circ}$ since there is a reduction in the electrostriction effect and the overall water structure is enhanced;¹⁷ (b) hydrophilic–hydrophobic interactions between the head groups of the amino acid and the methyl groups of NMF or between the $-\text{CONH}-$ group of NMF and the hydrophobic group of the amino acid; and (c) hydrophobic–hydrophobic interactions between the hydrophobic group of the amino acid and the methyl groups of NMF. Interactions of types

Table 1. Densities (ρ) and Apparent Molar Volumes (V_{ϕ}) of Glycine in Aqueous NMF Solutions Having Various Molalities (m) at 298.15 K

m_{Gly} mol·kg ⁻¹	ρ g·cm ⁻³	V_{ϕ} cm ³ ·mol ⁻¹	m_{gly} mol·kg ⁻¹	ρ g·cm ⁻³	V_{ϕ} cm ³ ·mol ⁻¹	m_{gly} mol·kg ⁻¹	ρ g·cm ⁻³	V_{ϕ} cm ³ ·mol ⁻¹
$m = 0.1996 \text{ mol}\cdot\text{kg}^{-1}$			$m = 0.5044 \text{ mol}\cdot\text{kg}^{-1}$			$m = 0.9919 \text{ mol}\cdot\text{kg}^{-1}$		
0	0.99754	—	0	0.99828	—	0	0.99946	—
0.1243	1.00148	43.22	0.1088	1.00172	43.31	0.1081	1.00286	43.45
0.2170	1.00437	43.30	0.1637	1.00344	43.35	0.1530	1.00426	43.46
0.2795	1.00629	43.42	0.2003	1.00458	43.38	0.2465	1.00713	43.59
0.3804	1.00936	43.52	0.3138	1.00806	43.51	0.3069	1.00898	43.64
0.4827	1.01241	43.64	0.4214	1.01129	43.64	0.4053	1.01192	43.77
0.5621	1.01476	43.71	0.5115	1.01397	43.73	0.5127	1.01512	43.84
$m = 1.5053 \text{ mol}\cdot\text{kg}^{-1}$			$m = 2.0112 \text{ mol}\cdot\text{kg}^{-1}$			$m = 2.5131 \text{ mol}\cdot\text{kg}^{-1}$		
0	1.00065	—	0	1.00179	—	0	1.00286	—
0.1136	1.00421	43.53	0.1036	1.00503	43.69	0.1127	1.00636	43.81
0.1571	1.00556	43.58	0.1611	1.00680	43.73	0.1625	1.00789	43.82
0.2197	1.00748	43.66	0.2282	1.00885	43.80	0.2094	1.00932	43.88
0.3270	1.01074	43.77	0.3082	1.01128	43.86	0.3184	1.01262	43.94
0.3963	1.01281	43.83	0.4082	1.01425	43.98	0.3998	1.01504	44.03
0.5016	1.01593	43.93	0.5038	1.01706	44.07	0.5017	1.01801	44.15
$m = 3.0496 \text{ mol}\cdot\text{kg}^{-1}$			$m = 3.4987 \text{ mol}\cdot\text{kg}^{-1}$			$m = 3.9924 \text{ mol}\cdot\text{kg}^{-1}$		
0	1.00395	—	0	1.00481	—	0	1.00574	—
0.1023	1.00712	43.88	0.1057	1.00807	44.01	0.1125	1.00918	44.23
0.1516	1.00863	43.93	0.1695	1.01002	44.05	0.1485	1.01027	44.26
0.2278	1.01095	43.98	0.2226	1.01163	44.09	0.2126	1.01220	44.29
0.3112	1.01345	44.05	0.3090	1.01422	44.13	0.3030	1.01490	44.35
0.4034	1.01618	44.16	0.4049	1.01706	44.21	0.4052	1.01791	44.41
0.5285	1.01983	44.26	0.5008	1.01987	44.27	0.5064	1.02084	44.49

Table 2. Densities (ρ) and Apparent Molar Volumes (V_{ϕ}) of L-Alanine in Aqueous NMF Solutions Having Various Molalities (m) at 298.15 K

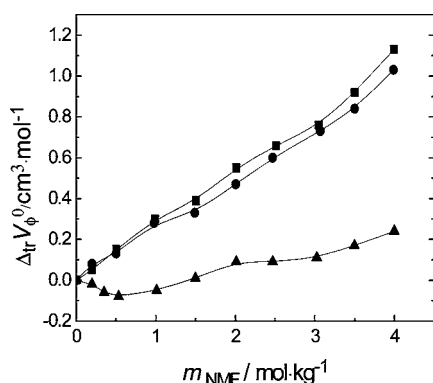
m_{Ala} mol·kg ⁻¹	ρ g·cm ⁻³	V_{ϕ} cm ³ ·mol ⁻¹	m_{Ala} mol·kg ⁻¹	ρ g·cm ⁻³	V_{ϕ} cm ³ ·mol ⁻¹	m_{Ala} mol·kg ⁻¹	ρ g·cm ⁻³	V_{ϕ} cm ³ ·mol ⁻¹
$m = 0.2000 \text{ mol}\cdot\text{kg}^{-1}$			$m = 0.3493 \text{ mol}\cdot\text{kg}^{-1}$			$m = 0.5343 \text{ mol}\cdot\text{kg}^{-1}$		
0	0.99753	—	0	0.99791	—	0	0.99834	—
0.1074	1.00060	60.44	0.1143	1.00117	60.40	0.1011	1.00123	60.39
0.1651	1.00222	60.50	0.1742	1.00285	60.47	0.1646	1.00302	60.43
0.2866	1.00558	60.62	0.2310	1.00443	60.53	0.2180	1.00451	60.48
0.354	1.00742	60.65	0.3126	1.00667	60.61	0.3123	1.00709	60.59
0.4001	1.00865	60.72	0.3884	1.00873	60.65	0.4020	1.00952	60.67
0.4833	1.01087	60.76	0.4721	1.01095	60.73	0.5034	1.01222	60.73
$m = 1.0109 \text{ mol}\cdot\text{kg}^{-1}$			$m = 1.4994 \text{ mol}\cdot\text{kg}^{-1}$			$m = 2.0118 \text{ mol}\cdot\text{kg}^{-1}$		
0	0.99949	—	0	1.00063	—	0	1.00179	—
0.1228	1.00299	60.40	0.1047	1.00361	60.47	0.1094	1.00489	60.53
0.1528	1.00383	60.46	0.1587	1.00513	60.49	0.1645	1.00643	60.55
0.2062	1.00532	60.48	0.2203	1.00684	60.54	0.2066	1.00759	60.60
0.3053	1.00804	60.58	0.3272	1.00976	60.62	0.3043	1.01027	60.67
0.4073	1.01080	60.64	0.4137	1.01209	60.69	0.4061	1.01302	60.71
0.5119	1.01358	60.72	0.5269	1.01508	60.78	0.5015	1.01554	60.79
$m = 2.4699 \text{ mol}\cdot\text{kg}^{-1}$			$m = 3.0225 \text{ mol}\cdot\text{kg}^{-1}$			$m = 3.4960 \text{ mol}\cdot\text{kg}^{-1}$		
0	1.00277	—	0	1.00390	—	0	1.00481	—
0.1059	1.00576	60.56	0.1067	1.00691	60.57	0.1004	1.00764	60.62
0.1494	1.00698	60.55	0.1621	1.00845	60.60	0.1540	1.00913	60.63
0.2047	1.00851	60.62	0.2017	1.00954	60.65	0.2028	1.01047	60.68
0.3082	1.01133	60.71	0.2979	1.01216	60.72	0.3027	1.01319	60.75
0.4054	1.01394	60.77	0.4097	1.01515	60.82	0.4137	1.01615	60.84
0.4977	1.01637	60.84	0.5038	1.01762	60.89	0.5015	1.01846	60.88
$m = 3.9967 \text{ mol}\cdot\text{kg}^{-1}$								
0	1.00573	—						
0.1096	1.00881	60.69						
0.1549	1.01006	60.72						
0.2022	1.01135	60.76						
0.3145	1.01439	60.86						
0.4019	1.01671	60.92						
0.5160	1.01969	61.00						

Table 3. Densities (ρ) and Apparent Molar Volumes (V_ϕ) of L-Serine in Aqueous NMF Solutions Having Various Molalities (m) at 298.15 K

m_{Ser} mol·kg ⁻¹	ρ g·cm ⁻³	V_ϕ cm ³ ·mol ⁻¹	m_{Ser} mol·kg ⁻¹	ρ g·cm ⁻³	V_ϕ cm ³ ·mol ⁻¹	m_{Ser} mol·kg ⁻¹	ρ g·cm ⁻³	V_ϕ cm ³ ·mol ⁻¹
$m = 0.2000 \text{ mol}\cdot\text{kg}^{-1}$			$m = 0.5018 \text{ mol}\cdot\text{kg}^{-1}$			$m = 0.9779 \text{ mol}\cdot\text{kg}^{-1}$		
0	0.99755	—	0	0.99828	—	0	0.99942	—
0.1020	1.00205	60.69	0.1222	1.00366	60.79	0.1142	1.00443	60.88
0.1475	1.00404	60.74	0.1590	1.00525	60.83	0.1602	1.00642	60.97
0.2070	1.00661	60.80	0.2140	1.00761	60.95	0.2172	1.00886	61.03
0.2986	1.01050	60.95	0.3329	1.01265	61.07	0.3085	1.01272	61.17
0.4170	1.01546	61.09	0.3893	1.01498	61.20	0.4067	1.01682	61.25
0.5283	1.02005	61.17	0.4992	1.01950	61.30	0.5086	1.02099	61.37
$m = 1.4995 \text{ mol}\cdot\text{kg}^{-1}$			$m = 2.0063 \text{ mol}\cdot\text{kg}^{-1}$			$m = 2.4969 \text{ mol}\cdot\text{kg}^{-1}$		
0	1.00062	—	0	1.00179	—	0	1.00277	—
0.1146	1.00567	60.99	0.1069	1.00646	61.08	0.1014	1.00719	61.20
0.1564	1.00822	61.06	0.1590	1.00870	61.19	0.1587	1.00965	61.26
0.2640	1.00945	61.08	0.2024	1.01055	61.25	0.2135	1.01198	61.35
0.3706	1.01411	61.22	0.3010	1.01470	61.39	0.3112	1.01607	61.48
0.4357	1.01839	61.37	0.3957	1.01861	61.51	0.4219	1.02062	61.63
0.5199	1.02211	61.50	0.4745	1.02183	61.60	0.4984	1.02371	61.74
$m = 3.0684 \text{ mol}\cdot\text{kg}^{-1}$			$m = 3.4995 \text{ mol}\cdot\text{kg}^{-1}$			$m = 3.9886 \text{ mol}\cdot\text{kg}^{-1}$		
0	1.00400	—	0	1.00482	—	0	1.00573	—
0.1014	1.00840	61.37	0.1047	1.00935	61.47	0.1063	1.01030	61.71
0.1556	1.01072	61.44	0.1547	1.01148	61.53	0.1579	1.01249	61.75
0.2046	1.01280	61.50	0.2156	1.01405	61.61	0.2040	1.01443	61.79
0.3091	1.01716	61.63	0.3030	1.01770	61.69	0.3119	1.01891	61.89
0.4060	1.02113	61.77	0.4195	1.02246	61.85	0.4208	1.02336	61.99
0.4995	1.02492	61.85	0.4988	1.02564	61.95	0.5005	1.02654	62.09

Table 4. Standard Partial Molar Volume, Transfer Partial Molar Volume and Hydration Number of Glycine, L-Alanine and L-Serine in Aqueous Solutions of NMF at 298.15 K

glycine				L-alanine				L-serine			
m mol·kg ⁻¹	V_ϕ° cm ³ ·mol ⁻¹	$\Delta_{\text{tr}}V_\phi^\circ$ cm ³ ·mol ⁻¹	N_{h}	m mol·kg ⁻¹	V_ϕ° cm ³ ·mol ⁻¹	$\Delta_{\text{tr}}V_\phi^\circ$ cm ³ ·mol ⁻¹	N_{h}	m mol·kg ⁻¹	V_ϕ° cm ³ ·mol ⁻¹	$\Delta_{\text{tr}}V_\phi^\circ$ cm ³ ·mol ⁻¹	N_{h}
0	43.03 ^a	0	2.68	0	60.37 ^a	0	3.45	0	60.49 ^a	0	3.90
0.1996	43.08	0.05 ± 0.04	2.66	0.2000	60.35	-0.02 ± 0.05	3.46	0.2000	60.57	0.04 ± 0.05	3.89
0.5044	43.18	0.15 ± 0.04	2.63	0.3493	60.31	-0.06 ± 0.04	3.47	0.5018	60.62	0.05 ± 0.04	3.88
0.9919	43.33	0.30 ± 0.06	2.58	0.5343	60.29	-0.08 ± 0.04	3.48	0.9779	60.77	0.16 ± 0.06	3.85
1.5053	43.42	0.39 ± 0.09	2.55	1.0109	60.32	-0.05 ± 0.06	3.47	1.4995	60.82	0.27 ± 0.06	3.81
2.0112	43.58	0.55 ± 0.08	2.50	1.4994	60.38	0.01 ± 0.05	3.45	2.0063	60.96	0.40 ± 0.04	3.77
2.5131	43.69	0.66 ± 0.05	2.46	2.0118	60.46	0.09 ± 0.04	3.43	2.4969	61.09	0.49 ± 0.06	3.74
3.0496	43.79	0.76 ± 0.07	2.43	2.4699	60.46	0.09 ± 0.06	3.42	3.0684	61.22	0.70 ± 0.05	3.67
3.4987	43.95	0.92 ± 0.05	2.37	3.0225	60.48	0.11 ± 0.07	3.41	3.4995	61.33	0.81 ± 0.07	3.63
3.9924	44.16	1.13 ± 0.07	2.30	3.4960	60.54	0.17 ± 0.05	3.39	3.9886	61.52	1.00 ± 0.06	3.57
				3.9967	60.61	0.24 ± 0.06	3.37				

^a Data from ref 13.**Figure 1.** Transfer volumes as functions of the molality of aqueous NMF solutions at 298.15 K: ■, glycine; ▲, L-alanine; ●, L-serine.

(b) and (c) would lead to a negative value of $\Delta_{\text{tr}}V_\phi^\circ$ because the methyl groups provide an additional tendency for hydrophobic–hydrophilic and hydrophobic–hydrophobic interactions, resulting in a reduction in the structure of water.¹⁷

The observed positive $\Delta_{\text{tr}}V_\phi^\circ$ values for glycine and L-serine suggest that the interactions of type (a) predominate over the interactions of type (b); the increase in transfer volume with increasing NMF concentration further strengthens this view. The

$\Delta_{\text{tr}}V_\phi^\circ$ value for glycine is a little larger than that for L-serine, reflecting the fact that the interactions between the $-\text{CH}_2\text{OH}$ group of L-serine and the methyl groups of NMF make a much larger contribution to $\Delta_{\text{tr}}V_\phi^\circ$ than the interactions between the $-\text{CH}_2\text{OH}$ group of L-serine and the $-\text{CONH}-$ group of NMF. On the whole, however, the contribution of $-\text{CH}_2\text{OH}$ to $\Delta_{\text{tr}}V_\phi^\circ$ is small. This further implies that the interactions between the charged end groups of L-serine and NMF are much stronger than those between the $-\text{CH}_2\text{OH}$ group and NMF.

In the case of L-alanine, the $\Delta_{\text{tr}}V_\phi^\circ$ values are negative at lower concentrations of NMF (m less than about $1.5 \text{ mol}\cdot\text{kg}^{-1}$), suggesting that the association of the $-\text{CH}_3$ group of L-alanine and NMF reduces the hydrophilic–hydrophilic interactions between the amino acid and NMF. In NMF solutions with m greater than about $1.5 \text{ mol}\cdot\text{kg}^{-1}$, the $\Delta_{\text{tr}}V_\phi^\circ$ values of L-alanine are positive, and a slight increase in $\Delta_{\text{tr}}V_\phi^\circ$ was observed. NMF is liable to form chainwise associations through intermolecular hydrogen bonds,¹⁸ and with an increase in the concentration of NMF, the association tendency is strengthened and the dipole moment of NMF increased,¹⁹ enhancing the hydrophilic–hydrophilic interactions between L-alanine and NMF.

Hydration Number. The hydration number (N_{h}) reflects the electrostriction effect of the charge center of the amino acid on the nearby water molecules. The hydration numbers of the amino

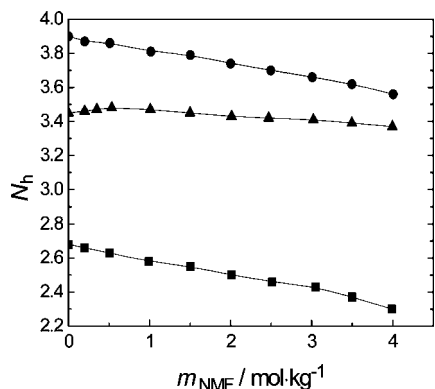


Figure 2. Hydration numbers as functions of molality of aqueous NMF solutions at 298.15 K: ■, glycine; ▲, L-alanine; ●, L-serine.

acids in aqueous NMF solutions were estimated using the method reported by Shahidi et al.²⁰

$$\Delta_{\text{tr}}V_{\phi}^{\circ} = [N_{\text{h}}(\text{in water}) - N_{\text{h}}(\text{in NMF solution})] \times 3.0 \quad (5)$$

According to Millero et al.,²¹ the hydration number of an amino acid in water can be evaluated by the following equation:

$$N_{\text{h}}(\text{in water}) = \frac{V_{\text{elect}}}{V_{\text{e}}^{\circ} - V_{\text{b}}^{\circ}} \quad (6)$$

where V_{e}° is the molar volume of electrostricted water and V_{b}° is the molar volume of bulk water. The value of $V_{\text{e}}^{\circ} - V_{\text{b}}^{\circ}$ is approximately $-3.3 \text{ cm}^3 \cdot \text{mol}^{-1}$ at 298.15 K.²¹ The electrostriction partial molar volume (V_{elect}) can be estimated from the measured V_{ϕ}° value of the amino acid using the following equation:²¹

$$V_{\text{elect}} = V_{\phi}^{\circ} - V_{\text{int}}^{\circ} \quad (7)$$

The intrinsic molar volume V_{int}° of the amino acid can be estimated from the crystal volume (V_{cryst}°) according to²¹

$$V_{\text{int}}^{\circ} = \frac{0.7}{0.634} V_{\text{cryst}}^{\circ} \quad (8)$$

and the crystal volume can be calculated from the density of the dry-state amino acid.²² The hydration numbers of the amino acids in water and in aqueous NMF solutions are given in Table 4 and illustrated in Figure 2.

The hydration numbers of glycine and L-serine in NMF solutions are less than those in water and decrease with increasing NMF concentration, which again indicates that the increase in solute–cosolute interactions reduces the electrostriction effect of the amino acids. It also suggests that NMF has a dehydration effect on the two amino acids. On the basis of a comparison with the N_{h} values for the amino acids in DMA solutions,¹³ it can be concluded that DMA has a little larger dehydration effect on glycine and L-serine than NMF. In NMF solutions with $m < 1.5 \text{ mol}\cdot\text{kg}^{-1}$, the hydration number of L-alanine is almost unaffected by the concentration of NMF, which further indicates that the CH_3 group in L-alanine reduces the hydrophilic–hydrophilic interactions

between L-alanine and NMF, and on the whole, the interaction between L-alanine and NMF has little influence on the hydration number of L-alanine. In NMF solutions with $m > 1.5 \text{ mol}\cdot\text{kg}^{-1}$, the dehydration effect of NMF on L-alanine increases as a result of the association between NMF molecules.

Conclusion

The interactions between amino acids and NMF have been reported on the basis of volumetric properties. The positive $\Delta_{\text{tr}}V_{\phi}^{\circ}$ of glycine and L-serine suggests that hydrophilic–hydrophilic interactions are predominant and that NMF has a dehydration effect on the two amino acids. The negative $\Delta_{\text{tr}}V_{\phi}^{\circ}$ of L-alanine in NMF solutions with $m < 1.5 \text{ mol}\cdot\text{kg}^{-1}$ shows that the $-\text{CH}_3$ group of L-alanine weakens the interaction between its charged group and the hydrophilic group of NMF, thereby enhancing the hydrophobic–hydrophobic and hydrophobic–hydrophilic interactions; this was confirmed by the changes in hydration number. In NMF solutions with $m > 1.5 \text{ mol}\cdot\text{kg}^{-1}$, the $\Delta_{\text{tr}}V_{\phi}^{\circ}$ value for L-alanine is positive, and the dehydration effect of NMF increases as a result of association between NMF molecules.

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