

# Dielectric Constants for Binary Amino Acid–Water Solutions from (278.15 to 313.15) K

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Dielectric constants for aqueous solutions of L-proline, glycine, L-alanine, and L-serine were measured from (278.15 to 313.15) K in different molalities up to  $0.35 \text{ mol}\cdot\text{kg}^{-1}$ . Results indicated that the logarithmic values of the dielectric constants for these amino acid–water solutions increase with increasing molalities of amino acids and conversely decrease as the temperature rises. At given molalities, the relationship of the dielectric constant to the temperature can be expressed by a linear equation for L-proline–water and L-alanine–water solutions and by a quadratic equation for glycine–water and L-serine–water solutions. At given temperatures, dependence of the dielectric constant on the mole fraction can be described by a linear equation for L-proline–water, L-alanine–water, and L-serine–water solutions and by a quadratic equation for glycine–water solutions. An empirical equation is proposed and used to relate  $\log \epsilon$  for the amino acid–water solutions to the temperature and compositions of the solutions.

## Introduction

Amino acids are of importance in industrial processes and can be utilized as food additives and constituents of pharmaceutical products. The thermodynamic study of aqueous systems containing amino acids is of much importance. Densities, viscosities, and dielectric constants have a special interest because they are critical for solution chemistry.<sup>1</sup> Those properties can be very useful as a support for the efficient design and simulation of separation processes.<sup>2,3</sup> Additionally, density and dielectric constants can be used to calculate the activity coefficients.<sup>1</sup>

In our previous work,<sup>4</sup> volumetric and viscosity properties of aqueous amino acid solutions at 298.15 K were studied. A perusal of the literature on the amino acid–water mixtures revealed that the dielectric constant measurements for amino acid–water systems are scarce. With an aim to carry out a systematic investigation involving the thermodynamics of amino acid–water mixtures through measurements of scarcely reported physical properties, this paper reports the dielectric constants for aqueous solutions of L-proline, glycine, L-alanine, and L-serine at different molalities and temperatures, and some empirical formulas are proposed to express the relationships of dielectric constants to the temperatures or/and the compositions of amino acids in solutions.

## Experimental Section

**Chemicals.** L-Proline, glycine, L-alanine, and L-serine were obtained from Sigma Chemical Company (USA). They were dried under vacuum to constant weight and then stored over  $\text{P}_2\text{O}_5$  in desiccators. The deionized water was doubly distilled over  $\text{KMnO}_4$ . The water sample with a conductivity of  $0.8 \cdot 10^{-4} \text{ S}\cdot\text{cm}^{-1}$  to  $1.0 \cdot 10^{-4} \text{ S}\cdot\text{cm}^{-1}$  was used throughout the experiments.

**Measurement of Dielectric Constants.** Solution dielectric constants were measured using a dielectric constant meter (model BI-870, Brookhaven Instrument Co., USA), which was

**Table 1. Values of Dielectric Constants  $\epsilon$  and Their Logarithmic Values  $\log \epsilon$  for L-Proline + Water Mixtures at Different Molalities and Temperatures**

T/K	$\epsilon$	$\log \epsilon$	T/K	$\epsilon$	$\log \epsilon$	T/K	$\epsilon$	$\log \epsilon$
$m_A = 0.1000 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.1500 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.2000 \text{ mol}\cdot\text{kg}^{-1}$		
278.15	88.1	1.9450	278.15	89.1	1.9499	278.15	90.1	1.9547
283.15	86.2	1.9355	283.15	87.3	1.9410	283.15	88.2	1.9455
288.15	84.3	1.9258	288.15	85.3	1.9310	288.15	86.3	1.9360
293.15	82.4	1.9159	293.15	83.4	1.9212	293.15	84.4	1.9263
298.15	80.6	1.9063	298.15	81.5	1.9112	298.15	82.4	1.9159
303.15	78.7	1.8960	303.15	79.7	1.9015	303.15	80.6	1.9063
308.15	76.9	1.8860	308.15	77.9	1.8915	308.15	78.8	1.8965
313.15	75.1	1.8756	313.15	76.1	1.8814	313.15	77.0	1.8865
$m_A = 0.2500 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.3000 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.3500 \text{ mol}\cdot\text{kg}^{-1}$		
278.15	91.2	1.9600	278.15	92.3	1.9652	278.15	93.2	1.9694
283.15	89.3	1.9509	283.15	90.3	1.9557	283.15	91.2	1.9600
288.15	87.4	1.9415	288.15	88.3	1.9460	288.15	89.2	1.9504
293.15	85.4	1.9315	293.15	86.4	1.9365	293.15	87.2	1.9405
298.15	83.5	1.9217	298.15	84.5	1.9269	298.15	85.3	1.9310
303.15	81.6	1.9117	303.15	82.6	1.9170	303.15	83.4	1.9212
308.15	79.8	1.9020	308.15	80.7	1.9069	308.15	81.5	1.9112
313.15	77.9	1.8915	313.15	78.9	1.8971	313.15	79.7	1.9015

described elsewhere.<sup>5</sup> The accuracy of temperature was controlled within  $\pm 0.02 \text{ K}$  by using a low-temperature thermostat (model DC-2006, Shanghai Hengping Instrument Factory). The dielectric constant meter was calibrated with pure water (the dielectric constant of water was taken to be 78.54 at 298.15 K<sup>6</sup>). The uncertainty of molalities of amino acids is evaluated to be about  $\pm 0.2 \text{ wt } \%$ . The uncertainty in dielectric constant was estimated to be  $\pm 0.1$ .

## Results and Discussion

**Relationship between Dielectric Constant and Temperature.** The experimentally measured dielectric constants and their logarithms for amino acid–water solutions at different molalities and temperatures are shown in Tables 1 to 4 indicating that the

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**Table 2. Values of  $\epsilon$  and  $\log \epsilon$  for Glycine + Water Mixtures at Different Molalities and Temperatures**

$T/K$	$\epsilon$	$\log \epsilon$	$T/K$	$\epsilon$	$\log \epsilon$	$T/K$	$\epsilon$	$\log \epsilon$
$m_A = 0.1000 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.1500 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.2000 \text{ mol}\cdot\text{kg}^{-1}$		
278.15	88.2	1.9455	278.15	89.4	1.9513	278.15	90.7	1.9576
283.15	86.3	1.9360	283.15	87.5	1.9420	283.15	88.7	1.9479
288.15	84.4	1.9263	288.15	85.5	1.9320	288.15	86.7	1.9380
293.15	82.5	1.9165	293.15	83.6	1.9222	293.15	84.6	1.9274
298.15	80.6	1.9063	298.15	81.7	1.9122	298.15	82.7	1.9175
303.15	78.7	1.8960	303.15	79.7	1.9015	303.15	80.6	1.9063
308.15	76.9	1.8859	308.15	77.8	1.8910	308.15	78.6	1.8954
313.15	75.1	1.8756	313.15	75.8	1.8797	313.15	76.4	1.8831
$m_A = 0.2500 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.3000 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.3500 \text{ mol}\cdot\text{kg}^{-1}$		
278.15	91.6	1.9619	278.15	92.9	1.9680	278.15	93.7	1.9717
283.15	89.6	1.9523	283.15	90.8	1.9581	283.15	91.6	1.9619
288.15	87.6	1.9425	288.15	88.7	1.9479	288.15	89.4	1.9513
293.15	85.4	1.9315	293.15	86.5	1.9370	293.15	87.2	1.9405
298.15	83.4	1.9212	298.15	84.3	1.9258	298.15	84.9	1.9289
303.15	81.2	1.9096	303.15	82.0	1.9138	303.15	82.4	1.9159
308.15	79.0	1.8976	308.15	79.7	1.9015	308.15	79.9	1.9026
313.15	76.8	1.8854	313.15	77.1	1.8871	313.15	77.2	1.8871

**Table 3. Values of  $\epsilon$  and  $\log \epsilon$  for L-Alanine + Water Mixtures at Different Molalities and Temperatures**

$T/K$	$\epsilon$	$\log \epsilon$	$T/K$	$\epsilon$	$\log \epsilon$	$T/K$	$\epsilon$	$\log \epsilon$
$m_A = 0.1000 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.1500 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.2000 \text{ mol}\cdot\text{kg}^{-1}$		
278.15	88.2	1.9455	278.15	89.4	1.9513	278.15	90.7	1.9576
283.15	86.3	1.9360	283.15	87.5	1.9420	283.15	88.7	1.9479
288.15	84.4	1.9263	288.15	85.6	1.9325	288.15	86.8	1.9385
293.15	82.5	1.9165	293.15	83.7	1.9227	293.15	84.9	1.9289
298.15	80.8	1.9074	298.15	81.9	1.9133	298.15	83.1	1.9196
303.15	78.9	1.8971	303.15	80.0	1.9031	303.15	81.2	1.9096
308.15	77.1	1.8871	308.15	78.2	1.8932	308.15	79.3	1.8993
313.15	75.4	1.8774	313.15	76.3	1.8825	313.15	77.4	1.8887
$m_A = 0.2500 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.3000 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.3500 \text{ mol}\cdot\text{kg}^{-1}$		
278.15	91.8	1.9628	278.15	93.0	1.9685	278.15	94.2	1.9741
283.15	89.8	1.9533	283.15	91.0	1.9590	283.15	92.2	1.9647
288.15	87.9	1.9440	288.15	89.0	1.9494	288.15	90.2	1.9552
293.15	85.9	1.9340	293.15	87.1	1.9400	293.15	88.3	1.9460
298.15	84.1	1.9248	298.15	85.3	1.9310	298.15	86.3	1.9360
303.15	82.2	1.9149	303.15	83.3	1.9207	303.15	84.3	1.9258
308.15	80.3	1.9047	308.15	81.4	1.9106	308.15	82.4	1.9159
313.15	78.4	1.8943	313.15	79.5	1.9004	313.15	80.4	1.9053

**Table 4. Values of  $\epsilon$  and  $\log \epsilon$  for L-Serine + Water Mixtures at Different Molalities and Temperatures**

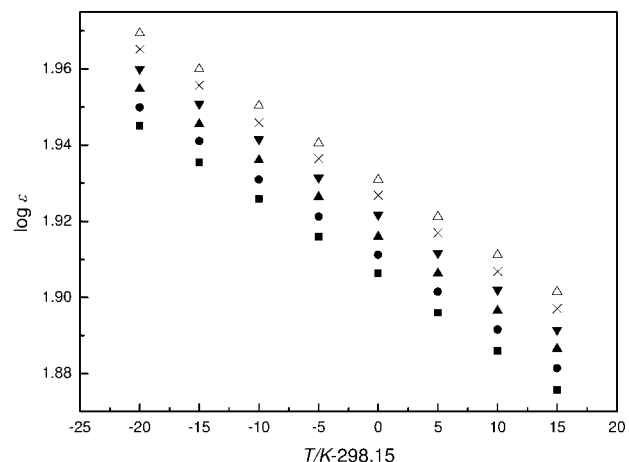
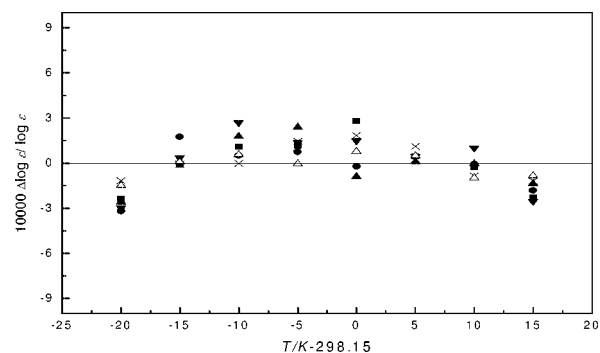
$T/K$	$\epsilon$	$\log \epsilon$	$T/K$	$\epsilon$	$\log \epsilon$	$T/K$	$\epsilon$	$\log \epsilon$
$m_A = 0.1000 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.1500 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.2000 \text{ mol}\cdot\text{kg}^{-1}$		
278.15	88.2	1.9455	278.15	89.3	1.9509	278.15	90.6	1.9571
283.15	86.3	1.9360	283.15	87.4	1.9415	283.15	88.6	1.9474
288.15	84.5	1.9269	288.15	85.5	1.9320	288.15	86.6	1.9375
293.15	82.6	1.9170	293.15	83.6	1.9222	293.15	84.7	1.9279
298.15	80.7	1.9069	298.15	81.7	1.9122	298.15	82.8	1.9180
303.15	78.8	1.8965	303.15	79.8	1.9020	303.15	80.7	1.9069
308.15	76.9	1.8859	308.15	77.9	1.8915	308.15	78.7	1.8960
313.15	75.0	1.8751	313.15	75.8	1.8797	313.15	76.5	1.8837
$m_A = 0.2500 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.3000 \text{ mol}\cdot\text{kg}^{-1}$			$m_A = 0.3500 \text{ mol}\cdot\text{kg}^{-1}$		
278.15	91.6	1.9619	278.15	92.8	1.9676	278.15	93.9	1.9727
283.15	89.6	1.9523	283.15	90.8	1.9581	283.15	91.9	1.9633
288.15	87.7	1.9430	288.15	88.8	1.9484	288.15	89.9	1.9538
293.15	85.7	1.9330	293.15	86.8	1.9385	293.15	87.7	1.9430
298.15	83.7	1.9227	298.15	84.7	1.9279	298.15	85.6	1.9325
303.15	81.4	1.9106	303.15	82.5	1.9165	303.15	83.3	1.9207
308.15	79.1	1.8982	308.15	80.2	1.9042	308.15	81.0	1.9085
313.15	76.6	1.8842	313.15	77.6	1.8899	313.15	77.8	1.8910

logarithmic values of dielectric constants increase with increasing molalities of amino acids and decrease with the rising of the temperature. As far as know, the dielectric constants for amino acid–water systems have not been reported in literature.

The dielectric constant of water was related to the temperature by<sup>6</sup>

$$\epsilon = 78.54[1 - 4.579 \cdot 10^{-3}(t - 25) + 11.9 \cdot 10^{-6}(t - 25)^2 + 28 \cdot 10^{-9}(t - 25)^3] \quad (1)$$

where  $\epsilon$  and  $t$  are the dielectric constant and degree centigrade, respectively. For dioxane–water solutions, the dielectric constant is within the temperature range from 0 to 80 by<sup>7</sup>

**Figure 1. Variation of  $\log \epsilon$  with temperatures at different molalities of proline: ■, 0.1000; ●, 0.1500; ▲, 0.2000; ▼, 0.2500; ×, 0.3000; Δ, 0.3500  $\text{mol}\cdot\text{kg}^{-1}$ .****Figure 2. Fractional deviations  $\Delta \log \epsilon / \log \epsilon = \{\log \epsilon(\text{exptl}) - \log \epsilon(\text{calcd})\} / \log \epsilon(\text{calcd})$  of the values of  $\log \epsilon(\text{exptl})$  for the proline–water system from eq 3 as a function of  $T$ .  $m_A$ : ■, 0.1000; ●, 0.1500; ▲, 0.2000; ▼, 0.2500; ×, 0.3000; Δ, 0.3500  $\text{mol}\cdot\text{kg}^{-1}$ .****Table 5. Coefficients of Equation 3**

$m/\text{mol}\cdot\text{kg}^{-1}$	composition				
	$x$	$w$	$A_1$	$10^3 B_1$	$10^4 \text{SD}^a$
Proline + Water					
0.1000	0.001797	0.01138	1.906	1.982	4
0.1500	0.002693	0.01698	1.911	1.965	3
0.2000	0.003587	0.02251	1.916	1.957	3
0.2500	0.004480	0.02798	1.921	1.959	4
0.3000	0.005371	0.03339	1.927	1.947	3
0.3500	0.006261	0.03873	1.931	1.945	2
Alanine + Water					
0.1000	0.001797	0.008831	1.907	1.948	3
0.1500	0.002693	0.01319	1.913	1.960	5
0.2000	0.003587	0.01751	1.919	1.956	5
0.2500	0.004480	0.02179	1.924	1.950	4
0.3000	0.005371	0.02603	1.930	1.939	5
0.3500	0.006261	0.03024	1.936	1.961	6

<sup>a</sup> SD, standard deviation of the fit.

$$\log \epsilon = A - Bt \quad (2)$$

where  $A$  and  $B$  are empirical constants. Owen et al.<sup>8</sup> expressed the dielectric constant of water as a function of temperature and pressure and obtained the same relationship as eq 2.

At given molalities, the relationship between the dielectric constant and temperature for L-proline–water and L-alanine–water solutions can be expressed as (see Figures 1 and 2 for L-proline–water, as an example)

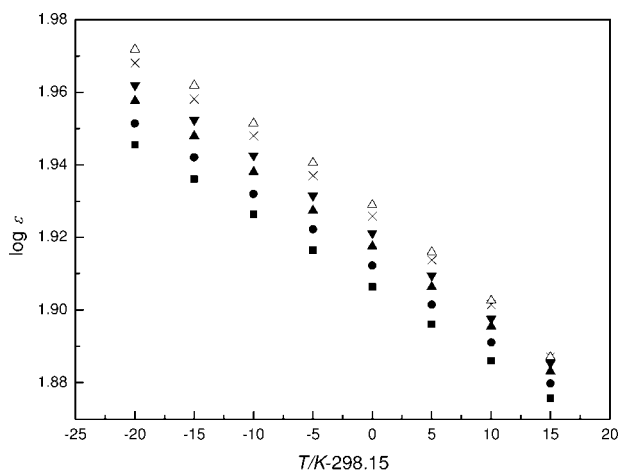
$$\log \epsilon = A_1 - B_1(T/K - 298.15) \quad (3)$$

where  $T$  is the absolute temperature and  $A_1$  and  $B_1$  are empirical constants, whose values were obtained by the fit of experimental

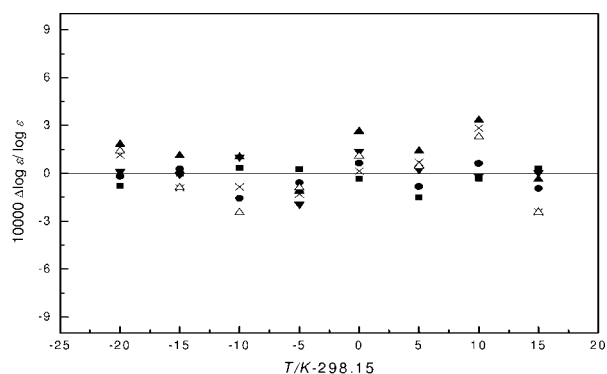
data and are included in Table 5. However, for glycine–water and L-serine–water solutions, the following equation was needed to express well experimental data (see Figures 3 and 4 for glycine–water, as an example)

$$\log \varepsilon = A_2 - B_2(T/K - 298.15) + C_2(T/K - 298.15)^2 \quad (4)$$

where  $A_2$  and  $B_2$  are empirical constants, whose values obtained by the fit are included in Table 6. Apparently,  $A_1$  and  $A_2$  are the values of  $\log \varepsilon$  at 298.15 K for given amino acid–water solutions. It has been observed in Tables 5 and 6 that  $B_1$  and  $B_2$  are almost fixed values for each of the amino acid–water solutions.



**Figure 3.** Variation of  $\log \varepsilon$  with temperatures at different molalities of glycine: ■, 0.1000; ●, 0.1500; ▲, 0.2000; ▼, 0.2500; ×, 0.3000; △, 0.3500 mol·kg<sup>-1</sup>.

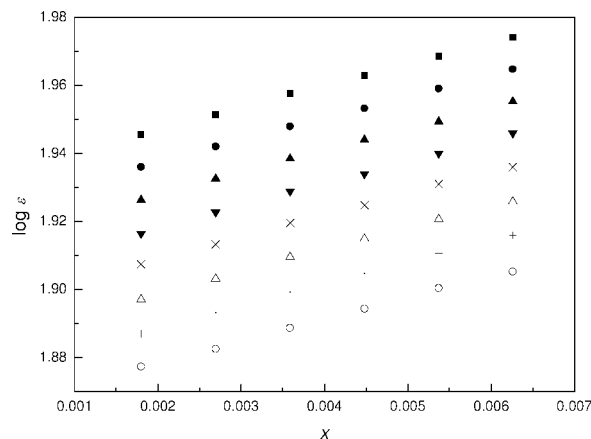


**Figure 4.** Fractional deviations  $\Delta \log \varepsilon / \log \varepsilon = \{\log \varepsilon(\text{exptl}) - \log \varepsilon(\text{calcd})\} / \log \varepsilon(\text{calcd})$  of the values of  $\log \varepsilon(\text{exptl})$  for the glycine–water system from eq 4 as a function of  $T$ .  $m_A$ : ■, 0.1000; ●, 0.1500; ▲, 0.2000; ▼, 0.2500; ×, 0.3000; △, 0.3500 mol·kg<sup>-1</sup>.

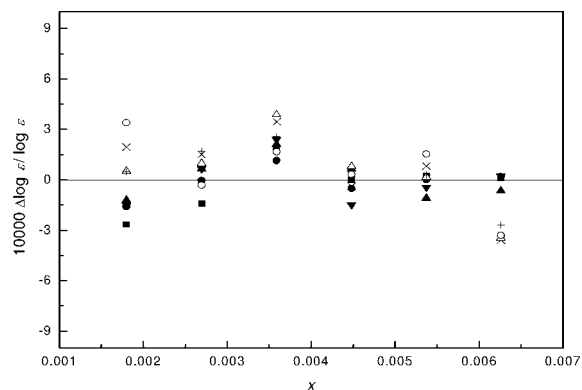
**Table 6.** Coefficients of Equation 4

composition			$A_2$	$10^3 B_2$	$10^6 C_2$	$10^4 \text{SD}^a$
$m/\text{mol} \cdot \text{kg}^{-1}$	$x$	$w$				
Glycine + Water						
0.1000	0.001797	0.007451	1.906	2.014	-2.667	1
0.1500	0.002693	0.01114	1.912	2.070	-5.329	2
0.2000	0.003587	0.01479	1.917	2.152	-6.950	3
0.2500	0.004480	0.01842	1.921	2.232	-9.183	2
0.3000	0.005371	0.02203	1.926	2.359	-12.95	4
0.3500	0.006261	0.02560	1.929	2.485	-17.36	4
Serine + Water						
0.1000	0.001797	0.01040	1.907	2.039	-5.660	1
0.1500	0.002693	0.01552	1.912	2.052	-6.513	3
0.2000	0.003587	0.02059	1.918	2.120	-8.050	4
0.2500	0.004480	0.02560	1.922	2.273	-15.73	5
0.3000	0.005371	0.03056	1.928	2.265	-14.88	5
0.3500	0.006261	0.03548	1.933	2.375	-19.82	12

<sup>a</sup> SD, standard deviation of the fit.



**Figure 5.** Variation of  $\log \varepsilon$  with molar fractions ( $x$ ) of alanine at different temperatures: ■, 278.15 K; ●, 283.15 K; ▲, 288.15 K; ▼, 293.15 K; ×, 298.15 K; △, 303.15 K; +, 308.15 K; ○, 313.15 K.



**Figure 6.** Fractional deviations  $\Delta \log \varepsilon / \log \varepsilon = \{\log \varepsilon(\text{exptl}) - \log \varepsilon(\text{calcd})\} / \log \varepsilon(\text{calcd})$  of the values of  $\log \varepsilon(\text{exptl})$  for the alanine–water system from eq 5 as a function of  $x$ .  $T$ : ■, 278.15 K; ●, 283.15 K; ▲, 288.15 K; ▼, 293.15 K; ×, 298.15 K; △, 303.15 K; +, 308.15 K; ○, 313.15 K.

**Table 7.** Coefficients of Equation 5

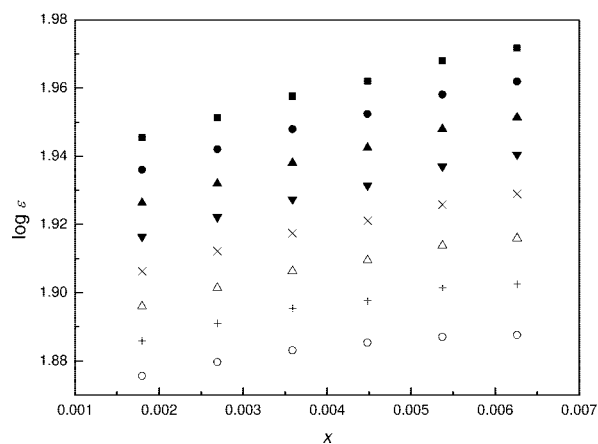
$T/\text{K}$	$\log \varepsilon_0^a$	$B_3$	$10^4 \text{SD}^b$
Alanine + Water			
278.15	1.9347	6.282	3
283.15	1.9249	6.357	2
288.15	1.9150	6.443	3
293.15	1.9050	6.536	3
298.15	1.8951	6.645	2
303.15	1.8851	6.612	2
308.15	1.8751	6.604	4
313.15	1.8650	6.531	5
Proline + Water			
278.15	1.9347	5.613	3
283.15	1.9249	5.720	2
288.15	1.9150	5.780	5
293.15	1.9050	5.831	6
298.15	1.8951	5.852	6
303.15	1.8851	5.885	5
308.15	1.8751	5.877	5
313.15	1.8650	5.920	4
Serine + Water			
278.15	1.9347	6.094	3
283.15	1.9249	6.164	2
288.15	1.9150	6.238	3
293.15	1.9050	6.220	7
298.15	1.8951	6.131	8
303.15	1.8851	5.827	9
308.15	1.8751	5.447	13
313.15	1.8650	4.547	21

<sup>a</sup>  $\varepsilon_0$  was taken from ref 6. <sup>b</sup> SD, standard deviation of the fit.

**Table 8. Coefficients of Equation 6**

T/K	$\log \varepsilon_0^a$	$B_4$	$C_4$	$10^4 \text{SD}^b$
Glycine + Water				
278.15	1.9347	6.481	-77.22	7
283.15	1.9249	6.701	-116.7	5
288.15	1.9150	6.839	-153.2	5
293.15	1.9050	6.815	-177.2	4
298.15	1.8951	7.017	-252.7	5
303.15	1.8851	6.903	-307.8	5
308.15	1.8751	6.992	-409.2	6
313.15	1.8650	6.883	-520.4	10

<sup>a</sup>  $\varepsilon_0$  was taken from ref 6. <sup>b</sup> SD, standard deviation of the fit.



**Figure 7.** Variation of  $\log \varepsilon$  with molar fractions of glycine at different temperatures: ■, 278.15 K; ●, 283.15 K; ▲, 288.15 K; ▼, 293.15 K; ×, 298.15 K; Δ, 303.15 K; +, 308.15 K; ○, 313.15 K.

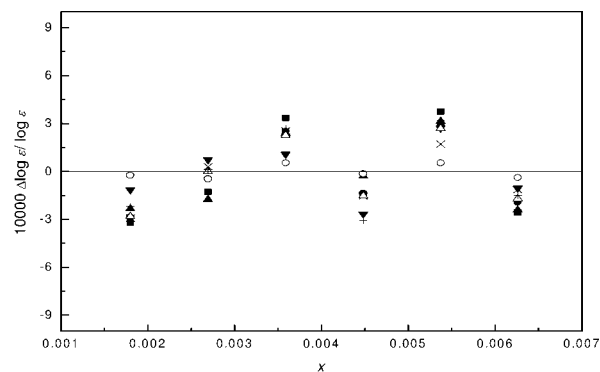
The dielectric constant not only is closely related to the macroscopic properties such as solubility, reaction rate constant, etc., but also has a strong dependence on the microscopic molecular orientational distribution as well.<sup>9</sup> The dielectric constant decreases as the temperature increases, indicating that the molecular ordering becomes weak at the high-temperature region.

**Relationship between Dielectric Constant and Composition.** Figure 5 shows that the logarithmic values of the dielectric constants for the amino acid–water mixtures increase with

**Table 9. Coefficients of Equation 7 and the Standard Deviations of the Fit**

$P_{ij}$	composition scale			composition scale		
	$x$	$m$	$w$	$x$	$m$	$w$
Alanine + Water						
$P_{00}$	1.895	1.896	1.895	1.896	1.896	1.895
$P_{01}$	$-1.953 \cdot 10^{-3}$	$-1.953 \cdot 10^{-3}$	$-1.953 \cdot 10^{-3}$	$-1.990 \cdot 10^{-3}$	$-1.989 \cdot 10^{-3}$	$-1.990 \cdot 10^{-3}$
$P_{02}$	--	--	--	--	--	--
$P_{10}$	6.434	0.1149	1.342	5.641	0.1007	0.9207
$P_{11}$	$2.226 \cdot 10^{-4}$	$3.957 \cdot 10^{-6}$	$4.711 \cdot 10^{-5}$	$7.561 \cdot 10^{-3}$	$1.350 \cdot 10^{-4}$	$1.236 \cdot 10^{-3}$
$P_{12}$	--	--	--	--	--	--
$P_{20}$	--	--	--	--	--	--
$P_{21}$	--	--	--	--	--	--
$P_{22}$	--	--	--	--	--	--
$\text{SD}^a$	$5 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
Serine + Water						
$P_{00}$	1.897	1.897	1.896	1.894	1.894	1.893
$P_{01}$	$-1.868 \cdot 10^{-3}$	$-1.869 \cdot 10^{-3}$	$-1.863 \cdot 10^{-3}$	$-1.961 \cdot 10^{-3}$	$-1.960 \cdot 10^{-3}$	$-1.965 \cdot 10^{-3}$
$P_{02}$	$1.589 \cdot 10^{-6}$	$1.545 \cdot 10^{-6}$	$1.803 \cdot 10^{-6}$	$-1.795 \cdot 10^{-6}$	$-1.762 \cdot 10^{-6}$	$-1.900 \cdot 10^{-6}$
$P_{10}$	5.725	0.1022	1.019	7.742	0.1388	1.879
$P_{11}$	$-7.914 \cdot 10^{-2}$	$-1.413 \cdot 10^{-3}$	$-1.408 \cdot 10^{-2}$	$-8.214 \cdot 10^{-3}$	$-1.671 \cdot 10^{-4}$	$-1.134 \cdot 10^{-3}$
$P_{12}$	$-3.315 \cdot 10^{-3}$	$-5.920 \cdot 10^{-5}$	$-5.897 \cdot 10^{-4}$	$-4.248 \cdot 10^{-6}$	$-6.424 \cdot 10^{-7}$	$2.356 \cdot 10^{-5}$
$P_{20}$	--	--	--	-339.2	-0.1097	-19.57
$P_{21}$	--	--	--	-12.09	$-3.820 \cdot 10^{-3}$	-0.7508
$P_{22}$	--	--	--	-0.3909	$-1.237 \cdot 10^{-4}$	-0.02416
$\text{SD}^a$	$7 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$4 \cdot 10^{-4}$
Glycine + Water						
$P_{00}$	1.897	1.894	1.893	1.894	1.894	1.893
$P_{01}$	$-1.868 \cdot 10^{-3}$	$-1.869 \cdot 10^{-3}$	$-1.863 \cdot 10^{-3}$	$-1.961 \cdot 10^{-3}$	$-1.960 \cdot 10^{-3}$	$-1.965 \cdot 10^{-3}$
$P_{02}$	$1.589 \cdot 10^{-6}$	$1.545 \cdot 10^{-6}$	$1.803 \cdot 10^{-6}$	$-1.795 \cdot 10^{-6}$	$-1.762 \cdot 10^{-6}$	$-1.900 \cdot 10^{-6}$
$P_{10}$	5.725	0.1022	1.019	7.742	0.1388	1.879
$P_{11}$	$-7.914 \cdot 10^{-2}$	$-1.413 \cdot 10^{-3}$	$-1.408 \cdot 10^{-2}$	$-8.214 \cdot 10^{-3}$	$-1.671 \cdot 10^{-4}$	$-1.134 \cdot 10^{-3}$
$P_{12}$	$-3.315 \cdot 10^{-3}$	$-5.920 \cdot 10^{-5}$	$-5.897 \cdot 10^{-4}$	$-4.248 \cdot 10^{-6}$	$-6.424 \cdot 10^{-7}$	$2.356 \cdot 10^{-5}$
$P_{20}$	--	--	--	-339.2	-0.1097	-19.57
$P_{21}$	--	--	--	-12.09	$-3.820 \cdot 10^{-3}$	-0.7508
$P_{22}$	--	--	--	-0.3909	$-1.237 \cdot 10^{-4}$	-0.02416
$\text{SD}^a$	$7 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	$7 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$4 \cdot 10^{-4}$

<sup>a</sup> SD, standard deviation of the fit.



**Figure 8.** Fractional deviations  $\Delta \log \varepsilon / \log \varepsilon = \{\log \varepsilon(\text{exptl}) - \log \varepsilon(\text{calcd})\} / \log \varepsilon(\text{calcd})$  of values of  $\log \varepsilon(\text{exptl})$  for the glycine–water system from eq 6 as a function of  $x$ . T: ■, 278.15 K; ●, 283.15 K; ▲, 288.15 K; ▼, 293.15 K; ×, 298.15 K; Δ, 303.15 K; +, 308.15 K; ○, 313.15 K.

increasing molalities of amino acids at given temperatures. The dependence of  $\log \varepsilon$  on the mole fraction ( $x$ ) of amino acids (proline, alanine, and serine) can be described as

$$\log(\varepsilon/\varepsilon_0) = B_3 x \quad (5)$$

where  $\varepsilon_0$  is the dielectric constant of pure water and  $B_3$  is the empirical constant. Values of  $B_3$  were obtained by the fits and are included in Table 7. Figure 6 shows that  $\log \varepsilon$  calculated by eq 5 coincides well with those in the experiment. The dielectric constants for glycine–water solutions can be related to compositions by the following equation (see Figures 7 and 8)

$$\log(\varepsilon/\varepsilon_0) = B_4 x + C_4 x^2 \quad (6)$$

where  $B_4$  and  $C_4$  are the empirical constants, whose values were obtained by the fits and are included in Table 8.

It is shown in Tables 5 to 8 that these empirical constants are not only as functions of the temperature but also as functions of the composition. Consequently, the following empirical equation was proposed and used to relate  $\log \varepsilon$  for amino acid–water mixtures to the temperature and the composition of mixtures [which can be expressed as the mole fraction ( $x$ ), molality ( $m$ ), or weight fraction ( $w$ )]:

$$\log \varepsilon = \sum_{i=0}^n \sum_{j=0}^m P_{ij} X^i (T/K - 298.15)^j \quad (7)$$

where  $P_{ij}$  is the empirical constant. Equation 7 can work well for alanine-water and praline-water mixtures when  $n = 1$  and  $m = 1$ , for serine-water mixtures when  $n = 1$  and  $m = 2$ , and for glycine-water mixtures when  $n = 2$  and  $m = 2$ . The  $P_{ij}$  values obtained are given in Table 9, along with the standard deviations of the fits (note: the standard deviations are those of  $\log \varepsilon$ ).

The standard deviations of the fit in Table 9 can be converted into those of  $\varepsilon$ . Results show that the converted values are smaller than 0.2. This indicates that eq 7 with parameters in Table 9 is able to evaluate accurately values of the dielectric constants for the studied systems at any temperature and composition in the experimental ranges.

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