International Journal of Thermophysics, Vol. 13, No. 5, 1992

Thermal Properties of Some α-Amino Acids in Aqueous Solutions

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Received March 13, 1992

The thermal properties (thermal conductivity, thermal diffusivity, and volumetric heat capacity) of aqueous solutions of α-amino acids [$R-CH(NH_2)COOH$]—glycine, DL-alanine, L-valine, and DL-leucine, were measured in the temperature range 20–90°C using the hot-wire technique. The results show that the values of the thermal properties depend mainly on the amino acid concentration in the medium, the substituted alkyl group of the substances under investigation, and the temperatures. The mechanism of heat transfer is discussed, and the roles of both radiation and convection are taken into consideration.

KEY WORDS: DL-alanine; DL-leucine; glycine; heat capacity; hot-wire technique; L-valine; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

It is well-known that amino acids are essential to all life. They usually exist as polymers known as polypeptides and proteins. Proteins serve as nutrients, regulate metabolism, assist in the absorption of oxygen, play important roles in the functioning of the nervous system, provide the mechanical basis for muscle contraction, represent a major support material for the body, and assist in the transfer of genetic information [1].

The present work presents the results of the measurements of thermal properties—thermal conductivity (λ), thermal diffusivity (a), and volumetric heat capacity ρ_c—of α-amino acids such as glycine, DL-alanine, L-valine, and DL-leucine in water by the hot-wire technique in the temperature range 20–90°C [2].

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0195-928X/92/0900-0827$06.50/0

A knowledge of thermal conductivity is helpful in understanding the conduction mechanism in such materials, and the results of heat capacity measurements indicate any existence of possible transitions in these materials. The transient hot-wire method has the advantage that the effect of convective heat transfer in the measurement of the thermal conductivity can be rendered negligible by the proper design and operation of the instrument, while the radiative heat transfer contribution can be minimized.

2. EXPERIMENTAL SETUP

An apparatus for the simultaneous absolute measurement of the thermal conductivity, thermal diffusivity, and specific heat capacity of solutions by the AC heated-wire (strip) technique was described by Atalla *et al.* [3]. From the plane temperature wave method (strip), the thermal activity ($\lambda/\sqrt{a}$) can be determined, and from the radial heat flow method (wire), the thermal diffusivity can be calculated. As a result of this combination, the investigated thermal properties of the solution were determined. The temperature oscillation field can be confined around the sensor in a liquid layer thin enough to suppress the hydrodynamic currents.

Aqueous solutions of glycine (Prolabo), DL-alanine (Aldrich), L-valine (Fluka-Garantie), and L-leucine (Koch-Light) of various concentrations were prepared using distilled water.

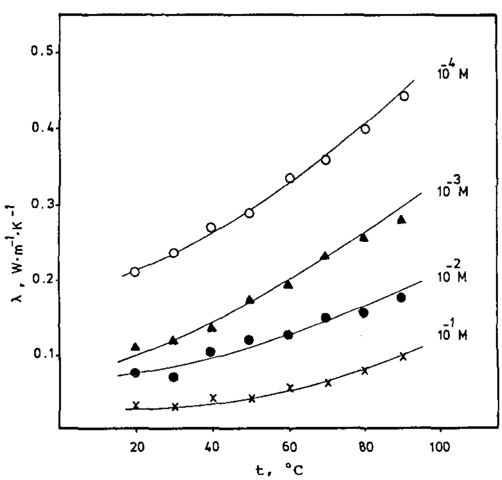

Fig. 1. Variation of thermal conductivity of glycine solutions (in aqueous media) with temperature for various concentrations.

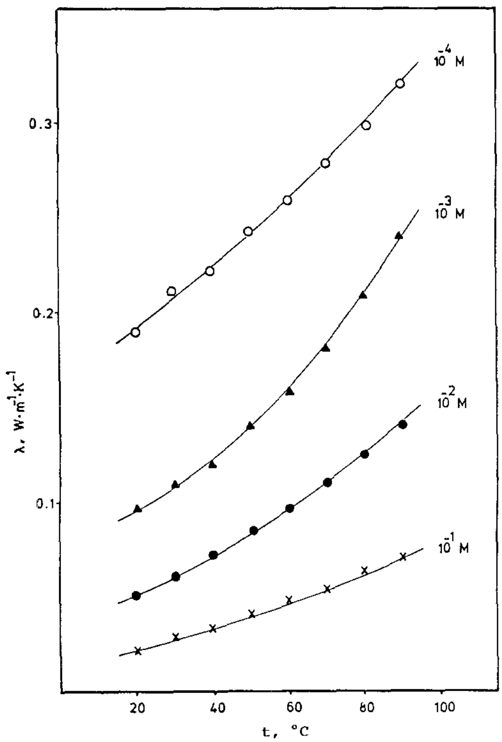

Fig. 2. Variation of thermal conductivity of DL-alanine solutions (in aqueous media) with temperature for various concentrations.

3. RESULTS AND DISCUSSION

3.1. Thermal Conductivity

Thermal conductivity results for aqueous solutions of α-amino acids (glycine, DL-alanine, L-valine, and DL-leucine) at different concentrations (from 10^{-4} to $10^{-1}\,\mathrm{mol\cdot L^{-1}}$) in the temperature range 20–90°C are presented in Figs. 1–4. As shown, the values of thermal conductivity decrease with amino acid concentration and increase with temperature. Increasing the molecular chain length of the amino acids causes a decrease in its thermal conductivity. Thus the increase in the values of thermal conductivity becomes greater in the order

glycine > DL-alanine > L-valine > DL-leucine

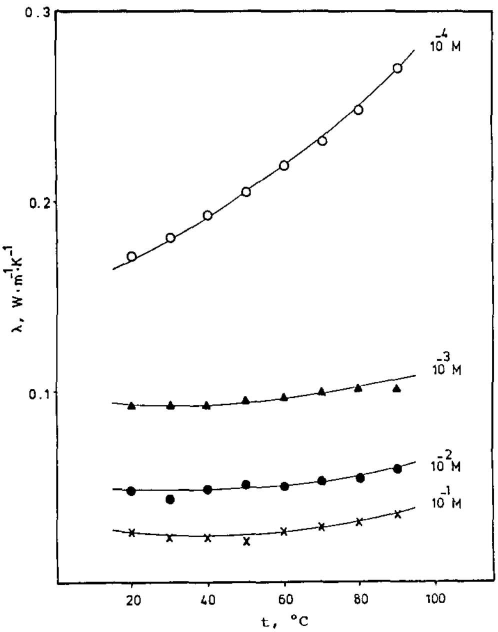

Fig. 3. Vatiation of thermal conductivity of L-valine solutions (in aqueous media) with temperature for various concentrations.

The results obtained may be attributed to the nature of the solvation of α-amino acids in aqueous solution, since in the solid state, amino acids exist as zwitterions (i.e., dipolar ions). In these zwitterions the carboxy group has transferred a proton to the amino group

Nonionic form; idealized amino acid	Zwitterion; amino acid as found in the solid state
$H_2N-C(CO_2H)(R)-H$	$H_3N^+-C(CO_2^-)(R)-H$

In an aqueous solution glycine, $H_3N^+CH_2CO_2^-$, for example, is slightly acidic because the acidic group of the zwitterion ($-NH_3^+$) is more acidic than the basic group ($-CO_2^-$) is basic.

$$H_3N^+-CH_2CO_2^- + H_20 \rightarrow H_2N-CH_2CO_2^- + H_3O^+$$

Reaction of glycine with water

This means that the increase in the thermal conductivity parameter on decreasing the substituted alkyl group of the amino acids depends on the

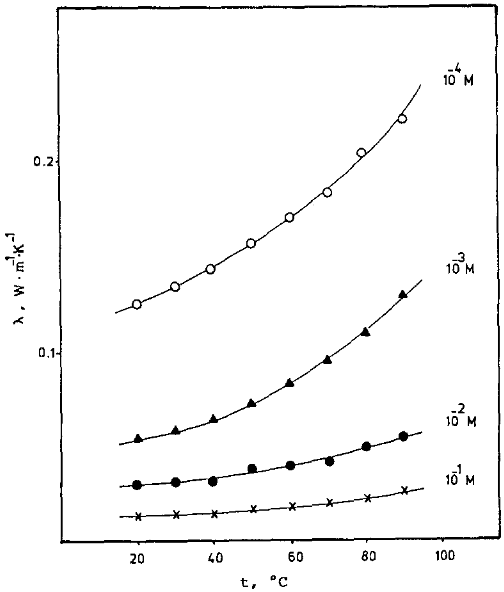

Fig. 4. Variation of thermal conductivity of DL-leucine solutions (in aqueous media) with temperature for various concentrations.

proton-transfer reactions, i.e., the dissociation constants (see Table I), of the investigated substances in aqueous solutions.

3.2. Thermal Diffusivity

The results of the thermal diffusivity for the investigated samples are presented in Figs. 5–8. We can see that thermal diffusivity decreases with increasing temperature and concentration of the amino acid in the system.

Table I. Proton-Transfer Reactions of α-Amino Acids [R – CH(NH_2)COOH] in water at 25°C [4] [a]

Name	R	pK_1	pK_2
Glycine (protonated cation)	H^-	2.35	9.78
α-Alanine (protonated cation)	CH_3-	2.34	9.87
Valine (protonated cation)	$(CH_3)_2$–CH–	2.29	9.74
Leucine (protonated cation)	$(CH_3)_2$–CH–CH_2–	2.33	9.74

[a] R is the substituted alkyl group of the amino acid [R–CH(NH_2)COOH]. pK_1 and pK_2 are the negative logarithms of the first and the second acidic dissociation constants of the amino acid.

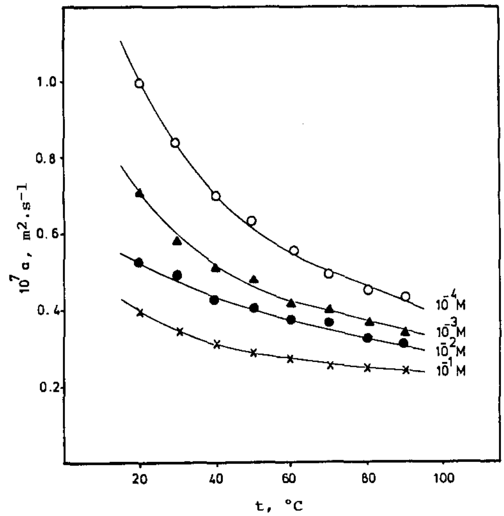

Fig. 5. Variation of thermal diffusivity of glycine solutions (in aqueous media) with temperature for various concentrations.

The increase in the values of thermal diffusivity is in the following order:

glycine > DL-alanine > L-valine > DL-leucine

The results obtained indicate that the substituted alkyl group of the amino acids affects the thermal diffusivity parameter of the investigated materials in aqueous solutions.

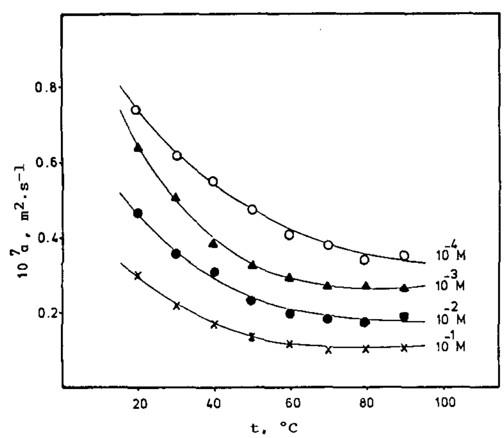

Fig. 6. Variation of thermal diffusivity of DL-alanine solutions (in aqueous media) with temperature for various concentrations.

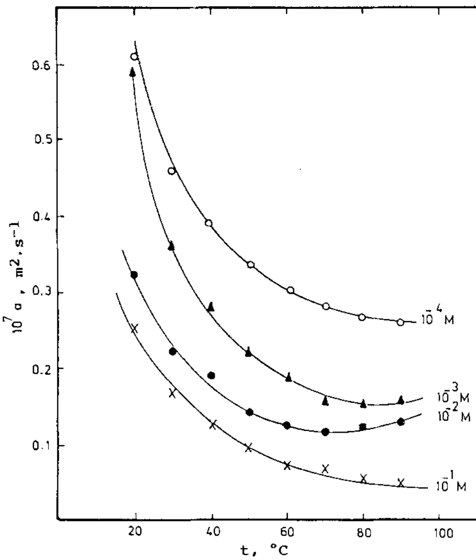

Fig. 7. Variation of thermal diffusivity of L-valine solutions (in aqueous media) with temperature for various concentrations.

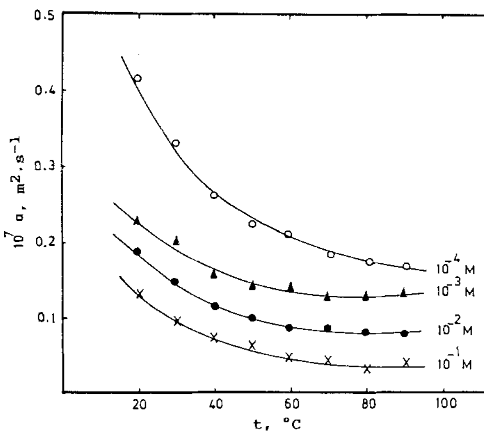

Fig. 8. Variation of thermal diffusivity of DL-leucine solutions (in aqueous media) with temperature for various concentrations.

3.3. Volumetric Heat Capacity

The results of the measurements of volumetric heat capacity with temperature of the amino acids with various concentrations are shown in Table II. It was observed that as the concentration of amino acid increases, the volumetric heat capacity decreases; however, ρ_c increases with increasing temperature. The increase in the values of heat capacity may be confirmed from the following relation:

$$\rho_c = \lambda / a$$

As shown, ρ_c increases as λ increases.

From the above results, it can be concluded that the behavior of the parameters studied (thermal conductivity, thermal diffusivity, and heat

Table II. Volumetric Heat Capacity, $10^{-6}\rho_c$ ($J \cdot m^{-3} \cdot K^{-1}$), of Various Concentrations of α-Amino Acid Solutions with Temperature

	T(°C)							
Conc. ($mol \cdot L^{-1}$)	20	30	40	50	60	70	80	90
				(a) Glycine				
10^{-1}	0.09	0.09	0.14	0.18	0.20	0.29	0.30	0.41
10^{-2}	0.14	0.15	0.25	0.28	0.36	0.46	0.53	0.58
10^{-3}	0.16	0.21	0.26	0.43	0.46	0.63	0.75	0.83
10^{-4}	0.20	0.31	0.34	0.46	0.61	0.75	0.88	0.97
				(b) DL-Alanine				
10^{-1}	0.08	0.14	0.25	0.28	0.40	0.43	0.54	0.59
10^{-2}	0.11	0.17	0.29	0.38	0.44	0.63	0.69	0.74
10^{-3}	0.15	0.23	0.32	0.48	0.52	0.66	0.77	0.62
10^{-4}	0.26	0.37	0.44	0.53	0.67	0.72	0.83	0.90
				(c) L-Valine				
10^{-1}	0.08	0.16	0.26	0.30	0.39	0.41	0.55	0.63
10^{-2}	0.15	0.20	0.30	0.40	0.45	0.60	0.69	0.75
10^{-3}	0.16	0.26	0.35	0.49	0.54	0.69	0.79	0.90
10^{-4}	0.28	0.39	0.49	0.56	0.73	0.78	0.85	1.03
				(d) DL-Leucine				
10^{-1}	0.12	0.19	0.27	0.31	0.45	0.46	0.59	0.60
10^{-2}	0.16	0.25	0.31	0.38	0.54	0.56	0.70	0.76
10^{-3}	0.22	0.34	0.45	0.51	0.65	0.70	0.84	0.98
10^{-4}	0.32	0.40	0.55	0.61	0.77	0.83	1.08	1.20

capacity) for α-amino acid solutions depends on the length of the alkyl group attached to the functional groups of the amino acids and also on the concentration of the investigated materials and the temperatures.

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