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Thermal Properties of Aminopolycarboxylic Acid Solutions in the Temperature Range 20–80°C

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The thermal properties (thermal conductivity, thermal diffusivity, and volumetric heat capacity) of aminopolycarboxylic acids, nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), triethylenetetraminehexaacetic acid (TTHA), 1,2-diaminocyclohexanetetraacetic acid (DCTA), and ethyleneglycol-bis-(2-aminoethylether) tetraacetic acid (EGTA), in dilute solutions of sodium hydroxide were measured in the temperature range 20–80 C. The measurements were performed with a hot-wire (strip) technique. The results show that the values of the thermal properties depend on the number of nitrogen atoms and the number of carboxyalkyl groups, which are bounded to the nitrogen atom, of the aminopolycarboxylic acid and also on the concentration of the investigated compounds in the medium and the temperatures. The mechanism of heat transfer is discussed and the role of convection is taken into consideration.

KEY WORDS: 1,2-diaminocyclohexanetetraacetic acid; diethylenetriaminepentaacetic acid; ethylenediaminetetraacetic acid; ethyleneglycol-bis-(2-aminoethyl ether) tetraacetic acid; heat capacity; hot-wire technique; nitrilotriacetic acid; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

Amino acids are compounds essential to all life [1]. To these compounds belongs the large group of aminopolycarboxylic acids, in which several carboxyalkyl groups are bound to the nitrogen atom. This class of compounds is very useful, especially in some fields of analytical applications [2].

The present work reports thermal properties, namely, thermal conductivity (λ), thermal diffusivity (a), and volumetric heat capacity (ρC_p),

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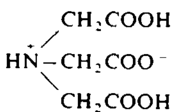
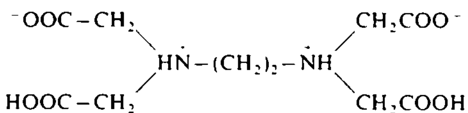
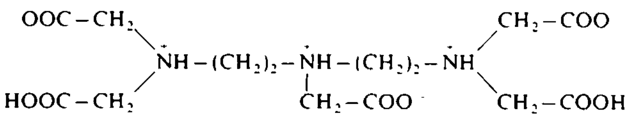
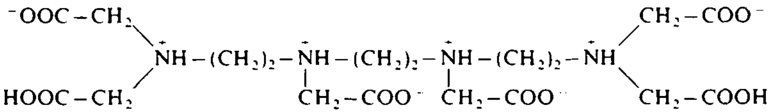
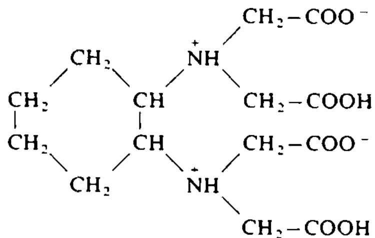
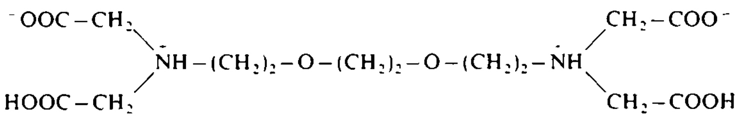
Table I. Dissociation Constants of Some Aminopolycarboxylic Acids [2][a]

Name and structural formula	Dissociation constant				
	pK_1	pK_2	pK_3	pK_4	pK_5
Nitrilotriacetic acid (NTA) 	1.89	2.49	9.73		
Ethylenediaminetetraacetic acid (EDTA) 	2.00	2.76	6.16	10.26	
Diethylenetriaminepentaacetic acid (DTPA) 	2.14	2.38	4.26	8.60	10.53

Triethylenetetraminehexaacetic acid (TTHA) 	—	—	—	—	—
1,2-Diaminocyclohexanetetraacetic acid (DCTA) 	2.4	3.52	6.12	11.7	
Ethyleneglycol-bis-(2-aminoethylether)tetraacetic acid (EGTA) 	2.00	2.68	8.85	9.43	

[a] pK_1, pK_2, pK_3, pK_4, and pK_5 are the negative logarithms of the first, second, third, fourth, and fifth acidic dissociation constants of the aminopolycarboxylic acid.

of aminopolycarboxylic acids such as nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), triethylenetetraminehexaacetic acid (TTHA), 1,2-diamino-cyclohexanetetraacetic acid (DCTA), and ethyleneglycol-bis-(2-amino-ethylether) tetraacetic acid (EGTA) dissolved in sodium hydroxide solutions by the hot-wire technique in the temperature range 20–80°C [3]. Since these properties have not yet been studied in the measured temperature range, measurement of their thermal properties at various temperatures and concentrations is helpful in understanding the conduction mechanism in such compounds.

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 previously described by Atalla et al. [3]. By the plane temperature wave method (strip), the thermal activity ($\lambda/a^{1/2}$) can be determined, and by the radial heat-flow method (wire), the thermal diffusivity can be calculated. As a result of this combination, the thermal properties ($\lambda, a, \rho C_p$) of the solutions were determined.

In this technique, the temperature oscillation field can be confined around the sensor in a solution layer thin enough to suppress the hydrodynamic currents, thus eliminating the convective heat transport. The calculated systematic errors of the thermal-activity measurements are of the order of 1.5% for plane wave heat flow and 2.0% for radial heat flow. For thermal diffusivity and heat capacity coefficients, these errors are not more 2.5%. Maximum errors for the thermal conductivity measurements were 2.2% [3].

The aminopolycarboxylic acids, nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), triethylenetetraminehexaacetic acid (TTHA), 1,2-diaminocyclohexanetetraacetic acid (DCTA), and ethyleneglycol-bis-(2-aminoethylether) tetraacetic acid (EGTA), were of 99.90% purity. Their structural formulae and dissociation constant values are given in Table I. The measurements were performed at various concentrations of aminopolycarboxylic acids (from 10^{-5} to 10^{-2} M) using 0.02 N NaOH solutions in the temperature range 20–80°C.

Table III. Thermal Diffusivity, $10^6 a$ ($m^2 \cdot s^{-1}$), of Various Concentrations of Aminopolycarboxylic Acid Solutions with Temperature

Conc. (M)	pH	T (°C) 20	30	40	50	60	70	80
		(a) Nitrilotriacetic acid (NTA)						
10^{-2}	3.864	0.140	0.150	0.160	0.170	0.160	0.165	0.160
10^{-3}	11.288	0.200	0.180	0.190	0.180	0.175	0.180	0.180
10^{-4}	11.328	0.210	0.200	0.200	0.190	0.200	0.195	0.190
10^{-5}	11.333	0.220	0.207	0.210	0.210	0.209	0.210	0.215
		(b) Ethylenediaminetetraacetic acid (EDTA)						
10^{-2}	2.940	0.172	0.144	0.129	0.100	0.110	0.129	0.144
10^{-3}	11.227	0.210	0.205	0.170	0.150	0.166	0.160	0.175
10^{-4}	11.296	0.220	0.210	0.190	0.180	0.188	0.180	0.185
10^{-5}	11.289	0.230	0.220	0.220	0.210	0.220	0.210	0.200
		(c) Diethylenetriaminepentaacetic acid (DTPA)						
10^{-2}	2.899	0.175	0.170	0.180	0.175	0.160	0.170	0.180
10^{-3}	11.191	0.190	0.195	0.180	0.185	0.182	0.179	0.180
10^{-4}	11.294	0.210	0.215	0.214	0.220	0.216	0.210	0.200
10^{-5}	11.309	0.230	0.235	0.220	0.225	0.235	0.220	0.225
		(d) Triethylenetetraminehexaacetic acid (TTHA)						
10^{-2}	8.505	0.175	0.180	0.170	0.169	0.160	0.162	0.170
10^{-3}	11.271	0.195	0.190	0.190	0.180	0.190	0.175	0.180
10^{-4}	11.313	0.225	0.220	0.210	0.205	0.202	0.201	0.201
10^{-5}	11.338	0.230	0.225	0.220	0.215	0.216	0.212	0.210
		(e) 1,2-Diaminocyclohexanetetraacetic acid (DCTA)						
10^{-2}	9.773	0.120	0.100	0.090	0.070	0.080	0.090	0.100
10^{-3}	11.386	0.140	0.120	0.110	0.115	0.120	0.128	0.130
10^{-4}	11.384	0.150	0.145	0.150	0.140	0.150	0.156	0.170
10^{-5}	11.354	0.200	0.190	0.180	0.150	0.180	0.170	0.180
		(f) Ethyleneglycol-bis-(2-aminoethylether)tetraacetic acid (EGTA)						
10^{-2}	9.544	0.145	0.108	0.100	0.080	0.078	0.078	0.100
10^{-3}	11.385	0.160	0.150	0.145	0.140	0.135	0.130	0.140
10^{-4}	11.386	0.180	0.175	0.170	0.175	0.160	0.175	0.170
10^{-5}	11.351	0.200	0.190	0.180	0.190	0.200	0.190	0.187

3. RESULTS AND DISCUSSION

3.1. Volumetric Heat Capacity

The results obtained for the variation of the volumetric heat capacity with temperature for the investigated samples with various concentrations are shown in Table II. It was observed that as the concentration of aminopolycarboxylic acids increases, the volumetric heat capacity decreases; however, the value of this property increases with increasing temperature. The increase in the values of volumetric heat capacity is in the following order:

$$\text{TTHA} > \text{DTPA} > \text{EDTA} \simeq \text{NTA} > \text{EGTA} > \text{DCTA}$$

The results obtained indicate that the number of functional groups of the aminopolycarboxylic acid affects the heat capacity parameter of the investigated compounds in dilute sodium hydroxide solutions.

3.2. Thermal Diffusivity

The results of the measurements of thermal diffusivity with temperature of the aminopolycarboxylic acids at various concentrations are presented in Table III. Generally, the thermal diffusivity decreases with increasing temperature and concentration of the aminopolycarboxylic acid in the medium. The same trend was reported previously in the case of α-amino acids in aqueous solutions [4]. The values of the thermal diffusivity increase in the order

$$\text{TTHA} > \text{DTPA} > \text{EDTA} \simeq \text{NTA} > \text{EGTA} > \text{DCTA}$$

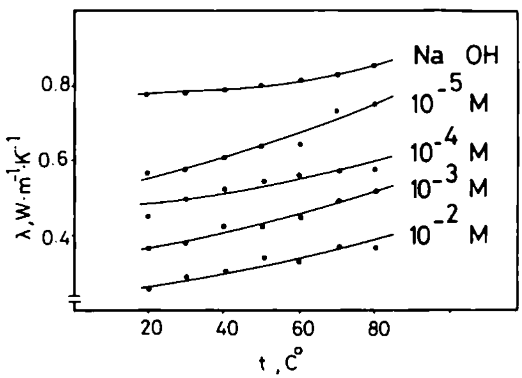


Fig. 1. Variation of thermal conductivity of nitrilotriacetic acid (NTA) solutions (in 0.02 *N* NaOH solutions) with temperature for various concentrations.

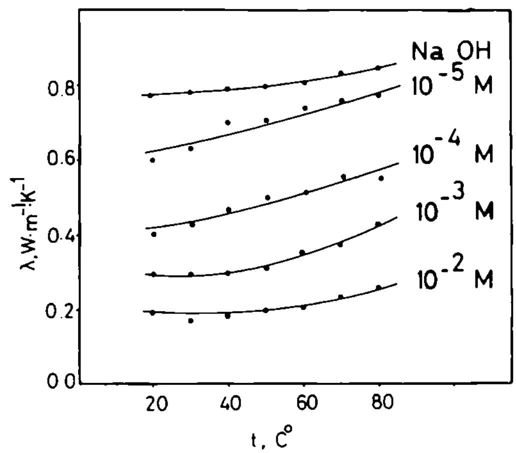


Fig. 2. Variation of thermal conductivity of ethylenediaminetetraacetic acid (EDTA) solutions (in 0.02 *N* NaOH solutions) with temperature for various concentrations.

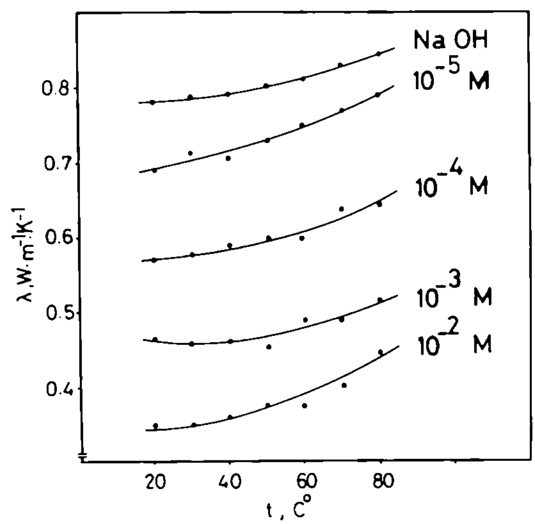


Fig. 3. Variation of thermal conductivity of diethylenetriaminepentaacetic acid (DTPA) solutions (in 0.02 *N* NaOH solutions) with temperature for various concentrations.

The results obtained indicate that the number of nitrogen atoms and hence the number of carboxyalkyl groups, which are bounded to the nitrogen atom of the aminopolycarboxylic acids, affect the behavior of the thermal diffusivity of the investigated samples in aqueous solutions of sodium hydroxide.

3.3. Thermal Conductivity

Figures 1–6 illustrate the thermal-conductivity results for solutions of aminopolycarboxylic acids (NTA, EDTA, DTPA, TTHA, DCTA, and EGTA) at different concentrations (from 10^{-5} to 10^{-2} M) in the temperature range 20–80°C. As shown, the values of thermal conductivity decrease with aminopolycarboxylic acid concentration and increase with temperature. The values of thermal conductivity increase in the order

$$\text{TTHA} > \text{DTPA} > \text{NTA} > \text{EDTA} > \text{EGTA} > \text{DCTA}$$

The results indicate that the values of thermal conductivity depend on the dissociation constants of the aminopolycarboxylic acid, i.e., proton-transfer reactions (see Table I). Dissociation of the protons from the carboxyl groups takes place easily, so that such compounds are fairly strong acids. The dissociation of a single carboxyl group increases the acidity of another carboxyl group, so that two protons dissociate in a single step. Thus, the first two values of dissociation constants for the investigated compounds are fairly close together. This means that increasing the number of carboxyl

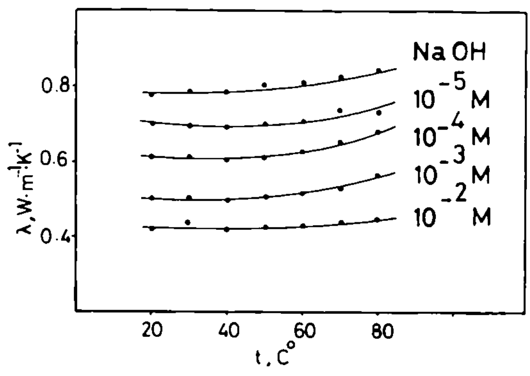


Fig. 4. Variation of thermal conductivity of triethylenetetraminehexaacetic acid (TTHA) solutions (in 0.02 N NaOH solutions) with temperature for various concentrations.

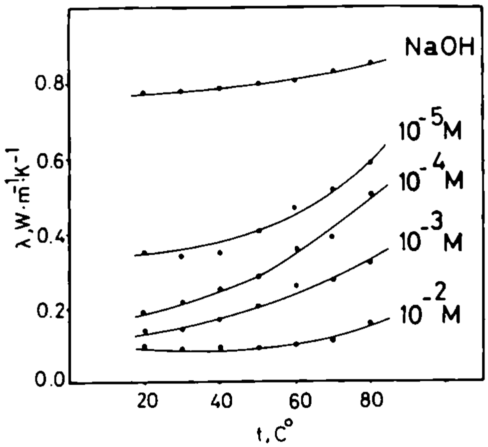


Fig. 5. Variation of thermal conductivity of 1,2-diaminocyclohexanetetraacetic acid (DCTA) solutions (in 0.02 *N* NaOH solutions) with temperature for various concentrations.

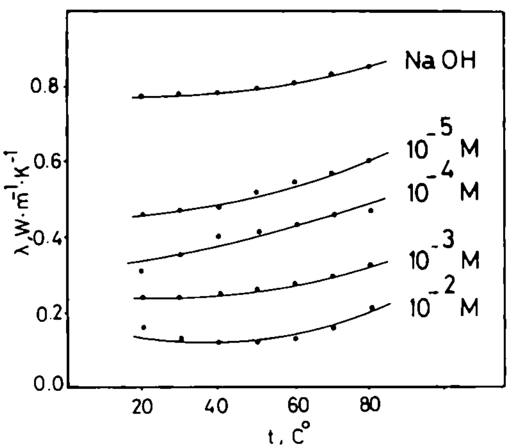


Fig. 6. Variation of thermal conductivity of ethyleneglycol-bis-(2-aminoethylether) tetraacetic acid (EGTA) solutions (in 0.02 *N* NaOH solutions) with temperature for various concentrations.

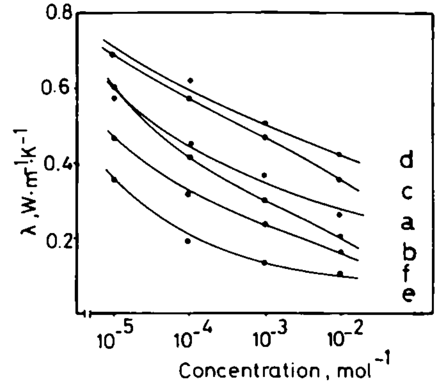
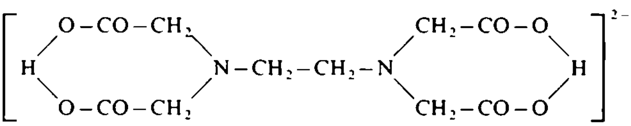


Fig. 7. Relation between thermal conductivity and different concentrations of aminopolycarboxylic acids at 20°C: (a) NTA; (b) EDTA; (c) DTPA; (d) TTHA; (e) DCTA; (f) EGTA.

groups as well as the number of nitrogen atoms of the aminopolycarboxylic acid causes an increase in its thermal conductivity. However, the higher values of thermal conductivity for NTA than for EDTA, as shown in Fig. 7, may be attributed to the secondary anion structure of the latter [5]:



4. CONCLUSION

From the above results, it can be concluded that the behavior of the thermal conductivity, thermal diffusivity, and heat capacity for aminopolycarboxylic acids in dilute sodium hydroxide solutions depends on the number of nitrogen atoms and the number of carboxyalkyl groups, which are bounded to the nitrogen atom, of the aminopolycarboxylic acid and also on the concentration of the investigated compounds and the temperature.

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