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# Ion Solvent Interaction of Amino Acids

## Part II. Amino Acids in Aqueous Solution in the Cationic, Anionic and Zwitterionic Forms

By

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The viscosities of aqueous solutions of several $\alpha$, $\beta$ and $\gamma$-amino acids at three different pH's have been measured at temperatures between 30 – 40 °C in the concentration range 0.005 to 0.1 molal, and the $B$-coefficients have been calculated using the equation $\eta/\eta_0 = 1 + Bc$. The corresponding activation energies for viscous flow have been calculated with the help of the Feakins, Freemantle and Lawrence equation. The $B$-coefficients for all the amino acids at the three pH's follow the sequence $B_{(\text{in } H_2O)} > B_{(\text{in NaOH})} > B_{(\text{in HCl})}$ over the above temperature range. The gradual decrement of $B$-coefficients from water to HCl has been discussed in terms of decreasing electric field of the ions concerned. From the temperature coefficient of $B$ it has been inferred that the simultaneous influence of polar and non polar parts is responsible for the extra structure enhancement by the $\gamma$-amino acids in aqueous solution.

Die Viskositäten wäßriger Lösungen einiger $\alpha$-, $\beta$- und $\gamma$-Aminosäuren bei drei verschiedenen pH-Werten wurden bei Temperaturen von 30 – 40 °C und Konzentrationen zwischen 0,005 und 0,1 molal gemessen. Die Koeffizienten $B$ der Gleichung $\eta/\eta_0 = 1 + Bc$ wurden berechnet. Die zugehörigen Aktivierungsenergien des viskosen Fließens wurden mit der Gleichung von Feakins, Freemantle und Lawrence ermittelt. Die Koeffizienten $B$ folgen für jede Aminosäure der Reihenfolge $B$ (in Wasser) > $B$ (in NaoH) > $B$ (in HCl) im angegebenen Temperaturbereich. Die schrittweise Abnahme der Koeffizienten von Wasser zu Salzsäure hin wurde hinsichtlich des abnehmenden elektrischen Feldes der Ionen diskutiert. Aus dem Temperaturkoeffizienten von $B$ wurde geschlossen, daß der gleichzeitige Einfluß polarer und unpolarer Molekelteile für die besondere strukturelle Erhöhung bei den $\gamma$-Aminosäuren in wäßriger Lösung verantwortlich ist.

## Introduction

The study of the properties of aqueous solutions of amino acids has gained interest recently since in the biological environment they exist as charged molecules, and actively interact with water [1]. Amino acids in the

aqueous medium exist in the dipolar or zwitterionic form. There are several other forms [2, 3] of amino acids, viz., the amino acid cation ($A^+$), the neutral amino acid form ($A$), the amino acid anion ($A^-$); and the relative concentrations of these different forms depend strongly on the pH of the medium. A study of the aqueous solutions of amino acids at different pH's from the standpoint of the viscosity $B$-coefficient should throw light on the nature of ion-solvent interactions involved in these processes.

The viscosity $B$-coefficient of simple strong electrolytes is obtained from the well-known Jones-Dole equation [4]

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc \tag{1}$$

where the square root term represents the long range ionic interaction [5]. For non-electrolytes and dipolar molecules at the isoelectric point (or, in neutral aqueous solution) at low concentrations, the following equation [6, 7] is applicable:

$$\eta/\eta_0 = 1 + Bc\,. \tag{2}$$

The $B$-coefficient is well established as a measure of solute-solvent interactions, and is directly dependent on the size, structure and charge of the molecules. As already stated, an amino acid can exist in several ionic forms depending on the pH of the medium; a study of the effect of ionic charge on the $B$-coefficient, without altering the size and structure, would therefore be possible. Few experimental studies in this regard are recorded in literature [8].

The zwitter-ionic form of an amino acid may be thought of as a bar magnet, having a similar pattern of lines of force [9] around it. The total energy in this field is not so large as that associated with the two small separate ions but is somewhat less. Thus, it is interesting to see how far an amino acid in the changing environment interacts with water and modifies the solvent structure.

Feakins, Freemantle, and Lawrence [10] have applied the theory [11] of absolute reaction rate to the phenomenon of viscous flow of electrolyte solutions to calculate the contribution per mole of the solute to the total energy of activation for the viscous flow process at infinite dilution, $\Delta\bar{H}_2^{\circ *}$. The expression for $\Delta\bar{H}_2^{\circ *}$ is given by the following equation:

$$\frac{dB}{dT} = -\frac{\bar{V}_1^{\circ}}{1000}\left(\frac{\Delta\bar{H}_2^{\circ *} - \Delta\bar{H}_1^{\circ *}}{RT^2}\right) \tag{3}$$

where $\Delta\bar{H}_1^{\circ *}$ and $\bar{V}_1^{\circ}$ are respectively the energy of activation for viscous flow, and the molar volume of the pure solvent.

In a previous communication [12] we have reported the viscosity behavior of *dl* α-alanine in water, 0.1 (N) HCl and 0.1 (N) NaOH solutions at 35 °C and 45 °C respectively. In the present paper we report the same for glycine, *dl* α-alanine, β-alanine, *dl*-2-amino butyric acid and 4-amino butyric acid in the above mentioned media, at temperatures between 30 – 40 °C. The earlier

reported measurements on *dl* α-alanine were repeated in the context of our improved experimental set up. In addition, glycine was studied at two other pH's (0.5 and 13.5) at 30°C, in view of the fact that it is known to exist almost wholly in the cationic and anionic forms respectively under the said conditions, as revealed from a pH dependent NMR study [2].

## Experimental

### Purification of the materials and preparation of the solutions

A saturated solution of medicinal glycine (E. Merck) in warm water was shaken with decolorising carbon, filtered, and precipitated by the addition of methyl alcohol; the operation was repeated. The white crystalline product was dried at 110° for 12 h. Analytical grade (Reanal) *dl* α-alanine was used without further purification. β-Alanine (E. Merck), *dl* 2-amino butyric acid (BDH) and 4-amino butyric acid (Fluka, 'Purum') were purified similarly as in the case of glycine, precipitations being done with ethyl alcohol. All the amino acids were dried at 100°C for about two hours before being dissolved in doubly distilled water (from an all pyrex still), or 0.1 N HCl, or 0.1 N NaOH, as appropriate, and the solutions were prepared and dilutions made (with water, or the above acid or alkali) on a molal basis. As a result of this method of solution preparation, the concentration of the amino acid hydrochloride, or the sodium salt, changed gradually, but the ionic strength of the medium remained effectively constant. Three to five solutions of each of the amino acids were prepared in the concentration range 0.005 to 0.1 M. {Only five solutions in NaOH [three for glycine (two at 35° and one at 40°C), and one each for α-alanine and 4-amino butyric acid, at 35°C], and one in HCl (glycine at 30°C) had slightly larger amino acid concentration.}

#### *Viscosity measurements*

The viscosities of the solutions were measured with a suspended level Ubbelohde viscometer (Schott & Gen, Mainz) having a flow time of 823.91 s for water at 30°C. Kinetic energy correction was made by using the table of Hagenbach corrections for KPG Ubbelohde viscometers supplied by the manufacturers. Flow times were measured to an accuracy of 0.1 s; at least three measurements being made for each solution, rarely differing mutually by more than 0.2 s. Flow times for water were measured once at the beginning and again at the end of each set of measurements. The densities of the solutions were measured in a 50 $cm^3$ specific gravity bottle, and are precise to $\pm 0.0001$ g $cm^{-3}$. A constant temperature bath, controlled to within $\pm 0.005$°C was used at three different temperatures: 30°, 35° and 40°C. The literature values [13] of the density of water used in the calculations were

0.99568, 0.99406 and 0.99220 g $cm^{-3}$ at 30°, 35° and 40° C respectively. The relative viscosities of the solutions were calculated with the usual relation $\eta_1/\eta_2 = d_1 t_1/d_2 t_2$. For amino acids in HCl or NaOH solutions, $\eta_{rel}$ values were calculated relative to the corresponding HCl or NaOH solution. The experimental results are recorded in Table 1.

Table 1. *Viscosity data for amino acids between 30–40° C*

| 30° C | | | | | |
|---|---|---|---|---|---|
| $10^2$ C | $(\eta/\eta_0 - 1)$ | $10^2$ C | $(\eta/\eta_0 - 1)$ | $10^2$ C | $(\eta/\eta_0 - 1)$ |
| Water | | | | | |
| Glycine | | α-Alanine | | 4-Amino butyric acid | |
| 3.34 | 0.0047 | 8.34 | 0.0202 | 8.05 | 0.0251 |
| 2.26 | 0.0036 | 4.44 | 0.0106 | 7.30 | 0.0224 |
| 1.74 | 0.0024 | 2.44 | 0.0064 | 4.25 | 0.0122 |
| | | 1.22 | 0.0030 | 3.61 | 0.0106 |
| 0.1 (N) NaOH $\eta_{NaOH}/\eta_{H_2O} = 1.0200$ | | | | | |
| 7.71 | 0.0097 | 7.49 | 0.0170 | 6.71 | 0.0184 |
| 4.19 | 0.0045 | 5.78 | 0.0129 | 5.64 | 0.0154 |
| 2.22 | 0.0023 | 3.75 | 0.0085 | 3.28 | 0.0079 |
| | | 1.31 | 0.0025 | 1.92 | 0.0043 |
| (NaOH of pH 13.5) | | | | | |
| 14.82 | 0.0103 | | | | |
| 9.02 | 0.0057 | | | | |
| 6.24 | 0.0035 | | | | |
| 3.05 | 0.0006 | | | | |
| 0.1 (N) HCl $\eta_{HCl}/\eta_{H_2O} = 1.0076$ | | | | | |
| | | 5.02 | 0.0090 | 5.27 | 0.0073 |
| | | 3.14 | 0.0058 | 4.84 | 0.0064 |
| | | 2.03 | 0.0041 | 1.46 | 0.0012 |
| (HCl of pH 0.5) | | | | | |
| 11.64 | 0.0106 | | | | |
| 3.65 | 0.0035 | | | | |
| 1.40 | 0.0016 | | | | |

Table 1. (continued)

| 35 °C | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $10^2$ C | $(\eta/\eta_0-1)$ | $10^2$ C | $(\eta/\eta_0-1)$ | $10^2$ C | $(\eta/\eta_0-1)$ | $10^2$ C | $(\eta/\eta_0-1)$ | $10^2$ C | $(\eta/\eta_0-1)$ |
| Water | | | | | | | | | |
| Glycine | | α-Alanine | | β-Alanine | | Butyrine | | 4-Amino butyric acid | |
| | | 14.47 | 0.0355 | 8.15 | 0.0178 | 3.52 | 0.0106 | 6.97 | 0.0215 |
| | | 9.64 | 0.0224 | 5.26 | 0.0110 | 1.69 | 0.0049 | 4.16 | 0.0128 |
| | | 8.85 | 0.0208 | 2.50 | 0.0047 | 0.77 | 0.0020 | 2.52 | 0.0074 |
| | | 2.74 | 0.0062 | | | | | | |
| 0.1 (N) NaOH $\eta_{NaOH}/\eta_{H_2O} = 1.0210$ | | | | | | | | | |
| 20.21 | 0.0260 | 15.06 | 0.0317 | 8.98 | 0.0180 | 3.66 | 0.0100 | 13.66 | 0.0387 |
| 14.68 | 0.0178 | 10.27 | 0.0218 | 8.73 | 0.0169 | 2.21 | 0.0062 | 8.04 | 0.0215 |
| 5.54 | 0.0056 | 4.67 | 0.0097 | 5.80 | 0.0110 | 1.05 | 0.0025 | 6.29 | 0.0169 |
| | | | | 4.64 | 0.0082 | 0.50 | 0.0007 | 3.42 | 0.0087 |
| 0.1 (N) $\eta_{HCl}/\eta_{H_2O} = 1.0080$ | | | | | | | | | |
| 10.26 | 0.0101 | 8.19 | 0.0142 | 6.41 | 0.0072 | 2.88 | 0.0073 | 8.71 | 0.0151 |
| 5.45 | 0.0049 | 5.75 | 0.0106 | 3.25 | 0.0035 | 1.80 | 0.0045 | 6.82 | 0.0119 |
| 3.46 | 0.0028 | 2.50 | 0.0050 | 1.37 | 0.0013 | 0.94 | 0.0023 | 4.70 | 0.0078 |
| | | | | | | 0.50 | 0.0009 | | |
| 40 °C | | | | | | | | | |
| Water | | | | | | | | | |
| 20.24 | 0.0292 | 7.98 | 0.0184 | 15.80 | 0.0348 | 4.52 | 0.0142 | 7.94 | 0.0229 |
| 10.80 | 0.0148 | 6.30 | 0.0144 | 9.29 | 0.0203 | 3.43 | 0.0106 | 4.62 | 0.0138 |
| 3.89 | 0.0055 | 3.64 | 0.0077 | 6.22 | 0.0136 | 1.92 | 0.0062 | 4.45 | 0.0129 |
| | | | | 3.68 | 0.0078 | 1.62 | 0.0055 | 1.55 | 0.0047 |
| 0.1 (N) NaOH $\eta_{NaOH}/\eta_{H_2O} = 1.0216$ | | | | | | | | | |
| 11.96 | 0.0143 | 8.77 | 0.0165 | 8.78 | 0.0169 | 2.76 | 0.0066 | 6.37 | 0.0158 |
| 8.35 | 0.0093 | 8.31 | 0.0149 | 6.51 | 0.0122 | 1.88 | 0.0044 | 5.32 | 0.0131 |
| 5.38 | 0.0052 | 4.68 | 0.0085 | 3.97 | 0.0072 | 0.93 | 0.0019 | 4.58 | 0.0109 |
| | | 4.26 | 0.0076 | 2.97 | 0.0050 | | | | |

Table 1. (continued)

| 40 °C | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $10^2$ C | $(\eta/\eta_0-1)$ | $10^2$ C | $(\eta/\eta_0-1)$ | $10^2$ C | $(\eta/\eta_0-1)$ | $10^2$ C | $(\eta/\eta_0-1)$ | $10^2$ C | $(\eta/\eta_0-1)$ |
| 0.1 (N) HCl $\eta_{HCl}/\eta_{H_2O} = 1.0086$ | | | | | | | | | |
| Glycine | | α-Alanine | | β-Alanine | | Butyrine | | 4-Amino butyric acid | |
| 9.23 | 0.0086 | 4.30 | 0.0081 | 9.10 | 0.0105 | 3.33 | 0.0081 | 5.73 | 0.0093 |
| 6.83 | 0.0063 | 3.63 | 0.0066 | 5.84 | 0.0063 | 2.21 | 0.0055 | 4.77 | 0.0081 |
| 4.19 | 0.0036 | 3.06 | 0.0061 | 4.54 | 0.0050 | 0.85 | 0.0019 | 3.58 | 0.0063 |
| 3.48 | 0.0027 | | | 2.01 | 0.0017 | | | 2.07 | 0.0034 |

## Result and discussion

As mentioned above, in the present experimental situation the concentration of the amino acid (hydrochloride or sodium salt) changes gradually, but the total ionic strength of the solution remains constant. Further, the Fuoss-Onsager theory [14] of mixed electrolyte solutions [Eq. (3)] shows [15] that the $A$-coefficient is in fact not strictly constant, but depends (although only very slightly) on the mixture composition:

$$\eta-\eta_0 = \eta^* = A'(P-Q_n)\sqrt{I} = a'\sqrt{I} \tag{3}$$

where

$$A' = 0.362\sqrt{2}\left(\frac{1}{DT}\right)^{1/2}, \quad P = \sum_{i=1}^{s} \varkappa_i Z_i/\lambda_i \quad \text{and} \quad Q_n = 4[\mathrm{R}] \sum_{n=0}^{\infty} C_n S^{(n)}, \varkappa_i$$

being the ional fraction of the $i$th type ion: $C_i Z_i^2/\Sigma C_i Z_i^2$, $Z_i$ the (absolute) value of its valence, $\lambda_i$ the ionic equivalent conductance, $D$ the dielectric constant, $T$ the absolute temperature, $C_n$ the bionomial coefficients, $[R]$ and $S^{(n)}$ matrices whose elements are functions of the ional fractions and the ionic mobilities and '$n$' the number of recursions.

The net electrostatic contribution in the experimentally measured quantity is then given by:

$$\frac{\eta_{mix}-\eta_{HCl}}{\eta_{HCl}} = \frac{(\eta_{mix}-\eta_0)-(\eta_{HCl}-\eta_0)}{\eta_{HCl}}$$

$$= \frac{(a'_{mix}-a'_{HCl})}{\eta_{HCl}}\sqrt{I} \approx (A_{mix}-A_{HCl})\sqrt{I}\,.$$

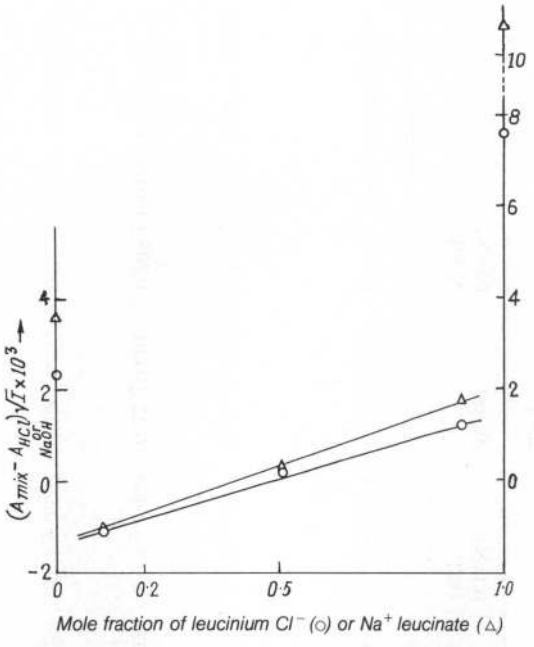


Fig. 1. Variation of the theoretically calculated quantity $(A_{mix} - A_{HCl\ or\ NaOH})\cdot\sqrt{I}$ with the mixture composition in case of leucinium $Cl^-$: (○) HCl and NaOH – Na-leucinate mixtures (△), according to the Fuoss-Onsager theory of viscosity of mixed electrolyte solutions

As a result, the simple $(\eta/\eta_0 - 1)/\sqrt{c}$ vs. $\sqrt{c}$ plot of the Jones Dole Eq. (1) to determine the value of $A$ would be inapplicable here. (In fact, unreliable negative $A$ values were obtained.) The proper course would then to calculate theoretically, the respective electrostatic contribution $(A_{mix} - A_{HCl\ or\ NaOH})\sqrt{I}$ quantities, to deduct the same from the $(\eta/\eta_0 - 1)$ values, and then to plot the residual $(\eta/\eta_0 - 1)$ vs. $c$ in order to see whether a linear fit [Eq. (2)] is obtained. Unfortunately, the required ion conductance data of both the cationic and anionic forms of the different amino acids used could not be traced in the literature. Only the said values for leucine were obtained [16], which were used for some representative calculations of the corresponding $(A_{mix} - A_{HCl\ or\ NaOH})\sqrt{I}$ quantities for different compositions of leucine hydrochloride: HCl, and sodium leucinate: NaOH mixtures (total electrolyte concentration 0.1 N); the results are shown in Fig. 1. Since the ion-conductance values in Eq. (3) are not critical, the results obtained would also hold generally for the amino acids of the present study.

It is seen that the calculated quantities are generally small in comparison with the experimentally measured $(\eta/\eta_0 - 1)$ values over most of the composition range, being of the order of a few ten percents (minus or plus)

Table 2. *Viscosity B-values for amino acids at various temperatures*

| 30 °C | | | 35 °C | | | 40 °C | | |
|---|---|---|---|---|---|---|---|---|
| Water | 0.1 (N) NaOH | 0.1 (N) HCl | Water | 0.1 (N) NaOH | 0.1 (N) HCl | Water | 0.1 (N) NaOH | 0.1 (N) HCl |
| Glycine | | | | | | | | |
| 0.137 ± 0.009 | 0.136 ± 0.005<br>0.082 ± 0.002<br>(pH = 13.5) | 0.088 ± 0.002<br>(pH = 0.5) | 0.139* | 0.138 ± 0.002 | 0.107 ± 0.0003 | 0.145 ± 0.004 | 0.138 ± 0.00004 | 0.102 ± 0.001 |
| α-Alanine | | | | | | | | |
| 0.240 ± 0.008 | 0.233 ± 0.004 | 0.167 ± 0.001 | 0.243 ± 0.004 | 0.212 ± 0.001 | 0.162 ± 0.003 | 0.247 ± 0.001 | 0.189 ± 0.003 | 0.163 ± 0.005 |
| β-Alanine | | | | | | | | |
| | | | 0.232 ± 0.001 | 0.217 ± 0.002 | 0.117 ± 0.00001 | 0.22 ± 0.001 | 0.205 ± 0.002 | 0.123 |
| Butyrine | | | | | | | | |
| | | | 0.313 ± 0.0008 | 0.294 ± 0.015 | 0.263 ± 0.007 | 0.300 ± 0.005 | 0.255 ± 0.001 | 0.249 ± 0.005 |
| 4-Amino butyric acid | | | | | | | | |
| 0.329 ± 0.004 | 0.300 ± 0.005 | 0.165 ± 0.005 | 0.316 ± 0.002 | 0.293 ± 0.004 | 0.182 ± 0.001 | 0.285 ± 0.004 | 0.273 ± 0.001 | 0.162 ± 0.006 |

* Ref. [17]

Table 3. *Energy of activation of viscous flow for amino acids at 35°C ($\Delta\bar{H}_2^{0*}$/kJ)*

| | Glycine | α-Alanine | α-Alanine | Butyrine | 4-Amino butyric acid |
|---|---|---|---|---|---|
| $H_2O$ | −19.8 | −15.5 | 102.0 | 119.4 | 206.4 |
| 0.1 (N) NaOH | 6.1 | 207.2 | 119.8 | 355.8 | 132.7 |
| 0.1 (N) HCl | 59.1 | 69.5 | −45.5 | 137.6 | 28.6 |

even in the most unfavourable cases of the lowest amino acid concentrations (mole fraction ~0.2) in HCl solutions.

It can thus be concluded from theoretical considerations that the electrostatic contribution should generally be small over the mixture composition range studied. The question whether the calculated electrostatic contributions are above the experimental error range, and if so, by how much and over which particular composition range, can only be answered through similar calculations as above using proper ion-conductance values.

In the mean-time, the simple linear plots according to Eq. (2) (with $c$ = concentration of amino acids) were found to lead to interesting results. Computorised least square fits were made, and it was found that the $(\eta/\eta_0 - 1)$ vs. $c$ plot gave a better fit, with a vanishingly small intercept [cf. Eq. (2)]. The $B$-coefficient values at the three different pH's and the three different temperatures, together with the corresponding standard deviations, are presented in Table 2. The activation energies for viscous flow of the amino acids are shown in Table 3.

The $B$-coefficient obtained for glycine in water at 30°C (0.137) is slightly larger than Tsangaris and Martin's [17] value at 30°C (0.131), but their value at 40°C (0.144) agrees with ours (0.145) at the same temperature. The value is comparatively smaller, on the other hand, than those obtained by Devine and Lowe [7], Tyrell and Kennerly [6] and Mason *et al.* [18]. The value obtained for α-alanine in water (0.243) at 35°C is also slightly higher than that of Mason *et al.* [18] (0.236). Extrapolation of Devine and Lowe's [7] results for 4-amino *n*-butyric acid in water at 15° and 25°C gives a $B$-coefficient value for 30°C which is less than that reported here. The discrepancy between their results and those of Tsangaris and Martin [17] was noted by Tyrell and Kennerly for glycine (also for sarcosine etc.). The $B$-coefficients reported by Daniel and Cohn [19] for glycine (0.152) and β-alanine (0.253) at 25°C are based on measurements at high concentrations and are larger than those of Mason *et al.* [18] and those reported in Table 2. Such small discrepancies were ignored by Tyrell and Kennerly. Their discussion is mainly concerned with comparisons between values for different solutes.

The temperature coefficient for β-alanine agrees with that obtained by Mason *et al.* [18] for the temperature range 25° to 35°C, although a disagreement is observed in the case of α-alanine. However, a similar disagreement between Devine and Lowe's results and those of Mason *et al.* [18] is also observed for β-alanine.

In accordance with our previous observation [12] with α-alanine, the *B*-coefficients of the other amino acids studied here (in water, NaOH and HCl), also decrease in the order $B_{(\text{in } H_2O)} > B_{(\text{in NaOH})} > B_{(\text{in HCl})}$, over the temperature range 30 – 40°C (all *B*'s positive). This clearly indicates that the dipolar form of the amino acids always has the largest *B*-coefficient compared to that of the other (ionic) species. This larger value is ascribed to the fact that the comparatively larger electrical field around the dipolar ion compared with that around any of the two ionic forms causes more water molecules to be oriented in its co-sphere.

In acidic or alkaline media on the other hand, the amino acid remaining either solely positively charged or solely negatively charged the *B*-coefficient values would be expected to be more or less identical, since the size and structure of the molecular ion remains almost unaltered. From a study of the pH dependent NMR spectra of $^{15}$N-enriched glycine [2], it has been shown that the glycine cation ($G^+$) is the principal species at pH 0.5 (99.99%), the zwitterion ($G^{\pm}$) at pH 6.4, and the anion ($G^-$) at pH 13.6 (99.99%). In 0.1 (N) HCl (pH = 1.2) and 0.1 (N) NaOH (pH = 12.4) there exists a mixture, predominantly of $G^+$ or $G^-$ respectively, with some $G^{\pm}$. The reason why the amino acids show a smaller *B*-coefficient in 0.1 (N) HCl compared to that in 0.1 (N) NaOH may be the presence of a comparatively smaller percentage of $G^{\pm}$ in it, so that the net total charge is lower. In support of the above argument we have determined the *B*-coefficient values of glycine at pH 0.5 and 13.5 at 30°C, and found a close agreement between the two values (0.088 and 0.082 respectively).

Table 2 shows the variation of the *B*-coefficient of the amino acids with temperature. The temperature coefficient for glycine in water is positive, indicating that the two charge centres of the molecule are of dominating influence in disrupting the water structure around it [7], and that the structure enhancing effect due to the $CH_2$ group is masked. This disordering effect of the two charged groups still predominates for α-alanine in water, but gets swamped in the 2-amino and 4-amino butyric acids, which show a negative temperature coefficient in water. As explained by previous workers [7, 18], the net structure enhancement in the latter cases is not due to any influence of charge, but to the predominance of the effect of the non-polar part of the molecule. According to Frank *et al.* [20], when a molecule with non-polar and polar parts dissolves in water at room temperature, the water adjacent to the non-polar part becomes more ice-like than normal, and this effect increases with the size of the non-polar part of the molecule.

In 0.1 (N) NaOH, the *B*-coefficient of glycine is almost temperature independent, whereas $dB/dT$ for the other acids is negative. This may be attributed to the fact that for glycine in NaOH, the total charge, and hence possibly its influence, being somewhat reduced compared to that in water, the effect due to the non-polar and polar parts are evenly poised. In the other amino acids which contain more $CH_2$ groups than glycine, the influence of the non-polar part predominates, and this is clearly shown by the large negative temperature coefficients.

In 0.1 (N) HCl there is a considerable reduction in the type of interaction considered, for $\beta$-alanine and 4-aminobutyric acid compared to their $\alpha$-isomers, as is shown by the respective *B*-coefficient values. In all these cases the temperature coefficients are negative (except for $\beta$-alanine). Even in glycine, the lowest number in the series, the absence of any significant charge influence in the acid medium is noticeable, as is indicated by the negative temperature coefficient. In the context of considerable (total) charge reduction compared to that in water, the structure disruption effect gets lessened in HCl, and the influence of the non-polar part becomes operative.

From a study of the apparent molal heat content [21], entropy of dilution [22] and viscosity measurements of higher amino acids in aqueous solution, it has been inferred that the hydrocarbon part plays an important role in modifying the solvent structure by introducing extra ice-likeness [20] into it. The relatively small negative temperature coefficient in 0.1 (N) HCl for all the four amino acids (except 2-amino butyric acid), and for 4-amino butyric acid in particular, permits us to speculate that in water both the polar and the non-polar parts of the amino acids play important roles in structure modification. Thus, for 4-amino butyric acid in water, the structure disruption by the polar part causes extra enhancement of structure by the non polar part in a like manner as is done by a mixture of NaCl and KCl in water [23]; this type of structure promotion is characteristic of $\beta$ or $\gamma$-acids, and is also proportional to the size of the non-polar part. In HCl, where the (total) charge reduction is maximum, this type of structure enhancement becomes minimum; a rise in temperature may not, therefore, cause any substantial depolymerisation around the molecule which is already stripped of extra structure.

It is interesting to note that the *B*-value of 2-amino butyric acid in 0.1 (N) HCl is not significantly reduced compared to the value in water, contrary to what is observed in the case of $\beta$-alanine and 4-amino butyric acid. The considerable bulk of the larger side chain (the non-polar part of the $\alpha$-acid) renders the molecule very much like an uncharged particle [19]; as a result, charge variation does not seem to impart any significant effect on the molecule compared to that in the $\gamma$-isomer.

The view that the $\gamma$-acids exhibit more structure enhancement than the $\alpha$-isomers is supported by the fact that the values of the differential entropy of dilution in aqueous solutions differ between $\alpha$ and $\beta$ acids, and that the $\gamma$-position of the $NH_3$ group gives the most negative values [22]. Now since in

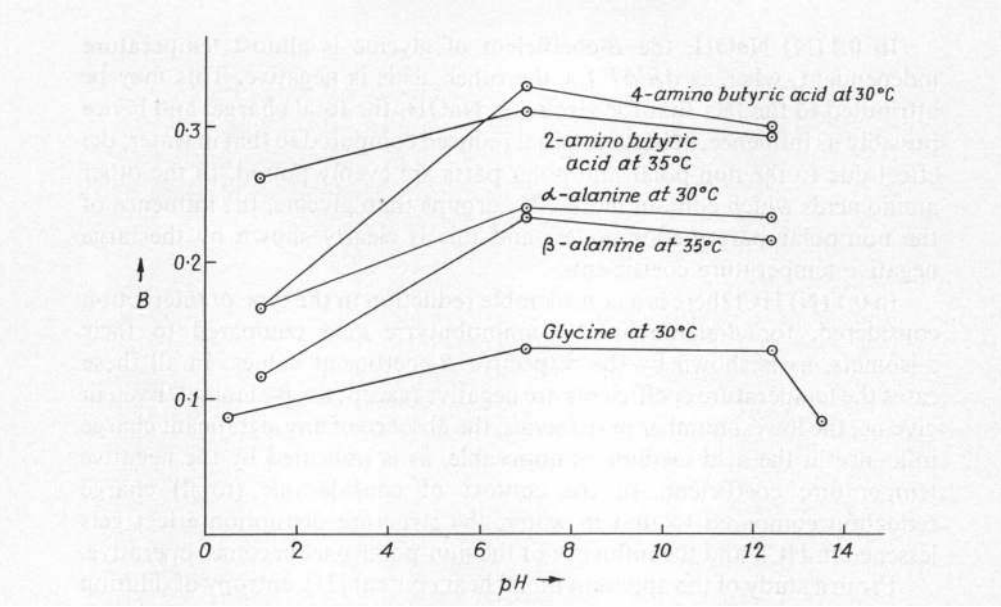


Fig. 2. Variation of $B$-coefficients of amino acids with pH

$\gamma$ acid the two charge ends are maximally separated and the non-polar part accompanying structure disruption by the other, takes place more favourably than that in $\alpha$-acid.

The change of $B$-coefficient with pH (or charge) at 30° and 35°C is depicted in Fig. 2. This variation is similar for glycine, $\alpha$-alanine and butyrine in the pH range 0.5 to 12.4. This may be due to the fact that for all these acids, being $\alpha$-acids, the charge density changes similarly with the change in environment. For $\beta$-alanine and 4-amino butyric acid, the initial rise in $B$-coefficient value is rather sharp. The larger separation between the two charge centres ($\beta$ and $\gamma$ acids) may be the possible reason for this abrupt change. Unlike in the case of the complex platinum salts [8], the $B$-coefficients of all these amino acids varies with charge in aqueous solution.

From Table 3 it is seen that both glycine and $\alpha$-alanine exhibit the lowest negative values of the energy of activation for viscous flow in their zwitterionic forms, in comparison to that in the other ionic forms. As the temperature is increased, the water molecules become more susceptible to orientation about the ions causing an increase in the $B$-coefficient value. The comparatively larger positive value of the activation energy for viscous flow in water for 4-amino butyric acid compared to that of its $\alpha$-isomer is, as stated earlier, also an indication that the extra ice-likeness is not due to the influence of the non-polar part of the molecule only.

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