

## Ion-Solvent Interaction of Amino Acids. $\alpha$ -Alanine in Aqueous Solution in the Cationic, Anionic and Zwitterionic Forms

(Received January 7, 1980)

*Ion-solvent interaction / B-coefficient /  $\alpha$ -Alanine / Amino acids*

The viscosities of *dl*- $\alpha$ -Alanine at three different pH's have been measured at 35° and 45° C 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 Nightingale-Benck equation. The effect of ionic charge on the *B*-coefficient of  $\alpha$ -Alanine in its three different ionic forms has been discussed on the basis of ion-solvent interaction.

Viskositäten von *dl*- $\alpha$ -Alanin wurden bei drei verschiedenen pH-Werten und bei 35 und 45° C gemessen und die *B*-Koeffizienten aus der Gleichung  $\eta/\eta_0 = 1 + Bc$  berechnet. Die zugehörigen Aktivierungsenergien für viskoses Fließen wurden aus der Nightingale-Benck-Gleichung berechnet. Der Einfluß der Ionenladung auf den *B*-Koeffizienten von  $\alpha$ -Alanin in seinen drei Formen wurde im Hinblick auf die Ion-Lösungsmittel-Wechselwirkung diskutiert.

### Introduction

Amino acids in aqueous medium (at the isoelectric point) remain as dipolar ions or Zwitterions and the viscosity *B*-coefficient of such electrically neutral molecules is found to be given at low concentrations by the equation [1, 2]

$$\frac{\eta}{\eta_0} = 1 + Bc. \quad (1)$$

For higher concentrations [3] a " $c^2$ " term is to be included. Electrically charged species such as electrolytes require, on the other hand, a  $\sqrt{c}$  term in the viscosity equation (Jones-Dole equation [4]):

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc. \quad (2)$$

The *B*-coefficients in Eqs. (1) and (2), although not identical, are well established as the manifestation of solute-solvent interaction. The *B*-coefficient is directly dependent on the size, structure and charge of the ions,

and it is interesting to study the effect of charge only on the  $B$ -coefficient keeping the other two factors constant. Few experimental studies [5] have been done in this regard. Since an amino acid molecule may exist once as positively charged, at another time as negatively charged and at yet other times as a neutral molecule, depending upon the pH of the medium only, i.e., without otherwise drastic alteration of the environment in which the molecule finds itself, it would appear that the amino acid molecule would serve this purpose eminently well. This prompted us to investigate the viscosity behavior of amino acids under the above different conditions.

Nightingale and Benck [6] have applied the theory of absolute reaction rate [7] to the phenomenon of viscous flow of electrolyte solutions and calculated the energy of activation for viscous flow for the electrolyte  $\Delta E^*$  with the help of the following equation:

$$\Delta E^* = \Delta E_0^* + R \frac{d \ln(1 + Bc)}{d(1/T)}$$

where  $\Delta E_0^* \left( = R \frac{d \ln \eta_0}{d(1/T)} \right)$  is the energy of activation for viscous flow of the solvent. The free energy of activation and the entropy of activation for viscous flow can also be calculated by use of the pertinent equations. The significance of these thermodynamic parameters is that they lead to an insight into the order or disorder producing effect of the ions in the solvent structure.

We report here the values of the viscosity  $B$ -coefficient of *dl*- $\alpha$ -alanine in water, 0.1(N) HCl and 0.1(N) NaOH solution [8] at 35°C and 45°C respectively and therewith the calculated value of the energy of activation of viscous flow. The calculation of the values of the other thermodynamic parameters could not be carried through in absence of required pertinent information.

### Experimental

The *dl*- $\alpha$ -Alanine used was analytical grade (Reanal, Budapest) and was used without further purification. The salt was dried at 100°C for about 2 h each time before being dissolved in double distilled water for preparing solutions on the molal basis. The densities of the solutions were measured at 35°C and 45°C with 50 ml specific gravity bottles and are precise to  $\pm 0.0001 \text{ g/cm}^3$ . All viscosity and density measurements were carried out in a constant temperature bath controlled to within  $\pm 0.01^\circ \text{C}$ . An Ostwald viscometer with a flow time for water at 35°C of 373.5 s was used. Flow times were measured to an accuracy of 0.1 s with a stopwatch. At least three measurements for each solution were made, and in most cases these rarely differed mutually by more than 0.2 s. Flow times for water were measured twice for each set of measurements, once at the beginning and the other at the end.

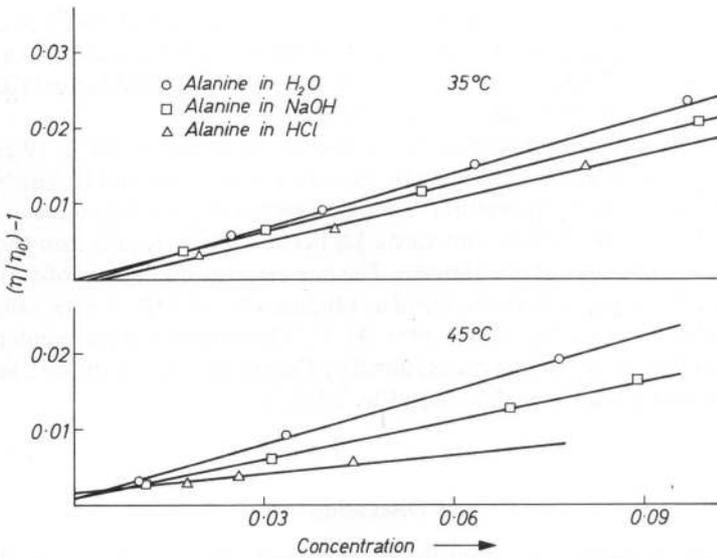


Fig. 1. Relative viscosity contribution as function of concentration

The viscosity of the solutions was calculated with the help of the usual relation  $\eta_1/\eta_2 = d_1 t_1/d_2 t_2 \cdot \eta_{rel}$  for alanine in HCl or NaOH solutions were calculated relative to the corresponding HCl or NaOH solution. Kinetic energy corrections were calculated by means of the usual relation  $\eta/\rho = Ct - K/t$ , where  $C$  and  $K$  are the characteristic viscometer constants. The absolute viscosity values of water [9] used at 35°C and 45°C were 0.7194 and 0.5963 centipoise respectively. The corresponding densities [10] were 0.99406 and 0.99020 g/ml respectively. Four to six solutions of  $\alpha$ -alanine were prepared in the concentration range 0.006 to 0.1 (M) for each set of experiments (acid, alkaline and neutral media) at the two temperatures. (For HCl, only three solutions were made.) The experimental results are presented in Fig. 1.

## Results

The  $B$ -coefficients for  $\alpha$ -alanine in water (isoelectric point 6.1) were calculated by means of Eq. (1) whereas in the cases of  $\alpha$ -alanine in HCl and NaOH both Eqs. (1) and (2) were tried. Computerised least square fits were made, and it was found, curiously, that Eq. (1) gave a better fit. The  $B$ -coefficient values at the three different pH's and the two different temperatures together with the corresponding standard deviations are as follows: [35°C:  $B_{inH_2O} = 0.244 (\pm 0.01)$ ,  $B_{inNaOH} = 0.205 (\pm 0.009)$ ,  $B_{inHCl} = 0.196 (\pm 0.014)$ ; 45°C:  $B_{inH_2O} = 0.238 (\pm 0.017)$ ,  $B_{inNaOH} = 0.169 (\pm 0.005)$ ,

$B_{\text{inHCl}} = 0.079 (\pm 0.001)$ ]. The  $B_{\text{ion}}$  values at 35° C for the cationic and anionic forms of alanine have been calculated on the basis of the usual assumption ( $B_{\text{K}^+} = B_{\text{Cl}^-}$  at all temperatures [11]) using the  $B$ -coefficient values of KCl [12] and NaCl [13] at 35° C ( $B_{\text{anion}} = 0.120$ ;  $B_{\text{cation}} = 0.191$ ).

The  $B$ -coefficient obtained for  $\alpha$ -alanine in water at 35° C (0.244) is slightly greater than that obtained by Mason, Kampmeyer and Robinson [14] (0.236) at the same temperature. A similar discrepancy for  $\beta$ -alanine at 25° C was also noted by Devine and Lowe [2] between their results and those of Mason, Kampmeyer and Robinson. The temperature coefficient of  $\alpha$ -alanine as found by us agrees with the trend as obtained by M.K.R. for the same salt between the temperature range 25° – 35° C. The temperature dependence of the  $B$ -coefficient for  $\beta$ -alanine as found by Devine and Lowe shows a reverse trend as compared with that found by M.K.R.

### Discussion

It is interesting to note that the  $B$ -coefficient of the dipolar ion is always larger than those of the other two ionic forms at both the temperatures. According to Gurney [15], dipolar ions, in general, possess a stronger field compared to that associated with the fields of two small separate ions. So the relatively large field around the dipolar ion accounts for the largest  $B$ -coefficient of alanine in aqueous solution. Laurence and Wolfenden [16] also observed the  $B$ -coefficient of the acetate ion to be much larger than that of acetic acid in aqueous solution at 25° C and concluded the larger value of the acetate ion to be due to its order producing property. Thus in both these cases, the charge factor actually plays the dominant role in influencing the  $B$ -coefficient since the size remains sensibly constant.

The calculated ( $\Delta E^* - \Delta E_0^*$ ) values for alanine at the three different pH's are all found to be positive (141.5 cal/mol in water, 593.9 cal/mol in NaOH, 1948.0 cal/mol in HCl), and it is interesting to note that the dipolar ion has the lowest value. This phenomenon can be explained in the following manner. As the temperature increases relative loosening of water structure around the dipolar ion is less presumably due to its stronger field compared to the weaker field of the other two molecular ions in the above temperature range. All these ions with positive  $B$ -coefficient and positive energy of activation may be included in the category of class I ions as proposed by Nightingale [17].

Nightingale and Kuecker [5] during their investigations of the effect of ionic charge on the viscosity  $B$ -coefficient of substituted chloroamminoplatinum salts in aqueous solution in the temperature range 20° – 30° C observed the ionic  $B$ -coefficient for most of the larger ions ( $r > 4 \text{ \AA}$ ) to be independent of the ionic charge. (A peripheral hydration with positive energy of activation for viscous flow; class IV ions.) On the other hand, the  $B$ -coefficients for smaller ions with crystal radii in the range 0.6–1.1 Å

increase with increase in charge if the radius remains more or less constant because on the average, a larger number of water molecules are peripherally oriented in the stronger electric field of the highly charged ions. Similar also is the effect of smaller polyatomic anions like  $\text{XO}_4^{z-}$  ions with radius 2.9 Å (and with approximately 50%  $\pi$ -character in the X–O bond) on the solvent structure, determined mostly by the surface charge density.

Our preliminary findings with *dl*- $\alpha$ -alanine reported above seem to suggest that  $\alpha$ -alanine in the three different ionic forms under the conditions mentioned above interacts with the solvent very likely in the above manner.

### Acknowledgement

The award of a Teacher-Fellowship to one of the authors (MMB) by the U.G.C., Govt. of India, under the Faculty Improvement Programme is gratefully acknowledged.

### References

1. J. V. Tyrell and M. Kennerly, *J. Chem. Soc. (A)* **1968**, 2724.
2. W. Devine and B. M. Lowe, *J. Chem. Soc. (A)* **1971**, 2113.
3. J. M. Tsangaris and R. B. Martin, *Arch. Biochem. Biophys.* **112** (1965) 267.
4. G. Jones and M. Dole, *J. Am. Chem. Soc.* **51** (1929) 2950.
5. E. R. Nightingale, Jr. and J. F. Kuecker, *J. Phys. Chem.* **69** (1965) 2197.
6. E. R. Nightingale and R. F. Benck, *J. Phys. Chem.* **63** (1959) 1777.
7. S. Glasstone, K. J. Laidler and H. Eyring, *The Theory of Rate Processes*. McGraw Hill, New York 1941, 494.
8. J. Webb, R. W. Strickland, F. S. Richardson, *Tetrahedron* **29** (16) (1973) 2499.
9. J. R. Coe and T. B. Godfrey, *J. Appl. Phys.* **15** (1944) 625.
10. L. W. Tilton and J. K. Taylor, *J. Res. Natl. Bur. Stand.* **18** (1937) 205.
11. M. Kaminsky, *Disc. Faraday Soc.* **24** (1957) 171.
12. W. E. Joy and J. H. Wolfenden, *Proc. R. Soc. A* **134** (1931) 413.
13. M. Kaminsky, *Z. Phys. Chem. Neue Folge* **8** (1956) 173.
14. L. S. Mason, P. M. Kampmeyer and A. L. Robinson, *J. Am. Chem. Soc.* **74** (1952) 1287.
15. R. W. Gurney, *Ionic Processes in Solution*. McGraw Hill, London 1953, 118.
16. V. D. Laurence and J. H. Wolfenden, *J. Chem. Soc. (London)* **1934**, 1144.
17. E. R. Nightingale, Jr., *Chemical Physics of Ionic Solutions*, B. E. Conway and B. G. Barradas, Ed., John Wiley and Sons, Inc., New York 1964, 87.

M. M. Bhattacharya and M. Sengupta

Department of Chemistry, University College of Science, Calcutta-9, India