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Surface properties of aqueous solutions of L-leucine

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Abstract

The surface tension, σ, of solutions of L-leucine $(CH_3)_2CHCH_2CH(NH_2)COOH$ in water, as well as in aqueous solutions of NaOH and HCl were measured in the temperature range between 278 and 308 K using the Wilhelmy plate method. L-Leucine was found to be a very weak surfactant, which can be understood if assuming strong interactions of this solute with the water structure. Striking differences were observed in the surface entropy of L-leucine solutions in water, 0.5 M HCl and 0.5 M NaOH. Moreover, surface activity of the solute is much lower than that supposed taking into account the hydrophobicity of this amino acid. It was concluded that the observed phenomena are caused by the water structure changes close to the side chain of leucine, caused by enforced hydrophobic hydration, i.e. formation of clathrate-like hydrates.

Keywords: Air–liquid interface; Surface tension; Surface entropy; Aqueous solutions; Liquid structure; L-Leucine

1. Introduction

Variation in surface energy, which can be calculated from surface tension data, depends almost equally on variation in molecular forces and that of the density of packing or molecular size [1]. On the other hand, hydrophobic hydration effects, manifesting in an enhancement of water structure and a significant entropy decrease [2], determine the molecular structure of diluted aqueous solutions of many polar solutes with hydrocarbon side chains, like alcohols, acids and amines. At higher concentrations an entropy-driven 'hydrophobic attraction' between solute molecules appears. The interactions of hydrophobic parts of solute molecules also manifest in liquid–air surface properties of aqueous solutions of them, where the hydrocarbon tails are much closer to one another and there are no water molecules screening the interactions.

The aim of this paper is to find how surface properties of aqueous solutions of a hydrophobic

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amino acid reflect the ionization of the hydrophilic part of the guest molecules adsorbed at the liquid–air interface. L-Leucine was chosen as the solute because its molecule is rather small and structurally very similar to those of short-chained normal alcohols investigated recently. On the other hand, the existence of two neighboring hydrophilic groups in the amino acid molecules could imply specific interactions between them, as well as with bulk water structure, strongly changing the surface activity of the solute under investigation.

2. Experimental

2.1. Chemicals

L-Leucine (99%, Aldrich) was used without additional purification. Solutions were prepared by weighing using doubly distilled water. Stock solutions (0.5 M) were prepared by dilution of NaOH Titrisol (Merck) and HCl Fixanal (Riedel & Haen).

2.2. Temperature stabilization

The thermostat Haake F6 was used, and the stabilization of temperature during measurements can be estimated as better than ± 0.05 K.

2.3. Surface tension measurements

The processor tensiometer K12 (Krüss) and Wilhelmy plate method were used [3]; the probe was a standard platinum plate 20 mm wide. Absolute accuracy, as estimated from the standard deviation of the results presented below, was undoubtedly much better than ± 0.2 mN/m. Surface tensions were measured changing the temperature between 278 and 308 or 313 K (with 2.5–5-K intervals).

Extreme care was taken with the platinum plate and experimental vessel. Before and after a measurement, the plate was tested using the same water which was used for preparing the solutions, in every case the surface tension being equal, in limits of experimental error, to that reported in the literature and equal to 72.8 mN/m at 20°C.

3. Results and discussion

Solubility of L-leucine in water is limited: that reported in the literature is 2.2 g/100 g H_2O at 25°C [4], the number corresponding to molar concentration of this amino acid close to C = 0.17 M. No data were found in the literature concerning solubility of this amino acid in aqueous solutions of acids or bases. It was found by us that L-leucine

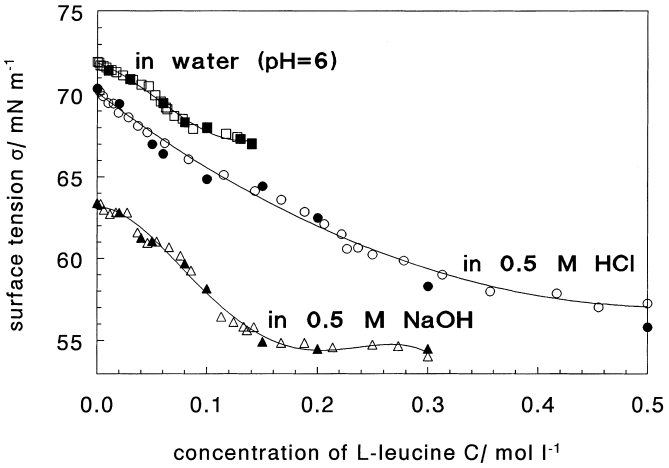

Fig. 1. Surface tension, σ, vs. L-leucine concentration in water, 0.5 M HCl and 0.5 M NaOH at 25°C. The open points were obtained by addition of concentrated solution to the known amount of solvent and the solvent to the known amount of the concentrated solution. The filled points were obtained by interpolation of the temperature dependencies.

dissolves in 0.5 M NaOH up to and above 0.3 M, and in 0.5 M HCl much above 0.5 M.

Fig. 1 presents the dependencies of surface tensions, σ, on concentration of L-leucine at 25°C. The curves were obtained by a gradual dilution of a known amount of concentrated solutions by a solvent and, in the second turn, by addition of the concentrated solution to it. The values of σ for 0.5 M NaOH and 0.5 M HCl are in good agreement with the literature data [5]. At first sight, a very weak effect of the solute on the surface tension is surprising. The weakest is the decrease of σ for pure water solvent, although one could suppose the strongest one in this case.

The surface activity of a solute is strongly linked with its hydrophobicity. That of L-leucine is very high, compared to other amino acids. Independent of the method of evaluation [6–8], leucine is one of the most hydrophobic amino acids. Remembering the method of evaluation of amino acids' relative hydrophobicities of Radzicka and Wolfenden [6], according to which the L-leucine molecule is an analogue of isobutanol or isobutanoic acid [9], one could suppose that addition of this compound to pure water would cause a rapid decrease of the surface tension.

It was demonstrated [10] that anions of organic acids with long hydrocarbon chains adsorb at the water–air surface at concentrations much higher than the corresponding non-dissociated acids. On the other hand, there is almost no difference in the surface properties of acids and alcohols with the same hydrocarbon end, which proves that only the hydrophobic parts of surfactant molecules decide the structure of the monolayer formed at the surface [11].

Another experiment was performed with individually prepared solutions. Their surface tensions, σ, were measured between 278 and 308 K to obtain the temperature dependencies. For all the systems and concentrations tested σ was linear with temperature, at least in the limits of experimental accuracy. Note that the points obtained by interpolation of these temperature dependencies to 25°C are also shown in Fig. 1.

It is a well-known fact that, with a particular choice of dividing surface, the temperature

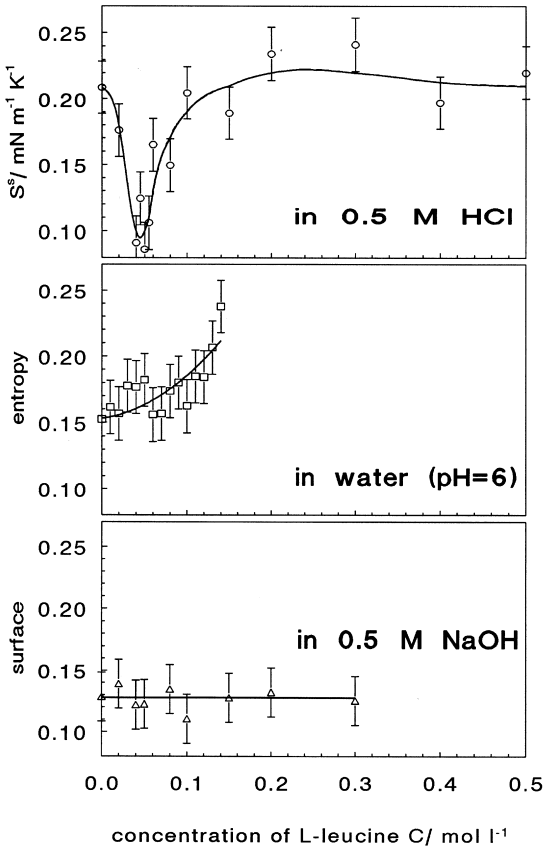

Fig. 2. Entropy of surface formation, S^S, vs. L-leucine concentration in water, 0.5 M HCl and 0.5 M NaOH.

derivative of surface tension corresponds to excess surface entropy per unit area [12]:

$$S^S = -\partial\sigma/\partial T \quad (1)$$

More precisely it was shown [13,14] that S^S represents the variation of entropy per unit area due to the interface formation. This equation is valid at constant surface concentration of the solute, not the bulk one, but changing the temperature in a rather narrow range should not change the surface composition too much. The surface entropies of L-leucine solutions [calculated from Eq. (1)] are drawn in Fig. 2 as a function of molar concentration of the solute.

The differences between $S^S = f(C)$ shown in

Fig. 2 are striking. The surface entropy is concentration-independent for the base solution, increases in pure water and passes through a sharp minimum for acidic solution. Note that the isoelectric point of L-leucine is pH 5.98 [15]; this was the same as the experimentally determined pH of the aqueous solutions under test. While at this point the amino acid molecule has formally no electric charge, one could suppose, by analogy with aqueous solutions of short-chained alcohols [16], that after an initial rapid increase, the surface entropy will pass through a maximum. On the other hand, in HCl or NaOH solutions, L-leucine is charged and should not strongly affect the surface entropy, at least in low concentrations [10]. However, the above is true only for the 0.5 M NaOH solvent.

The most interesting seems the sharp minimum in S^S vs. L-leucine concentration in 0.5 M HCl. Its location, at $C \cong 0.02$ mol/l, suggests that this concentration, corresponding to the water/leucine molecular ratio $\cong 2700$ has a special meaning. This value is a few orders higher than, for example, the hydration number of L-leucine, which was estimated by Suzuki et al. [17] to be, on average, three water molecules for each CH_2- for straight alkyl side chains and slightly less for a branched side chain, i.e. approximately 11. On the other hand, the existence of a well-defined hydrophobic group in the L-leucine molecule suggests formation of a water clathrate-like cage around it, whose size increases in the order of increasing hydrophobicity of amino acid solutes, as deduced by Hecht et al. [18] from infrared spectroscopy measurements. The number of water molecules forming such a clathrate hydrate (136 or even more) is evidently much higher than the hydration number found by Suzuki et al. but still very low compared to 2700. Note also that in this paragraph we discuss not the aqueous solution of L-leucine, but that in 0.5 M HCl, where hydration of H^+ and Cl^- ions competes with that of amino acid. Undoubtedly, this system needs further investigation.

Finally it should be mentioned that Ide et al. [19], on the basis of Raman spectroscopy and ^{1}H-NMR, concluded that although the structure of water in solutions of various amino acids did not depend on the nature of side chains at neutral pH, it did at basic and acidic conditions. The above allows to suppose that the phenomena observed by us originate from the bulk water structure rather than from the formation of different structures of leucine adsorbed at the water–air interface. If this explanation was true, our results would be the first known example of direct relations between structural processes occurring in the bulk, namely formation of clathrate hydrates around the hydrophobic side chain, and the surface properties of a liquid system. For more information on the typical structures and stoichiometries of clathrate hydrates refer to the paper by Dyadin [20].

The hydrophobic tail of the amino acid under investigation resembles very much that of *n*-butyl alcohol or *n*-butylamine. However, the surface properties of *n*-butanol and L-leucine are different. For the former, surface entropy passes through two maxima located around an alcohol mole fraction of 0.01 [16]. This phenomenon was explained in terms of the rapidly changing structure of the monomolecular layer of alcohol molecules adsorbed at the interface. While no such maxima are observed for the amino acid under investigation, one could suppose that a relatively large size of the hydrophilic part, $-CH(NH_2)COOH$, makes impossible the creation of a close-packed adsorbed layer, thus preserving it against any more sophisticated structural rearrangements. Note also that electrostatic interactions undoubtedly play an important role in dumping the structural modifications of the layer of adsorbed solute molecules, too: aqueous solutions of 1,2-pentanediol, i.e. a solute with only slightly less hydrophobic and hydrophilic parts but almost no charge on them, exhibits a maximum of surface entropy similar to that observed for the water/*n*-propanol system [21].

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