J. Chem. Thermodynamics 74 (2014) 227–230

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Mutual diffusion coefficients of L-lysine in aqueous solutions

M. Melia Rodrigo [a,1], Artur J.M. Valente [b], Marisa C.F. Barros [b], Luis M.P. Verissimo [b], Carmen Romero [c], Miguel A. Esteso [a,1], Ana C.F. Ribeiro [b,*]

[a] U.D. Química Física, Facultad de Farmacia, Universidad de Alcalá, 28871 Alcalá de Henares, Madrid, Spain
[b] Department of Chemistry, University of Coimbra, 3004-535 Coimbra, Portugal
[c] Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Bogota, Colombia

ARTICLE INFO

Article history:
Received 28 November 2013
Received in revised form 11 February 2014
Accepted 12 February 2014
Available online 22 February 2014

Keywords:
Diffusion coefficients
Transport properties
Amino acids
L-lysine

ABSTRACT

Mutual diffusion coefficients, D, were determined for aqueous solutions of L-lysine at $T = 298.15$ K at concentrations from (0.001 to 0.100) mol · dm^{-3}. From these experimental results, the hydrodynamic radius R_h, diffusion coefficients at infinite dilution D^0, the thermodynamic factors and activity coefficients γ, by using the Hartley equation, have been estimated, permitting us to have a better understanding of the thermodynamic of these systems of L-lysine in aqueous solutions.

1. Introduction

Considerable interest has been given to the study of physicochemical properties of aqueous solutions of amino acids as they are small molecules that constitute the building blocks of proteins. They have been considered model compounds that can give useful information to understand the role of (solute + solvent) interactions in the stability of proteins in aqueous solution. Additionally, they have several applications in food industry and play a fundamental role in human nutrition [1].

L-lysine (Lys) is a basic essential amino acid with a significant number of applications other than those arising from metabolic needs and its dissociation can be represented by the following equations [2]:

$$CO_2H(NH_3)^+CH(CH_2)_4NH_3^+ + H_2O \leftrightarrows CO_2^-(NH_3)^+CH(CH_2)_4NH_3^+ + H_3O^+ \quad pK_{a,1} = 2.21,$$

$$CO_2^-(NH_3)^+CH(CH_2)_4NH_3^+ + H_2O \leftrightarrows CO_2^-(NH_2)CH(CH_2)_4NH_3^+ + H_3O^+ \quad pK_{a,2} = 9.19,$$

$$CO_2^-(NH_3)^+CH(CH_2)_4NH_3^+ + H_2O \leftrightarrows CO_2^-(NH_2)CH(CH_2)_4NH_3^+ + H_3O^+ \quad pK_{a,3} = 10.75.$$

L-lysine can be used to form hydrogels [3], and polycationic complexes used for, *e.g.*, probiotics encapsulation in food industry [4] and bio-analysis [5], and drug encapsulation as well [6]. L-lysine can also be used as a precursor for the synthesis of polylisine that can be used for controlled drug and gene delivery [7,8]. An example of latter was reported by Aldawsari *et al.* [9]. These authors shown that intravenous administration of L-lysine-containing polyethylenimine (PEI- a gene delivery system) lead to a significant increase (at least three fold higher than that obtained with unmodified PEI) of gene expression in a tumour [9].

Recently, L-lysine has been used to synthesize "green" amino acid–based amphiphiles.

The synthesis of these surfactants opens the possibility, by substituting conventional surfactants, of applications in areas such as cosmetics and nanotempling chemistry [10,11]. The knowledge of the physicochemical properties of aqueous solutions of L-lysine is of great interest not only for fundamental and theoretical purposes but also in order to be used in many practical applications (*e.g.*, the development of sensors [12,13]). Although information on the structure and solvation of L-lysine, in aqueous solutions, can be found in the literature (*e.g.*, [14]) at the best of our knowledge no data on differential mutual diffusion coefficients, D (interdiffusion coefficients), for L-lysine in aqueous systems have been published. In this study the differential mutual diffusion coefficients parameters for L-lysine in aqueous systems are reported in

* Corresponding author. Tel.: +351 239 854460; fax: +351 239 827703.
E-mail addresses: mmelia.rodrigo@uah.es (M. Melia Rodrigo), avalente@ci.uc.pt (A.J.M. Valente), marisa.barros@gmail.com (M.C.F. Barros), luisve@gmail.com (L.M.P. Verissimo), cmromeroi@unal.edu.co (C. Romero), miguel.esteso@uah.es (M.A. Esteso), anacfrib@ci.uc.pt (A.C.F. Ribeiro).
[1] Tel.: +34 91 88548 61; fax: +34 91 88547 63.

http://dx.doi.org/10.1016/j.jct.2014.02.008
0021-9614/

the concentration range from (0.001 to 0.100) mol · dm^{-3} at T = 298.15 K, using the Taylor dispersion technique [15–20]. From the results obtained, structural, thermodynamic and transport parameters, such as hydrodynamic radius of L-lysine in aqueous solutions, the limiting diffusion coefficients and activity coefficients have been determined, contributing in this way to a better understanding of the thermodynamic behaviour of small solutes such as L-lysine in aqueous solution.

2. Experimental

2.1. Materials

L-lysine (CAS 56-87-1) was used as received (table 1). The solutions for the diffusion measurements were prepared in calibrated volumetric flasks using Millipore-Q water. The amino acid solutions, in the concentration range: (0.001 to 0.100) mol · dm^{-3}, were freshly prepared and de-aerated, by using a Sonorex RK106 ultrasonic bath, for about 30 min before each set of runs.

2.2. Taylor dispersion method

The Taylor dispersion method is well described in the literature (*e.g.*, [21,22]), so in this work, only the most relevant points on the experimental determination of binary diffusion coefficients will be presented.

The method [21,22] is based on the dispersion of small amounts of solution injected into laminar carrier streams of solvent or solution of different composition, flowing through a long capillary tube of radius and length $(3.2799 \pm 0.0001) \cdot 10^4$ mm and (0.5570 ± 0.0003) mm, at $T = (298.15 \pm 0.01)$ K in an air thermostat.

At the start of each run, a 6-port Teflon injection valve (Rheodyne, model 5020) was used to introduce 0.063 mL of solution into the laminar carrier stream of slightly different composition. A flow rate of 0.17 mL · min^{-1} was maintained by a metering pump (Gilson model Minipuls 3) to give retention times of about $1.1 \cdot 10^4$ s. The dispersion tube and the injection valve were kept at $T = (298.15 \pm 0.01)$ K in the air thermostat.

Dispersion of the injected samples was monitored using a differential refractometer (Waters model 2410) at the outlet of the dispersion tube. Detector voltages for a interval of time, $V(t)$, were measured as a function of timer at 5 s intervals with a digital voltmeter (Agilent 34401 A) with an IEEE-488 interface. Binary diffusion coefficients, D, were evaluated by fitting the dispersion equation

$$V(t) = V_0 + V_1 t + V_{\max}(t_R/t)^{1/2} \exp[-12D(t - t_R)^2/r^2 t], \quad (1)$$

to the detector voltages, being r the radius of the dispersion tube. The additional fitting parameters were the mean sample retention time t_R, peak height $V_{\max}$, baseline voltage V_0, and baseline slope V_1.

The concentrations of the injected solutions $(\bar{c} + \Delta c)$ and the carrier solutions $(\bar{c})$ differed by ±0.150 mol · dm^{-3} or less. Solutions of different composition were injected into each carrier solution to confirm that the measured diffusion coefficients were independent of the initial concentration difference and therefore represented the differential value of D at the carrier-stream composition.

The *pH* measurements were carried out with a Jenway 3510 pH meter with a924005 combined *pH* electrode and a 27500 automatic temperature compensation probe; the *pH* was measured in fresh solutions at T = 298.15 K and the electrode was calibrated immediately before each experimental set of solutions using IUPAC-type 4 and 9.2 *pH* buffers; $u(pH)$ = 0.02.

TABLE 1
Provenance and mass fraction purity of the sample studied.

Chemical name	CAS number	Source	Mass fraction purity
L-lysine	56-87-1	Sigma	0.99

3. Experimental results and discussion

Mutual diffusion coefficients of L-lysine in aqueous solutions together with the standard deviations of the mean at T = 298.15 K are summarized in table 2, where D is the mean value of six independent experiments, with an uncertainty under the 3%, in accordance with the previous reported data [23].

The dependence of the measured diffusion coefficients on concentration was fitted by least squares to a linear equation to obtain by extrapolation the limiting diffusion coefficient D^o at infinite dilution.

$$D/(10^{-9}\text{m}^2 \cdot \text{s}^{-1}) = 0.665 - 0.393c. \quad (2)$$

The goodness of the adjustment, done with a confidence interval of 98% can be assessed by the good correlation coefficient (R^2 = 0.993) and the low percentage of standard deviations (<1%) for the intercept.

Two different effects, the ionic mobility and the gradient of the free energy, can control the diffusion process, assuming that D is a product of both kinetic, F_M (or molar mobility coefficient of a diffusing substance) and thermodynamic, F_T ($F_T = c\partial\mu/\partial c = (1 + c(\partial \ln\gamma/\partial c))$, factors where μ and γ represent the chemical potential and the thermodynamic activity coefficient of the solute, respectively.

That is,

$$D = F_M F_T, \quad (3)$$

where

$$F_M = (D^0 + \Delta_c + \Delta_a) = (2000RT\overline{M}/c), \quad (4)$$

with the subscripts c and a representing the cation and anion, respectively, and $(\overline{M}/c)$ is given by equation (5)

$$\frac{\overline{M}}{c} = 1.0741 \cdot 10^{-20} \frac{\lambda_c^0 \lambda_a^0}{|z_c| \nu_c \Lambda^0} + \frac{\Delta\overline{M'}}{c} + \frac{\Delta\overline{M''}}{c}, \quad (5)$$

where λ^0 and Λ^0 are the ionic and molar conductivity, respectively, at infinite dilution. In equation (5), the first- and second-order electrophoretic terms, $\Delta\overline{M'}/c$ and $\Delta\overline{M''}/c$ are given by

$$\frac{\Delta\overline{M'}}{c} = \frac{(|z_a|\lambda_c^0 - |z_c|\lambda_a^0)^2}{|z_c z_a|^2 (\Lambda^0)^2} \frac{3.132 \cdot 10^{-19}}{\eta(\varepsilon T)^{1/2}} \frac{c\sqrt{2I}}{1 + ka}, \quad (6)$$

TABLE 2
Mutual diffusion coefficients, D, of L-lysine in aqueous solutions at different concentrations, c, at T = 298.15 K and at atmospheric pressure and the respective standard deviations, S_D.

c/mol · dm^{-3}	$10^9 \cdot (D \pm S_D)$/(m^2 · s^{-1})[a]
0.001	0.666 (±0.004)
0.005	0.662 (±0.018)
0.010	0.661 (±0.009)
0.020	0.659 (±0.009)
0.030	0.652 (±0.009)
0.050	0.646 (±0.006)
0.100	0.626 (±0.007)
	$D^0 = 0.665 \cdot 10^{-9}$ m^2 · s^{-1}[b]

[a] D and S_D are the mean diffusion coefficients for 6 experiments and the respective standard deviations of that mean.; $u(c)$ = 0.001 mol · dm^{-3}; $u(D) = 0.02 \cdot 10^{-9}$ m^2 · s^{-1}; $u(T)$ = 0.01 K.
[b] The limiting D^0 value calculated by extrapolating experimental data to $c \to 0$ (table 2).