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Dependence of Equilibrium Constants of *L*-Valine on Ionic Strength According to Guggenheim, Scatchard and Pitzer Models

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Summary. A systematic study of the dependence of acid-base stoichiometric constants on the ionic strength has been carried out for the aminoacid *L*-valine in ClK and BrK solutions. The observed dependence has been interpreted by using Guggenheim, Scatchard and Pitzer models for the activity coefficients of the species involved in the equilibria.

Keywords. Interaction parameters; Potentiometry; Stoichiometric constants; *L*-Valine.

Die Abhängigkeit von Gleichgewichtskonstanten des *L*-Valin von der Ionenstärke entsprechend den Modellen von Guggenheim, Scatchard und Pitzer

Zusammenfassung. Es wurde an *L*-Valin in KCl- und KBr-Lösungen eine systematische Studie der Abhängigkeit der Säure-Base-Stöchiometrie von der Ionenstärke durchgeführt. Die beobachteten Abhängigkeiten wurden aufgrund der nach den Modellen von Guggenheim, Scatchard und Pitzer erhaltenen Aktivitätskoeffizienten der an den Gleichgewichten beteiligten Spezies interpretiert.

Introduction

Thermodynamic equilibrium constants (K^T) are related to stoichiometric constants (K^*) by means of the activity of coefficients (γ_i) as:

$$K^* = K^T \Pi(\gamma_i)^{v_i}$$

where i refers to the species that appear in the equilibrium considered, v_i are the corresponding stoichiometric coefficients, and γ_i are functions of the ionic strength (I) of the medium.

From this equation it is possible to ascertain the reliability of some existing models for the activity coefficients of the species present in the medium, in order to explain the experimental observed dependence of pK^* as a function of the ionic strength of the solution.

In this work, the activity coefficients corresponding to the equilibrium of *L*-valine in solutions of ClK and BrK at different values of the ionic strength have been expressed according to the well known models of Guggenheim, Scatchard and Pitzer and the dependence of pK^* vs. I was analyzed.

L-valine is a neutral amino acid present in natural waters, so it is interesting to study the influence of the saline composition of the medium on relevant equilibria; moreover, in this way it is also possible to test the way in what zwitter-ionic species can interact with the environment.

Theory

The acid-base equilibrium of any amino acid with two dissociable groups, like L-valine, can be written as:

$$AH_2^+ \longleftrightarrow Z + H^+ \quad \text{and} \tag{1}$$

$$Z \longleftrightarrow A^- + H^+, \tag{2}$$

where Z represents the zwitter-ion, AH_2^+ is the protonated molecule of the amino acid and A^- is the anion. The correspondent constants are:

$$K_1^T = \frac{(Z)(H^+)}{(AH_2^+)} = \frac{\gamma_z \gamma_H}{\gamma_{AH_2^+}} \frac{[Z][H^+]}{[AH_2^+]} = \frac{\gamma_z \gamma_{H^+}}{\gamma_{AH_2^+}} K_1^* \quad \text{and} \tag{3}$$

$$K_2^T = \frac{(A^-)(H^+)}{(Z)} = \frac{\gamma_{A^-} \gamma_{H^+}}{\gamma_Z} \frac{[A^-][H^+]}{[Z]} = \frac{\gamma_{A^-} \gamma_{H^+}}{\gamma_Z} K_2^*, \tag{4}$$

where K^T refers to the thermodynamic equilibrium constants and K^* to the stoichiometric ones.

The activity coefficients can now be expressed by the different models.

1. *Guggenheim's Model*

This theory was developed by Guggenheim in the thirties [1]. He took into account the Debye–Hückel equation and the specific interaction theory proposed by Bronsted. According to this model the activity coefficients of the species present in the equilibria in a medium with an excess of an inert 1:1 electrolyte KX, would be:

$$\ln \gamma_{AH_2^+} = -A \frac{I^{1/2}}{1 + 1.5I^{1/2}} + 2\beta(AH_2^+, X^-)I,$$

$$\ln \gamma_{H^+} = -A \frac{I^{1/2}}{1 + 1.5I^{1/2}} + 2\beta(H^+, X^-)I,$$

$$\ln \gamma_{A^-} = -A \frac{I^{1/2}}{1 + 1.5I^{1/2}} + 2\beta(A^-, K^+)I,$$

$$\ln \gamma_Z = 2\lambda I,$$

where A is the constant of the Debye–Hückel limiting law and β is a constant which accounts for the interaction between the indicated species. With regard to the activity coefficient of the zwitter-ion, some authors have shown that for large dipolar ions with sufficient separation between positive and negative centers it can be considered that the charges exhibit an independent behavior [2]; however, as it will be shown below by the analysis of experimental data for *L*-valine, it can be supposed that the charges are not sufficiently separated and the behaviour is the same as a neutral molecule.

Then, if the activity coefficients are substituted in Eqs. (3) and (4), and decimal logarithms are used, one finds:

$$pK_1^* = pK_1^T + \varepsilon_1 I, \tag{5}$$

$$pK_2^* = pK_2^T - 2A'\frac{I^{1/2}}{1+1{,}5I^{1/2}} + \varepsilon_2 I, \tag{6}$$

where:

$$\varepsilon_1 = \frac{2}{\ln 10}[\lambda - \beta(AH_2^+, X^-) + \beta(H^+, X^-)] \quad \text{and}$$

$$\varepsilon_2 = \frac{2}{\ln 10}[-\lambda + \beta(A^-, K^+) + \beta(H^+, X^-)].$$

Therefore, the plot pK_1^* vs. I is a straight line, however, the plot pK_2^* vs. I is different due to the presence of a term arising from the Debye–Hückel limiting law. Conversely, if the behaviour of the zwitter-ionic species is considered as two independent charges, and if γ_Z is considered as in Ref. [2], the following expressions are valid:

$$pK_1^* = pK_1^T - 2A'\frac{I^{1/2}}{1+1.5I^{1/2}} + \varepsilon_1' I, \tag{7}$$

$$pK_2^* = pK_2^T + \varepsilon_2' I. \tag{8}$$

2. *Scatchard's Theory*

If the species that appear in the first equilibrium are taken into account, the constant can be written as:

$$K_1^T = K_1^* \frac{\gamma(z) \cdot \gamma_\pm^2(HX)}{\gamma_\pm^2(AH_2X)}, \tag{9}$$

where it has been multiplied and divided by γ_X because Scatchard's theory (developed in the sixties) uses mean activity coefficients. If equations of Ref. [3] are used, the activity coefficients of the species of the equilibrium (Eq. 9) can be written as:

$$2\ln\gamma_\pm(XH) = A_{XH} + \alpha_{XK} + B^0_{XH,XK} - B^1_{XH,XK},$$

$$2\ln\gamma_\pm(AH_2X) = A_{AH_2X} + \alpha_{XK} + B^0_{AH_2X,XK} - B^1_{AH_2X,XK},$$

$$\ln\gamma_Z = h_0 I + 1/2 h_1 I^2,$$

where the contribution to the ionic strength due to the amino acid has been neglected, and its activity coefficient has been considered just like Scatchard proposed for amino acids in Ref. [4] (we have wrote $1/2h_1$, because it is more convenient in the following equations, although some authors think that this coefficient can be neglected [5]). After substitution of the above expressions in Eq. (9), we have:

$$\ln K_1^T = \ln K_1^* + \ln \gamma_Z + A_{XH} - A_{AH_2X} + B^0_{XH,XK} - B^1_{AH_2X,XK} + B^1_{AH_2X,XH} - B^1_{XH,XK}.$$

If A and B are expressed as a function of the ionic strength [6], using the terms with I^2 and $a_J = 1.5$ for all electrolytes, one finds:

$$pK_1^* = pK_1^T - A_1(I/\ln 10) - B_1(I^2/2\ln 10), \tag{10}$$

where:

$$A_1 = (a^{(1)}_{AH_2X} + b^{(0,1)}_{AH_2X,XK} - a^{(1)}_{XH} - b^{(0,1)}_{XH,XK} - h_0),$$

$$B_1 = (a^{(3)}_{AH_2X} - a^{(2)}_{XH} + b^{(0,2)}_{AH_2X,XK} - b^{(0,2)}_{XH,XK} + b^{(1,2)}_{XH_2XK} - b^{(1,2)}_{AH_2X,XK} - h_1)$$

The second constant is:

$$K_2^T = \frac{[A^-][H^+]}{[Z]} \frac{\gamma_{A^-} \cdot \gamma_{H^+}}{\gamma_Z} = K_2^* \frac{\gamma^2_{\pm AH}}{\gamma_Z}, \tag{11}$$

if the value of each activity coefficient is substituted in Eq. (11) and decimal logarithms are used it is found:

$$pK_2^* = pK_2^T + \frac{2SI^{1/2}}{\ln 10(1 + aI^{1/2})} + A_2(I/\ln 10) + B_2(I^2/2\ln 10), \tag{12}$$

where

$$A_2 = (a^{(1)}_{AH} + a^{(1)}_{XK} + b^{(0,1)}_{AH,XK} - h_0) \quad \text{and}$$
$$B_2 = (a^{(2)}_{AH} + 2a^{(2)}_{XK} + b^{(0,2)}_{AH,XK} - b^{(1,2)}_{AH,XK} - h_1).$$

All "*a*" and "*b*" parameters are independent on ionic strength in this theory. Beside, pK_1^* is a quadratic function on I (Eq. 10); however, the dependence of pK_2^* on I shows a term that arises from the limiting law.

3. *Pitzer's Model*

The activity coefficients of the species involved in the equilibria can be expressed by the theory that Pitzer developed in the seventies [7, 1]:

$$\ln \gamma_{H^+} = f^\gamma + 2I(B_{XH} + IC_{XH}) + I^2(B'_{XK} + C_{XK}) + I(2\theta_{HK} + I\psi_{HXK}),$$
$$\ln \gamma_{AH_2^+} = f^\gamma + 2I(B_{XAH_2} + IC_{XAH_2}) + I^2(B'_{XK} + IC_{XK}) + I(2\theta_{AH_2K} + I\psi_{AH_2XK}),$$
$$\ln \gamma_Z = 2\lambda_{Z,K}I_K + 2\lambda_{Z,X}I_X = 2\lambda_{Z,XK}I,$$
$$\ln \gamma_{A^-} = f^\gamma + 2I(B_{AK} + IC_{AK}) + I^2(B'_{XK} + IC_{XK}) + I(2\theta_{AX} + I\psi_{AXK}),$$

where f^γ:

$$f^\gamma = -0.392\left[\frac{I^{1/2}}{1 + 1.2I^{1/2}} + \frac{2}{1.2}\ln(1 + 1.2I^{1/2})\right]$$

and I is the molality of an 1:1 electrolyte, KX, in excess with respect to the other species in the medium. Moreover, the zwitter-ion has been considered again as a neutral molecule [9], so the $\ln\gamma_Z$ term is a linear function of the ionic strength. In this model, all parameters are supposed to be constant except B and its derivative B':

$$B_{MX} = \beta^0_{MX} + \frac{\beta^1_{MX}}{2I}[1-(1+2I^{1/2})\exp(-2I^{1/2})],$$

$$B'_{MX} = \frac{\beta^1_{MX}}{2I^2}[-1+(1+2I^{1/2}+2I)\exp(-2I^{1/2})].$$

If decimal logarithms are used in the expression of the first equilibrium constant and each value of $\ln\gamma$ is substituted in this equations one obtains:

$$pK_1^* = pK_1^T - \frac{2}{\ln 10} I\left(\beta^{(0)}_{XAH_2} - \lambda_{Z,XK} - \beta^{(0)}_{HX}\right) - (\beta^{(1)}_{XAH_2} - \beta^{(1)}_{HX}) g/\ln 10, \tag{13}$$

where

$$g = [1-(1+2I^{1/2})\exp(-2I^{1/2})],$$

and for the second equilibrium:

$$pK_2^* = pK_2^T + \frac{2}{\ln 10} f^\gamma + [\beta^{(1)}_{AK} + \beta^{(1)}_{XH} - \beta^{(1)}_{XK}] \frac{g}{\ln 10} + \frac{2}{\ln 10} \beta^{(1)}_{XK} I \exp(-2I^{1/2})$$
$$+ \frac{2}{\ln 10} I [\beta^{(0)}_{AK} - \lambda_{Z,XK} + \beta^{(0)}_{XH}], \tag{14}$$

where θ, ψ, y, C have been neglected. This simplification is commonly used for $I < 2M$ [7].

It is worth noting that the dependence pK^* vs. I, in this theory, is more complicated than it is in the other models. This is due to the exponential terms arising from the dependence of B on the ionic strength. In addition, Pitzer adds a new term to the limiting law.

Experimental Part

All reagents were Merck p.a. and the water necessary for the solutions was purified using a Milipore-Mili-Q system.

The concentration of *L*-valine was approximately 0.01*M* in all experiments and different amounts of BrK and ClK were added to keep the ionic strength constant.

The experiments were carried out in a cell with double wall with a stream of water from a thermostat at 25.0 ± 0.1 °C. Purified nitrogen (99.999%) is bubbled into the cell to remove CO_2 and to stir the solution. An automatic burette CRISON microBU 2030 with syringes of 10 ml and 2.5 ml was used to deliver the titrant (controlled by a TANDON PAC 286/10-PW computer by means of the ALIA program [10]); a *pH*-meter CRISON micropH 2002 was connected to an electrode RADIOMETER GK2401C. The calibration of the glass electrode was carried out according to established procedures [11, 12]. The program MINIQUAD [13] was used for the calculation of pK_i^*.

Results and Discussion

The obtained pK_1^* and pK_2^* values are shown in Table 1. The ionic interaction parameters proposed by the three models are calculated with this data. The statistical program SOLO [14] was used to carry out the fits pK^* versus the different functions of the ionic strength in each theory and the obtained parameters are shown in Tables 1–4.

It can be noticed that there are large errors in some parameters, however, the fit itself is good, lying within the accepted experimental margin of error for acid-base pK^* values reported in specialized texts [15] (ca. 0.06 pK^* units). On the other hand,

Table 1. Values of pK_1^* and pK_2^* obtained at different values of ionic strengths in ClK and BrK[1,2]

I(ClK)	pK_1^*	pK_2^*
0	2.286	9.719
0.10	2.303 ± 0.001	9.548 ± 0.004
0.25	2.252 ± 0.004	9.457 ± 0.046
0.51	2.280 ± 0.002	9.480 ± 0.002
0.72	2.326 ± 0.022	9.474 ± 0.014
1.03	2.282 ± 0.031	9.469 ± 0.015
1.25	2.280 ± 0.023	9.480 ± 0.016
1.46	2.305 ± 0.003	9.511 ± 0.003
1.68	2.352 ± 0.035	9.518 ± 0.019
I(BrK)	**pK_1^***	**pK_2^***
0	2.286	9.719
0.25	2.297 ± 0.023	9.487 ± 0.011
0.51	2.231 ± 0.005	9.461 ± 0.007
0.72	2.347 ± 0.002	9.482 ± 0.003
1.04	2.361 ± 0.010	9.497 ± 0.003
1.26	2.377 ± 0.009	9.528 ± 0.019
1.48	2.399 ± 0.003	9.550 ± 0.004
1.70	2.429 ± 0.002	9.563 ± 0.003

[1] pK^T values were taken from Ref. [16]

[2] The transformations from molarity to molality for pK^* and for ionic strength were carried out with data from Ref. [8]

Table 2. Guggenheim parameters obtained from Eqs. (5) and (6)

	pK_1^*	ε_1	σ_1
ClK	2.261 ± 0.018	0.09 ± 0.04	0.042
BrK	2.283 ± 0.008	0.18 ± 0.02	0.015
	pK_2^*	**ε_2**	**σ_2**
ClK	9.734 ± 0.011	0.32 ± 0.02	0.020
BrK	9.729 ± 0.007	0.40 ± 0.02	0.013

Table 3. Scatchard parameters obtained from Eqs. (10) and (12)

	ClK	BrK
pK_1	2.281 ± 0.024	2.287 ± 0.012
A_1	+0.09 ± 0.16	−0.15 ± 0.07
B_1	−0.21 ± 0.17	−0.04 ± 0.08
σ_1	0.042	0.016

	ClK	BrK
PK_2	9.726 ± 0.015	9.722 ± 0.010
A_2	+0.40 ± 0.09	+0.46 ± 0.07
B_2	−0.09 ± 0.10	−0.07 ± 0.08
σ_2	0.024	0.013

Table 4. Pitzer parameters obtained from Eqs. (13) and (14)

	ClK	BrK
pK_1	2.290 ± 0.032	2.286 ± 0.014
β^1_{XAH2}	0.70 ± 0.37	0.39 ± 0.16
$\beta^0_{XAH2} - \lambda_{Z,XK}$	0.06 ± 0.07	0.10 ± 0.03
σ_1	0.042	0.016

	ClK	BrK
pK_2	9.722 ± 0.019	9.721 ± 0.012
β^1_{AK}	0.54 ± 0.21	0.40 ± 0.14
$\beta^0_{AK} - \lambda_{Z,XK}$	0.01 ± 0.04	0.04 ± 0.03
σ_2	0.024	0.014

any of the three theories is better than the others to explain the experimental behaviour, as it is observed in the plots pK^* vs. I (Figs. 1 and 2). Besides it must be noticed that the behaviour of pK^* vs. I is different for both pK^*; in this way, in the plot $pK_2^* - I$ (Fig. 2) a very important increase can be observed when $I \rightarrow 0$, but this is not observed in the first pK^*. To understand this behaviour and its relation with the activity coefficient of the zwitter-ion it is interesting to study the derivative of the function $pK_1^*(I)$ when $I \rightarrow 0$, which can be obtained from Eq. (13) for the Pitzer equations:

$$\mathrm{d}(pK_1^*)/\mathrm{d}I = -\frac{2}{\ln 10}(\beta^{(0)}_{XAH_2} - \lambda_{Z,XK} - \beta^{(0)}_{\mathrm{H}X}) - \frac{2}{\ln 10}(\beta^{(1)}_{XAH_2} - \beta^{(1)}_{\mathrm{H}X}).$$

For the Scatchard equations from Eq. (10) one finds:

$$\mathrm{d}(pK_1^*)/\mathrm{d}I = -A_1/\ln 10.$$

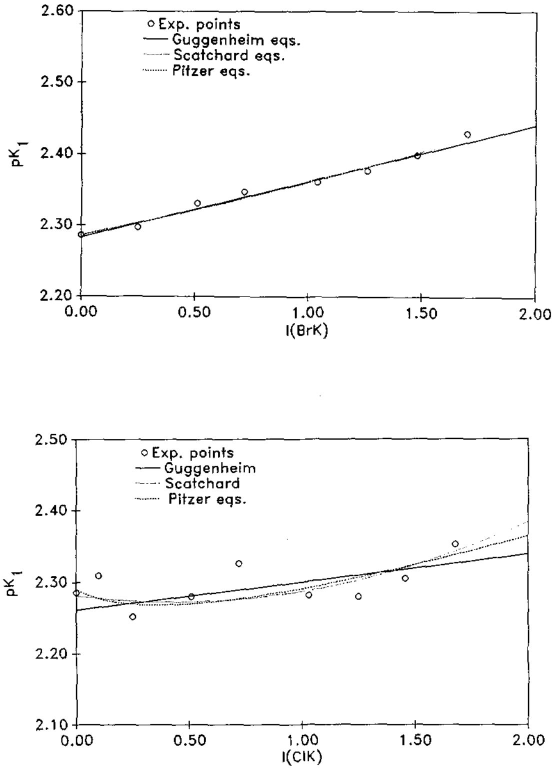

Fig. 1. pK_1^* vs. I according to several models for *L*-valine in ClK and BrK as background electrolytes

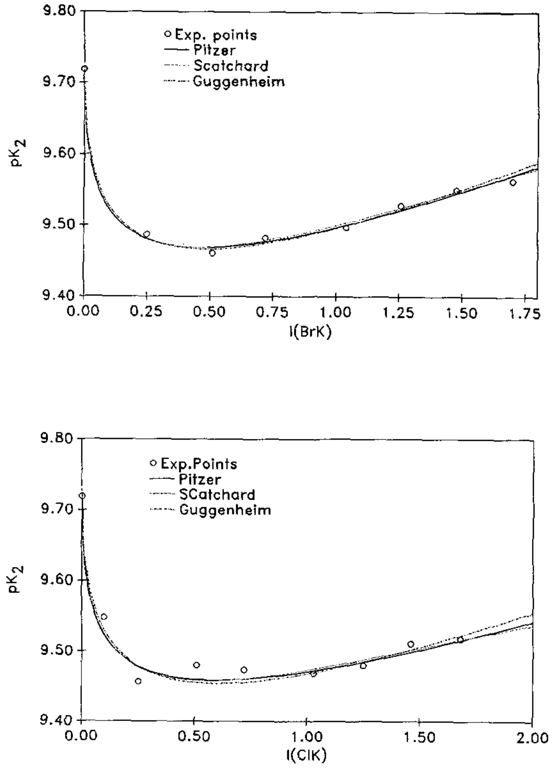

Fig. 2. pK_2^* vs. I according to several models for *L*-valine in ClK and BrK as background electrolytes

In the function $pK_2^*(I)$ appears a new term for any of the three theories. In the Pitzer model this function is:

$$f^{\gamma} = -A_{\phi}[I^{1/2}/(1 + 1.2I^{1/2}) + (2/1.2)\ln(1 + 1.2I^{1/2})].$$

When $I \to 0$, $\partial f^{\gamma}/\partial I = -\infty$, so $\lim_{I \to 0} \mathrm{d}(pK_2^*)/\mathrm{d}I = -\infty$.

For the other theories the new term corresponds to the Debye–Hückel limiting law:

$$S[I^{1/2}/(1 + aI^{1/2})]$$

(this is the same for Scatchard and Guggenheim theories because $A = -S = A'/\ln 10$), thus one obtains:

$$\lim_{I \to 0} \mathrm{d}(pK_2^*)/\mathrm{d}I = -\infty, \quad \text{because } S < 0.$$

It should be noticed that with this value of the slope ($-\infty$) an important increase can be expected in the plot $pK_2^* - I$ when $I \to 0$, on the other hand the plot $pK_1^* - I$ should not exhibit this behaviour; this is actually observed in Figs. 1 and 2. Conversely, if the zwitter-ion of *L*-valine was supposed to behave as two independent charges as it was done in Ref. [2] for other dipolar compounds, the behaviour would be just the opposite for both pK^*: an important increase in pK_1^* when $I \to 0$, but not in pK_2^*. So, from this analysis of pK^* vs. I data, it can be concluded that the zwitter-ionic form of *L*-valine interacts with its surroundings just like a neutral molecule.

References

[1] Pitzer K. S. (1979) Theory: Ion Interaction approach in Pytkowicz R. M. (ed.) Activity Coefficients in Electrolyte Solutions. C.R.C. Boca Ratón

[2] Salvatore F., Ferri D., Palombari R. (1986) J. Sol. Chem. **15**(5): 423

[3] Scatchard G. (1961) J. Am. Chem. Soc. **83**: 2636

[4] Scatchard G. (1943) In: Cohn E. J., Edsall, J. T. (eds.) Proteins, Aminoacids and Peptides as Ions and Dipolar Ions, Chap. 3. Reinhold, New York, U.S.A.

[5] Long F. A., McDevit W. F. (1952) Chem. Rev. **51**: 119–169

[6] Wu Y. C., Rush R. M., Scatchard G. (1968) J. Phys. Chem. **72**: 4048

[7] Pitzer K. S. (1973) J. Phys. Chem. **77**(2): 268

[8] C.R.C. Handbook of Chemistry (1976) CRC Press 1986–1987

[9] Pitzer K. S., Silvester L. F. (1976) J. Sol. Chem. **5**: 269

[10] Penedo F., Arce F. Unpublished results

[11] Linder P. W., Torrington R. G., Williams D. R. (1984) Analysis Using Glass Electrodes. Open University Press (1984)

[12] Braibanti A., Ostaroli G., Paoleti P., Pettit D., Sammartano S. (1987) Pure App. Chem. **12**: 1721

[13] Vacca A., Sabatini A. (1985) Miniquad y Miquv In: Legget D. J. (ed.) Computational Methods for the Determination of Formulation Constants. Plenum N.Y.

[14] Statistical Package SOLO. Distributed by BMDP Statistical Software Inc. Versión 03 8/88

[15] Albert A., Serjeant E. P. (1984) The Determination of Ionization Constants. Chapman and Hall, Cambridge

[16] Robinson R. A., Stokes R. H. (1959) Electrolyte Solutions. Butterworths, London

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