Research Article

Equilibrium constants from absolute hardness: the hydrolysis reactions of Li^+, Na^+ and K^+

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Abstract The present work is dedicated to explore the relations between the absolute hardness for the group 1 cations (Li^+, Na^+ and K^+) and their acidic (hydrolysis) properties in aqueous media. A series of empirical equations were derived, among them: $pK_a = -0.042\eta^+ + 15.078$ (η^+ is the cation absolute hardness, in eV and pK_a is the equilibrium constant for the hydrolysis of Li^+, Na^+ and K^+). It is shown that there are straightforward relationships involving the cation absolute hardness and the M-O distance, with reflections on their acidity, spectroscopic data and Jones-Dole coefficient.

Keywords Hydrolysis, group 1 cations, absolute hardness, Jones-Dole coefficient

Introduction

In aqueous solutions, many cations are able to promote the hydrolysis of molecules [1], making the medium acidic, as follows:

$$[M(H_2O)_n]^{z+} + H_2O \Leftrightarrow [M(H_2O)_{n-1}(OH)]^{(z-1)+} + H_3O^+ \qquad (1)$$

As recently shown [2] there is a straightforward relation between the absolute hardness (η) for a given cation and its interaction with water molecules, affecting, for example, the hydration enthalpy.

The present work is dedicated to explore the relations between the absolute hardness for group 1 cations (Li^+, Na^+ and K^+) and their acidic (hydrolysis) properties in aqueous media.

All employed auxiliary data are summarized in Table 1.

Table 1: Auxiliary data

Specie	η^+/eV	pK_a
$Li^+_{(g)}$	35.12	-
$Na^+_{(g)}$	21.08	-
$K^+_{(g)}$	13.64	-
$Li^+_{(aq)}$	-	13.6
$Na^+_{(aq)}$	-	14.2
$K^+_{(aq)}$	-	14.5

Methodology, Results and Discussion

When the pK_a values for the hydrolysis of Li^+, Na^+ and K^+ are plotted as function of the respective absolute hardness values (eV), the curve shown in Figure 1 is obtained, from which the following equation (r= 0.9999) is derived:

$$pK_a = -0.042\eta^+ + 15.078 \qquad (2)$$
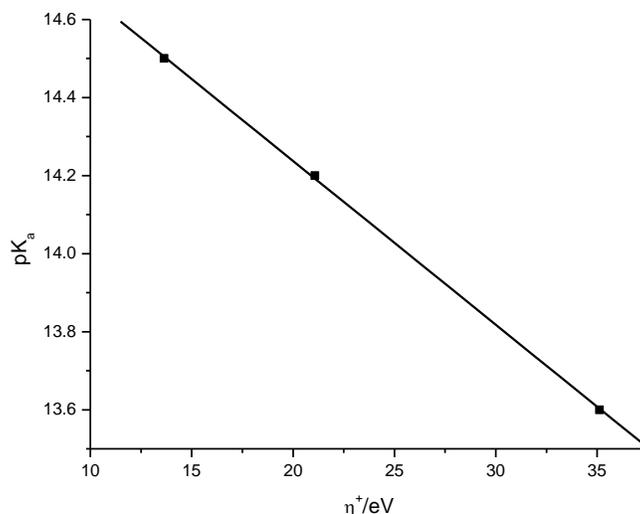
Figure 1: Hydrolysis constants (pK_a) as function of absolute hardness for Li^+, Na^+ and K^+.

Eq. (2) shows clearly that there are a straightforward relationship between acidic constants and absolute hardness for the considered cations. Of course, such relation shows that the chemical equilibrium expressed in Eq. (1) can be understood in terms of a chemical hardness equilibrium.

The number of water molecules in the coordination sphere increases form Li^+ to Cs^+ [3]. Whereas Li^+ is four coordinated, Na^+ and K^+ have six and eight water molecules in their coordination spheres [3]. The metal-oxygen (M-O) bond distances (pm) for $[Li(H_2O)_4]^+$, $[Na(H_2O)_6]^+$ and $[K(H_2O)_8]^+$ are 195, 243 and 284, respectively [3].When the pK_a values are plotted as function of the M-O distances, the curve shown in Figure 2 (r= 0.9895) is obtained, form which the following equation is derived:

$$pK_a = 0.010\ (d\text{M-O}) + 11.650 \tag{3}$$
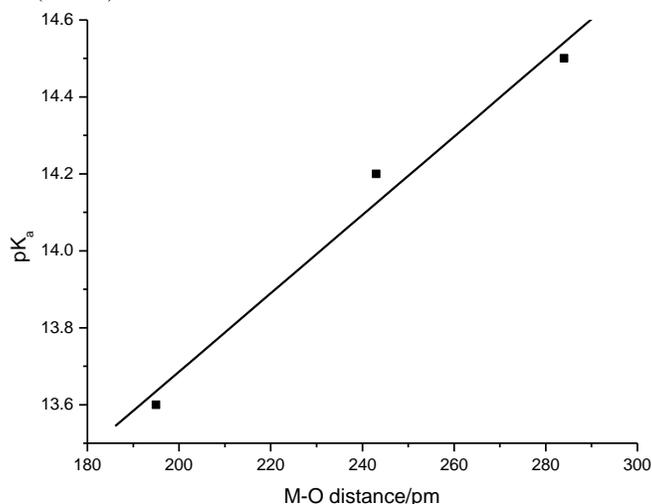
Figure 2: Hydrolysis constants (pK_a) as function of the M-O bond distance for $[Li(H_2O)_4]^+$, $[Na(H_2O)_6]^+$ and $[K(H_2O)_8]^+$.

Mähler and Persson [4] have studied the hydration of the alkali metal ions in aqueous solution by large angle X-ray scattering (LAXS) and double difference infrared spectroscopy (DDIR). If the pK_a values are plotted as function of the affected spectra peaks (cm^{-1}) obtained for $LiClO_4$, NaI and KI (aqueous media), respectively, 2626, 2566 and 2559 cm^{-1}, the curve shown in Figure 3 (r= 0.9717) is obtained, from which the following equation is derived:

$$pK_a = -0.012\ a + 45.340 \tag{4}$$

where *a* is the affected spectra (affected spectra extrapolated to infinite dilution) peak (cm^{-1}).
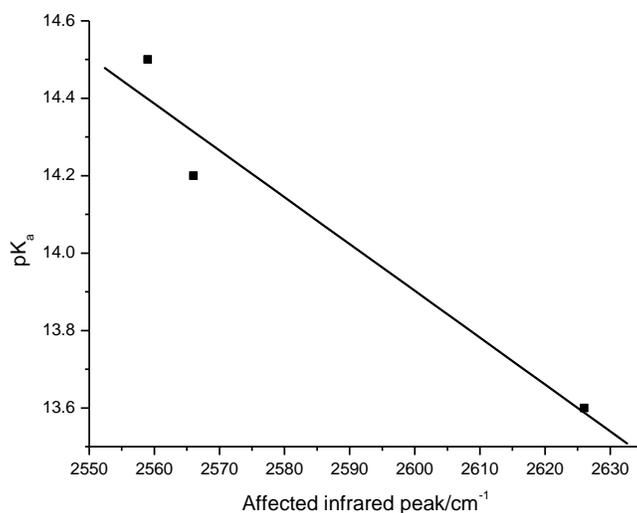
Figure 3: Hydrolysis constants (pK$_a$) as function of the affected spectra peaks (cm^{-1}) obtained for LiClO$_4$, NaI and KI (aqueous media)

Together, Eq. (2), (3) and (4) shows that there are straightforward relations involving the cation absolute hardness and the M-O distance, with reflections on their acidity and their experimental infrared spectra.

Of course, Eq.(2), (3) and (4) can be combined to obtain straightforward relation between the several parameters. For example, combining Eq. (2) and (4) and making the suitable algebraic manipulations, we obtain:

$$\eta^+ = (0.012\ a - 30.262)/0.042 \qquad (5)$$

Such equation, of course, relates η^+, a parameters calculated by using ionization energies with a, a parameter derived from experimental infrared data. Hence, it is stablished a straightforward relationship between an electronic parameter and an infrared one. In other words, a straightforward relation between UV-Vis and vibrational spectroscopy.

When the pK$_a$ values are plotted as function of the hydrated cations radius (pm): Li$^+$ (340), Na$^+$ (276) and K$^+$ (201) [8] the curve shown in Figure 4 (r= 0.9723) is obtained, from which the following equation is derived:

$$pK_a = -0.006r + 15.844 \qquad (6)$$

where r is the cation hydrated radius.

When the pK$_a$ values are plotted as function of the Jones-Dole parameter (dm^{3}mol^{-1}) for Li$^+$ (0.15), Na$^+$ (0.085) and K$^+$ (-0.007) [5] the curve shown in Figure 5 (r= 0.9585) is obtained, from which the following equation is derived:

$$pK_a = -5.568\ B + 14.526 \qquad (7)$$

where B is the Jones-Dole coefficient.
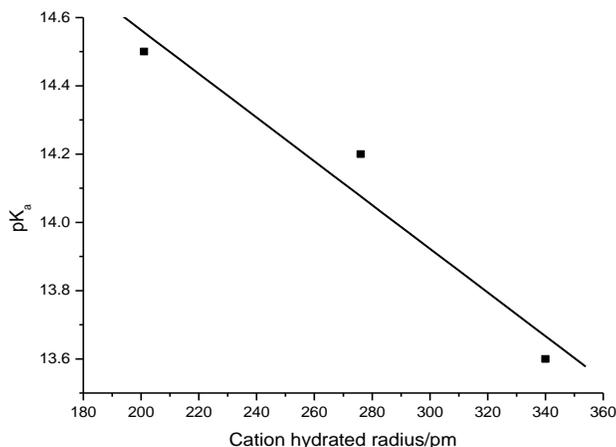
Figure 4: Hydrolysis constants (pK$_a$) as function of the cation hydrated radius for Li$^+$, Na$^+$ and K$^+$.
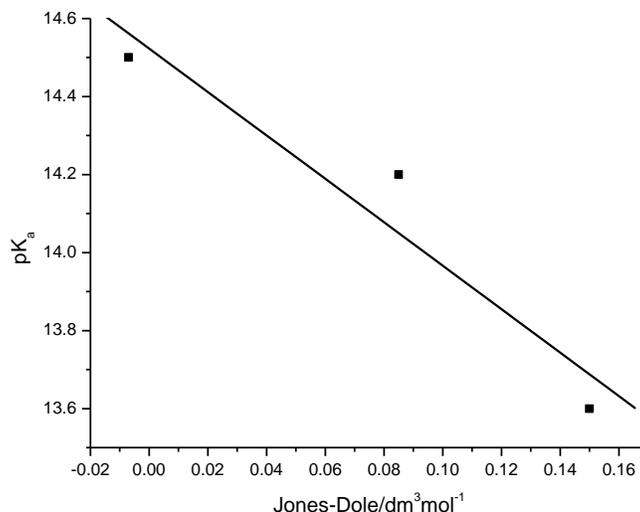
Figure 5: Hydrolysis constants (pK$_a$) as function of the cation Jones-Dole parameter for Li$^+$, Na$^+$ and K$^+$.

Eq. (7) shows that, besides the viscosity influences expressed by Jones-Dole coefficient, the acidic nature/force of the cations must be considered in their ability to permeate trough the a filtration membrane [5] (and, presumably, trough the cell membrane, in a biological system).

Combining Eq. (2) and (7), we have:

$$B = (0.042\eta^+ - 0.052)/5.568 \qquad (8)$$

Eq. (8) shows that cations with higher chemical absolute hardness will be the ones with higher Jones-Dole coefficient.

In Jones-Dole equation:

$$(\eta/\eta_o) = 1 + AC^{1/2} + BC \qquad (9)$$

η is the viscosity of the solution (at a fixed temperature and pressure), η_0 is the viscosity of the solvent at the same temperature and pressure, A is a coefficient that describes the impact of charge-charge interactions on the viscosity of a solution (it is usually positive) and can be calculated from Debye-Hückel theory; B is a coefficient that characterizes the solute-solvent interactions (at a defined temperature and pressure) and C is the solute concentration. Hence, in is clearly shown, by Eq.(9) that the absolute chemical hardness is closely related, in the hydrolysis process, with the cation-water interactions.

Using molecular simulations, the microscopic processes driving the Nuclear Magnetic Resonance (NMR) relaxation of quadrupolar cations in water have been investigated [6]. It was verified that the fluctuations of the Electric Field Gradient (EFG) experienced by alkaline and magnesium cations, which determine the NMR relaxation time, are mainly due to the dynamics of water molecules in their solvation shell.

When the pK$_a$ values are plotted as function of the spectral density at zero frequency of the external electric field gradient (10^{27} SI) for Li$^+$, Na$^+$ and K$^+$ aqueous ions with their normal masses: 9.37, 3.11 and 2.19, respectively [6] the curve shown in Figure 6 (r= 0.9585) is obtained, from which the following equation is derived:

$$pK_a = -0.115J + 14.660 \qquad (10)$$

A linear relationship is also obtained if the pK$_a$ values are plotted as function of the spectral density at zero frequency of the external electric field gradient for the aqueous ions with their infinitely heavy isotope, J$^\infty$: 12.9, 4.26 and 2.62, respectively [6].

Linear relationships are also verified between pK$_a$ and the characteristic times for the decay of the survival probability (S$_c$) (ps) and the reorientation (C$_{reor}$) of water molecules (ps) [6]. When pKa is plotted as a function of the characteristic time for the reorientation (C$_{reor}$) of water molecules, the curve shown in Figure 7 is obtained, from which the following equation is derived:

$$pK_a = -0.189C_{reor} + 16.214 \qquad (11)$$
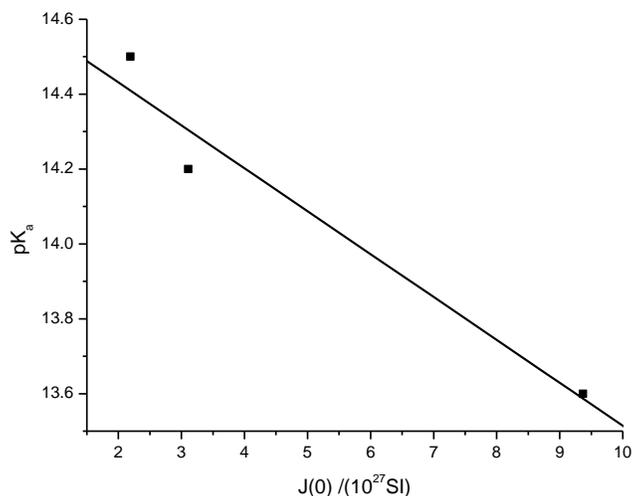
Figure 6: Hydrolysis constants (pKₐ) as function of the spectral density at zero frequency of the external electric field gradient for Li⁺, Na⁺ and K⁺.
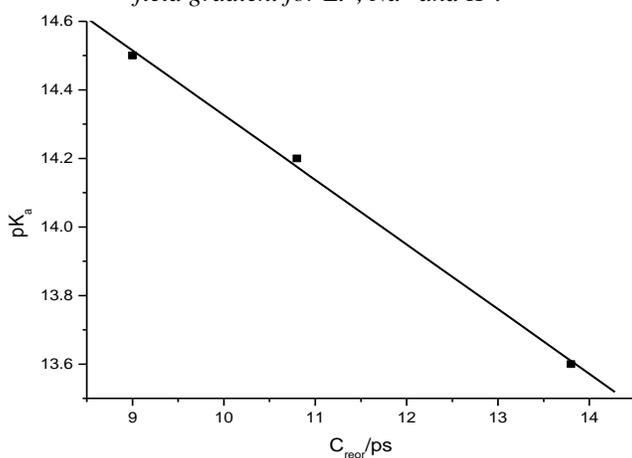
Figure 7: Hydrolysis constants (pKₐ) as function of the spectral density at zero frequency of the external electric field gradient for Li⁺, Na⁺ and K⁺.

Of course, Eq. (2)-(8) and (10,11) shows that all considered physicochemical parameters are very closed related with each other, and particularly related with pK_a and with the absolute hardness of the investigated ions. Presumably, analogous equation can be derived toother ions, including transition metal ones.

Of course, starting from Eq. (2)-(8) and (10,11), a series of another derived equations can be obtained, relating two or more parameters with each other. For example, if Eq.(2) and (11) are equated, we have:

$$C_{reor} = (0.042\eta^+ + 1.136)/0.189 \tag{12}$$

showing that the time (ps) required for the reorientation of water molecules will be greater for harder cations.

References

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