INTRINSIC PROTONATION CONSTANTS OF CHELATING ION EXCHANGE RESIN

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ABSTRACT The intrinsic protonation constants of three steps of chelating ion exchange resin D751 containing iminodiacetic groups in water and ethanol-water mixtures have been determined at 25°C by potentiometric titration and by means of the extrapolation procedure without the assumption on the activity coefficients of charged species in the resin phase. The changes in the acid-base properties of the chelating resin D751 in the water and the ethanol-water mixtures have been observed, and the observed effects are explained. The variation of apparent protonation constants with the degree of neutralization has been demonstrated.

Keywords: Chelating ion exchange resin, Apparent protonation constant, Intrinsic protonation constant, Ethanol-water mixture solvent

1 INTRODUCTION

In 1982, Szabadka^[1] derived the general equation which described the protonation equilibria of *N*-basic groups attached to an insoluble polymer matrix and found that the consecutive steps of protonation of iminodiacetic acid groups of chelating resin are well separated and can be considered as individual steps. Therefore, apparent protonation constant, $\log K_{a_i}$ were calculated from equation

$$\log K_{a_i} = \overline{\text{pH}} + \log \frac{4 - \alpha^* - i}{\alpha^* - 3 + i} \quad (i = 1, 2, 3) \quad (1)$$

where $\overline{\text{pH}} = -\log(\text{H}^+)$, (H^+) is the calculated proton activity, in the resin phase α^* is the real degree of titration, the values $\log K_{a_i}$ obtained were independent of α^* .

In 1990, the equation (1) was used to determine the protonation constants $\log K_{a_i}$

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of technical and of pure ion exchange resins containing iminodiacetic acid groups, and the constancy for the $\log K_{int}$ were substantiated by Huhn and Szabadka *et al* ^[2].

In 1985, Marinsky ^[3] theoretically treated the effect of ionic strength on measurable potentiometric properties of weakly acidic (basic) resin $\overline{HA}$ -simple neutral electrolyte MX system as a direct consequence of Donnan potential term, and the correction for this term leads to the resolution of intrinsic protonation constant of weakly acidic resins. In this theoretical treatment, the intrinsic protonation constant was defined by

$$\log K_{int} = \overline{pH} + \log \frac{1 - \alpha^*}{\alpha^*} - \log \overline{y}_{A-} \quad (2)$$

$$pH = -\log \overline{c}_H - \log \overline{y}_{H+}$$

where $\overline{c}_H$ denotes the concentration of H^+ in the resin phase, $\overline{y}_{A-}$ and $\overline{y}_{H+}$ are the activity coefficients of the designated species in the resin phase, the activity coefficient of associated HA was considered to be unity. Choosing the same standard state in both resin and external solution phases, the following relationship holds

$$p\overline{M} - pH = \overline{pM} - \overline{pH} + \frac{0.4343\pi}{RT} (V_H - V_M) \quad (3)$$

where $\overline{pM}$ is $-\log \overline{a}_{M+}$, pM is $-\log a_{M+}$ and $\overline{a}_{M+} = \overline{c}_{M+} \overline{y}_{M+}$, $\overline{y}_{M+}$ is the activity coefficient of M^+ in the resin phase, π is the osmotic pressure of the solvent in the resin phase, V is the partial molar volume. Since the $0.4343\pi/RT$ term is small enough to be neglected, the $\log K_{int}$ assumes the following form

$$\log K_{int} = pH - pM - \log \frac{\alpha^*}{1 - \alpha^*} - \log \overline{c}_{M+} - \log \overline{y}_{M+} - \log \overline{y}_{A-} \quad (4)$$

Providing that $\overline{y}_{M+} = \overline{y}_{H+}$, Eq. (4) can thus be rewritten as

$$\begin{aligned} \log K^{app} &= \log K_{int} + \log \overline{y}_{H+} + \log \overline{y}_{A-} \\ &= pH - \log \frac{\alpha^*}{1 - \alpha^*} - pM - \log \overline{c}_{M+} = \overline{pH} - \log \frac{\alpha^*}{1 - \alpha^*} \end{aligned} \quad (5)$$

A plot of the sum of the terms on the right hand side of Eq. (5) as a function of α^* should yield an intercept value of ordinate at $\alpha^* = 0$, the $\log K_{int}$ therefore can be obtained by means of the extrapolation procedure since both $\overline{y}_{H+}$ and $\overline{y}_{A-}$ approach unity as α^* approaches zero. This extrapolation procedure is reasonable and unquestionable, but there is no experimental evidence to support the assumption that $\overline{y}_{M+} = \overline{y}_{H+}$ in any cation exchange system, and there is also no experimental evidence to support the assumption that $\overline{y}_{X-} = \overline{y}_{OH-}$ in any anion exchange system. $\overline{y}_{X-}$ and $\overline{y}_{OH-}$ are the activity coefficients of the small anion X^- and hydroxyl OH^- in resin phase respectively. Thus the applicability of this extrapolation procedure deserves further consideration.

As a matter of fact, this assumption $\bar{y}_{M+} = \bar{y}_{H+}$ in cation exchange system or $\bar{y}_{X-} = \bar{y}_{OH-}$ in anion exchange system is not necessary for this extrapolation procedure. The $\log K_{i, n, i}$ can be obtained by means of the extrapolation procedure just the same as long as the $\bar{y}_{M+}$ and $\bar{y}_{A-}$ approach unity as α approaches zero. If $\bar{y}_{H+} \neq \bar{y}_{M+}$ (or $\bar{y}_{X-} \neq \bar{y}_{OH-}$), the right hand side of Eq (5) is merely not equal to $\log K^{a, p}$.

In addition, the constancy for the $\log K_{a, i}$ of every step of protonation of iminodiacetic acid groups attached to a matrix is questionable^[1, 2], since the variation of the $\log K_{a, 1}$ and $\log K_{a, 2}$ with the degree of titration was observed by Leyden and Underwood^[4] and it is not consistent with the "polyelectrolyte effect"

In view of the fact mentioned above, the aim of the present paper is to test the validity of the extrapolation procedure without the assumption $\bar{y}_{M+} = \bar{y}_{H+}$ or $\bar{y}_{X-} = \bar{y}_{OH-}$, and the validity of the constancy for the apparent protonation constant, $pK_{a, i}$. In the first two protonation steps of the iminodiacetic acid groups, the chelating ion exchange resin acts as a cation exchanger, while in the third step, the chelating resin acts as an anion exchange resin. That is why the chelating ion exchange resin D751 containing iminodiacetic acid groups was chosen from the various kinds of ion exchange resin.

2 EXPERIMENTAL

The macroporous chelating resin, D751 was obtained from Shanghai Resin Factory in Na form as 0.5 mm to 0.63mm beads. After the resin was treated and converted into the neutral zwitterion form in a regular way, it was put in a shallow glass dish which was then placed inside a desiccator over the saturated NaCl solution until a constant weight was reached. The desiccator was placed in an air thermostat ($25 \pm 2^\circ\text{C}$).

The dry weight of the resin was determined by heating aliquot portions of the moist resin to a constant weight at 105°C . The weight capacity of this resin was determined by adding standard alkali to a weighted quantity of the resin and back titrating the excess alkali, and it was given as $Q = 2.81 \pm 0.02 \text{ mmol}$ of active group per g of dry zwitterion form resin.

To study the deprotonation and protonation of the resin, a batch method^[5] was used to ensure that the full equilibration was reached. Known masses of the resin samples were weighted into 50ml glass-stoppered flasks. For the study of deprotonation, increasing amounts of potassium or sodium hydroxide were added to the samples, the ionic strength and the 50ml final volume were adjusted by adding a calculated quantity of water and ethanol, and a concentrated solution of potassium or sodium chlorides. For the study of protonation, the procedure was the same except that alkali was replaced by hydrochloric acid. The systems were shaken for 7 days at 25°C .

After equilibration, the pH of the solution phase was measured as rapidly as possible by using a Model PXSJ-216 Ion Analysis Meter (Shanghai Rex Instruments

Factory) and Model 231 glass electrode. The sensitivity of the meter was 0.001 pH unit and the reproducibility of the data was 0.002 pH unit. After the pH measurement, the resin phase was separated from the solution by filtration and dried to a constant weight at 105°C. The solvent content was calculated with reference to lg of the neutral dry resin. After the determination of solvent content, the resin was transferred to a small glass column, and the invasive potassium or sodium chloride was eluted with water and collected in a standard flask. The amount of the invasive electrolyte was obtained from a Mohrs chloride determination. Then the chemically bound cation or anion was eluted from the resin with a known amount of standard acid or alkali and collected in a standard flask. Finally the amount of chemically bound cation or anion was obtained by titration of the acid or alkali left in the solution.

3 RESULTS AND DISCUSSION

The titration curves of the chelating resin in water and in ethanol--water binary mixtures at different ionic strength (I) were obtained and have two inflection points. The $\overline{G}_K$, amount of chemically bound potassium (sodium) and chloride ions, the $\overline{G}_I$, amount of electrolyte (NaCl or KCl) invading the resin phase from external solutions (in mmol per g of resin) and the $\overline{H_2O}$ and $\overline{Solv}$, water content and ethanol--water content (in g per g of resin) were determined respectively. From the $\overline{G}_K$, $\overline{G}_I$ and $\overline{H_2O}$ or $\overline{Solv}$, the (G) , concentration of counter ions in imbibed water or ethanol--water solvent in resin phase (in mmol per g) was calculated by

$$(G) = \frac{\overline{G}_K + \overline{G}_I}{\overline{H_2O} \text{ (or } \overline{Solv})} \quad (6)$$

The proton activity in the resin phase, (H^+) was calculated by

$$(H^+) = [H^+] \left(\frac{(G)}{a_G} \right)^{\pm 1} \quad (7)$$

where $[H^+]$ and a_G are the activities of the proton and the counter-ions in the external solution phase, the sign of the exponent is positive when the counter-ion is a cation, and negative when the counter-ion is an anion. The a_G was given as $a_G = m_G \gamma_G$, m_G is the molality and γ_G is the activity coefficient, the γ_G in the water was obtained from the literature [5], and γ_G in the ethanol--water mixtures was calculated by using Debye-Huckel equation [6] to the first approximation.

From the charge and mass balance equations, the real degree of titration in the resin, α^* can be calculated by

$$\alpha^* = 1 \pm \frac{\overline{G}_K}{Q} + \frac{(H^+) - (OH^-)}{Q/\overline{H_2O} \text{ (or } \overline{Solv})} \quad (8)$$

In equation (8), the remarks apply for the $\pm$ sign as for equation (7). From a large number of data of $\overline{pH}$ and α^* , the apparent protonation constants of the three

steps can be obtained by Eq. (1). The plots of $\log K_{ai}$ against $\bar{\alpha}^*$ are shown in the Figs. 1, 2 and 3

As can be seen from the Fig. 1, in the aqueous solution, all three $\log K_{ai}$ show a definite tendency to increase with increasing real degree of titration $\bar{\alpha}^*$. This inconstancy of $\log K_{ai}$ with the degree of neutralization has been observed with other ion exchange resins [4, 7, 8].

All the $\log K_{ai}$ values obtained with two different concentration of KCl fall on a single straight line, though the $\text{pH} + \log(3 - \bar{\alpha}^*) / (\bar{\alpha}^* - 2)$ and $\text{pH} + \log(2 - \bar{\alpha}^*) / (\bar{\alpha}^* - 1)$ points at higher ionic strength, fall on a lower single straight line and those at lower ionic strength

Fig. 1 Variation of the calculated $\log K_{ai}$ values as a function of the real degree of titration $\bar{\alpha}^*$ (water). $I = 0.0$ —○, $I = 1.0$ —●

Fig. 2 Variation of the calculated $\log K_{ai}$ values as a function of the real degree of titration $\bar{\alpha}^*$ (50% (v/v) ethanol-water), $I = 0.3$ —○, $I = 0.4$ —●

Fig. 3 Variation of the calculated $\log K_{ai}$ values as a function of the real degree of titration $\bar{\alpha}^*$ (72% (v/v) ethanol-water), $I = 0.2$ —○, $I = 0.3$ —●

fall on an upper one respectively, while the $\text{pH} + (1 - \bar{\alpha}^*) / \bar{\alpha}^*$ points at two different ionic strengths fall on two single lines with reverse positions. These results are in quantitative accord with the prediction of the Donnan model and provide strong confirmation of the validity of the Donnan model of ion exchange system. [3]

As can be seen from Figs. 2 and 3, the plots of $\log K_{ai}$ vs. $\bar{\alpha}^*$ in the 50% and 72% (v/v) ethanol-water mixtures are essentially similar to those in the aqueous solution. Compared with Fig. 1, these $\log K_{ai}$ vs. $\bar{\alpha}^*$ straight lines in various sol-

vents differ in their slopes and positions. The more water the solvent contains, the steeper all plots $\log K_{a1}$ vs. $\bar{\alpha}^*$ become. The more water the solvent contains, the higher the plots $\log K_{a2}$ vs. $\bar{\alpha}^*$ and $\log K_{a3}$ vs. $\bar{\alpha}^*$ become, on the contrary, the lower the plots $\log K_{a1}$ vs. $\bar{\alpha}^*$ become. These results imply that the more water the solvent contains, the more flexible the chelating resin D751 becomes, the less acidic the carboxyl group of D751 becomes, and the less basic the amine group of the resin D751 becomes.

The straight lines $\log K_{a2}$ vs. $\bar{\alpha}^*$ and $\log K_{a3}$ vs. $\bar{\alpha}^*$ should thus yield the intercept values of the ordinate at $\bar{\alpha}^* = 1$ by means of extrapolation procedure, and the intercept values can be unambiguously identified with intrinsic protonation constants $\log K_{int2}$ and $\log K_{int3}$, since the resin phase becomes neutral and the activity coefficients of charged species becomes unity at $\bar{\alpha}^* = 1$.

The straight lines $\log K_{a1}$ vs. $\bar{\alpha}^*$ should also yield the intercept values of the ordinate at $\bar{\alpha}^* = 2$, but whether these values can be unambiguously identified with intrinsic protonation constants $\log K_{int1}$ is still a question since the resin phase does not become neutral and the active group of chelating resin carries one negative charge. However, the reliability of these intrinsic protonation constants $\log K_{int1}$ is supported by the facts that the straight lines of $\log K_{a1}$ vs. $\bar{\alpha}^*$ at two different ionic strengths coincide either in the water or in the ethanol-water mixtures and that the $\log K_{int1}$ value in the aqueous solution is in agreement with the 8.88^[9] of *N*-benzylimidodiacetic acid (BIMDA). The $\log K_{int, i}$ values are given in Table 1.

Table 1 Intrinsic Protonation Constant

	Water	50% (v/v) ethanol-water	72% (v/v) ethanol-water
K_{int1}	8.95	7.22	7.22
K_{int2}	3.26	2.81	2.60
K_{int3}	1.94	2.40	2.72

The protonation constant of active groups of the chelating ion exchange resin depends on the dielectric constant and the proton affinity of the solvent. Since there is a good reason to believe that the proton in the ethanol-water mixtures is hydrated at least to H_3O^{+} ^[10], the effect of the water and the various ethanol-water mixtures depends only on the dielectric constant. As shown in Table 2, increasing the proportion of ethanol in solvents lowers the dielectric constant thus favouring the formation of $-COO^- \cdots M^+$ ion pairs and the removal of a proton from $-COOH$, thus the $\log K_{int,1}$ and $\log K_{int,2}$ decrease^[11]. On the other hand, the association between acid and base probably occurs by hydrogen bonding^[10] and the more ethanol the solvent contains, the more association occurs and $\log K_{int,3}$ thus increases with increasing the proportion of ethanol in the solvent. Nevertheless it is still a question that whether or not these $\log K_{int, i}$ can be unambiguously identified with intrinsic protonation constants.

tant since the resin phase does not become neutral and the active group of chelating resin carries one negative charge at $\bar{\alpha}^* = 2$

4 CONCLUSIONS

(1) The intrinsic protonation constants of the three steps of the chelating ion exchange resin D751 in the water and in the 50% and 72% (v/v) ethanol-water mixtures at 25°C have been determined.

(2) The extrapolation procedure for evaluation of the intrinsic protonation constant proposed by Marinsky has been discussed, and it is pointed out that the assumption on the value of activity coefficients of the charged species is not necessary

(3) The more water the solvent contains, the less acidic the carboxyl group, and less basic the amine group of D751 become. The observed effects of solvent are explained

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整合离子交换树脂的本征质子化常数

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摘要 在 25°C, 分别在水及乙醇-水混合溶剂中, 用电位滴定法研究了国产的含有胺亚二乙酸功能基的大孔整合树脂 D751 的质子化反应. 在对树脂相中各组分的活度系数不作任何假定的前提下, 用外推法从表观质子化常数的对数值与滴定度间的关系, 求得了该树脂的三级本征质子化常数. 本文肯定了表观质子化常数对滴定度的依赖性, 合理地解释了在不同溶剂中树脂的酸碱性的变化.

关键词: 整合离子交换树脂 表观质子化常数 本征质子化常数 水-乙醇混合溶剂