in aqueous solution, and many attempts have been made to interpret the corresponding enthalpies and entropies. However, all the theories proposed to explain the stepwise protonation enthalpies of polyamines [1, 2] account poorly for the successive protonation enthalpies in several cases [3].

The protonation reaction of an amine group in water can be formally divided in different processes

$$R–NH_{2(aq)} + H^+_{(aq)} \rightleftarrows R–NH^+_{3(aq)}$$

involving a solvation (or desolvation) enthalpy or a bond formation enthalpy. The desolvation of the proton is not explicitly included since it is a constant for all the studied reactions. The bond formation enthalpy (E_B) is connected with the formation of the N–H$^+$ bond for the insulated amine and its value is proportional to the N and H charges [3]. As concerns the solvation enthlapy (E_S) we use a continuous model of the solvent and consider only the electrostatic contribution since the studied compounds are highly polar. In this model the solvation enthalpy reads:

$$E_S = \frac{1-\epsilon_o}{\epsilon_o}\left(\sum_i \frac{Q_i}{2R_i} + \sum_{i<j} \frac{Q_iQ_j}{R_{ij}}\right)$$

where R_i is the 'effective' radius of atom i, Q_i its charge and R_{ij} the distance between the atoms i and j [4]. Figure 1 presents a plot of $\Delta H^o_{calc} = E_B + E_S$ *versus* ΔH^o_{exp} for several diamines. Despite the crudeness of the computational method the correlation is very good. As a second step we performed a conformational analysis: the results indicate that first protonation leads to more folded conformations with respect to neutral molecules, while the second protonation leads to very rigid full extended conformations.

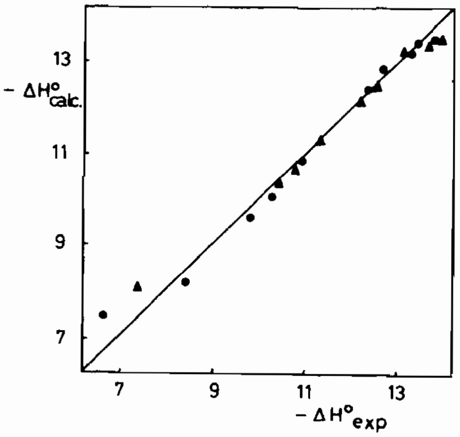

Fig. 1. Comparison between calculated and experimental-enthalpies of protonation of diamines (kcal mol^{-1}). ▲, first protonation; ●, second protonation.

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Thermodynamic Studies on the Protonation and Complex Formation of New Tertiary Amino Polymers in Aqueous Solution

LEONE OLIVA, ROLANDO BARBUCCI, VINCENZO BARONE
Istituto Chimico, via Mezzocannone 4, 80134 Naples, Italy

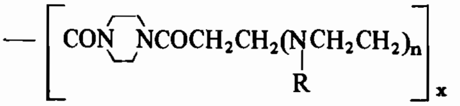
and PAOLO FERRUTI
Facoltà di Chimica Industriale, Università di Bologna, Italy

In previous studies we have found that polymers having a poly(amido–amine) structure show interesting properties in aqueous solution as far as their protonation and complex formation are concerned [1–4]. We thought it interesting to study a second class of poly(amido–amines) with enitrely linear macromolecular chains. The structures of the polymers are reported in Fig. 1 together with the protonation and stability constants of the second class of poly(amido–amines).

The new polymers have been synthesized by polyaddition of pyperazine and NN'-dimethylethylenediamine to NN'-diacriloyl NN'-diethylethylenediamine (polymers I and II) or divinylsulphone (polymer III). Also in the case of these new polymers on the contrary to most polyelectrolytes 'sharp' basicity constants have been obtained. The results for polymers I and II are very close to those of the corresponding polymers of the first class: this means that the presence of a ring structure in the main chain is irrelevant with respect to protonation. Also for polymer III 'sharp' constants have been obtained despite the short distance between basic nitrogens of different monomeric units; these constants are very low. A close similarity exists also between the stability constants of both classes of polymers.

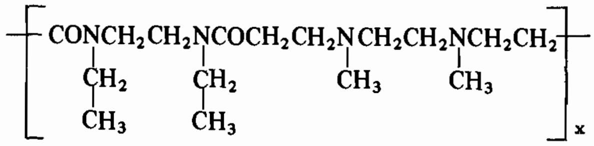
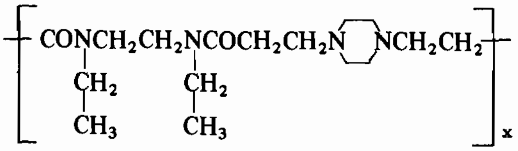
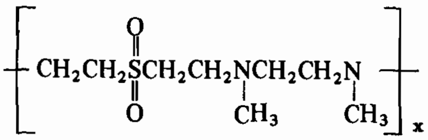
A Cu^{2+} complex may be formed in aqueous solution also with polymer III. The stability constant of this complex, however, is much lower than that with polymer I.

first class



n = 1,2,3
R = $-CH_3$ or
$-CH_2CH_2N(CH_3)_2$

second class

		HL	H_2L	CuL
I		8.09	4.53	8.72
II		6.94	3.08	–
III		6.30	2.34	3.93

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Formation des Isopolycomplexes Hydroxylés et Carbonatés de l'Ion Uranyle, en Solution Aqueuse

J. HURWIC, N. K. PONGI et G. DOUBLE

Laboratoire de Diélectrochimie, Université de Provence, 3, place Victor-Hugo, F-13331 Marseille Cedex 3, France

L'utilisation d'un programmateur électromécanique pour réactions liquide–liquide [1] nous a permis de reprendre l'étude de l'hydrolyse de l'ion uranyle par les bases fortes: nous avons ainsi vérifié et complété les nombreux résultats, souvent divergents, rencontrés dans la littérature.

Nous avons effectué une série de titrages potentiométriques (15 s à plusieurs heures entre deux ajouts de réactif titrant) de solutions de nitrate d'uranyle (0.00012 *M* à 0.1 *M*) par de l'hydroxide de sodium (1 *M*) en présence de $NaNO_3$ *0.2 M* comme sel de fond. Sur le réseau obtenu, les courbes de concentrations supérieures à 0.001 *M* se coupent au point isohydrique [2] situé au pH = 7.8 et correspondant au rapport molaire Na/U = 2.33. En ce point, l'espèce isopolycondensée, prépondérante et la plus probable, est $(UO_2)_3(OH)_7^-$, qui implique un rapport OH/U = 2.33. Les autres espèces formées en milieu acide et provenant de la précédente, sont: $(UO_2)_3(OH)_6$, $(UO_2)_3(OH)_5^+$, $(UO_2)_3(OH)_4^{2+}$ et $(UO_2)_2(OH)_2^{2+}$. Le mécanisme réactionnel peut être résumé comme suit. Le cation $UO_2\cdot aq^{2+}$ résultant de l'ionisation dans l'eau des sels d'uranyle est un acide qui subit la dissociation au cours de l'alcalinisation:

$$UO_2\cdot aq^{2+} \rightleftarrows UO_2OH\cdot aq^+ + H^+.$$

La polymérisation résultant de la formation probable de liaisons coordinatives par les groupements hydroxyles est favorisée par l'alcalinisation. Ainsi l'ajout ultérieur d'ions OH^- entraîne-t-il la dimérisation du cation formé:

$$2UO_2OH\cdot aq^+ \rightleftarrows (UO_2)_2(OH)_2\cdot aq^{2+}.$$

Par association avec le cation libre non dissocié, le dimère donne le trimère:

$$(UO_2)_2(OH)_2\cdot aq^{2+} + UO_2\cdot aq^{2+} \rightleftarrows (UO_2)_3(OH)_2\cdot aq^{4+}$$