For the above reasons we thought it useful to study systematically the complexes of alkali-metal ions with carboxylic and hydroxycarboxylic acids. The formation constants have been determined potentiometrically by alkalimetric titrations of the acids using KNO_3, $NaNO_3$, $NaClO_4$, $LiNO_3$, $CsNO_3$ and tetraethylammonium bromide as background in the concentration range 0.03–1.0 mol dm^{-3} at 25° and 37 °C. Citrate, tartrate, malate, oxalate, malonate, phthalate and succinate ligands were investigated. The potentiometric data have been analyzed by using modified versions of ACBA [2] and MINIQUAD [3] least squares computer programs.

All the ligands considered form complexes with alkali-metal ions and the stability constants show the trends citrate > tartrate > malate and oxalate > malonate ~ phthalate > succinate for hydroxycarboxylic and carboxylic acids respectively. As regards the metal ion the trend is Li > Na > K > Cs. The hydroxycarboxylic acids form protonated species too.

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Mixed Metal Complexes in Solution. Thermodynamic Study of Heterobinuclear Metal(II)–Citrate Complexes in Aqueous Solution

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Though the formation of mixed ligand ternary complexes is well known in the literature, the study in solution of mixed metal complexes having one ligand and two different metal ions has been very little developed. The formation of this type of ternary species might explain a number of apparently anomalous data and some interferences in analytical procedures.

We have previously reported the stability constants of heterobinuclear copper(II)–L-histidinate complexes with nickel(II), zinc(II) or cadmium(II) in aqueous solution [1]. Such mixed metal complexes are formed by another imidazole derivative too [2]. Now we are extending our investigation to another set of ligands, namely hydroxypolycarboxylic acids, widely used as buffers, which are of relevant importance in the analytical field and also in biofluids. In this work we report the thermodynamic parameters for the formation of heterobinuclear complexes of citrate (cit^{3-}) with Cu(II)–Ni(II), Ni(II)–Zn(II), Cu(II)–Zn(II) ion couples, determined in aqueous solution at 25 °C and 0.1 mol dm^{-3} ($K[NO_3]$). The alkalimetric titration curves of solutions containing citric acid and two different metal ions exhibit two buffer regions, one in the acidic and the other in the neutral–alkaline range. By comparing the experimental curves with those calculated taking into account only the binary species, the existence of heterobinuclear complexes in the acidic region was excluded, whilst it was strongly evident in the neutral–alkaline region. The species present in the latter pH range, when considering the binary systems, are of the type $[M_2(cit)_2H_{-2}]^{4-}$, (M = Cu(II), Ni(II) or Zn(II)); graphical analysis and computer calculations showed the presence of the $[MM'(cit)_2H_{-2}]^{4-}$ for each couple of metal considered. The stability constants corresponding to the equilibrium: $M^{2+} + M'^{2+} + 2\ cit^{3-} \rightleftarrows [MM'(cit)_2H_{-2}]^{+}\ 2H^{+}$ are:

Cu(II)–Ni(II)	$\log\beta = 1.55 \pm 0.05$
Ni(II)–Zn(II)	$\log\beta = -2.92 \pm 0.08$
Cu(II)–Zn(II)	$\log\beta = 1.51 \pm 0.11$

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Theoretical Studies on the Protonation of Diamines in Aqueous Solution

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A considerable amount of thermodynamic work has been carried out on protonation of polyamines 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.

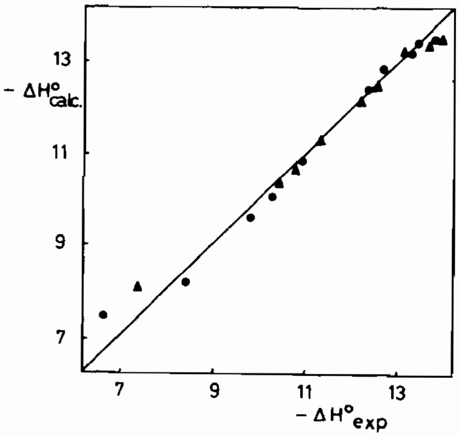

Fig. 1. Comparison between calculated and experimental enthalpies of protonation of diamines (kcal mol^{-1}). ▲, first protonation; ●, second protonation.

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

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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.