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