CrossMark

Potentiometric studies on ternary complexes involving some divalent transition metal ions, gallic acid and biologically abundant aliphatic dicarboxylic acids in aqueous solutions

Abdelatty Mohamed Radalla

Department of Chemistry, Faculty of Science, Beni-Suef University, Beni-Suef 62111, Egypt

ARTICLE INFO

ABSTRACT

Formation of binary and ternary complexes of the divalent transition metal ions, Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} with gallic acid and the biologically important aliphatic dicarboxylic acids (adipic, succinic, malic, malonic, maleic, tartaric and oxalic acids) were investigated by means of the potentiometric technique at 25 °C and $I = 0.10$ mol dm^{-3} NaNO$_3$. The acid-base properties of the ligands were investigated and discussed. The acidity constants of gallic acid and aliphatic dicarboxylic acids were determined and used for determining the stability constants of the binary and ternary complexes formed in the aqueous medium under the above experimental conditions. The formation of the different 1:1 and 1:2 binary complexes and 1:1:1 ternary complexes are inferred from the corresponding potentiometric pH-metric titration curves. The ternary complex formation was found to occur in a stepwise manner. The stability constants of these binary and ternary systems were calculated. The values of Δ log K, percentage of relative stabilization (%R.S.) and log X were evaluated and discussed. The concentration distribution of the various complex species formed in solution was evaluated and discussed. The mode of chelation of ternary complexes formed was ascertained by conductivity measurements.

1. Introduction

Gallic acid is commonly used in the pharmaceutical industry because many in vivo and in vitro studies in humans, animals, and cell culture have provided evidence for cytotoxicity against cancer cells, without harming healthy cells (Elvira et al., 2006). Gallic acid exists in two forms as the free molecule and as part of tannins. Pure gallic acid is a colorless crystalline organic powder. Green tea is the most abundant source of tea phenolics, mostly in the form of simple hydroxybenzoic acids and propyl gallate and its catechin derivatives (epigallocatechin-3-gallate, epigallocatechin, epicatechin-3-gallate, and epicatechin). One of the most common moieties in the structure of tea phenolics, besides hydroxyl groups, is the gallic acid moiety. Green tea catechins and phenolic acids have been shown to demonstrate profound biochemical and pharmacological activities including

---

antioxidant activities, modulation of carcinogen metabolism, and inhibition of cell proliferation (Barbosa, 2007; Chiu-Lan et al., 2007; Cook et al., 1995; Hurrell et al., 1999; Jittawan and Sirithon, 2008; Kuroda and Hara, 1999; Min et al., 2002; Misao et al., 2007; Rajalakshmi and Narasimban, 1996). Extracts derived from green tea have the potential to reduce the oxidation of food products and extend their shelf life. The antioxidant action was shown to be dependent on the ability of their constituent phenolic compounds to scavenge free radicals and to chelate and the metal ion chelating ability of polyphenols is related to the presence of *ortho*-dihydroxy polyphenols, i.e., molecules bearing catechol or galloyl groups metals (Moran et al., 1997; Morck et al., 1983). Coordination of metal ions by gallic acid may be desirable in view of potential clinical significance (Ziano and Roberts, 1977). Aliphatic carboxylic acids are biologically abundant and important and versatile binding ligands (Inezedy, 1976).

As a continuation of our research program oriented to study the binary and ternary complexes of biologically active ligands (Radalla, 2010; Radalla and Khalil, 1998; Radalla et al., 1997, 2009a, 2009b, 2009c, 2013, 2014), the formation of binary and ternary complexes of the divalent transition metal ions, Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} with gallic acid and the biologically important aliphatic dicarboxylic acids (adipic, succinic, malic, malonic, maleic, tartaric and oxalic acids) was investigated by means of the potentiometric and conductometric techniques at 25 °C and $I = 0.10$ mol dm-3 NaNO$_3$. The mode of chelation of ternary complexes formed was ascertained by conductometric measurements.

2. Experimental section

2.1. *Materials and solutions*

The gallic acid used in this study was a commercially available chemical (TCI Co., LTD, Tokyo, Japan) and used without further purification. Aliphatic dicarboxylic acids were analytical-grade (Aldrich or Merck) products. The purity of these compounds and the concentrations of the stock solutions were determined by Gran's method (Gran, 1952). The metal salts were provided by BDH as nitrates or chlorides. Stock solutions of the metal salts were prepared in deionized water, and the metal ion concentrations were determined complexometrically using EDTA and suitable indicators (Welcher, 1965). Carbonate-free sodium hydroxide (titrant, prepared in 0.10 mol dm^{-3} NaNO$_3$ solutions) was standardized potentiometrically with KH phthalate (Merck AG). A nitric acid solution (≈ 0.016 mol dm^{-3}) was prepared and used after standardization. Sodium hydroxide, nitric acid, and sodium nitrate were from Merck p.a.

2.2. *Apparatus and procedure*

Potentiometric *pH*-metric titrations were performed using a Metrohm 702 SM automatic titrator equipped with a 665 dosimat, combined glass electrode and magnetic stirrer (Switzerland). The precision of the instrument was (±0.001) *pH* unit. The *pH* titrations were carried out in an 80 cm^3 commercial double-walled glass vessel. The ionic strength of the

solutions is maintained at a constant level by using the desired concentration of NaNO$_3$ solution as supporting electrolyte. Generally, the titrated solutions were thermostated at a constant temperature and the temperature was adjusted inside the cell at the desired temperature, by circulating water using a water-thermostat set up. The calibration of the electrode system was carried out by means of a strong acid (base)/strong base (acid) titration under the same temperature and ionic strength used in the investigation. A computer program (GLEE, glass electrode evaluation (Gans and O'Sullivan, 2000) has been used to calibrate the glass electrode by means of a strong acid-strong base titration under the same temperature and ionic strength used in the investigation. This program provides an estimate of the carbonate contamination of the base, the pseudo-Nernstian standard potential and slope of the electrode, and optionally, the concentration of the base and pK$_w$. The autoprotolysis of water ($2H_2O = H_3O^+ + OH^-$, K_w) at 25 °C and ionic strength of 0.1 mol dm^{-3} of NaNO$_3$ were ($1.05 \times 10^{-14} \pm 1.01 \times 10^{-16}$ or pK$_w$ = 13.97 ± 0.01), ($1.05 \times 10^{-14} \pm 1.02 \times 10^{-16}$ or pK$_w$ = 13.98 ± 0.01) and ($1.04 \times 10^{-14} \pm 1.0 \times 10^{-16}$ or pK$_w$ = 13.99 ± 0.01) which averaged to ($1.06 \times 10^{-14} \pm 1.00 \times 10^{-16}$ or pK$_w$ = 13.97 ± 0.02). The combination electrode involves the use of a 3 M KCl salt bridge between the internal reference and the external solution. This salt bridge reduces the 4junction potential, but it does not become zero (Longhi et al., 1990). This potential varies from one solution to another, and this variability increases the uncertainty of the measured pH with respect to that obtained by the other methods. For this reason, the reported accuracy cannot be better than (0.02 pH/pKa units).

The investigated solutions were prepared (total volume 50 cm^3) and titrated potentiometrically against standard CO$_2$-free NaOH (0.20 mol dm^{-3}) solution. A stream of nitrogen was passed throughout the course of the experiment in order to exclude the adverse effect of atmospheric carbon dioxide. Magnetic stirring was used during all titrations. The ligand concentrations were varied in the range $1\cdot10^{-3}$—$6\cdot10^{-3}$ mol dm^{-3}. Three to four different metal-to-ligand ratios for binary systems and 1:1:1 and 1:2:2 (metal: primary ligand: secondary ligand) ratios for the ternary systems were used in the investigation. The initial estimates of the ionization constants of the ligands and the stability constants of binary and ternary complexes were calculated by adopting *Irving* and Rossotti technique (Irving and Rossotti, 1953, 1954). Part of information required for determining the metal complex stability constants is the acid dissociation constant (pKa). Therefore, the pKa values were calculated from Eq. (1) where β is the proton-ligand formation constant of the ligand and ^n_H is the average number of protons associated per mole of ligand at several *pH* values.

$$\overline{n}_H = \beta\left[H^+\right]\left(1 + \beta\left[H^+\right]\right)^{-1} \tag{1}$$

Eq. (2) was used for calculation of the ^n_H values from the titration curves corresponding to solutions 1, 2, and 4, where y is the number of dissociable protons (y = 2 in case of all ligands studied).

$$\overline{n}_H = \left\{ yC_L + \frac{[(V_a - V_b) or (V_a - V_d)]C_b}{V_o} \right\}(C_L)^{-1} \tag{2}$$