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Activity coefficients, acid–base properties and weak Na^+ ion pair formation of some resorcinol derivatives

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ABSTRACT

Setschenow coefficients of resorcinol (1,3-benzenediol), 2-methylresorcinol (2-methyl-1,3-benzenediol) and 4-chlororesorcinol (4-chloro-1,3-benzenediol) were determined in $NaCl_{(aq)}$ (0–3 mol L^{-1}) at 25 °C by distribution (2-methyl-1-propanol/water) measurements. Moreover, the protonation constants in $NaCl_{(aq)}$ and in $Me_4NCl_{(aq)}$ were determined potentiometrically, at different salt concentrations (0–3 mol L^{-1}). The dependence on ionic strength of the protonation constants was modelled by Debye-Hückel, SIT (Specific ion Interaction Theory) and Pitzer approaches. From distribution measurements at different ionic strengths Setschenow coefficients were determined and, therefore, the activity coefficients of the neutral species. By the dependence on ionic strength of the protonation constants the activity coefficients of charged species can be calculated. The differences between protonation constants of the resorcinols in $NaCl_{(aq)}$ and $Me_4NCl_{(aq)}$ ($NaCl_{(aq)} \ll Me_4NCl_{(aq)}$) were also interpreted in terms of weak complexes formation. Enthalpy changes for the protonation of these compounds were determined by calorimetric titrations in $NaCl_{(aq)}$ at different salt concentrations (0–3 mol L^{-1}) at 25 °C. The strength of proton ligand interactions is similar to that of phenols and very different from that of another class of O-ligands, namely carboxylates. This difference comes from the enthalpic contribution, whilst the entropic contribution to the stability is very similar for the two O-ligands classes.

In general it was found that the resorcinols here studied behave in a similar way and can be considered a homogeneous class of O-ligands.

1. Introduction

The knowledge and understanding of weak electrolyte and non-electrolyte activity coefficients are fundamental for any study of salt effects upon chemical or electrochemical processes. In previous works we mainly paid our attention on a critical evaluation of thermodynamic parameters for the protonation of some classes of ligands such as amines, amino acids and carboxylates [1–6]. In this work we extended the study to another class of organic compounds, namely the resorcinols.

The applications of resorcinol (1,3-benzenediol) and its derivatives are very frequent in many industrial fields. Thus, they are used in resins as UV absorbers [7], in manufacturing as fluorescent and leather dyes and adhesives. In the pharmaceutical field they are used to treat acne and other greasy skin conditions in combination with other acne treatments, such as sulphur. Typically, they are used in the formulation of hair dyes and colours (as anti-dandruff agent in shampoo and sunscreen cosmetics) [8–10]. Resorcinol is also used as indicator, known as lacmoid, for acid–base titrations when it reacts with sodium nitrite [11]. An emerging use of resorcinol is a template molecule in supramolecular chemistry [12]. The –OH groups on resorcinol form hydrogen bonds to target molecules holding them in the proper orientation for a reaction. Many reactions can be carried out in the solid state, thereby reducing or eliminating the use of solvents that may be harmful to the environment. In the light of these considerations resorcinol and its derivatives hold an important role from an applicative point of view, and the study of their acid–base properties is fundamental to understand the behaviour of those compounds. However, few data are reported in literature dealing with the acid–base properties of resorcinols in water solution, and often published data are not consistent [13–24]. For this reason, we undertook a systematic study on the chemico-physical behaviour of resorcinols in various ionic media at different ionic strengths. In this paper we report the distribution coefficients in $NaCl_{(aq)}$; the protonation constants in $NaCl_{(aq)}$ and $Me_4NCl_{(aq)}$ at different ionic strengths; the sodium ion pair formation constants; and the relatives protonation enthalpies obtained by direct calorimetric titrations, in $NaCl_{(aq)}$. The whole data were analyzed by SIT and Pitzer type equations in order to determine the activity coefficients.

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2. Experimental section

2.1. Chemicals

Resorcinol (1,3-benzenediol), 2-methylresorcinol (2-methyl-1,3-benzenediol) and 4-chlororesorcinol (4-chloro-1,3-benzenediol) (Sigma–Aldrich) were purified as recommended by Perrin et al. [25], and their purity, checked alkalimetrically, was found to be always >99%. Sodium chloride solutions were prepared by weighing the pure salt (Fluka, p.a.) previously dried in an oven at 110 °C. Tetramethylammonium chloride, $(CH_3)_4NCl$ (Fluka), was recrystallized from methanol. Hydrochloric acid and sodium hydroxide solutions were prepared from concentrated ampoules (Fluka) and standardized against sodium carbonate and potassium hydrogen phthalate, respectively. All the solutions were preserved from atmospheric $CO_{2(g)}$ by means of soda lime traps. Grade A glassware and twice-distilled water were employed in the preparation of all the solutions.

2.2. Apparatus and procedure

Distribution measurements were carried out by dissolution of known amount of ligand (C_L = 10–20 mmol L^{-1}) in the salt aqueous solution (NaCl)/organic phase (2-methyl-1-propanol) mixtures (25 mL of ligand plus; 25 mL of organic phase); the mixtures were shaken for at least four hours and after successive separation of two immiscible phases, potentiometric titrations were performed, in order to calculate the distribution ratio of the ligands.

The free hydrogen ion concentration was measured with a Metrohm model 713 potentiometer (resolution 0.1 mV, reproducibility 0.15 mV) connected to a Metrohm 665 automatic burette and to a model 8101 Ross type Orion electrode, coupled with a standard calomel electrode. The potentiometer and the burette were connected to a personal computer which, using a suitable software, allows automatic data acquisition. The measurement cells were thermostated at (25.0 ± 0.1) °C. Purified $N_{2(g)}$ was bubbled into the solutions in order to exclude the presence of $CO_{2(g)}$ and $O_{2(g)}$. To avoid systematic errors, some measurements were carried out using a different apparatus (Metrohm model 809 titrando) and software (Metrohm TiAMO 1.0) for the automatic data acquisition. ISE-H^+ measurements for the determination of protonation constants were carried out by titrating 25 mL of solutions, containing each ligand (C_L = 5–15 mmol L^{-1}) and $Me_4NCl_{(aq)}$ or $NaCl_{(aq)}$ at different concentrations, with standard $NaOH_{(aq)}$. For each experiment, the standard electrode potential E° and the junction potential coefficient j_a ($E_j = j_a$ [H^+]) were determined by titrating a strong acid solution with standard base, under the same medium and ionic strength conditions as the systems to be investigated. In this way, the pH scale used was the free proton concentration one, $pH \equiv -\log_{10}[H^+]$. The reliability of the calibration in the alkaline range was checked by calculating pK_w values.

Calorimetric measurements were carried out at 25.000 ± 0.001 °C by titrating 50 mL of the solution containing each ligand (C_L = 4–5 mmol L^{-1}) and $NaCl_{(aq)}$ (in order to obtain the pre-established ionic strength values), with $HCl_{(aq)}$ standard solutions. Before each experiment, the heat of dilution was measured under the same ionic strength condition. The apparatus consisted of a Model 450 Tronac isoperibol titration calorimeter coupled with a Keithey 196 system digital multimeter. Titrant was delivered by a 2.5 mL capacity Hamilton syringe (model 1002TLL). The apparatus was connected to a PC, and automatic titrations were performed using a suitable computer program to control calorimetric data acquisition. The repeatability of the calorimetric apparatus was checked by titrating Tris [tris-(hydroxymethyl)aminomethane] with $HCl_{(aq)}$, and was estimated to be $Q \pm 0.008$ J and $V \pm 0.001$ mL.

2.3. Calculations

All calculations relative to the refinement of parameters (protonation constants, analytical concentration of reagents, formal electrode potential) of the ligands investigated in this paper were carried out by the computer program ESAB2M [26]; this program was also used to check the ligands purity. Calorimetric data were analyzed by the computer program ES5CM [27]. The general least squares computer program LIANA [28] was used for the refinement of the parameters for the dependence on ionic strength of protonation constants and distribution parameters. Protonation constants, concentrations and ionic strengths are expressed in the molar or molal concentration scales. Molar to molal conversions were made as described elsewhere [29]. The protonation equilibria of resorcinols can be expressed by:

$$H^+ + L^{2-} = HL^- \quad (1)$$

$$H^+ + HL^- = H_2L^0 \quad (2)$$

and the relative protonation constants, K_i^H are given by:

$$K_1^H = \frac{[HL^-]}{[L^{2-}][H^+]} \quad (3)$$

$$K_2^H = \frac{[H_2L^0]}{[HL^-][H^+]} \quad (4)$$

dissociation constants, K_{ai}, are related to protonation constants by:

$$pK_{ai} = \log K_{3-i}^H \quad (5)$$

3. Results and discussion

3.1. Distribution measurements

When two phases are in equilibrium (aqueous and organic phases), the chemical potentials of the components are the same in each phase, so that we have [30,31]:

$$\frac{m_0}{m} = K_D \quad (6)$$

where m_0 is the concentration of the ligand in the organic phase and m is the concentration in aqueous solution (in the molal concentration scale), and then K_D is the distribution ratio of the components between the two phases. When no salt is added to the aqueous phase,

$$K_D^0 = \lim_{m_{salt} \to 0} K_D \quad (7)$$

and

$$\frac{K_D}{K_D^0} = \frac{\gamma_N}{\gamma_0} \quad (8)$$

where K_D^0 is the distribution ratio between pure water and 2-methyl-1-propanol, and γ_0 is the activity coefficient of neutral species in the organic phase, and γ_N is the relative activity coefficient in aqueous phase. If the concentration in the organic phase is low enough, we can assume that the activity coefficients in this phase are $\gamma_0 \approx 1$, and taking logarithms of both sides, we have:

$$\log \gamma_N = \log \frac{K_D}{K_D^0} \quad (9)$$

by considering the Setschenow equation [32] we have:

$$\log \gamma_N = k_m m_{salt} \quad (10)$$

where γ_N is activity coefficient of neutral species, k_m represents the Setschenow parameter and m_{salt} is the salt concentration (in