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# Solubility, activity coefficients and acid–base properties of three naphthol derivatives in $NaCl_{(aq)}$ at different ionic strengths and at $T = 298.15$ K

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ABSTRACT

Total and intrinsic solubilities of three naphthol derivatives (1-Naphthol, 1,5-Dihydroxynaphthalene and 1-Amino-2-Naphthol-4-Sulfonic acid) were determined in $NaCl_{(aq)}$ at different salt concentrations (0–3 mol $L^{-1}$) and in pure water at $T = 298.15$ K. To characterize the acid–base properties of these naphthols, the protonation constants were determined potentiometrically in the same conditions. The solubility of neutral species in pure water is −1.978, −2.886, −2.594 (expressed in logarithmic scale) for 1-Naphthol, 1,5-Dihydroxynaphthalene and 1-Amino-2-Naphthol-4-Sulfonic acid, respectively. The values of Setschenow coefficients ($k_m$) for these three ligands, are 0.209, 0.158 and 0.369. The dependence on the ionic strength of protonation constants $K_i^H$ from potentiometric measurements was studied using three models, namely Debye–Hückel, SIT (Specific ion Ionic Interaction) and Pitzer equations. Therefore infinite dilution $K_i^H$ and interaction coefficients (SIT and Pitzer) were calculated. The activity coefficients were obtained from solubility and protonation data, in the molal concentration scale. Activity coefficients in $NaCl_{(aq)}$ shown the same behaviour found for other O-donors ligands, previously studied.

## 1. Introduction

Substituted polycyclic aromatic hydrocarbons (PAHs) are widely used in several industries, and it is well-known that these compounds are pollutants due to their slow degradation and high toxicity (they can cause cancer and other health effects [1–4]). Naphthol and some of its derivatives are used as dye precursors in oxidative hair colorants, but they are also present in different applications in industrial field. These compounds contain protonable or deprotonable groups and generally show low solubility: therefore a study of the acid–base behaviour is very important to model industrial and environmental processes. In this work we considered three naphthalene derivatives (see Fig. 1): 1-Naphthol (L1), 1,5 Dihydroxynaphthalene (L2) and 1-Amino-2-Naphthol-4-Sulfonic acid (L3). 1-Naphthol is a toxic metabolite of the PAH naphthalene; it is a major component of the pesticide napropamide and the main degradation product of the pesticide carbaryl. Recently it has been reported associations between urinary 1-Naphthol levels and several intermediate measures of male reproductive health, namely sperm motility, serum testosterone levels, and sperm DNA damage [5]. 1,5 Dihydroxynaphthalene is used as corrosion inhibitor [6]; it acts as base for epoxy resin to produce carbon films [7]. 1-Amino-2-Naphthol-4-Sulfonic acid was adopted as a reagent for the determination of arsenic and phosphorus [8], and also of molybdate-reactive silica [9]; it reacts in presence of aniline to form nanotubes of polyaniline [10]. In the last years we were involved in the study of aqueous solubility (one of the most important physico-chemical factors) of different classes of compounds [11–17]. In this work we have determined total and intrinsic solubilities, and the protonation constants from potentiometric measurements in sodium chloride at different ionic strengths at $T = 298.15$ K, for the three ligands. In Table 1 and in Table 2 literature data of protonation constants [18–20], solubility and Setschenow coefficients [21–26] of some naphthol derivatives are reported.

## 2. Experimental section

### 2.1. Chemicals

1-Naphthol, 1,5 Dihydroxynaphthalene and 1-Amino-2-Naphthol-4-Sulfonic acid (Aldrich products) were used without further purification and their purity, checked alkalimetrically, was found to be >99%. Sodium chloride solutions were prepared by weighing pure salt (Fluka, p.a.) previously dried in an oven at $T = 383.15$ K. Sodium hydroxide solutions were prepared from concentrated NaOH (Fluka puriss. Electrochemical grade) and standardized against potassium biphthalate. Hydrochloric acid solutions were prepared from concentrated ampoules (Fluka) and standardized against sodium carbonate. All solutions were preserved from atmospheric $CO_2$ by means of soda lime traps. Grade A glassware and twice-distilled water were employed in the preparation of all the solutions.

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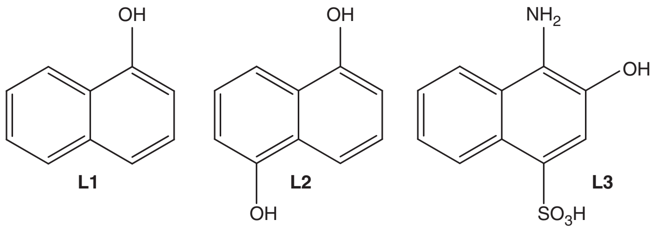

**Fig. 1.** Molecule structures of 1-Naphthol (L1); 1,5-Dihydroxynaphthalene (L2); 1-Amino-2-Naphthol-4-Sulfonic acid (L3).

### 2.2. Apparatus

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 suitable software, allows automatic data acquisition. The measurement cells were thermostatted at (298.15 ± 0.1) K. Purified $N_2$ was bubbled into the solutions in order to exclude the presence of $CO_2$ and $O_2$. 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.

### 2.3. Procedure

Saturated solutions of 1-Naphthol (L1), 1,5 Dihydroxynaphthalene (L2) and 1-Amino-2-Naphthol-4-Sulfonic acid (L3) were prepared in the following way: an amount of ligand in a small excess was added to a solution of sodium chloride at a pre-established concentration of salt (0 to 3 mol L$^{-1}$). These solutions were stirred at $T = 298.15$ K for at least 24 h. From preliminary conductivity measurements on saturated solutions we established that a so long time of stirring was unnecessary, and after 4–6 h of stirring equilibrium conditions were reached. Saturated solutions were centrifuged and filtered through a cellulose membrane filter (Ø = 0.45 μm). A volume of 25 ml of the filtered solution was titrated with standard NaOH. Separate titrations of HCl at the same ionic strength as the sample under study were carried out to determine the standard electrode potential $E^0$, and the junction potential coefficient $j_a$ ($E_j = j_a$ [H$^+$]). To avoid systematic errors, independent experiments were performed at least three times.

**Table 1**
Some of literature data for protonation constants of naphthol derivatives.

| Ligand | log$K_1$ | Ligand | log$K_1$ | log$K_2$ |
|---|---|---|---|---|
| 1-Naphthol | 9.20[a]<br>9.416[c] | 6-Methyl-2-Naphthol | 9.70[a] | |
| 1-Naphthol-4-($CH_3$) | 9.64[b] | 7-Methyl-2-Naphthol | 9.64[a] | |
| 1-Naphthol-(H) | 9.39[b] | 1-Cl-2-Naphthol | 7.97[a] | |
| 1-Naphthol-4-(Cl) | 8.80[b] | 6-Br-2-Naphthol | 9.23[a] | |
| 1-Naphthol-4-(Br) | 8.72[b] | 1-Br-2-Naphthol | 7.89[a] | |
| 1-Naphthol-3-($NO_2$) | 7.86[b] | 2-Cl-1-Naphthol | 7.76[a] | |
| 1-Naphthol-4-($C_6H_5CO$) | 7.33[b] | 4-Cl-1-Naphthol | 8.75[a] | |
| 1-Naphthol-4-(CN) | 7.08[b] | 1-Amino-2-Naphthol-4-Sulfonic acid[c)] | 8.80[d] | 3.10[d] |
| 1-Naphthol-4-(CHO) | 6.53[b] | 2,3-Dihydroxynaphthalene [c)] | 10.90[e] | 8.34[e] |
| 1-Naphthol-4-($NO_2$) | 5.73[b] | 1,2-Dihydroxynaphthalene-4-sulfonic acid[c)] | 12.64[f] | 8.12[f] |
| 1-Naphthol-4-(NO) | 8.18[b] | 2,3-Dihydroxynaphthalene-6-Sulfonic acid[c] | 12.16[g] | 8.19[g] |
| 2-Naphthol | 9.45[a] | | | |

[a] Rosenberg et al. [18] , values at $I = 0$ mol L$^{-1}$ at $T = 298.15$ K.
[b] Creamer et al. [19], values at $I = 0$ mol L$^{-1}$ at $T = 298.15$ K.
[c] Pettit and Powell [20].
[d] Values of log$K_2$ and log$K_3$ at $I = 0.1$ mol L$^{-1}$, $KNO_3$ at $T = 293.15$ K.
[e] Values at $I = 0.2$ mol L$^{-1}$, $NaClO_4$ at $T = 303.15$ K.
[f] Values at $I = 0.1$ mol L$^{-1}$, $NaClO_4$ at $T = 298.15$ K.
[g] Values at $I = 0.1$ mol L$^{-1}$, KCl at $T = 293.15$ K.

### 2.4. Calculation

All calculations relative to the refinement of parameters (protonation constants, analytical concentration of reagents, formal electrode potential) of ligands investigated in this paper were performed by the computer program BSTAC; this program was also used to check the ligands purity. The general least squares computer program LIANA was used for the refinement of both the parameters for the dependence of protonation constants on ionic strength and on ligand concentrations and of the solubility. Computer programs used in this laboratory are described in reference [27].

## 3. Results

### 3.1. Solubility measurements

The treatment of solubility data was already described in previous works [11–17], and here we remind just the essential aspects. Owing to proton dissociation/association equilibria, the total solubility of the ligands is due to the sum of all the species in solution, namely, the neutral and deprotonated or partially protonated species, in fact, we have:

$$S^T = \left[HL^0\right] + [L^-] \tag{1}$$

$$S^T = \left[H_2L^0\right] + [HL^-] + \left[L^{2-}\right] \tag{1a}$$

$$S^T = \left[H_3L^+\right] + \left[H_2L^0\right] + [HL^-] + \left[L^{2-}\right] \tag{1b}$$

for L1, L2 and L3, respectively, where $S^T$ is the total solubility, $[H_nL^0] = S^0$ (solubility of neutral species, or specific solubility). By rearranging the Eqs. (1)–(1b) and considering the protonation constants ($K_i^H$) (see hereafter), we have:

$$S^T = S^0\left(1 + \frac{1}{K_1^H[H^+]}\right) \tag{2}$$

$$S^T = S^0\left(1 + \frac{1}{K_2^H[H^+]} + \frac{1}{K_1^H K_2^H[H^+]^2}\right) \tag{2a}$$

$$S^T = S^0\left(1 + \frac{1}{K_2^H[H^+]} + \frac{1}{K_1^H K_2^H[H^+]^2} + K_3^H\left[H^+\right]\right) \tag{2b}$$

and then the values of $S^0$ can be calculated.

By using Eqs. (2) and (2a) for L1 and L2, we found coincidence between the total solubilities ($S^T$) and the solubilities of the neutral species ($S^0$), whose values are reported in Table 3. For L3 different values of the total solubility and the solubility of the neutral species were obtained, as reported in Table 4.

Solubility data were fitted to the function:

$$\log S^T = \log S_0^T + a \cdot c_{MX} \tag{3}$$

where $c_{MX}$ is the salt concentration expressed in the molar concentration scale [Eq. (3) can be applied to the molal concentration scale by