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Solvent effect on heats of protonation of some amines

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Abstract

The heats of protonation of *n*-pentylamine, dipentylamine, tributylamine and heats for the first protonation step of 1,8-diamino-3,6-dioxaoctan, diazacrownether 22 and cryptand 222 in pure acetonitril and propylene carbonate and of diazacrownether 22 and dibenzosubstituted ligand 22BB in water + acetonitrile mixtures have been measured at 298.15 K using calorimetric titrations. The values of the reaction enthalpies in the solvents as well as the data in aqueous and methanol solutions reported in literature are analysed in terms of the simple electrostatic model and thermodynamic parameters of transfer (solvation) of the reactants. Estimation of the electrostatic and covalent contributions to standard enthalpy of transfer of the reactions from water to non-aqueous and mixed solvents has been made.

Keywords: Amines; Heat of protonation; Solvent effect; Electrostatic model

1. Introduction

Acid–base interactions play a key role in most chemical and biological processes. The acid–base properties of a solute in solution depend on a definite balance between the intrinsic acidity/basicity of the solute in the gas phase and the ability of the solvent to stabilize neutral and charged species [1–3]. One of the classical problems of physical chemistry is solvent induced inversion of the basicity in the order of primary, secondary and tertiary aliphatic amines as comparing with the gas phase. In water hydration effect changes the order basicity of the amines in the direction opposite to inductive effect of alkyl groups. The anomalous order in aqueous solution and also in other media is generally explained on the base of Born–Haber type cycles by comparing the thermodynamic parameters of solvation (transfer) of the reagents and products of the reactions [4,5]. The same approach is also widely used at the analysis of thermodynamic data for ion-molecular complexation [6]. Estimation of electrostatic and nonelectrostatic contributions to thermodynamic parameters of reactions give a valuable information about the nature of interactions in solutions [7,8]. In the last years more detailed description of solvent effects became possible due to advances of modern theoretical methods (QM, MD, Monte Carlo) [9]. Nevertheless, proton affinities of amines with complex molecular structures as well as in various reaction media often cannot be explained in detail or predicted *apriori* because many factors influence them still far from an understanding. For polyfunctional macrocyclic and macrobicyclic nitrogen containing molecules like diazacrownethers and cryptands some additional effects such as conformational changes and mutual influence of the different functional groups can be necessary to take into account [10–14].

Protonation reactions of diazacrownethers (secondary diamines) and cryptands (tertiary diamines) have been mainly studied in protic solvents: water [15–17] and methanol [18]. In the present work, heats of protonation for some representative open and cyclic diazapolyethers, primary, secondary and tertiary aliphatic monoamines are determined in two aprotic solvents: acetonitrile and propylene carbonate at 298.15 K. Additionally, heats of the first protonation step for two diazacrownethers are measured in all composition range of ace-

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tonitrile + water mixtures. To gain further insight into physical nature of solvent effects a simple model for estimation of electrostatic and covalent (electrodynamic) contributions to enthalpies of transfer of the reactions from water to non-aqueous and mixed solvents is suggested.

2. Experimental

The following commercially available ligands *n*-pentylamine (PA) (Fluka, purity ≥97%), dipentylamine (DPA) (Acros Organics, purity 99%), tributylamine (TBA) (Fluka, purity ≥99.5%), 1,8-diamino-3,6-dioxaoctan (DAOO)(Merk, purity 98%), 1,10-diaza-4,7,13,16-tetraoxa-cyclooctadecane (Kryptofix 22, Merck), 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8] hexacosan (Kryptofix 222, Merck) were used without further purification. Dibenzosubstituted diazacrownether (Kryptofix 22BB) was kindly donated by Dr. R. Klinck (Merck, Darmstadt). The chemical structures of the amines are given on Fig. 1. Trifluoromethane sulfonic acid (Fluka, purity ≥99%) was used as purchased.

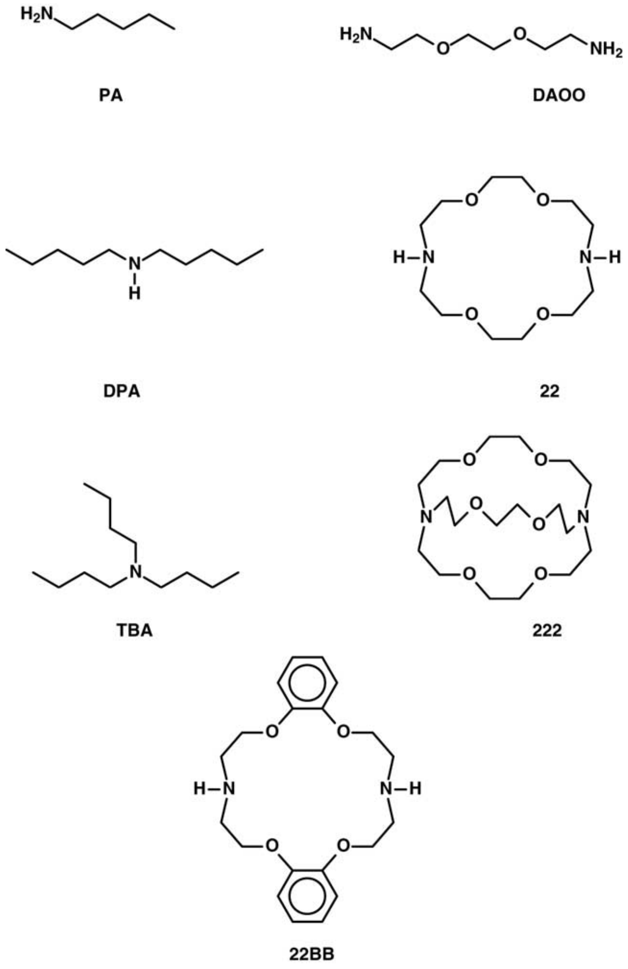

Fig. 1. Chemical structures of amines used in this work.

Acetonitrile, (AN) (Fluka, puriss. absolut, H_2O ≤0.01%) and propylene carbonate (PC) (Fluka, puriss. anhydrous, H_2O ≤0.005%) were used as solvents.

The reaction enthalpies were determined using a Tronac Model 450 calorimeter. During the calorimetric titration a solution of trifluoromethane sulfonic acid (0.01–0.04 M) was titrated continuously into 40 ml solution of amine (0.03–0.08 M) for one minute (burett rate 0.333 ml/min). In this case the actual proton concentration in the reaction vessel is much lower than the amine concentration. Under these experimental conditions only monoprotonation takes place. The measured heat after correction for all non-chemical effects depends on the number of moles and the reaction enthalpy of the monoprotonated amine formed during the titration. The reaction enthalpies (ΔH_1^0) were calculated from the experimental data by published procedures [19–21].

To determine the reaction enthalpy of the second protonation step of diamines it is necessary to provide much higher proton concentration in the reaction vessel compared with the amine concentration [22]. However, solutions of trifluoromethane sulfonic acid in PC have a limited stability [5]. The sum of the reaction enthalpies ($\Delta H_1^0 + \Delta H_2^0$) calculated from the experimental data in PC and also in AN proved to be unusually high. Probably, an additional exothermic process under titration of solutions with excess of the acid can be responsible for this effect. Under these conditions enthalpy values for the second protonation step cannot be accurately determined. Therefore, they are not considered in this paper.

3. Results and discussion

3.1. Experimental results

The reaction enthalpies for the protonation of mono- and diamines in AN and PC are given in Table 1. First enthalpies of protonation of 22 and 22BB in water + acetonitrile mixtures are given in Table 2. The value of reaction enthalpy for the in water slightly soluble dibenzosubstituted ligand 22BB was estimated from the measured values in mixed solvents by extrapolation to $X_{AN} = 0$.

Table 1
First protonation enthalpies for mono- and diamines in acetonitrile and propylene carbonate at 298.15 K

Amine	$-\Delta H_1^0$ (kJ mol^{-1})	
	Acetonitrile	Propylene carbonate
PA	126.7	103.9
DPA	118.4	90.0
TBA	113.2	82.5
DAOO	117.3	122.2
22	71.3	73.9
222	76.1	74.4