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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.

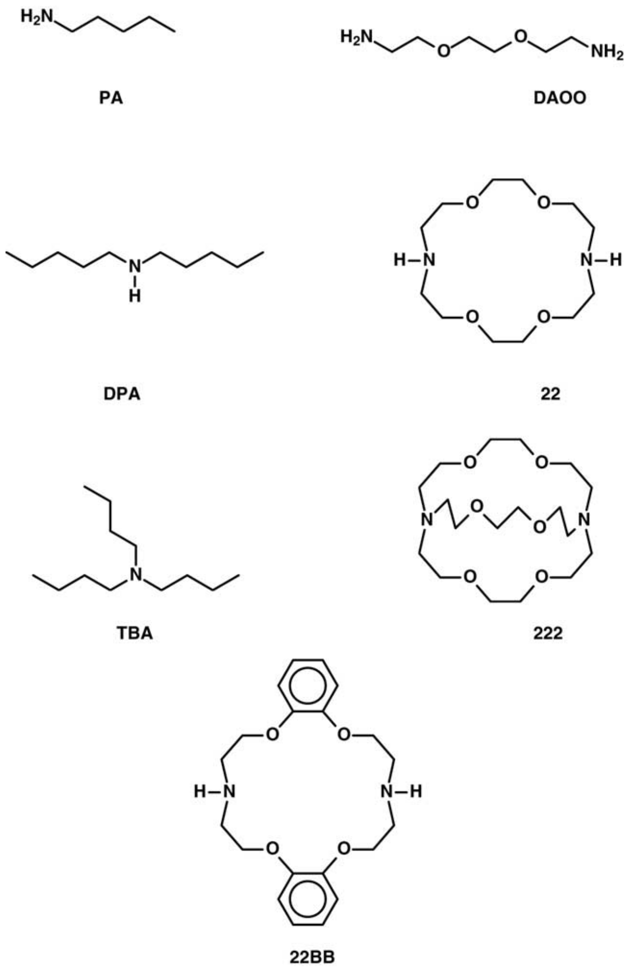

Fig. 1. Chemical structures of amines used in this work.

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

Table 2
First protonation enthalpies for 22 and 22BB in acetonitrile + water mixed solvents at 298.15 K

X_{AN}	$-\Delta H_1^0$ (kJ mol^{-1})	
	22	22BB
0.0	38.4[a]	35.3[b]
0.12	38.9	27.5
0.22	41.3	21.0
0.31	40.5	18.2
0.51	28.7	21.2
0.64	25.7	–
0.80	19.6	44.9
0.89	21.4	–
1.00	71.3	80.6

[a] [15].
[b] Extrapolated.

3.2. Method of analysis of solvent effect on the reaction enthalpies

Reaction enthalpy is closely related to energy of chemical bonds and can be considered as a measure of electrostatic and covalent interaction forces between the reacting species. As far as long-range electrostatic forces are non-specific (so-called universal forces), one can possibly estimate the electrostatic contribution to the solvent effect by "fixing" interaction energy between proton and ligand itself (reaction enthalpy) and considering only changes of the energy due to solvation (enthalpies of transfer) from a reference point (gas phase, aqueous solution) to other reaction media.

According to Coulomb law for interactions of two electric charges (Eq. (1)),

$$F = \frac{q_1 q_2}{4\pi\varepsilon_0\varepsilon_s r^2} \tag{1}$$

electrostatic forces are reduced by factor ε_s (dielectric constant of the medium) on transferring the charges from gas phase ($\varepsilon_{gas} = 1$) to the medium. The energy of electrostatic interactions (Eq. (2)) is obtained by integration of the general relation, $dE = F\,dr$ with respect to distance r:

$$E = \frac{q_1 q_2}{4\pi\varepsilon_0\varepsilon_s r} \tag{2}$$

Assuming proportionality between $\Delta_r H^0$ and the electrostatic bond energy ($E \cong \Delta_r H^0$), reaction enthalpies in all solvents (s) with $\varepsilon_s < \varepsilon_{water}$ should be larger (more negative) for enthalpy stabilized complexes than in water by factor equal to the ratio of corresponding values of dielectric constants of the solvents, for example, at transfer from water to methanol 79.5/32.7 = 2.4. Thus, if only electrostatic interactions take place then Eqs. (3) and (4) are valid

$$\Delta H_w^0 \varepsilon_w = \Delta H_s^0 \varepsilon_s = \Delta H_{gas}^0 \tag{3}$$

$$\Delta H_s^0 = \Delta H_w^0 \frac{\varepsilon_w}{\varepsilon_s} \tag{4}$$

Electrostatic contribution ($\Delta_{tr} H_{r,el}^0(W \to S)$) to enthalpy of transfer of the reaction from water to other solvents ($\Delta_{tr} H_r^0 = \Delta H_s^0 - \Delta H_w^0$) is defined as

$$\Delta_{tr} H_{r,el}^0(W \to S) = \Delta H_w^0 \left(\frac{\varepsilon_w}{\varepsilon_s} - 1\right) \tag{5}$$

In general, a covalent contribution can be also the part of $\Delta_{tr} H_r^0$. This can be calculated using the equation:

$$\Delta_{tr} H_{r,cov}^0 = \Delta_{tr} H_r^0 - \Delta_{tr} H_{r,el}^0 \tag{6}$$

Electrostatic contribution is determined here only by a macroscopic parameter (dielectric constant) and reflects the role of the solvent as a medium for electrostatic interactions. Covalent contribution relates to more strong and specific solute–solvent interactions reflecting the role of the solvent as a reagent. The dividing of transfer enthalpy on the two contributions should be considered as an approach to estimation of specific and nonspecific parts of solvent influence. Thus, the contribution named here conventionally as a "covalent contribution" relates not only to covalent interactions but also can include non-covalent short-range interactions connected to molecular nature of the solvent (dipole moment, polarizability, etc.).

3.3. Discussion

It is known that electrostatic factors of solvation are predominant for relatively weak molecular complexes as well as for relatively slow processes, for example in organic chemistry. In this cases different semiempirical correlations between stability constants or thermodynamic parameters of the reactions and dielectric constant of the solvent (ε_s^{-1}) are valid [1–3,23]. At the same time for most stable ion-molecular complexes as well as for fast complexation and proton transfer reactions in solution electrostatic models of solvent effect are generally not applicable. In this relation it is necessary to take into account the fact that the nature of solvent influence depends not only on properties of the solvent but also on a "power" of interactions between the reagents [2,14]. Therefore, the suggested model assumes as a first approximation that both electrostatic and covalent contributions of transfer enthalpy are proportional to the interaction energy between proton and ligand itself (reaction enthalpy in water as a reference solvent).

Electrostatic and covalent contributions to enthalpies of transfer from water to MeOH, AN and PC for the first protonation step of some diamines and for *n*-pentylamin are presented in Table 3. The reaction enthalpies in water and methanol for this calculation were taken from literature [15,16,18]. In all cases electrostatic contributions are favorable (negative) and increase in the order: PC ($\varepsilon_s = 65.1$), AN ($\varepsilon_s = 35.9$), MeOH ($\varepsilon_s = 32.7$) according to Eq. (5). Covalent contributions are much more specific because of the relation to changes at the first solvation shells of the reagents. Thus, positive covalent contributions indicate on increase of solvation at transfer of the reactions to MeOH and AN.

Table 3
First protonation transfer enthalpies of amines, $\Delta_{\mathrm{tr}} H_r^0$ (in kJ mol^{-1}), from water to non-aqueous solvents at 298.15 K and the corresponding electrostatic, $\Delta_{\mathrm{tr}} H_{r,\mathrm{el}}^0$, and covalent, $\Delta_{\mathrm{tr}} H_{r,\mathrm{COV}}^0$, contributions

Amines	PA	DAOO	22	222
W → MeOH				
$\Delta_{\mathrm{tr}} H_r^0$	−5.0	−9.9	−14.6	−4.6
$\Delta_{\mathrm{tr}} H_{r,\mathrm{el}}^0$	−83.9	−75.6	−54.1	−73.2
$\Delta_{\mathrm{tr}} H_{r,\mathrm{COV}}^0$	78.9	65.7	39.5	68.6
W → AN				
$\Delta_{\mathrm{tr}} H_r^0$	−67.2	−63.7	−32.9	−24.2
$\Delta_{\mathrm{tr}} H_{r,\mathrm{el}}^0$	−69.6	−62.7	−45.9	−60.7
$\Delta_{\mathrm{tr}} H_{r,\mathrm{COV}}^0$	2.4	−1.0	13.0	36.5
W → PC				
$\Delta_{\mathrm{tr}} H_r^0$	−44.4	−68.4	−35.5	−22.5
$\Delta_{\mathrm{tr}} H_{r,\mathrm{el}}^0$	−12.5	−11.3	−8.1	−10.9
$\Delta_{\mathrm{tr}} H_{r,\mathrm{COV}}^0$	−31.9	−57.1	−27.4	−11.6

Favorable electrostatic contributions at transfer from water to MeOH are compensated up to 70–90% by unfavorable covalent ones, leading to relatively small differences between reaction enthalpies in both solvents. At the same time, transfer to AN is mainly determined by favorable electrostatic contribution. Furthermore, covalent contributions for PA and DAOO in this case are close to zero. Both covalent and electrostatic contributions are favorable for transfer from water to PC with predominance of the former one.

A more representative picture is obtained from the analysis of enthalpies of transfer for the first protonation step of 22 and 22BB in water + acetonitrile mixed solvents (Fig. 2a). Electrostatic contributions for both amines in this case are nearly identical. They appear to be very close to enthalpy of transfer of H^+ in the system [24] and depend almost linearly on the mole fraction of AN (Fig. 2b). At the same time dependences of covalent contributions for 22 and 22BB from composition of the solvent are rather different with a maxima at 0.9 and 0.5 mole fraction of AN respectively. Positive values of the covalent contributions indicate the increase of solvation of the reacting sites of the amines in mixed solvents as comparing with pure water and acetonitril.

It should be noted that for complexes stabilized in water by entropy factor ($\Delta H_r^0 > 0$) without a covalent contribution (for example, cryptate complexes of La^{3+} [25]) Eqs. (4) and (5) predict more positive values of reaction enthalpy in solvents with $\varepsilon_{\mathrm{s}} < \varepsilon_{\mathrm{water}}$. However, in practice, favorable covalent contribution for such complexes in non-aqueous solvents becomes significant, leading to negative values of the reaction enthalpies.

It would be also interesting to discuss the electrostatic and covalent contributions to reaction enthalpy in terms of the structural differences of mono- and diamines as well as of primary, secondary and tertiary amines. However, it is difficult to make such a comparison at the moment because of a limited number of amines studied.

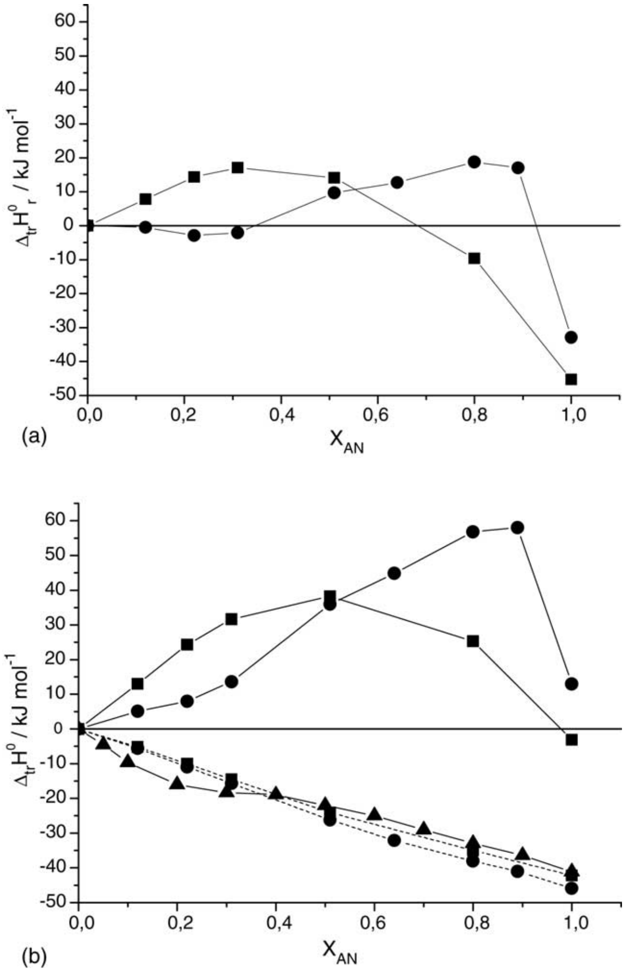

Fig. 2. First protonation transfer enthalpies, $\Delta_{\mathrm{tr}} H_r^0$(in kJ mol^{-1}), of 22 (●) and 22BB (■) from water to water + acetonitrile mixed solvents at 298.15 K as function of the mole fraction of AN (a), the corresponding electrostatic, $\Delta_{\mathrm{tr}} H_{r,\mathrm{el}}^0$, (- - - -), and covalent, $\Delta_{\mathrm{tr}} H_{r,\mathrm{COV}}^0$, (—) contributions and literature values of the enthalpy of transfer of H^+ (▲) (b) [24].

4. Conclusions

A new approach to analysis of solvent influence on the reaction enthalpies has been described. In the scope of the suggested model electrostatic contribution to enthalpy of transfer of the reactions relates to nonspecific Born-type solute–solvent interactions and proportional to the interaction energy between proton and ligand itself (reaction enthalpy in gas phase or water as a reference solvent). The sign and the value of the covalent contribution are determined by the peculiarities of specific solvation of the reactants. Electrostatic and covalent contributions of the enthalpies of transfer from water to MeOH, AN, PC and water + acetonitrile mixed solvents for protonation reactions of different mono- and diamines have been estimated. It has been shown that electrostatic contribution is favorable for the transfer of the reactions from water to the solvents with lower dielectric constants. Covalent contribution is favorable only at weak solvation of the reagents in non-aqueous solvent (PC) in comparison with water. In water + acetonitrile mixtures the reagents are solvated more strongly than in the pure solvents that leads to extremal dependences of the first protonation enthalpies of 22 and 22BB on the solvent composition.

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