# Protonation of Imines by Water in the Presence of Salts: Role of Cooperative Effects in Water-Shared Ion Pairs

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An IR spectroscopic study of lithium and magnesium salt solutions in acetonitrile in the presence of an organic base such 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) shows that this base may be protonated by water when added. The formation of a water-separated ion pair is essential to this protonation. The replacement of a solvent molecule by a DBU molecule in the first solvation shell of the cation in this solvent-separated ion pair leads to the elimination of protonated DBUH<sup>+</sup>X<sup>-</sup> ion pair.

#### Introduction

It has long been shown that in organic solvent solutions the water molecule bonding with both anions and cations increases its acidity through a cooperative effect.<sup>1</sup> This effect is reinforced when water forms solvent-shared ion pairs in organic solvents of low or average dielectric constant such as that of THF, CH<sub>3</sub>NO<sub>2</sub>, or CH<sub>3</sub>CN.<sup>1</sup> The cation cooperative effect on hydrogen bonding of water with solvents or anions has recently been reinvestigated more quantitatively by Luck and co-workers.<sup>2,3</sup> These authors have measured the cooperativity factors  $a_+$  from the slope (1 +  $a_+$ ) of the lines  $\Delta \nu_{+\dots OH \to B} / \nu_{vap}$  versus  $\Delta \nu_{OH \to B} / \nu_{vap}$ . According to the results of these authors with polar and nonpolar solvents B,  $\Delta v_{+-OH-B} = v_{OH,vap} - v_{+-OH-B}$  (where  $v_{+-OH-B}$  is the OH stretching frequency of the cation complex) and  $\Delta v_{OH-B} = v_{vap} - v_{OH-B}$  (where  $\nu_{OH-B}$  is the OH stretching frequency of the H-bond complex OH...B). These factors correlate well with the  $pK_a$  of the corresponding hydrates in water. They have thus found cooperativity factors  $a_+$  of 0.55 and 1.1 respectively for Li<sup>+</sup> and Mg<sup>2+</sup>, corresponding to the polarization of the water O-H bond by the cation and to the resulting acidity increase.

In this paper, we emphasize the importance of these effects that can lead to the protonation of organic bases of appropriate  $pK_a$ such as an imine such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). This compound has indeed been shown to be a reagent



of particular interest in synthetic organic chemistry.<sup>4</sup> These effects are important for a better understanding of the deprotonation reaction mechanism in organic synthesis<sup>5,6</sup> or may be of interest for biological reaction mechanisms such as the protonation of the imine group of photopigments (e.g., rhodopsin and bacterio-rhodopsin).<sup>7</sup>

#### **Experimental Section**

Our DBU samples were supplied by Janssen, and trifluoroacetic acid obtained from Prolabo. Acetonitrile (Prolabo, IR quality) was dried over Merck 4-Å molecular sieves. The salts LiBr (Koch-Light Laboratories),  $MgCl_2$  (Aldrich), and tetrabutylammonium bromide (Eastman) were dried by slow heating under vacuum and stored under argon. The anhydrous  $MgBr_2$  salt was prepared in THF solution by action of 1,2-dibromoethane on magnesium turnings. After THF filtration, washing with toluene, and finally evaporation, a white powder is obtained. Solutions were prepared in a drybox or under argon in a glovebag.

Infrared spectra were scanned on a Perkin-Elmer 983 spectrometer. The resolution was usually 3 cm<sup>-1</sup>, and the frequencies are given with a precision  $\pm 1$  cm<sup>-1</sup>. The cell was equipped with CaF<sub>2</sub> windows and had a thickness of 30  $\mu$ m; the temperature inside the spectrometer is about 30 °C.

## **Results and Discussion**

The DBU molecule has two main vibrational modes that are sensitive to the molecular interactions, the  $\nu$ (C=N) and  $\nu$ (CN) located at 1612 and 1313 cm<sup>-1</sup>, respectively, when the molecule is dissolved in CH<sub>3</sub>CN.

When a very well dried salt such as LiBr is added to a DBU solution in acetonitrile (Figure 1), a slight shift toward low frequencies and a broadening of the narrow  $\nu$  (C==N) band at 1613 cm<sup>-1</sup> are observed. Further addition of LiBr (equimolecular or more concentrated than the DBU solution) results in the appearance of a new band at 1607 cm<sup>-1</sup> and a corresponding decrease of the free DBU band at 1613 cm<sup>-1</sup>. Similarly, the  $\nu(CN)$  band at 1313 cm<sup>-1</sup> shifts to 1316 cm<sup>-1</sup> under the same conditions. These new bands characterize the complexation of the DBU molecule with the Li<sup>+</sup> cation. We had previously erroneously assigned this complexation to a band appearing at 1646 cm<sup>-1,6</sup> Indeed when large amounts of LiBr are added (Figure 1), a small band appears at 1646 cm<sup>-1</sup> due to trace amounts of water. This is demonstrated on Figure 2 where increasing quantities of water are added to an equimolecular solution of DBU and LiBr in CH<sub>3</sub>CN. The band previously observed at 1607 cm<sup>-1</sup> decreases in intensity, while the

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Figure 1. Infrared absorption spectra of DBU at the concentration of 0.3 M in CH<sub>3</sub>CN alone (--) or in the presence of increasing amounts of dry LiBr (-) 0.1 M,  $(\cdots)$  0.3 M, and (--) 0.75 M.



Figure 2. Infrared absorption spectra of an equimolecular solution of DBU and LiBr: 0.3 M in CH<sub>3</sub>CN in the presence of increasing amounts of water: (--) 0.005 M; (--) 0.05 M; (--) 0.1 M; and of an equimolecular solution of DBU and H<sub>2</sub>O (0.3 M) in CH<sub>3</sub>CN in the presence of an excess of LiBr (--) 0.75 M.



Figure 3. Infrared spectra of a 0.3 M CF<sub>3</sub>COOH solution in CH<sub>3</sub>CN (---), a 0.3 M DBU solution in CH<sub>3</sub>CN (---), and an equimolecular 0.3 M DBU and CF<sub>3</sub>COOH mixture in CH<sub>3</sub>CN.

band appearing at 1646 cm<sup>-1</sup> increases and is thus directly related to the presence of water. This band may be readily assigned to the  $\nu(C=N)$  vibration of protonated DBU for the following reasons: (1) The only bands appearing in the 1800–1600-cm<sup>-1</sup> region for solutions of CF<sub>3</sub>COOH and DBU in acetonitrile, respectively, are the  $\nu(C=O)$  band of CF<sub>3</sub>COOH····N $\equiv$ C-··CH<sub>3</sub> at 1786 cm<sup>-1</sup> and the  $\nu(C=N)$  band of DBU at 1612 cm<sup>-1</sup>. They disappear (Figure 3) in an equimolecular mixture of these two compounds in acetonitrile. The two new bands observed for this mixture at 1689 and 1643 cm<sup>-1</sup> are respectively assigned to the  $\nu_a(COO<sup>-</sup>)$  vibration of the trifluoroacetate anion<sup>8</sup> and to the  $\nu$ -(C=N) vibration of DBUH<sup>+</sup>. Thus, the DBU molecule is quantitatively protonated by the trifluoroacetic acid under these conditions. (ii) A similar frequency increase of 30 cm<sup>-1</sup> of the



Figure 4. Infrared absorption spectra of (--) a 0.3 M solution of DBU in CH<sub>3</sub>CN, in the presence of (--) MgCl<sub>2</sub>, not completely dry (H<sub>2</sub>O ~ 0.02 M) and at a concentration ~0.2 M, close to saturation in the presence of DBU, or in the presence of increasing amounts of incompletely dried MgBr<sub>2</sub>: (--) 0.3 M MgBr<sub>2</sub>-~0.06 M H<sub>2</sub>O; (--) 0.4 M MgBr<sub>2</sub>-~0.1 M H<sub>2</sub>O; (---) 0.4 M MgBr<sub>2</sub>-~0.3 M H<sub>2</sub>O.



Figure 5. Infrared absorption spectra of  $CH_3CN$  solutions: (---) 0.32 M  $H_2O$ , (---) 0.3 M  $H_2O$  in the presence of DBU 0.3 M, (--) 0.3 M  $H_2O$  in the presence of 0.3 M DBU and 0.28 M BrNBu<sub>4</sub>.

 $\nu(C=N)$  vibration due to the formation of an imminium salt has already been observed.<sup>9</sup> It has further been shown through deuteriation that this large frequency shift with protonation is due to a coupling of the  $\nu(C=N)$  mode with the  $\delta(NH^+)$  in plane bending mode of the imminium salt.<sup>10</sup> The  $\delta(NH^+)$  mode is indeed located at 1434 cm<sup>-1</sup> in (CH<sub>3</sub>)<sub>2</sub>CHCH=NH<sup>+</sup>CH(CH<sub>3</sub>)<sub>2</sub>BF<sub>4</sub><sup>-</sup> for which a  $\nu(C=N)$  frequency increase of 28 cm<sup>-1</sup> is observed through protonation of the corresponding imine. This frequency increase is only 9 cm<sup>-1</sup> through deuteriation.<sup>10</sup> In contrast, the complexation with a cation like Li<sup>+</sup> of the imine nitrogen lowers the  $\nu(C=N)$  frequency by 6 cm<sup>-1</sup>. This is confirmed by the complexation with the Mg<sup>2+</sup> cation of MgCl<sub>2</sub> or MgBr<sub>2</sub> (Figure 4) where the bands of the DBU protonated and complexed with the Mg<sup>2+</sup> cation are observed at 1646 and 1595 cm<sup>-1</sup>, respectively. The larger lowering of the  $\nu(C=N)$  frequency, 18 cm<sup>-1</sup> for Mg<sup>2+</sup>, compared to 6 cm<sup>-1</sup> for Li<sup>+</sup> is due to the higher polarizing power of the Mg<sup>2+</sup> cation (higher charge over radius ratio). The  $\nu(CN)$ 

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Figure 6. Infrared transmission spectra in the  $\nu(NH^+)$  and  $\nu(H_2O)$  region of water lithium bromide solutions in  $CH_3CN$ : (-----) 0.7 M LiBr, 0.9 M H<sub>2</sub>O, (---) 0.67 M LiBr, 0.3 M H<sub>2</sub>O, and of the same solutions with DBU 0.3 M added: (---) 0.7 M LiBr, 0.9 M H<sub>2</sub>O, (---) 0.67 M LiBr, 0.3 M H<sub>2</sub>O (the spectrum of the pure solvent is shown (---) and has not been subtracted due to its slight perturbations by the different solutes).

3500

cm

3000

vibration always increases in frequency with complexation since it is observed at 1316, 1318, and 1322 cm<sup>-1</sup> for complexation with Li<sup>+</sup>,  $Mg^{2+}$ , and protonation, respectively.

To interpret the protonation mechanism of DBU by water, we have considered the different interactions of DBU with water with or without tetrabutylammonium bromide. As seen on Figure 5, at a concentration of 0.32 M in the 1600-1700-cm<sup>-1</sup> range, we observe only a broad band at 1630 cm<sup>-1</sup> due to the bending vibration of water hydrogen bonded to two solvent molecules.<sup>1</sup> In the presence of DBU in equimolecular amount, the spectrum of DBU does not seem different from what it is in the absence of water, with the  $\nu$ (C=N) band at 1613 cm<sup>-1</sup> and a small band at 1660 cm<sup>-1</sup> probably due to an overtone or combination mode. The water bending mode is overwhelmed by the DBU  $\nu$ (C=N) band. With the addition of an equimolecular amount of tetrabutylammonium bromide, only a very small intensity decrease of the  $\nu$ (C==N) band is observed, but the 1646-cm<sup>-1</sup> band is not visible although it is known that under these conditions water is asymmetrically hydrogen bonded to a bromide ion and to a solvent molecule.<sup>1</sup> These facts confirm that the presence of a lithium cation is needed for the protonation of DBU. The interaction of water with salts in organic solvents such as acetonitrile has been extensively studied previously,<sup>1-3</sup> and the transmission spectra of water solutions in the presence of LiBr compared to the solvent spectrum shows two intense bands (Figure 6) at 3356 and 3520  $cm^{-1}$  in the  $\nu(OH)$  region that characterize the formation of water-separated ion pairs:



If we add DBU to these solutions at a 0.3 M concentration, the intensity of the  $\nu(OH_2)$  stretching modes of the water molecules strongly decreases if water is in excess of DBU. It tends to zero in the case where water is in an equimolecular amount with DBU, indicating an almost quantitative protonation of DBU by water activated both by Li<sup>+</sup> and Br<sup>-</sup> ions in the water-separated ion-pairs. Furthermore, the addition of DBU to the lithium bromide water mixture in acetonitrile induces the appearance of at least two new bands at 3320 and 3070 cm<sup>-1</sup> with probably another component at lower frequencies. As the solvent and DBU CH stretching

modes, appearing close to the new bands, may be slightly perturbed by the presence of salt, the substraction of the solvent spectrum and of the added DBU CH vibrations has not been attempted. The new bands may be assigned to the  $\nu(NH^+)$ -related absorptions expected around this position. Indeed for (CH<sub>3</sub>)<sub>2</sub>CHCH= NH<sup>+</sup>CH(CH<sub>3</sub>)<sub>2</sub>BF<sub>4</sub><sup>-</sup> in CD<sub>3</sub>CN similar absorptions have been observed at 3200, 3158, and 3100 cm<sup>-1</sup> with approximately equal intensities in the 3200 and 3100 cm<sup>-1</sup> components.<sup>10</sup> The complexity of this band may either be due to Fermi resonances or to conformations or dynamic effects.<sup>10</sup> Therefore, the lowering of the frequencies of the components of the  $\nu(NH^+)$  at 3070 cm<sup>-1</sup> and at lower frequency seems to indicate as previously observed with chlorine<sup>10</sup> that the =NH<sup>+</sup> group is hydrogen bonded to the Br<sup>-</sup> anion. The small component at 3320 cm<sup>-1</sup> is possibly due to a slight amount of free DBUH<sup>+</sup>...NCCH<sub>3</sub> solvated cation. The protonation mechanism of the imine DBU base by the waterseparated lihtium bromide ion pair is thus as follows:



There is probably formation of a short-lived reaction intermediate where one solvent molecule of the water-separated lithium bromide ion pair in the solvation shell of the lithium cation is replaced by a DBU molecule interacting by its imine nitrogen. Due to the strong  $pK_a$  of the organic base DBU, which like other guanidines is among the strongest organic bases, this short-lived intermediate species reacts through the protonation of the imine nitrogen of the DBU molecule to form an ion-pair aggregate involving a DBUH<sup>+</sup>...Br<sup>-</sup> and a Li<sup>+</sup>...OH<sup>-</sup> ion pair. This ion-pair aggregate further dissociates into a DBUH+...Br- ion pair and a lithium hydroxyde ion pair. This reaction is driven by the high  $pK_a$  in aprotic donor solvents of LiOH, which precipitates. It is thus shown that the acidity of a water molecule activated by both a Br<sup>-</sup> anion and a Li<sup>+</sup> cation is sufficient to protonate a base of  $pK_a$ =  $11.6^{12}$  such as DBU. If we compare the frequency increase of the different complexes formed by water with Li<sup>+</sup> and Br<sup>-</sup> ions in acetonitrile as measured by the  $\nu(OH)$  frequency of the HOD molecule,<sup>1</sup> we observe indeed that, compared to the water molecule hydrogen-bonded to the solvent,  $\nu(OH) = 3578 \text{ cm}^{-1}$ , the acidity indicated by the frequency decrease of the hydrogen-bonded OH involved into the bonding with ions increases when going from the simple activation by only a Li<sup>+</sup> ion 86 cm<sup>-1</sup> or a Br<sup>-</sup> ion 183 cm<sup>-1</sup> to the simultaneous action of a Li<sup>+</sup> ion and a Br<sup>-</sup> ion in the water-separated lithium bromide ion pair 223 cm<sup>-1</sup>. This cooperative effect is smaller than their simple addition, probably due to the less favorable interaction of both Li<sup>+</sup> and Br<sup>-</sup> ions with the water molecule in the solvent-separated ion pair due to their mutual attraction:



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#### Conclusions

We have shown that the  $pK_a$  of water in a lithium bromide water-separated ion pair is sufficient to protonate an imine nitrogen such as that of DBU. This protonation takes place by replacement of solvent molecule by a DBU molecule in the first solvation shell of the cation and proceeds through the concerted formation of two contact ion pairs: Li<sup>+</sup>OH<sup>-</sup> and DBUH<sup>+</sup>Br<sup>-</sup>.

Similar mechanisms may be responsible for the deprotonation of phosphonate esters leading to the formation of carbanions in mild conditions, by the use of single salts like lithium or magnesium salts with an appropriate base like DBU or an amine<sup>5,6,13,14</sup> or for the protonation mechanism of the imine pigments responsible for the vision.<sup>7</sup>

Registry No. DBU, 6674-22-2; LiBr, 7550-35-8; MgBr<sub>2</sub>, 7789-48-2; water, 7732-18-5.

# Simple Wave Effects in Two-Component Nonlinear Liquid Chromatography. Application to the Measurement of Competitive Adsorption Isotherms

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For a binary mixture injected as a wide rectangular pulse, the hodograph transform of the elution profiles (i.e., a plot of  $C_1$  versus  $C_2$  at the same time) results in two straight lines when the equilibrium isotherms follow the competitive Langmuir isotherm model. Moreover, the hodograph plot is universal and is independent of the column length, injection profile, and mass-transfer rate as long as a constant state is achieved. The slope and intercept values of the lines in the hodograph plot are used to derive the best fit Langmuir isotherm parameters for the binary mixture. Experimental results obtained in reversed phase chromatography with a mixture of 2-phenylethanol and 3-phenylpropanol show that by using these best fit parameters a better prediction of the individual elution profiles of the bands is obtained than by employing single-component Langmuir parameters in a competitive isotherm.

## Introduction

All chromatographic responses (whether it be the band profile of a single component, the individual band profiles of the components of a mixture, system peaks, or band profiles in a displacement train) depend primarily on the equilibrium isotherms of the components of the mixture between the two phases of the chromatographic system. A better understanding of the chromatographic separation process as well as the ability to predict the performance of a chromatographic procedure has become necessary for the development of preparative applications of chromatography which are acquiring a great importance in the pharmaceutical industry and the life sciences. Progress in this area requires a detailed knowledge of the competitive phase equilibria involving closely related compounds. Improving our knowledge on this important problem needs in turn the systematic acquisition of experimental data.

The determination of single-component isotherms by chromatographic methods has been extensively investigated in the past as a method of studying adsorption and solubility equilibria in thermodynamics and for process design in chemical engineering. The methods of frontal analysis,<sup>1,2</sup> frontal analysis by characteristic point,<sup>3</sup> and elution by characteristic point<sup>4</sup> were developed 30 years ago. The step and pulse method has been used successfully in gas<sup>5-7</sup> and liquid chromatography.<sup>8</sup> Comparison of the singlecomponent isotherms measured by each of these different methods shows excellent agreement.<sup>9,10</sup> They are also in agreement with isotherms determined by the static methods.<sup>7,9</sup> The validity of the equilibrium isotherms obtained by these methods is further

proven by the excellent agreement observed between the single compound band profiles predicted by exact models of elution<sup>10</sup> and displacement<sup>9,11</sup> chromatography and the profiles recorded experimentally.

Chromatography, however, is a separation method. The investigation of the simplest separation problem, the resolution of a binary mixture, requires the determination of binary competitive isotherms. Using the conventional, static methods, this would be a tedious and time-consuming task, requiring considerable amount of chemicals and solvents. Of the classical chromatographic methods, two have been extended to the measurement of competitive isotherms: the step and pulse method<sup>12,13</sup> and frontal analysis.14

Two implementations of the former method have been developed: the tracer-pulse technique<sup>12,15,16</sup> and the classical pulse technique.<sup>13,17,18</sup> Helfferich and Peterson have shown that if a

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