# Interaction energy in pairs of phthalazinium dibenzoylmethylid (PDBM)–protic solvent molecules estimated in the limits of the cell ternary solution model, by spectral means

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HIGHLIGHTS

▶ The cell model of ternary solutions was applied to homogeneous solutions of PDBM.
▶ The active solvent average statistic weight in the first salvation sphere of PDBM was computed.
▶ The hydrogen bond energy in pairs PA-PDBM and O-PDBM was estimated.

GRAPHICAL ABSTRACT
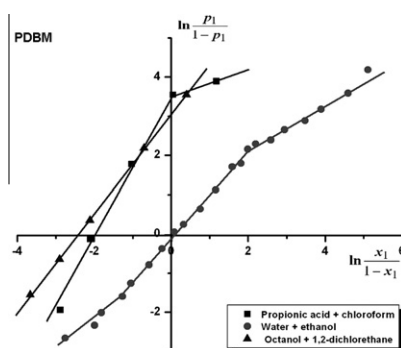
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ABSTRACT

The dipolar compound Phthalazinium-dibenzoylmethylid (PDBM) was used as spectrally active molecule in order to analyze the molecular interactions in ternary solutions containing at least one protic solvent. In PDBM + protic solvent (1) + aprotic solvent (2) ternary solutions, PDBM can be involved both in universal and specific interactions reflected in solvatochromic effects. The protic solvent (or the solvent with the higher electric permittivity) was considered as being active from the interactions point of view. The content of the first solvation sphere of the studied ylid has been established on the basis of the statistical cell model of ternary solutions. The active solvent molecules are dominant in the first solvation sphere of the PDBM molecules. The difference between the interaction energies in the PDBM–active solvent (1) and PDBM–inactive solvent (2) molecular pairs has been determined for three binary solvents water + ethanol (W + E), propionic acid + chloroform (PA + C) and octanol + 1,2 dichloroethane (O + DCE). The hydrogen bond formation energy of the PDBM–protic solvent complex has been estimated in the binary solvents PA + C and O + DCE containing one protic (PA and O, respectively) and one aprotic solvent with close electro-optical parameters refractive index and electric permittivity of the components.

Introduction

The molecules of phthalazinium-dibenzoylmethylid (PDBM) have a phthalazinium heterocycle as cationic part and the negative charge localized on the carbanion [1]. The stability of PDBM is assured by the negative charge delocalization on the ylid symmetrically disubstituted carbanion, by the resonance interactions and also by the Coulombian interactions between the opposite charged parts of the molecule [1–4].

Phthalazinium ylids can be used as precursors for obtaining new heterocycle compounds, in drug preparation, or as acid basic

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indicators [1,5–7]. The majority of the reactions take place in situ; for this reason the knowledge about the intermolecular interactions between phthalazinium ylid and the solvent molecules is of a great importance.

The aim of this study is to establish the applicability of the statistical cell model of ternary solution to the PDBM ternary solutions and to estimate the difference between the energies of interactions in pairs PDBM–protic solvent and PDBM–aprotic solvent molecules, in their ground state. When the binary solvent is made by two solvents (one protic and one aprotic) with close macroscopic parameters, the contribution of van der Waals interactions in the estimated difference is close to null and this difference approximates the energy of hydrogen bond formation in the pair PDBM–protic solvent molecules.

The statistical model of ternary solutions is a cell model in which the molecules are considered spheres arranged in solvation shells around the spectrally active molecule.

The instability from the liquid solutions generated by the small differences between the thermal energy (influencing Brownian motion) and the intermolecular energy determine a continuous modification of the content of the solvation shells. The time of the electronic spectra recording is very high compared with the life time of the solvation shells. Consequently, only statistical average weights defined below influence the spectral shifts measured in ternary solutions of the spectrally active molecules relative to their gaseous phase.

The solvent molecules, of the types (1) and (2), are chaotically distributed in PDBY solvation shells and their supply to the interaction energy with spectrally active molecules (considered as being in the centers of the solvation shells) depends on the statistical average weights of the type (1) and (2) molecules.

The cell model of the ternary solutions has been developed in order to describe the spectral shift of electronic spectra in binary solvent relative to the same spectrum recorded in each component of the binary solvent.

Experimental

PDBM under study was prepared as it is described elsewhere [1,5–7]. Briefly, the treatment of phthalazinium with phenacyl bromide afforded the corresponding bromide [7] and, in aqueous alkaline medium, it led to the corresponding phthalazinium-dibenzoylmethylid (PDBM).

The obtaining procedure and chemical structure of the studied PDBM compound are given in Fig. 1. The purity of the newly obtained PDBM was checked by chemical (elemental) and spectral (FTIR and NMR) analyses.

The solvents, achieved from Merck Company, were spectrally grade and used as received. Three binary solvents were used in this study: Water + Ethanol (W + E), containing two protic solvents; Propionic acid + Chloroform (PA + C) and Octanol + 1,2 Dichloroethane (O + DCE).

The binary solvent was achieved from one active (1) liquid and one inactive (2) liquid in variable volumetric ratios, in order to evidence the possibility of ylid to give hydrogen bond complexes and to estimate the energy of their formation. In binary solvent the
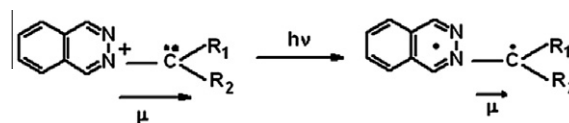

Fig. 2. Mechanism of intramolecular charge transfer (ICT) responsible for PDBM visible band appearance.

liquid with higher value of the electric permittivity (the protic liquid) is considered active from the interactions point of view. The parameters referring to this solvent are noted by (1). The inactive (or less active) solvent from the interactions point of view is indexed by (2).

The molar fractions of the solvents in the binary solvent were computed on the basis of the volumetric ratios [8,9]:

$$x_1 = \frac{C_1 \frac{\rho_1}{M_1}}{C_1 \frac{\rho_1}{M_1} + C_2 \frac{\rho_2}{M_2}} \quad \text{and} \quad x_2 = 1 - x_1 \tag{1}$$

In relations (1), C_1 and C_2, ρ_1 and ρ_2, and M_1 and M_2, respectively, are the volumetric concentrations, the densities and the molar masses of the two solvents composing the binary solvent. The PDBM concentration in solutions was very small, between 10^{-3} and 10^{-4} mol/l.

The solvent refractive index was measured with an Abbe refractometer and the electric permittivity with a RL Oehme DK-meter at 7 MHz. In order to assure a good precision, the refractive index and the electric permittivity were measured for each pure solvent and for the binary solvents.

Phthalazinium ylids have a visible electronic absorption band attributed to an intramolecular charge transfer (ICT) from the carbanion toward the heterocycle (Fig. 2). The electronic spectra of some phthalazinium dibenzoyl methylids in binary solutions [10] and in stretched polymer foils [11] were recently analyzed. The ICT process (Fig. 2) is accompanied by a decrease (or by change in orientation) of the molecular dipole moment.

The electronic absorption spectra were recorded by a Specord UV–Vis Spectrophotometer M22 Carl Zeiss Jena. The wavenumbers in the maximum of the ICT visible band of PDBM was measured by known methods [12].

Theoretical notions

Both universal interactions (of the type orientation, induction or dispersion) and specific interactions (hydrogen bond, proton charge transfer) can act between the PDBM and solvent molecules in solutions. The dipolar molecules of PDBM offer information regarding the composition of their first solvation shell in ternary solutions by the frequency modification in the visible electronic absorption spectra.

Ternary solutions are made by the solute spectrally active molecules (PDBM in our study) and a binary solvent achieved in variable volumetric ratios from one polar, protic (active from the point of view of orientation-induction or/and specific interactions) and one non-polar (inactive or less active from the intermolecular interactions point of view) liquids.
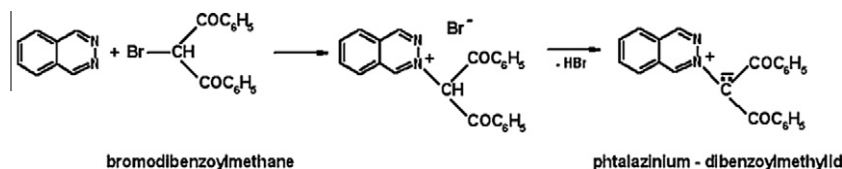

bromodibenzoylmethane · · · · · · · · · · · · phtalazinium - dibenzoylmethylid

Fig. 1. Obtaining reaction of PDBM.