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Dielectric polarization of 2-pyrrolidinone molecules in benzene solution - a quantum-chemical study

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Abstract: *Ab initio* quantum chemical calculations have been performed to study the problem of dielectric polarization of molecules in solutions. It is shown that the theoretical results obtained for 2-pyrrolidinone molecules reproduce quite well the experimantal data at low concentrations.

1. Introduction

Measurements of the dielectric polarization in solutions provide a unique information about association and self-association of solvated molecules by means of analysis of the dependence of the value of the apparent dipole moment square (μ^2_{app}) on the concentration of the solute. In the static dielectric studies μ^2_{app} is determined on the basis of measurements of the electric permittivity, density and refractive index [1], According to the definition, μ^2_{app} equals to the dipole moment of an isolated solute molecule and does not depend on the concentration of a solute only for non-interacting solvated systems, i.e. in the very simplified case. In real molecular solutions, especially those which undergo strong intermolecular interactions caused by formation of hydrogen bonds, μ^2_{app} depends on the concentration, and the shape of this dependence is related to the structure of molecular associates formed. Thus, the dependence of μ^2_{app} on the nominal concentration of the solute, C_0, is determined by the real concentration and the dipole moments of the associates and semi-associates.

Let us represent this dependence as follows:

where K_i and μ_i are, respectively, the equilibrium constant of formation and the dipole moment for a certain associate in the solvent. In principle, the thermodynamic expressions for each K_i could be taken into account and the equation (1) could be solved. In practice, however, the values of K_i and μ_i are usually determined from independent experiments or postulated [2], In consequence, the equation (1) is solved by finding the best fitting between the calculated and the experimental dependence of μ^2_{app} on concentration.

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In this report we propose another way of solving equation (1). We evaluate the necessary parameters of the equation (1) from *ab initio* quantum chemical calculations, which are now quite common to study chemical reactions in the gas phase. In the case of small molecules and intermolecular complexes, the use of the post Hartree-Fock approximations together with the extended basis sets, including polarization functions, allows one to obtain really 'experimental accuracy' for such characteristics of a molecule as its geometry, enthalpy, electronic density distribution, etc. The current performance of similar characteristics at the Hartree-Fock level for molecules of moderate and large sizes are also quite satisfactory. This allows one to get qualitative or semi-quantitative predictions for the molecular properties mentioned above. Similar realistic calculations of the influence a solvent [3] require substantially more computer time than the usual quantum chemical calculations. This is the reason why many simplified schemes, based on the continuum approximation, have been developed [4], They can provide qualitative or semi-quantitative data, depending on the level of complexity.

Below, we present the results of *ab initio* investigation for the dilute solutions of 2-pyrrolidinone in benzene, which system was extensively studied by other researchers using different techniques [2,5].

2. Calculation method

The *ab initio* Hartree-Fock calculations were performed with the GAMESS [6] program using the standard 6-31G* basis set. The interaction enthalpy at OK (ΔH_0) was calculated as the difference between the energy of the dimer (Ed) and the isolated monomer (E_m), corrected for the basis set superposition error (BSSE) by the counterpoise method and for the zero-point vibrational energy (ZPE) according to the expression:

$$\Delta H_0 = E_d - 2E_m + \Delta BSSE + ZPE_d - 2ZPE_m ,$$

where the indexes *d* and *m* belong to the monomer and the dimer, respectively.

To estimate the dependence of the electrostatic part of the solvation energy in the benzene solvent upon the relative energies of dimers, we applied the self-consistent reaction field method, implemented in the GAMESS program at the Onsager level [1]. We have used the electric permittivity value $\varepsilon = 2.2$, corresponding to benzene, and the cavity radius 4.09 A, which comes from the calculations of the molecular volume.

To estimate the equilibrium constants, the standard thermodynamic formula $K = e^{-\frac{\Delta G}{RT}}$ has been used. Because the entropy changes are usually much smaller then the changes of the enthalpy, and because the calculations of the entropy in solution are still out of real possibilities of the most of computers, the entropy changes have not been taken into account.

3. Results and discussion

According to the numerical experimental data, the self-association of 2-pyrrolididone in dilute benzene solutions is described as the interaction of monomeric 2-

pyrrolidinone molecules forming dimers[2,5]. Following these data, to interpret the dielectric properties of the 2-pyrrolidinone solutions, we assumed the simplest possible model, according to which the 2-pyrrolidinone molecules form two different types of dimers (Fig. 1). Thus, the following equation should be valid:

$$\text{Dimer A} \overset{K_d}{<\text{-----}>} 2\ \text{monomers} \overset{K_{d'}}{<\text{-----}>} \text{Dimer B} \tag{2}$$

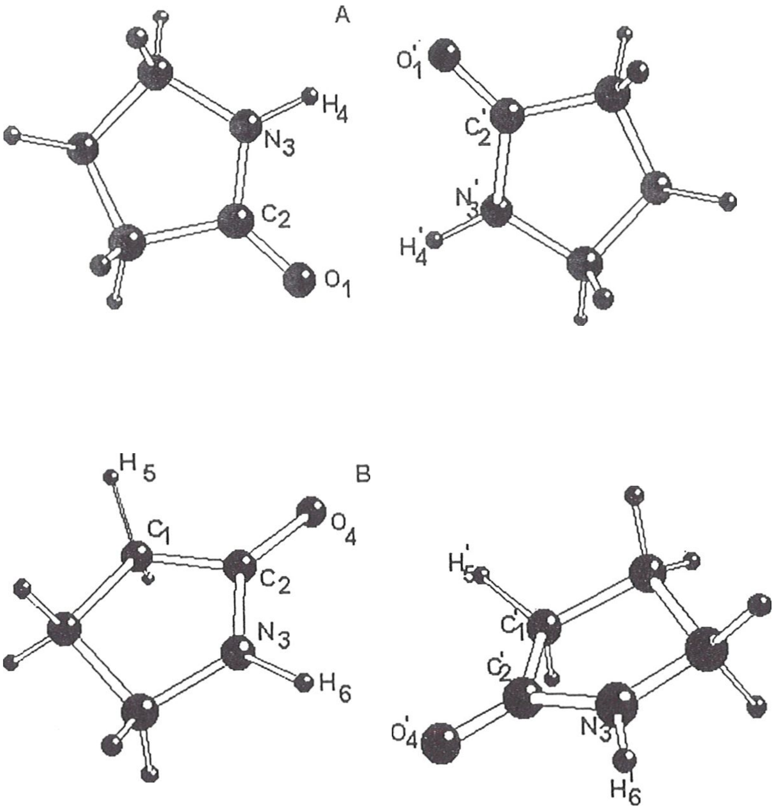

Figure 1. Structures of the two dimers considered in this paper.

If C_0 is the initial molar concentration (mol/dm^{-3}) of the lactam and C_m , C_d , $C_{d'}$ are the equilibrium concentrations of the monomers and the dimers respectively, then:

$$C_0 = C_m + 2\,C_d + 2\,C_{d'} \tag{3}$$

and

$$C_0\,\mu^2_{app} \equiv C_m\ \mu^2_m \quad + \quad C_d\,\mu^2_d \quad + \quad C_{d'}\,\mu^2_{d'} \tag{4}$$

Hence, the equation (1) can be presented as follows:

$$g(C_0) \equiv \mu_{app}^2/\mu_m^2 = 1/C_0(C_m + K_{d'} C_m^2 g_1), \qquad (5)$$

where:

$$C_m = \frac{-1+\sqrt{1+8\,(K_d+K_{d'})\,C_0}}{4\,(K_d+K_{d'})} \qquad (6)$$

and

$$g_1 = (\mu_{d'}/\mu_m)^2 \qquad (7)$$

As one can see, K_d, $K_{d'}$, μ_d and $\mu_{d'}$ should be calculated, to get the concentration dependence of $g(C_0)$.

We have also performed the analysis of geometrical parameters of the 2-pyrrolidinone dimers, because their geometry has been a subject of discussions [5],

3.1. Geometry of the dimer. The dimer having the lowest energy has cyclic structure with C_{2h} symmetry as it is drawn in Fig. 1A. It is easy to see that the dipole moment of this associate is zero, $\mu_d = 0$. So, it does not appear in any static dielectric measurements. The geometrical structure of the other dimer(s), having a non-zero dipole moment, still remains a subject of discussion [5] because, from a formal point of view, the possible dimers can have either open or cyclic structures. To our best knowledge, there has been no report about the geometrical parameters for 2-pyrrolidinone dimers neither any *ab initio* calculations of the hydrogen bonding for 2-pyrrolidinone are known to us. Thus, as a reference system we have chosen the formamide dimer, which has been extensively studied both theoretically [7] and experimentally [8], According to the very precise investigation of the hydrogen bonding of the formamide molecules [7a], there exist at least three types of hydrogen bonded dimers. All of them are cyclic and have: a) two NH...0 bonds (zero dipole moment, ΔE=11.4 kcal/mol at the MP2/DZP level, global minima between all the hydrogen bonded dimers); b) NH...0 and CH...0 bonds (non zero dipole moment, ΔE_d=7.1 kcal/mol at the MP2/DZP level); c) two CH...0 bonds (zero dipole moment, ΔE_d=2.8 kcal/mol at the MP2/DZP level).

In the case of the self association of the 2-pyrrolidinone, we have identified two local minima, drawn in the Fig 1, which correspond to the first two types of the hydrogen bonding of formamide molecule. The geometrical parameters of the minima drawn in Fig 1A are collected in Table 1, together with the available parameters for the formamide dimer. One can see that the corresponding geometrical parameters of the formamide and the 2-pyrrolidinone dimers are very close to each other. Therefore, we should conclude that the geometry of this type of the hydrogen bonded dimers does not depend too much on the chemical structure of the corresponding amides. The main difference, that we should emphasize, is the difference in the torsion angle $C_2O_1H'_4N'_3$. This means that unlike to the formamide dimer, the 2-pyrrolidinone dimer A (Fig. 1) is slightly nonplanar.

Parameter	6-31G*	6-31G** [7b]	MP2/6-31G** [7b]	X-ray [7b]
R_{C2N3}	1.338	1.333	1.343	1.318
R_{C2O1}	1.208	1.205	1.237	1.241
R_{N3H4}	1.005	1.004	1.021	1.010
$R_{C2C2'}$	4.137	4.153	4.081	4.183
$R_{O1N3'}$	2.995	2.995	2.900	2.948
$R_{O1H4'}$	1.998	-	-	-
$<_{O1C2N3}$	126.5	126.6	125.6	124.9
$<_{C2N3H4}$	121.0	120.6	120.6	119.6
$<_{C2C2'N3}$	62.7	63.6	61.4	60.7
$<_{C2N3O1'}$	115.2	113.0	117.4	118.5
$<_{N3H4O1}$	171.3	171.6	175.0	-
$<_{C2O1H4'}$	120.7	-	-	-
$<_{C2O1H4'N3'}$	8.8	0.0	0.0	0.0

Table 1. Selected geometrical parameters (bond lengths in A and bond angles in degrees) of the A-dimers of the 2-pyrrolidinone (column 2; Fig. 1A) and the a)-dimers of the formamide (columns 3-5).

Length	R_{C2N3}	$R_{C'2C'1}$	R_{C2O4}	$R_{C'2O'4}$	R_{N3H6}	$R_{O4H'5}$	$R_{H6O'4}$	$R_{C'1H'5}$
	1.344	1.516	1.203	1.205	1.003	2.452	2.031	1.081

Angle	$<_{O4C2N3}$	$<_{O'4C'2N'3}$	$<_{C2N3H6}$	$<_{C2C'1H'5}$	$<_{C2N3O4}$	$<_{C'2C'1O'4}$
	126.6	125.5	121.2	111.0	120.5	101.1
Angle	$<_{C'1H'5O4C2}$	$<_{H'5O'4C2}$	$<_{C'1H'5O4}$	$<_{N3H6O'4}$	$<_{H6O'4C'2}$	$<_{N3H6O'4C'2}$
	118.6	60.9	179.0	120.0	4.4	-5.8

Table 2. Selected geometrical parameters (bond lengths in A and bond angles in degrees) of 2-pyrrolidinone dimer (Fig. 1B).

The geometrical parameters of the dimer B of 2-pyrrolidinone are collected in the Table 2 and the geometrical structure is drawn in Fig. 1B. We can easy recognize the two hydrogen bonds (**$N_3H_6...O'_4$** and $C'_1H'_5...O_4$) knowing the typical interatomic distances for each of them [8], The non-planarity of this dimer, which is characterized by non-zero (and the opposite sign) of the $N_3H_6O'_4C'_2$ and $C'_1H'_5O_4C_2$ angles, should also be noted.

Molecule	E_{tot}	ΔE	BSSE	ZPE	ΔH_0	ΔE_{solv}	μ
Dimer A	-569.78094	-13.5 (-13.4)[b]	2.6	0.24215	-9.3 (-8.7-9,6)[b] (-7.2)[c]	0.0	0.0
Dimer B	-569.77327	-8.6	2.0	0.24132	-5.4 (-4.2)[b]	0.4	2.8 (2.3)[c]
Monomer	-284.87974	-	-	0.11979	-	2.8	4.3 (4.0)[c]

Table 3. Total energies (E_{tot}, a.u.), basis set superposition errors (BSSE, kcal/mol), zero-point vibration energies (ZPE, a.e.)[a] , interaction energies (ΔE, kcal/mol), enthalpies ($\Delta H_{0;}$ kcal.mol), energy of solvation (ΔE_{solv}, kcal/mol) and dipole moments (μ, D), calculated for the 2-pyrrolidinone dimers. [a] calculated at 3-21G* level; [b] from Ref. [7a]; [c] from ref [2c].

3.2. Interaction energies. The calculated values of the energies are presented in Table 3. The experimental data for self association of the 2-pyrrolidinone (available from [2c]) and the calculated data for the formamide dimer (from Ref. [7b]) are also collected there. The conclusions coming from the analysis of these data are as follows. *(i)* The agreement between the experimental and our theoretical results is quite good. *(ii)* Slightly weaker NH...O hydrogen bonding for the dimer B follows from the analysis of both the interatomic distances and the interaction energies data, *(iii)* The influence of the solvation manifests itself much stronger in the case of the monomer than in the case of the dimer. *(iv)* Finally, we should also emphasize the satisfactory correspondence between the experimental and the calculated dipole moment values.

3.3. Dielectric polarization of the 2-pyrrolidinone in the benzene solution. The analysis of the calculated geometrical and energetic parameters leads to the conclusion that all parameters that one needs to solve equation (5) are in a reasonable agreement with the experimental values. Below we apply these parameters to solve the equation (5).

The corresponding experimental and theoretical dependencies, for the temperature range from 20 to 50 °C and for the concentration of the 2-pyrrolidinone between 0.008 and 0.8 mol/dm^{-3}; are drawn in Fig. 2. One can see there that the *ab* *initio* calculated values of ΔH_0 and the dipole moments of the monomer and the dimers are able to reproduce quite well the experimentally obtained curves, $g(C_0)$, giving the quantitative agreement with the experimental data in the range of low concentrations, i.e. in the region where, probably, only the dimers coexist with the monomers. The agreement becomes semi-quantitative, when the concentration grows up; what we interpret as an indication of presence of higher multimers in the solution.

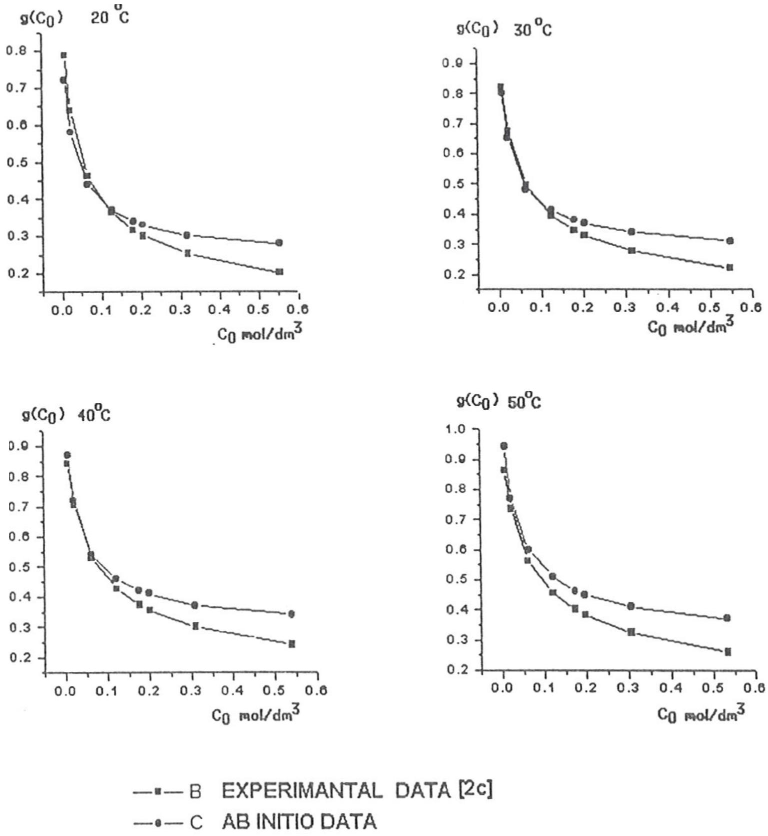

Figure 2. The experimental and theoretical dependence of the relative apparent dipol moment, $g(C_0)$, on the concentration of the 2-pyrrolidinone in benzene solution at four different temperatures.

4. Conclusions

This study is addressed mainly to outline the possibilities of *ab initio* calculations to solve theoreticaly the problem of dielectric polarization of molecules in solutions. The obtained agreement between the experimental data and the Hartree-Fock calculations looks very promising from this point of view. As a next step, the post-Hartree-Fock calculations for the dimers of similar sizes and the calculations of trimers and tetramers at the Hartree-Fock level are in progress. The use of the more sophisticated schemes to model the influence of the solvent is also under development.

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