

Electrostatic Potentials of Molecules and Prediction of the Lewis Acid-Base Properties of Solvents, Part I. General Considerations

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Summary. Electrostatic potentials in the vicinity of isolated molecules of typical nonaqueous solvents were computed in the MNDO approximation. It was found that the calculated dipole moments are in good agreement with experimental values. However, it turned out that in many cases electrostatic interactions of ions with solvent molecules cannot be described in the frame of ion-dipole interactions. Thus, two computable parameters, UN and UP describing short-range electrostatic interactions of a solvent molecule with a cation or an anion of radius R were proposed. The dependence of UN and UP upon R is analyzed in the context of ion-solvent interactions.

Keywords. Electrostatic interactions; MNDO calculations; Solvent effect.

Elektrostatistische Potentiale von Molekülen und Voraussage von Lewis-Säure-Base-Eigenschaften von Lösungsmitteln, 1. Mitt.: Allgemeine Grundlagen

Zusammenfassung. Es wurden die elektrostatischen Potentiale in der Umgebung von isolierten Molekülen typischer nichtwäßriger Lösungsmittel in der MNDO-Näherung berechnet. Die berechneten Dipolmomente waren in guter Übereinstimmung mit den experimentellen Werten. Es wurde jedoch beobachtet, daß in vielen Fällen die elektrostatischen Wechselwirkungen von Ionen mit Lösungsmittelmolekülen nicht im Rahmen von Ionen-Dipol-Wechselwirkungen beschrieben werden können. Dafür wurden zwei berechenbare Parameter UN und UP zur Beschreibung von elektrostatischen Wechselwirkungen im Nahbereich eines Lösungsmittelmoleküls mit einem Kationen- oder Anionenradius R vorgeschlagen. Die Abhängigkeit von UN und UP von R wurde im Zusammenhang von Ionen-Solvens-Wechselwirkungen untersucht.

Introduction

Although the effect of solvent on the rate and the position of equilibria of chemical reactions has been known since the last century, there are still no exact methods for quantitative prediction of such solvent effects [1–5]. Generally, many attempts have been made to correlate the chemical and physicochemical properties of the solutes with the parameters characterizing the solvents.

Quite often attention is paid to the macroscopic parameters, e. g. electric permittivity (ϵ) or refractive index. The solvent is considered as a homogeneous iso-

tropic continuum which surrounds the molecules of the solute, and, consequently, it is believed that the mentioned parameters control the so-called universal or non-specific (long-range) solvent-solute interactions. In fact, the electric permittivity describes only the ability of a solvent to separate electrical charges and to orient its dipolar molecules in the electric field. Then it is not surprising that for many solvents and solutes the correlations with ϵ are not obeyed; these systems often interact specifically and have to be treated accordingly.

Following this model, the medium is characterized as inhomogeneous and anisotropic, and these features should determine the solvent-solute interactions. In other words, it is believed that such interactions are chemical (short-range) in nature and consist of the formation of solvation complexes through donor-acceptor bonds which are localized and directed in space in a definite manner. So, the most important manifestation of specific interactions is regarded as being connected with the interactions of Lewis acids and bases.

Besides these two alternative viewpoints, the idea of so-called cooperative solvent-solute interactions has been developed. This case is considered intermediate between the specific and non-specific interaction mechanisms. Accordingly, numerous multiparametric relations have been proposed to describe various aspects of the solvent-solute interactions (for a recent review cf. Ref. [5]). The basic idea of these propositions is connected with the separation of the empirical solvent parameters into independent contributions arising from specific and non-specific forces. Is this differentiation possible, in fact?

There are linear trends between certain kinetic data and solvent acceptor numbers [6] which also include low dielectric media. Analyzing such relations, Mayer [7] has pointed out that the acceptor numbers, which express the Lewis acidities of solvents, possibly include contributions from long-range forces. This idea seems to be consistent with existing correlations between solvent acidity and the optical characteristics of solvated electrons [8]. Schmidt [9, 10] has proposed to combine the Lewis acidity and basicity parameters with $\log \epsilon$ in one equation. In Ref. [10] we can even read "...specific and non-specific interaction changes parallel each other, or, heretically, traditional electrostatic solvation – as a counterpart to specific solvation – does not exist at all or else is insignificant".

Kęcki et al. [11], analyzing critically the empirical systems used to describe solvent properties, have expressed the opinion that the parameters properly describing the solvent effects are those which are sensitive to the electron charge redistribution.

Recently, an important step forward was achieved by the application of factor analysis which led to very interesting results. Analyzing different basicity parameters of 22 aprotic solvents, Maria et al. [12] demonstrated clearly that the property defined as basicity should at least be described by two independent components named F_1 and F_2 . F_1 was recognized as a measure of the ability of a given molecule to form covalent bonds and to participate in charge-transfer interactions. The nature of F_2 is essentially electrostatic.

However, it appears to the present authors that even the problem of electrostatic interactions is still open for discussion. At least two questions should be answered. Does the dipole moment describe properly the electrostatic field operating around the molecules of commonly used solvents? Is it possible to introduce other parameters describing electrostatic interactions? We wish to report here our results on this subject.

Results and Discussion

Method of Computation

In order to obtain some information on the electrostatic properties of the molecules under study, we have used the semi-empirical method MNDO with geometry optimization [13–15]. This method is much less time-consuming than any ab initio procedure that gives results of comparable quality [14]. An additional advantage of MNDO calculations is the simplicity of obtaining $U(\mathbf{r})$, the electrostatic potential [16] around the molecule at the points of space indicated by the vector \mathbf{r} . The potential function is represented in the form of a multicenter multipole expansion [17]:

$$U(\mathbf{r}) = \sum_{nuclei} \left[\frac{q_A}{|\mathbf{r} - \mathbf{r}_A|} + \frac{\tilde{\mu}_A \cdot \mathbf{r}}{(|\mathbf{r} - \mathbf{r}_A|)^2} + \dots (\text{higher terms}) \right] \quad (1)$$

where q_A , $\tilde{\mu}_A$, ... are partial charge, dipole moment (and higher multipole moments) localized on nucleus A at \mathbf{r}_A .

Due to the assumption in the MNDO method (zero overlap of atomic orbitals), the lower multipoles centered at each nuclei of a given molecule can be easily calculated from the final bond-order matrix. Only very simple arithmetic operations are necessary and corresponding formulae are essentially the same as used during computing two-center integrals in MNDO calculations [13–15]. We have found, however, that in the distance range of interest the quadrupoles do not contribute markedly to the overall $U(\mathbf{r})$ values. Consequently, the expansion (1) was truncated at the dipole term.

Among limitations of the MNDO method we should note the lack of adequate parameterization for sulphur and phosphorus atoms [18]. This excluded from our study some important solvent molecules, e. g. dimethylsulfoxide and hexamethylphosphotriamide. However, this reduction seems not to be very serious as we were still able to perform the computations for many other representative molecules. It should be added in this place that all the calculations were carried out on an IBM XT personal computer equipped with a math co-processor.

At the beginning we have calculated the dipole moments of the molecules under study. The results of these computations together with corresponding experimental values extracted from the literature are collected in Table 1. Further, we have determined the standard deviation of experimental and calculated dipole moments

$$\mu_{exp} = (1.082 \pm 0.020) \mu_{calc} \quad (2)$$

which is moderate: $s_\mu = 1.50 \cdot 10^{-30} \text{ C m}$ (0.45 Debye). It is noteworthy that this s_μ value is comparable with the variation of dipole moments determined by various experimental techniques. The slope of the regression is close to unity with a correlation coefficient $r = 0.946$ for $N = 79$ data points. Thus, we can assume that our calculations reflect satisfactorily electrostatic properties of the molecules under consideration.

Properties of the Electrostatic Potentials

An analysis of the changes of electrostatic potentials calculated according to Eq. (1) is very suggestive. The function $U(\mathbf{r})$ depends on each of the three spatial coordinates

Table 1. Electrostatic parameters of the molecules of selected solvents

| No. | Solvent | $\mu_{calc.}^a$ | $\mu_{exp.}^b$ | UN^c | UP^d |
|-----|-----------------------------|-----------------|--------------------|--------|--------|
| 1 | Benzene | 0.00 | 0.00 | 15.8 | 4.5 |
| 2 | Carbon tetrachloride | 0.00 | 0.00 | 6.5 | 16.5 |
| 3 | 1,4-Dioxane | 0.00 | 0.00 | 49.5 | 31.2 |
| 4 | Cyclohexane | 0.00 | 0.00 | 0.4 | 0.1 |
| 5 | Tetramethylsilane | 0.00 | 0.00 | 2.1 | 7.9 |
| 6 | Biacetyl | 0.00 | 4.07 | 55.4 | 34.9 |
| 7 | 3,5-Dichloropyridine | 1.37 | 3.17 | 48.3 | 31.6 |
| 8 | Furan | 1.40 | 2.20 | 36.8 | 15.1 |
| 9 | N,N-Dimethylaniline | 1.77 | 5.37 | 36.6 | 14.4 |
| 10 | Dimethyl carbonate | 2.24 | 2.87 | 75.0 | 27.8 |
| 11 | Diethyl carbonate | 2.80 | 3.54 | 77.4 | 22.2 |
| 12 | Triethylamine | 3.04 | 2.74 | 42.7 | 21.1 |
| 13 | di- <i>n</i> -propyl ether | 3.57 | 3.94 | 58.6 | 25.1 |
| 14 | Diethylamine | 3.64 | 3.07 | 56.6 | 29.8 |
| 15 | Diethyl ether | 3.67 | 3.54 ^d | 57.6 | 25.7 |
| 16 | Phenol | 3.90 | 4.07 ^d | 50.6 | 42.7 |
| 17 | 1-Propanol | 4.64 | 5.54 | 61.6 | 44.6 |
| 18 | Chloroform | 4.67 | 3.47 ^d | 15.8 | 44.9 |
| 19 | Cyclopropylamine | 4.67 | 3.97 ^d | 60.1 | 44.2 |
| 20 | 1-Butanol | 4.70 | 5.30 | 61.9 | 43.8 |
| 21 | Anisole | 4.77 | 4.50 | 62.9 | 18.4 |
| 22 | Ethanol | 4.77 | 5.60 ^d | 61.4 | 44.3 |
| 23 | 2-Propanol | 4.84 | 5.60 | 62.5 | 41.9 |
| 24 | 2-Methyl-2-propanol | 4.94 | 5.50 | 64.2 | 35.4 |
| 25 | Methanol | 4.94 | 5.54 ^d | 61.6 | 46.5 |
| 26 | Tetrahydropyran | 5.04 | 5.27 ^d | 62.4 | 17.8 |
| 27 | Vinyl acetate | 5.27 | 5.84 | 74.0 | 28.5 |
| 28 | Methyl formate | 5.50 | 5.90 | 75.9 | 33.8 |
| 29 | Ethyl formate | 5.57 | 6.41 | 76.5 | 31.6 |
| 30 | 2,6-Dimethylpyridine | 5.70 | 5.54 | 68.7 | 20.4 |
| 31 | Ammonia | 5.87 | 4.90 ^d | 65.2 | 57.5 |
| 32 | Methyl acetate | 5.87 | 5.74 ^d | 78.8 | 26.0 |
| 33 | Tetrahydrofuran | 5.90 | 5.84 ^d | 66.9 | 18.9 |
| 34 | <i>o</i> -Dichlorobenzene | 5.90 | 8.47 | 24.4 | 30.2 |
| 35 | Water | 5.94 | 6.17 ^d | 66.9 | 60.3 |
| 36 | Tetramethylguanidine | 6.00 | - | 73.9 | 31.3 |
| 37 | 2,4,6-Trimethylpyridine | 6.04 | 6.44 | 68.0 | 19.4 |
| 38 | Ethyl acetate | 6.07 | 5.87 | 79.7 | 25.2 |
| 39 | 2-Chloroethanol | 6.17 | 5.80 | 39.5 | 59.5 |
| 40 | Chlorobenzene | 6.24 | 5.64 | 32.9 | 19.3 |
| 41 | Methylene chloride | 6.34 | 5.40 | 27.5 | 53.3 |
| 42 | Pyridine | 6.57 | 7.41 ^d | 71.6 | 22.2 |
| 43 | 4-Methylpyridine | 6.77 | 8.57 | 72.0 | 19.3 |
| 44 | <i>tert</i> -Butyl chloride | 7.47 | 7.11 | 46.3 | 28.1 |
| 45 | Ethylenediamine | 7.51 | 5.90 ^d | 65.3 | 54.6 |
| 46 | Ethyl monochloroacetate | 7.54 | 8.81 | 68.7 | 47.7 |
| 47 | 2-Aminoethanol | 7.57 | 10.17 ^d | 61.9 | 58.0 |
| 48 | Ethyl benzoate | 7.61 | 6.51 | 83.8 | 21.5 |

Table 1 (continued)

| No. | Solvent | $\mu_{calc.}^a$ | $\mu_{exp.}^b$ | UN^c | UP^d |
|-----|--------------------------------|-----------------|--------------------|--------|--------|
| 49 | N,N,N',N'-Tetramethylurea | 7.67 | 11.58 | 84.9 | 25.3 |
| 50 | Chloroacetonitrile | 7.77 | - | 55.1 | 58.6 |
| 51 | 2-Cyanoethanol | 7.87 | - | 67.2 | 62.6 |
| 52 | Ethyl trichloroacetate | 7.91 | 8.51 | 58.4 | 42.0 |
| 53 | 3-Pentanone | 8.01 | 9.04 | 76.5 | 34.7 |
| 54 | 2-Butanone | 8.21 | 9.27 ^d | 76.9 | 36.6 |
| 55 | Cyclopentanone | 8.21 | 11.01 ^d | 76.3 | 25.5 |
| 56 | Acetone | 8.37 | 9.47 | 77.3 | 38.6 |
| 57 | Cyclohexanone | 8.54 | 9.57 ^d | 77.6 | 30.6 |
| 58 | Epichlorhydrin | 8.57 | 6.00 | 61.3 | 46.8 |
| 59 | Acetonitrile | 8.81 | 13.08 ^d | 69.6 | 35.5 |
| 60 | Propionitrile | 9.04 | 13.51 ^d | 70.5 | 35.4 |
| 61 | Acetophenone | 9.07 | 10.01 | 81.3 | 24.6 |
| 62 | Benzyl cyanide | 9.41 | 11.58 | 70.4 | 33.9 |
| 63 | Benzaldehyde | 9.47 | 9.91 | 79.0 | 27.5 |
| 64 | N,N-Dimethylformamide | 10.64 | 12.88 | 91.3 | 44.0 |
| 65 | N,N-Dimethylacetamide | 10.71 | 12.64 | 93.6 | 39.6 |
| 66 | N-Methylformamide | 10.91 | 12.88 ^d | 92.8 | 46.6 |
| 67 | 1-Methyl-2-pyrrolidinone | 10.98 | 13.64 | 92.9 | 31.0 |
| 68 | γ -Pyrone | 11.14 | 12.41 | 91.9 | 36.6 |
| 69 | Benzonitrile | 11.18 | 14.65 | 74.6 | 27.5 |
| 70 | Formamide | 11.21 | 10.74 | 94.9 | 59.2 |
| 71 | 2-Pyrrolidinone | 11.21 | 11.84 | 93.9 | 32.9 |
| 72 | N-Methylimidazole | 12.34 | 12.44 | 95.0 | 47.7 |
| 73 | N,N-Dimethylchloroformamide | 12.38 | - | 76.5 | 50.0 |
| 74 | N,N,N',N'-Tetraethylurea | 12.41 | - | 102.3 | 38.7 |
| 75 | N,N-Dimethylcyanamide | 12.51 | 15.91 ^d | 86.0 | 43.5 |
| 76 | N,N'-Dimethylpropyleneurea | 12.71 | - | 103.5 | 38.1 |
| 77 | Pyridine-N-oxide | 13.01 | 13.78 ^d | 105.3 | 34.8 |
| 78 | 2,2,2-Trifluoroethanol | 13.11 | - | 56.1 | 96.3 |
| 79 | Hexafluoroisopropanol | 13.18 | - | 65.5 | 122.2 |
| 80 | N,N-Dimethyltrifluoroacetamide | 13.68 | - | 72.6 | 58.0 |
| 81 | Nitromethane | 13.88 | 11.54 | 74.6 | 71.3 |
| 82 | γ -Butyrolactone | 13.88 | 14.24 ^d | 90.2 | 48.1 |
| 83 | 2,6-Difluoropyridine | 14.01 | 12.74 ^d | 78.8 | 50.2 |
| 84 | 2-Cyanopyridine | 15.21 | 17.45 ^d | 75.0 | 45.0 |
| 85 | N-Methyl-oxazolidone | 15.61 | - | 99.9 | 54.0 |
| 86 | Ethylene carbonate | 15.75 | 16.25 | 90.5 | 72.1 |
| 87 | Propylene carbonate | 16.18 | 16.48 | 92.2 | 69.7 |
| 88 | Nitrobenzene | 16.75 | 14.14 | 80.5 | 44.7 |
| 89 | N-Methylsydnone | 21.31 | 24.35 ^e | 102.8 | 85.7 |

^a Dipole moment, in 10^{-30} C m

^b Experimental data, preferably for the gas phase, taken from Ref. [22] if not stated otherwise

^c Calculated, this work, in kJ/mol (see text)

^d Taken from Ref. [23]

^e Taken from Ref. [24]

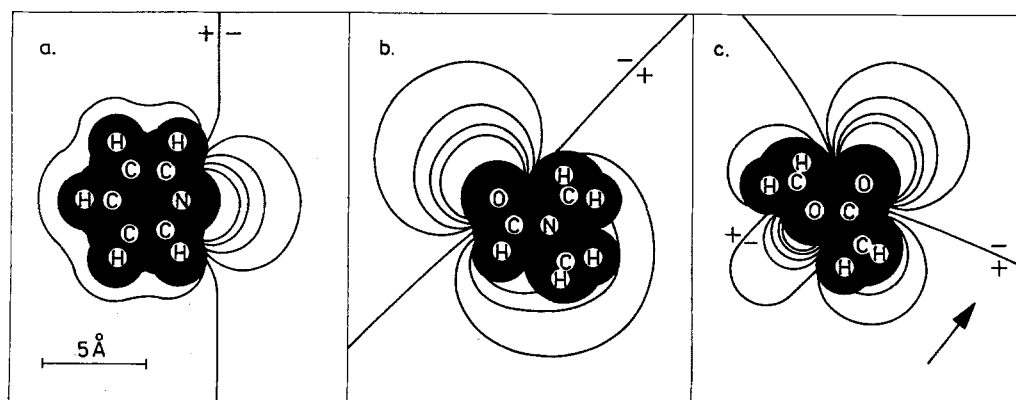


Fig. 1. Electrostatic potential in the vicinity of isolated molecules: pyridine (a), N,N-dimethylformamide (b) and methyl acetate (c) (for detailed explanation see text)

and generally it cannot be shown in a plane. However, one can show two-dimensional sections of it in a form of maps with contour lines connecting points of the same value of the potential. We show here (Fig. 1) the maps for three exemplary molecules: pyridine, N,N-dimethylformamide, and methyl acetate. These molecules are essentially planar and, therefore, we present only one section for each of them.

As a measure of the potential $U(\vec{r})$, we use the energy of interaction of the molecule with an elementary point charge ($z = +e$); this energy is expressed in kJ/mol units. The potential around a positive charge is assumed to be positive. The thick line corresponds to zero energy of interaction, the others mark energies of ± 25 , ± 50 , ± 75 , and ± 100 kJ/mol, respectively.

The space inside the van der Waals spheres of atoms is shadowed, because our multipole expansion should not be used at very small distances from the nuclei. The van der Waals radii of atoms have been extracted from [19], the van der Waals radius of hydrogen is assumed to be 110 pm.

Some further remarks ought to be done now. As we understand it today, the electrostatic potential near the pyridine ring is not a simple dipolar one, despite a high symmetry of the molecule. The regions of negative and positive potentials differ significantly; they may not be described with a single dipole. It seems to be a paradox that the potential in the vicinity of the non-symmetrical molecule of N,N-dimethylformamide (*DMF*) appears to be more regular. Also it is remarkable that the electrostatic potential near the nitrogen atom of *DMF* (above or below the plane in Scheme 1 b) is weakly positive, despite the negative partial charge of the nitrogen, while, as expected, it is strongly negative at the oxygen.

The most impressive observation may be done, however, for methyl acetate. There are two distinct regions of negative potential on the opposite sides of the ester group (oxygen atoms). The overall potential near the molecule looks like a potential of a quadrupole. Only ca. 2 nm apart, it starts to resemble a potential of a dipole, but then the energy of interaction is small, about 1 kJ/mol. Such a behavior cannot be easily predicted, as the calculated dipole moment of the molecule is significant and equals to $5.87 \cdot 10^{-30}$ C m (1.76 D; its direction is indicated in Fig. 1 c). Moreover, the electrostatic potential in the vicinity of the carbonyl oxygen is comparable with that of *DMF*, although the dipole moment of the latter molecule

is twice as large as that of methyl acetate. It is apparent that in this case the total dipole moment reproduces poorly the molecular electrostatic potential.

Do our results allow any simple description of electrostatic ion-solvent interactions?

Let us notice that when a nonpolarizable ion, i.e. a charged hard sphere of radius R , interacts with a molecule of solvent, their most probable configuration is obtained when the electrostatic energy of the system reaches a minimum. This energy may be calculated as extreme of the potential energy on the surface located at the distance R above the van der Waals surface of the molecule. In our case the extremes were found for given R and charge of the "probe" ion with the help of a simple computer program using the output of the original MNDO program. Typically the extremes were observed in perfect agreement with intuition; they were located in the vicinity of O or N atoms for probe cations and near C or H atoms for probe anions.

So, let us introduce two functions: $UN(R)$ and $UP(R)$. $UN(R)$ describes the negative side of a solvent molecule. For a given R , $UN(R)$ equals to the absolute value of energy of purely electrostatic binding of a cation ($z = +e$) with the radius R to the isolated solvent molecule. Similarly, $UP(R)$ is proper for anions ($z = -e$) and describes the positive side of the molecule. For convenience, both $UN(R)$ and $UP(R)$ will be expressed in kJ/mol units. Obviously, the energy of interaction of a polyvalent ion is proportionally larger than for a monovalent one. It is also clear that $UN(R)$ as well as $UP(R)$ decrease with an increase of R .

Certainly, the two functions of a single variable, $UN(R)$ and $UP(R)$, contain less information about the electrostatic potential of a molecule than the three-dimensional $U(\vec{r})$, but, as we shall see later, using them seems to be sufficient in many situations.

It would be very comfortable if we could find a functional form of $UN(R)$ and $UP(R)$, so let us have a look at Fig. 2. We may observe that both functions behave more regularly than one might expect remembering the complex patterns observed in Fig. 1. This indicates that we may look for a common functional approximation of them. The simplest approximations are often useful; so let us notice that in an ion radius range of 100–500 pm $UN(R)$ and $UP(R)$ vary roughly like $1/R$. Thus, knowing $UN(R_{ref})$ for a reference ion radius R_{ref} , we may reconstruct $UN(R)$ for other values via the formula

$$UN(R) = UN(R_{ref}) \frac{R_{ref}}{R} \quad (3)$$

Of course, *mutatis mutandis* the same may be told about $UP(R)$.

After careful analysis we suggest to use in both formulae [for $UN(R)$ as well as for $UP(R)$] $R_{ref} = 133$ pm. Later, we will refer to $UN(133 \text{ pm})$ and $UP(133 \text{ pm})$ simply as to scalar values UN and UP . 133 pm is equal to the crystal (Pauling) radius of the K^+ cation, and, at the same time to the radius of the F^- anion. Additional arguments for this selection of R_{ref} will be presented later. The UN and UP parameters for several dozen of molecules are contained in Table 1.

It is our experience that the error connected with applying formula (3) (with $R_{ref} = 133$ pm) instead of exact $UN(R)$ and $UP(R)$ is typically lower than 10% for the range $100 < R < 250$ pm. The error increases when $R < 100$ pm, but for small ions other effects (polarization of a solvent molecule, covalent bonding etc.) play

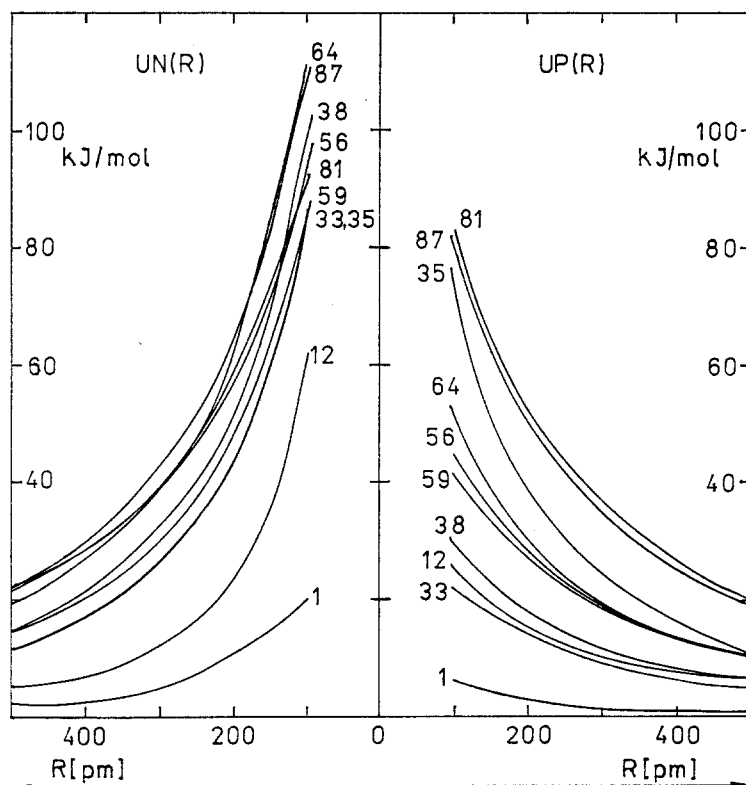


Fig. 2. Dependence of $UN(R)$ (left hand scale) and $UP(R)$ (right hand scale) on R for 10 representative solvents. For solvent numbers c. f. Table 1

also a significant role [4]. On the other hand, at larger distances the precision of Eq. (3) also gets worse but then the absolute error, expressed in kJ/mol, is smaller.

At present we do not know physical or chemical reasons for the $1/R$ form of Eq.(3). In many cases we observe just an *inverse* proportionality of various quantities related to ion solvation upon ionic radii as e. g. the free energies of transfer [20, 21]. Such dependences are usually treated in the frame of continuous dielectric theories (e. g. the Born equation and its consequences). However, it is difficult to explain why these theories give correct predictions when ions are smaller than solvent molecules. In the scope of our results it seems to be possible that the primary reason for the $1/R$ relations lies in the typical form of the molecular electrostatic

Table 2. Correlation coefficients between calculated parameters (number of correlated pairs: $N=89$; data from Table 1)

| Parameter | UN | UP | $\mu_{calc.}$ |
|---------------|-------|-------|---------------|
| UN | 1.000 | 0.311 | 0.713 |
| UP | 0.311 | 1.000 | 0.615 |
| $\mu_{calc.}$ | 0.713 | 0.615 | 1.000 |

potential, and the agreement with predictions of continuum theories is partially accidental.

At this point we must answer whether our electrostatic scalar parameters UN and UP (for $R_{ref} = 133$ pm!) are mutually independent and whether they are correlated with the dipole moments of molecules. Thus, Table 2 presents correlation coefficients between each pair of the UN , UP and μ_{calc} values. It can be seen that the UN and UP values are virtually linearly independent. This result stresses that the electrostatic binding of cations and anions to solvent molecules cannot be described with a single solvent parameter.

The correlation coefficients of both UN and UP with the dipole moments are not very high. This means that dipole moments are not effective in predicting electrostatic binding energies medium-sized ions to the typical solvent molecules. However, there is no contradiction with a fact that at the same time both correlations are statistically significant. Reasons for this are obvious: non-zero values of UN and UP imply some dipole moment of molecules, while non-vanishing μ imply some binding of ions. So, these variables are mutually dependent to some extent, and there are enough points involved in the calculation to observe this dependence.

Finally it should be mentioned that the results presented here can be discussed in the frame of Lewis acidity and basicity of solvents. Such a discussion will be presented in Part II of this study.

Acknowledgements

This work was supported as part of Program CPBP 01.15.

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Received December 6, 1990. Accepted August 5, 1991