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V. V. ZELINSKII and V. P. KOLOBKOV

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Abstract

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V. V. ZELINSKII and V. P. KOLOBKOV

ON THE APPLICABILITY OF THE DIELECTRIC CONSTANT FOR CHARACTERIZING INTERACTIONS IN SOLUTIONS

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Recently, in order to express the effect of a solvent on the electronic spectra of organic compounds, a number of authors ($^{1-9}$) have proposed formulas relating changes in the spectra to the dielectric constant ε and the refractive index n of the solvent. On the other hand, in works ($^{10-15}$) attention was drawn to facts of disagreement between changes in the positions of electronic spectra and changes in ε and n. In the present work we shall dwell on the question of how far attempts to express the interaction of molecules in solution through the dielectric constant of the medium are theoretically justified from the standpoint of general ideas about the forces acting between molecules in solution.

The quantity ε is introduced into formulas expressing the influence of the medium on spectra as a result of applying, for the calculation of this influence, the model proposed by Onsager (^{16}) for calculating the polarization of a dielectric in an external field. As Ya. I. Frenkel pointed out (^{17}), Onsager' s theory suffers from a number of shortcomings, the chief of which are the following: 1) Onsager uses an artificial and, moreover, crudely simplified model of a molecule*; 2) it is assumed that the dielectric constant of the medium retains an unchanged value right up to the molecule itself, i.e., the immediate environment of the molecule is regarded as a continuous medium with a macroscopic dielectric constant. Onsager' s model does not take into account the sharply expressed inhomogeneity of the field due to the fact that, in a real liquid, the distances between the nearest atoms of neighboring molecules are of the same order as the distances between neighboring atoms in an individual molecule.

In constructing a theory of the interaction of molecules in solutions, the actually occurring contacts of the molecules of the dissolved substance with the molecules of the solvent must be taken into account (^{18}). Substances in which a strong change in the positions of spectra is observed under the influence of the solvent have, to a greater or lesser degree, internally ionized molecules bearing charges of opposite sign at their ends, while the charges in the molecules of polar solvents are concentrated on individual atoms. Therefore the various possible contacts are energetically inequivalent, and it is precisely the interaction of these localized charges that must be considered first of all. Thus, unquestionably, a model in which the interaction of localized charges located at the ends of the molecule of the dissolved substance with their nearest environment is considered will correspond more accurately to the actual state of affairs.

Let us, using such a model, carry out an approximate calculation of the forces which owe their origin to the existence of a permanent dipol—

* Instead of considering the real distribution of charges in a molecule, Onsager assumes that the molecule is a point dipole located at the center of a cavity equal in volume to the corresponding molecule.

** The necessity of considering (in the case of large molecules), when calculating dispersion forces, the interaction of individual poles of a molecule with the nearest bonds of another molecule was pointed out by London ([19]).

of the dipole moment of the solvent molecules, which will act on the poles of the solute molecule. Let R denote the distance between the poles of the molecule of the solute under investigation (molecule A), r_1 the distance between a pole of molecule A and the nearest oppositely charged atom of the solvent, and r_2 the distance between two atoms of the same solvent molecule. As we have already indicated, in real solutions for which the influence of the solvent on the spectra is studied, $r_1 \approx r_2 \approx r$ and $R > r$. For simplicity we shall take the charges at both ends of molecule A to be equal and denote them by q_1. We shall likewise take the charges forming the dipole of the solvent molecule (molecule B) to be equal and denote them by q_2.

The force acting on a pole of molecule A from the molecules B enclosed within a certain solid angle with its vertex at the pole A is equal to

$$F = \sum_i f(L) \cos \alpha_i,$$

where $f(L)$ is the force due to a single molecule B, oriented along the field of the charge A and situated at a distance L from A; α is the angle formed by the axis of the dipole of molecule B with the intensity vector produced by charge A.

Let us consider the interaction of molecules B, situated close to the pole of molecule A, with pole A. The force due to the nearest atom of molecule B will be $f^1_{\mathrm{AB1}} = -q_1 q_2 / r_1^2$. When molecules B are oriented along the field of charge A, the force acting from the second atom, if the second charge of the dipole is concentrated on it, is $f^1_{\mathrm{AB2}} = +q_1 q_2/(r_1 + r_2)^2 = +q_1 q_2/(2r)^2$, i.e., four times smaller than that due to the first charge. Thus the force acting from the whole molecule belonging to the first layer, under the assumption that the charges are concentrated on two adjacent atoms, is $f^1_{\mathrm{AB}} = -q_1 q_2/r^2 + q_1 q_2/4r^2 = -{}^3/_4\, q_1 q_2/r^2$, i.e., even in this case the entire action of the nearest molecule will be determined mainly by the charge on the separate atom of the solvent molecule nearest to the pole of molecule A. It is clear that as the distance between the charges of the solvent molecule increases, the force due to molecule B approaches to an even greater degree the force due to a single nearest charge.

On the other hand, the magnitude ε is determined by the dipole moment of the molecule as a whole, which is the vector sum of all the elementary dipoles of the molecule. However, the same elementary dipoles, formed by identical charges, may be combined in the molecule in different ways, so that the total dipole moment of two different liquids and their dielectric constant will differ sharply, while the microfields of all atoms in the solvent molecules will be completely identical.* Hence it is clear that the magnitude ε cannot serve as a true indicator of the strength of interaction, and consequently of the interaction energy, between the nearest molecules of the solvent and the solute. The magnitude ε can serve only to characterize the action of sufficiently distant molecules. However, in constructing an approximate theory it makes sense to take the action of more distant molecules into account only if it is shown that this action constitutes a sufficiently large part of the total influence of the solvent molecule on the molecule

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* Let us consider the example of diethyl ether and dioxane. Both compounds are built from identical units, and there is no doubt that the charges on each carbon and oxygen atom in the molecules of both compounds are very close. A rough calculation, analogous to that presented above, shows that the action of a diethyl ether molecule, oriented radially with respect to the pole of molecule A, differs from the action of a dioxane molecule by no more than 10%. On the other hand, in the dioxane molecule the elementary dipoles are combined in such a way that they compensate one another, as a result of which the dipole moment and dielectric constant in the case of dioxane are considerably lower than for diethyl ether. Similar considerations were expressed by Lippert (^{5}) to explain the fact that the positions of the spectra in dioxane do not fit the proposed formulas relating changes in spectra to the magnitude ε.

of the solute*. Let us consider whether this actually takes place.

The action of the sum of molecules located in the second layer at a distance equal to the mean diameter of molecule B will be expressed by the sum $F^{\mathrm{II}} = \sum_i f^{\mathrm{II}}(\cos\alpha_i)^{\mathrm{II}} = N f^{\mathrm{II}}\overline{(\cos\alpha)}^{\mathrm{II}}$, where f^{II} is the force acting from the side of a molecule of the second layer oriented along the field of pole A; N is the number of molecules in the second layer. Since the first layer has a greater orientation in the field of the central charge, one always has $\overline{(\cos\alpha)}^{\mathrm{I}} > \overline{(\cos\alpha)}^{\mathrm{II}}$. Thus, the ratio of the forces of action of the molecules of the second and first layers falling within one and the same solid angle has the greatest value when $\overline{(\cos\alpha)}^{\mathrm{II}} = 1$, i.e., when all molecules of the second layer are completely oriented along the field of charge A. Then $F^{\mathrm{II}}/F^{\mathrm{I}} = N^{\mathrm{II}} f^{\mathrm{II}}\overline{(\cos\alpha)}^{\mathrm{II}}/N^{\mathrm{I}} f^{\mathrm{I}}\overline{(\cos\alpha)}^{\mathrm{I}} = N^{\mathrm{II}} f^{\mathrm{II}}/N^{\mathrm{I}} f^{\mathrm{I}}$. In this case the force of interaction of pole A with the nearest atom of molecule B, belonging to the second layer, will be equal to $f^{\mathrm{II}}_{\mathrm{AB1}} = -q_1 q_2/(r_1 + mr_2 + r_1)^2 = -q_1 q_2/(2r_1 + mr_2)^2$, where m is the number of bonds in molecule B.

If the charges are concentrated on two neighboring atoms of molecule B, then, correspondingly, the interaction of the pole with the second charge of molecule B of the second layer will be equal to $f^{\mathrm{II}}_{\mathrm{AB2}} = q_1 q_2/(r_1 + mr_2 + r_1 + r_2)^2 = q_1 q_2/[2r_1 + (m+1)r_2]^2$. The force of interaction of the whole molecule as a whole with pole A, for $r_1 \approx r_2 \approx r$, will be

$$f^{\mathrm{II}} = f^{\mathrm{II}}_{\mathrm{AB1}} + f^{\mathrm{II}}_{\mathrm{AB2}} = \left[-\frac{(5+2m)}{(2+m)^2(3+m)^2}\right] \times \left[\frac{q_1 q_2}{r^2}\right].$$

For example, in the case of a four-atom molecule B entering the second layer, the distances are $5r$ and $6r$. Correspondingly, the force of action of this molecule on pole A is $f^{\mathrm{II}} = -{}^{11}/_{900} q_1 q_2/r^2$, i.e., the force produced by one molecule of the second layer, oriented along the field, is approximately 60 times smaller than the force produced by one molecule of the first layer. Taking into account that the number of molecules in the second layer is 7** times greater than in the first layer, the total action of the molecules of the second layer is approximately 9 times less than the total action of the first layer. Thus, the total action of all molecules of the second layer, even in the case when all molecules are oriented in the most favorable way, is considerably less than the action produced by the first layer.

The expression for the force of action of the molecules composing the layer around pole A at any distance from it has the form $F^k = -\{[(2k+1) + 2(k-1)m](3k^2 - 3k + 1)/[k + (k-1)m]^2[(k+1) + (k-1)m]^2\} q_1 q_2/r^2$, where k is the number of the layer. It is easy to verify that the sum of the terms of this series, beginning with the second (for example, for a four-atom molecule), is less than the value of the term corresponding to the first layer. The decrease in the values of the terms of the series is very steep, so that the term corresponding to the fifth layer amounts to 0.03 of the value of the first term of the series.

In reality, complete orientation not only in the second but even in the first layer is, in the general case, not achieved. An exact calculation of the degree of orientation of the layer presents difficulty, but for the question of principle resolved in the present work the results of rough orientational calculations are sufficient.

If one neglects the inhomogeneity of the field created by the pole of the molecule, then the degree of orientation may be expressed according to the formula

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* The assumption that the action of the entire ensemble of solvent molecules considerably exceeds the action of the molecules directly surrounding the solute molecule underlies the viewpoints advanced in works (3-8) to explain the applicability of formulas connecting changes in the positions of spectra with changes in the dielectric constant of the solvent.

** The ratio of the number of molecules contained in the first and in the second layers within one and the same solid angle is taken as equal to the ratio of the volumes of these layers, i.e., ${}^4/_3\pi l^3$ and ${}^4/_3\pi(2l)^3 - {}^4/_3\pi l^3 = 7 \cdot {}^4/_3\pi l^3$, respectively, where l is the mean size of a molecule. If the number of molecules in the first layer is taken as 1, then in the layer with number k the number of molecules will be $k^3 - (k-1)^3 = 3k^2 - 3k + 1$.

Langevin*. Let us consider the case in which a very considerable degree of orientation of the solvent molecules may be expected. Suppose that molecule A is completely internally ionized, that one of its poles bears a negative charge $4.77 \cdot 10^{-10}$ CGSE, and the other pole an equal positive charge. Let us take, as an example, a sufficiently polar solvent—propyl chloride, with dipole moment $\mu = 2.1$ D. The distances from pole A to the charges on the molecules of the second layer will be $L_1 = (1.5+5+1.5)$ Å, $L_2 = (8+1.75)$ Å. The field strength produced by charge A at the position of the nearest charge of a molecule of the second layer will be equal to $E = q_1/L_1^2$; then $\mu E/kT = (2.1 \cdot 10^{-18} \cdot 4.77 \cdot 10^{-10})/(8^2 \cdot 10^{-16} \cdot 1.38 \cdot 10^{-16} \cdot 3 \cdot 10^2) = 3.8$, which corresponds to a degree of orientation $\overline{M}/\mu$ equal to 0.74. Thus, in the case of a completely internally ionized molecule A, the molecules of the second layer of propyl chloride still have a high degree of orientation. However, already in the third layer $\overline{M}/\mu = 0.3$, and in the fourth $\overline{M}/\mu = 0.18$. Accordingly, the force of the total action of the molecules belonging to the second and more distant layers is at least 4 times less than the force of action of the first layer.

In reality, complete internal ionization in organic molecules is more the exception than the rule. In the case when the charge at pole A is $1 \cdot 10^{-10}$ CGSE, the orientation already in the second layer for the case of propyl chloride is 0.28, and in the third layer 0.08, so that $\sum_{k=2}^{\infty} F^{(k)}(\overline{M}/\mu)^{(k)}$ is at least 20 times less than $F^1(\overline{M}/\mu)^1$. Thus, the total action on pole A of all molecules, beginning with the second layer, may be neglected.

Obviously, almost everything that has been said may be repeated for that component of the intermolecular interaction which owes its origin to the induction polarizability of the solvent molecules. Calculation shows that the total action of the second and more distant layers is negligibly small in comparison with the action of the first layer. Thus, the universal action on the solute molecule of large ensembles of solvent molecules is always less than the universal electrostatic action of the solvent molecules directly adjoining the poles of the solute molecule. In the case of small polarities of the solvent and solute, however, the influence of the entire ensemble reduces to a negligible correction to the action of the solvent molecules directly adjoining the poles of the solute molecule.

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* Allowance for the inhomogeneity of the field will lead to an even greater difference in the degree of orientation of the molecules nearest to pole A and those more distant.

Note: Figure translations are in progress. See original paper for figures.

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