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A SIMPLE MODEL FOR THE DIELECTRIC BEHAVIOUR OF POLAR SOLVENTS IN THE MEAN SPHERICAL APPROXIMATION

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION AVAILABILITY OF REPORT
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
Technical Report #26	

6a. NAME OF PERFORMING ORGANIZATION	6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION
Physics Department University of Puerto Rico		

6c. ADDRESS (City, State, and ZIP Code)	7b ADDRESS (City, State, and ZIP Code)
Río Piedras Puerto Rico 00931-3343	

8a. NAME OF FUNDING / SPONSORING ORGANIZATION Chemistry Office of Naval Research	8b OFFICE SYMBOL (If applicable) Code 472	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER RCT Project 4133002---05

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
Arlington Virginia 22217-5000	PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)
A SIMPLE MODEL FOR THE DIELECTRIC BEHAVIOUR OF POLAR SOLVENTS IN THE MEAN SPHERICAL APPROXIMATION

12 PERSONAL AUTHOR(S)
L. Blum and R. W. Fawcett

13a. TYPE OF REPORT	13b. TIME COVERED FROM _____ TO _____	14 DATE OF REPORT (Year, Month, Day) 1-15-93	15 PAGE COUNT 15

16. SUPPLEMENTARY NOTATION

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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20 DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. Robert Nowak	22b TELEPHONE (Include Area Code) (203) 696-4410	22c OFFICE SYMBOL ONR 472

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted
All other editions are obsolete

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Abstract

A simple model based on the mean spherical approximation is described for the dielectric properties of polar solvents. The molecular properties required are the dipole moment, the molecular polarizability, and the molecular diameter. It is shown that inclusion of a stickiness parameter accounting for other electrostatic features and non-sphericity in the real system leads to a simple analytical result from which the dielectric constant may be calculated. The stickiness parameter is shown to be correlated to the magnitude of dipole-dipole interactions in the system.

Introduction

Application of the mean spherical approximation (MSA) to the description of the dielectric properties of polar solvents dates from the work of Wertheim.[1] In this model, solvent molecules are represented as hard spheres with centrally located point dipoles. When applied to water, the estimated dielectric constant is considerably less than the experimental value.[2] Thus, one must replace the experimental dipole moment by a higher effective value in order to obtain the experimental dielectric constant from the MSA model.[2,3] It is generally recognized that the failure of models for water based on a hard sphere - point dipole description is due to the fact that this simple molecule has a more complex multipole character.[4] The complex electrostatic description leads to its well known hydrogen-bonded character.

Application of the MSA model to larger polar solvents is certainly expected to result in other problems. Thus, if one considers the series of normal alcohols, the representation of the molecule as a sphere with a central point dipole becomes worse as the length of the alkyl chain increases. Problems of a similar nature are encountered when one considers a series of aprotic solvents such as acetonitrile, and alkyl cyanides with larger alkyl groups. Thus, in general, one recognizes two problems with any model for a polar liquid based on hard spheres with centrally located point dipoles. The first is that the electrostatic description of the molecule may require that the quadrupole moment or higher order multipoles be considered. The second problem is that the molecule may not be well represented as a sphere.

One way of dealing with the above inadequacies is to introduce stickiness in the model. In this way, one can correct for the multipole nature of the polar molecule and its soft intermolecular interactions. The sticky interaction either aligns or misaligns the electrical dipoles of the solvent molecules, and therefore can be called a structure forming or structure breaking parameter. In the present paper, the original work of Wertheim[1] is extended by including a sticky interaction parameter in the description of the polar molecule. Otherwise, the solvent molecule is considered to be a hard sphere possessing a permanent point dipole and a polarizability. The model is applied

to representative polar solvents, including both aprotic and protic systems, in order to assess the role of the stickiness parameter in determining bulk dielectric properties.

The Model

On the basis of Wertheim's original work[1], one defines a polarization parameter, λ, by the relationship

$$\lambda^2 (\lambda + 1)^4 = 16 \, \varepsilon_s \tag{1}$$

where ε_s is the static dielectric constant of the polar liquid. The parameter, λ, also arises when the MSA is applied to the estimation of ion-dipole interactions in an infinitely dilute electrolyte solution[5], and is designed to take into account softness and nonspherecity of the solvent core. λ is obtained from the energy parameter, b_2, which comes from the solution of the MSA for dipole-dipole interactions for a system composed of hard spheres with centrally located point dipoles. The relationship between λ and b_2 is

$$\lambda = \frac{1 + b_2/3}{1 - b_2/6} \tag{2}$$

where

$$b_2 = 3\pi \, \rho_s \sqrt{\frac{2}{15}} \int_0^\infty dr \, \frac{\hat{h}^{112}(r)}{r} \, \sigma_s^3 \tag{3}$$

$\hat{h}^{112}(r)$ is the relevant coefficient from the invariant expansion of the total pair correlation function $h(r)$ which depends on the distance, r, between two dipolar spheres.[5] ρ_s is the number density of molecules in the liquid and σ_s, their diameter. The excess internal energy per unit volume for the liquid is given by

$$\frac{E}{V \, k_B \, T} = - \frac{d_2^2 \, b_2}{2\pi \, \sigma_s^3} \tag{4}$$

where

$$d_2^2 = \frac{4\pi \, \rho_s \, p^2}{3 k_B T} \tag{5}$$

Here, p, is the permanent dipole moment of the solvent molecule, and k_B, the Boltzmann constant. In the MSA, when the molecules are non-polarizable, one obtains the result

$$d_2^2 = \frac{\lambda^2 (\lambda+2)^2}{9} \left(1 - \frac{1}{\varepsilon_s}\right) \qquad (6)$$

Wertheim also studied the MSA and other approximations for the case of dipole hard spheres which are polarizable.[6] This work was reformulated to show that it is equivalent to a mixture of hard spheres of equal diameter but varying dipole moment.[7] As a result, when the molecules have a polarizability α, eq. (6) becomes

$$d_p^2 = \frac{\lambda^2 (\lambda+2)^2}{9} \left(1 - \frac{1}{\varepsilon_s}\right) \qquad (7)$$

where

$$d_p^2 = a^2 d_2^2 + 4\pi \, a \, \rho_s \, \alpha \qquad (8)$$

with

$$a^{-1} = 1 - \frac{4 \, b_2 \, \alpha}{3\sigma_s^3} \qquad (9)$$

Solving eq. (7) for the parameter λ, one obtains

$$\lambda = (1 + 3d_a)^{1/2} - 1 \qquad (10)$$

where

$$d_a = d_p / (1 - 1/\varepsilon_s)^{1/2} \qquad (11)$$

When one applies the above system of equations to water for which p is equal to 1.83 Debyes and α_1, to 1.47×10^{-3} nm³, one obtains the result that $d_p = 4.33$ and $\lambda = 2.75$. As a result, on the basis of eq. (1), the MSA estimate of ε_s for water at 25 °C is 93.7, which can be compared with the experimental result of 78.3. This suggests that a small correction to the contact correlation functions would yield good agreement with experiment. This is achieved here using the directional

sticky model described by Blum, Cummings and Bratko.[8] In its simplest dipolar version, introducing a longitudinal stickiness parameter t_o, eq. (7) becomes

$$d_p^2 = \frac{\lambda^2 (\lambda+2)^2}{9} \left[(1 - t_o/\lambda)^2 - \frac{1}{\epsilon_s} \right] \tag{12}$$

Having estimated d_p^2 on the basis of eq. (8), one can then determine the stickiness parameter t_o by solving eq. (12) using the value of λ obtained from the experimental value of ϵ_s (eq. (1)). One then has a self-consistent model in which the experimental value of ϵ_s is estimated from the molecular dipole moment and polarizability using the experimentally defined polarization parameter λ with an additional stickiness parameter t_o.

This model is now examined for selected polar solvents. However, before examining the static solvent permittivity, the high frequency permittivity, and the ability of the MSA to estimate the refractive index from the molecular polarizability are considered.

Solvent Permittivity at Optical Frequencies

At optical frequencies, the system only responds to an electrical field via its molecular polarizability. Thus, in this case the parameter d_p is given by the equation

$$d_p^2 = 4\pi a \rho_s \alpha \tag{13}$$

Furthermore, the polarization parameter, λ, is now calculated from the optical permittivity, ϵ_{op}, that is, from the equation

$$\epsilon_{op} = \lambda^2 (\lambda+1)^4 / 16 \tag{14}$$

where ϵ_{op} is the square of the refractive index. Thus, an alternate way to estimating d_p is via the equation

$$d_p^2 = \frac{\lambda^2 (\lambda+2)^2}{9} \left(1 - \frac{1}{\epsilon_{op}} \right) \tag{15}$$

The parameters b_2 and a defined above by equations (2) and (9), respectively, are now estimated using the value of λ obtained from eq. (14).

In the case of water at 25 °C, the valuer of ε_{op} is 1.7756. The corresponding high frequency value of the polarization parameter λ is 1.151 on the basis of eq. (14). One may now estimate the parameter d_p by using eq. (15) and then calculate the molecular polarizability on the basis of eq. (13). For water, the MSA estimate of α is 1.483×10^{-3} nm^3, a result which compares very well with the value, 1.471×10^{-3} nm^3, estimated on the basis of the Lorentz-Lorenz relationship.[9] In the latter case, the polarizability is calculated from the molar refraction R defined by the equation

$$R = \frac{\varepsilon_{op}-1}{\varepsilon_{op}+2} \, \bar{V} = \frac{4}{3} \, \pi \, N_o \, \alpha \qquad (16)$$

where $\bar{V}$ is the molar volume and N_o, the Avogadro constant. Keeping in mind the fact that the value of the polarizability depends very much on whether it is obtained from gas or liquid phase measurements[10], it seems appropriate that it be obtained from the refractive index of the liquid.

Values of α were calculated for all other solvents considered using both the MSA and the Lorentz-Lorenz relationship. In all cases, the MSA estimate is slightly higher, typically, by approximately 1%. Because the difference is so small, the MSA result was used in all further calculations and is tabulated in Table 1 together with other pertinent solvent data.

The Static Solvent Permittivity

The present model was applied to 20 different polar solvents, both protic and aprotic, chosen so that the role of the stickiness parameter could be assessed. Three solvent groups considered were water and the lower alcohols in which the polar group is -OH, the alkyl cyanides with $-C \equiv N$ as the polar group, and the amides whose dielectric parameters depend markedly on whether the solvent is protic or aprotic. The dielectric and other relevant parameters for these systems are summarized in Table 1. Some comment should be made about the values of the dipole moment chosen from the compilations of McClellan.[12] The value of this parameter depends somewhat on whether it was measured in the gas phase or in a dilute solution in a non-polar solvent. The chosen values for a group of solvents were obtained by one method, preferably using measurements from

one laboratory. The results obtained in the present study depend markedly on the value chosen for this parameter, so it is important that it properly reflect trends within a given group of solvents.

The stickiness parameter, t_0, also recorded in Table 1 was estimated from the dielectric data in the following way. Initially, the polarization parameter, λ, and the related energy parameter, b_2, were calculated from the bulk dielectric constant, ε_s, (eqs. (1) and (2)). Then the molecular parameter, d_2, was estimated on the basis of eqs. (5), (8) and (9) using the molecular polarizability found earlier, and the dipole moment, density, and molecular diameter tabulated in Table 1. Finally, the value of t_0 was obtained by solving eq. (12) using the above values of λ and d_p.

From the results, it is apparent that t_0 varies over a wide range from a low of -1.498 for formamide to a high of 0.495 for 1-propanol. Negative values of t_0 indicate that d_p is underestimated when it is calculated on the basis of eq. (8). It also follows that the MSA then underestimates the ordering effect of a given dipole on its neighbours. In the case of protic solvents such as water and formamide, this is attributed to the presence of hydrogen bonding, and important multipole contributions to the electrostatic description of the molecule. Negative values of t_0 are also found for all aprotic solvents considered. This also reflects the fact that the dipole moment cannot be considered to be centrally located in any of the polar solvent molecules considered.

It is interesting to follow the change in t_0 with the strength of the dipole-dipole interactions in the system. This can be seen for the water-alcohol series and also the alkyl nitrile series. Plots of t_0 against p^2/d^2 are linear for both series over a range of 4 kT (Fig. 1). What is interesting about these results is that t_0 becomes more positive as dipole-dipole interactions decrease in magnitude. This, in turn, can be related to the dipolar group in the solvent molecule moving further and further away from the molecular center. No such trend can be seen for the amides. Undoubtedly, this is due to the fact that the group of solvents considered includes both protic and aprotic systems so that the complete electrostatic description varies considerably among the members of this group. N-methylformamide is the only other solvent listed which has a positive value of t_0. Both formamide and N-methylformamide are systems which are extensively hydrogen bonded but with

quite different structures as a result of change in number of acidic hydrogens.[14] This change undoubtedly leads to the large difference in t_o for these solvents.

The remaining solvents listed in Table 1 are all aprotic and possess negative values of t_o. This parameter is plotted against the dipole-dipole interaction energy unit, p^2/d^3 in Fig. 2. There is clearly a correlation between these two quantities, the value of t_o becoming more negative as p^2/d^3 increases. This suggests that the smallest molecules with largest dipole moments depart most severely from the simple MSA result. This result reflects the fact that the tendency for local order is underestimated by the MSA. The scatter is much larger than that seen in Fig. 1 where molecules with the same polar group were considered. Not only are the polar groups different but the size and shape of the non-polar part of the molecule varies considerably among the solvents considered. In addition, systems like nitrobenzene and benzonitrile have very polarizable phenyl rings whereas the other molecules do not. In conclusion, the observed correlation is chiefly a result of the change in molecular size, and corrects the MSA model for the fact that the dipolar group is not centrally located in the solvent molecule.

Discussion

The MSA model for the dielectric properties of polar solvents described here is remarkably simple. Using the molecular dipole moment, polarizability, and diameter estimated from gas solubilities, one is able to calculate the relative permittivity with two additional parameters, namely, the polarization parameter, λ, and the stickiness parameter, t_o. The first of these, λ, is calculated directly from the static dielectric constant. Furthermore, the stickiness parameter, t_o, is clearly correlated to the ratio p^2/d^3 which is proportional to the dipole-dipole interaction energy. As the size of the non-polar group increases in a series of molecules with the same polar group, the ratio p^2/d^3 decreases, and t_o, increases. The correlation between these quantities is perfectly linear for a given series of compounds.

The limitations of the simple MSA in describing the properties of polar liquids are well known[15], the present extension adding very little to the complexity of the model. If one compares the results of the present model to those from molecular dynamics calculations, it is clear that the

latter approach only would yield reasonable results if a detailed electrostatic description of the solvent molecule is provided. The fact that the MSA provides an analytical model with empirical parameters which can be qualitatively related to known properties of the system suggests that it is a very good basis for describing the dielectric properties of polar liquids.

Acknowledgements

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Table 1. Summary of Relevant Solvent Parameters

Solvent	Relative Permittivity		Molar Volume	Dipole Moment[b]	Polarizability[c]	Molecular Diameter[d]	Stickiness Parameter
	Static ε_s	Optical[a] ε_{op}	V/cm^3 mol^{-1}	p/Debye	$10^3\alpha$/nm^3	d / nm	t_0
Water (w)	78.3	1.7756	18.07	1.83	1.48	0.274	-0.155
Alcohols							
Methanol (MeOH)	32.7	1.7596	40.73	1.66	3.29	0.371	0.366
Ethanol (EtOH)	24.6	1.8480	58.69	1.66	5.21	0.436	0.453
1-propanol (PrOH)	20.3	1.9146	75.14	1.66	7.10	0.498	0.495
Amides							
Formamide (F)	111.0	2.0932	39.89	3.82	4.26	0.345	-1.498
N-methylformamide (NMF)	182.4	2.0449	59.14	3.82	6.20	0.452	0.154
N,N-dimethylformamide (DMF)	36.7	2.0398	77.44	3.80	8.12	0.517	-0.600
N,N-dimethylacetamide (DMA)	37.8	2.0609	93.02	3.80	9.91	0.548	-0.359
Nitriles							
Acetonitrile (AN)	37.5	1.7999	52.86	3.47	4.48	0.427	-0.840
Propionitrile (PN)	29.6	1.8594	70.91	3.50	6.37	0.477	-0.632
Butyronitrile (BuN)	22.7	1.9099	87.87	3.50	8.29	0.532	-0.520
Benzonitrile (BzN)	25.2	2.3284	103.07	4.54	13.05	0.574	-0.654

Table I ...... cont......

Other Aprotic Solvents

Acetone (AC)	20.7	1.8387	74.04	2.87	6.51	0.476	-0.351
Dimethylsulfoxide (DMSO)	46.7	2.1824	71.30	3.96	8.24	0.491	-0.763
Hexamethylphosphoramide (HMPA)	30.0	2.1228	175.65	4.47	19.6	0.698	-0.153
Nitrobenzene (NB)	34.8	2.4025	102.73	4.28	13.5	0.574	-0.696
Nitromethane (NM)	35.8	1.9033	53.96	3.46	5.04	0.431	-0.885
N-methylpyrrolidinone (NMP)	32.2	2.1550	96.44	4.09	11.0	0.569	-0.608
Propylene carbonate (PC)	66.1	2.0190	85.21	4.98	8.80	0.536	-0.806
Tetramethylurea (TMU)	23.1	2.1005	102.76	3.40	13.1	0.544	-0.264

[a] The square of the refractive index measured at the sodium D line.

[b] From the compilations of McClellan[12]; 1 Debye = 3.335×10^{-30} C m.

[c] Calculated by the MSA using eqs. (13)-(15); see text for details.

[d] From gas phase solubilities[13]; when these data were not available, the solvent's diameter was estimated on the basis of a linear

correlation between existing experimental data and the cube root of the molar volume.

Legends for Figures

Figure 1. Plot of the stickiness parameter, t_0, against the dipole-dipole interaction energy factor p^2/d^3 for the lower alcohols and water, and for the alkyl cyanides. The abbreviations for the solvent given next to each point are defined in Table 1.

Figure 2. As in Figure 1, but for all aprotic solvents listed in Table 1.