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Dielectric Behaviour of Polar-Polarizable Solvents in Generic Mean Spherical Approximations: The Kirkwood g_K Factor

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Dielectric Behaviour of Polar-Polarizable Solvents in Generic Mean Spherical Approximations:
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Summary

The dielectric properties of polar solvents are considered within the context of generic mean spherical approximations. Given the molecular diameter in a spherical representation, the dipole moment, and molecular polarizability, the static permittivity of such a solvent is estimated on the basis of the Wertheim polarization parameter, and a stickiness parameter which accounts for other electrostatic features of the bulk system and non-sphericity of the actual solvent molecules. The stickiness parameter is related to the magnitude of dipole-dipole interactions for a series of solvents with the same polar group. This model is also used to estimate the Kirkwood structure factor. The values obtained are in excellent agreement with structural features of these systems obtained from experiment.

Introduction

In a previous paper[1] (referred to as I), we discussed the mean spherical approximation (MSA) with sticky association in a model for the dielectric properties of polar solvents. In this model, the molecules are represented as hard spheres with a permanent dipole moment, a polarizability, and an anisotropic stickiness parameter which leads to structure formation or break up in the liquid system. The idea of representing the complex molecules of which polar solvents are composed as spheres is useful for a large number of applications. The analytical solution of the MSA for polar[2] and polar-polarizable hard spheres[3,4] has opened up new perspectives for the simple representation of these rather complex systems.

Water in its liquid state has, presumably the local structure of ice I[5,6], in which a central water molecule is surrounded by four others in tetrahedral positions. Recently, we have shown[7] that an analytical potential with terms up to the octupole can represent very well the experimental atom-atom pair correlation functions. All of these works are based on the invariant expansion formalism[8,9] in which the pair (correlation, potential) functions are expanded in terms of rotationally invariant generalized spherical harmonics.

Picking a reference frame in which the intermolecular center to center vector is the z-axis, one can classify the harmonics by the periodicity of the functions for rotations around that intermolecular axis, very much like the so-called Hylleras molecular orbitals for the H_2^+ radical: the lowest term is the $\chi = 0$ (Σ orbital) coefficient[9], which corresponds to the cylindrically symmetric representation; the next $\chi = 1$ representation has the symmetry of cos ϕ, namely 1 node for a full rotation $0 < \phi < 2\pi$ around the z (intermolecular) axis. Only the $\chi = 0$ and $\chi = 1$ representations are necessary to obtain an almost quantitative representations of the structural pair correlation functions of water.[10]

The same representations are required to formulate the theory of the dielectric constant for polar-polarizable molecules.[11,12] Therefore, the Blum-Fawcett model[1], in which solvents are represented by hard spheres with a dipolar polarizability, and an orientational sticky parameter can be thought as being a mean field theory for the full molecule, which admittedly has many more directional interactions. The parameter t_0 of the sticky interaction is a sort of average of the effects of the very directional hydrogen bonds in water, which have the effect of aligning ($t_0 > 0$) or misaligning ($t_0 < 0$) the hydrogen bonds. In a way it is a realization of the structure forming structure breaking parameter of Frank and Wen.[13]

In I, the static dielectric permittivity of the polar liquid ε_s was related to the Wertheim polarization parameter λ using the equation[2]

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

This relationship is not quite correct in the presence of sticky directional interactions, and a new relationship is derived below. As a result, the parameterization for the solvents derived earlier[1] changes so that a new set of parameters are presented in this paper.

In the following section, we present a revised theory for the dielectric permittivity of a polar solvent. Then, the Kirkwood g_K factor is derived and its relation to older methods of estimating it is presented.

In the generic MSA (GEMSA)[11,12] approximations, the MSA closure relation is

$$c(r) = -\beta u(r) \quad \text{for} \quad r > A >> \sigma \tag{2}$$

where c(r) is the direct correlation function, u(r) the potential energy for dipole-dipole interactions, σ, the molecular diameter, A, a large distance which describes a sphere containing the system, and $\beta = 1/kT$. It has been shown that the GEMSA approximations all share the property that the Kirkwood g_K factor is internally consistent in the sense that the different ways of computing it yield the same result. On the other hand, this is not necessarily true for other approximations. An excellent and comprehensive discussion of the dielectric behaviour and its molecular origins can be found in the review by Stell, Patey and Høye.[12] Various methods of extracting the g_K factor and the infinite frequency limits are also considered in the following section.

The Dielectric Constant for the GEMSA

Consider a system of molecules with dipolar symmetry. The correlation and potential functions can be expanded using the invariant expansion.[2,8,9] In general,

$$f(1,2) = f^{000}(r_{12}) + \Phi^{110} f^{110}(r_{12}) + \Phi^{112} f^{112}(r_{12}) \tag{3}$$

where 1 is the shorthand for (r_1, θ_1, ϕ_1), the position and orientation of molecule 1and 2 is shorthand for (r_2, θ_2, ϕ_2), those of molecule 2. $\mathbf{r_{12}} \equiv |\mathbf{r_1} - \mathbf{r_2}|$ is the center to center distance. The invariants Φ^{110} and Φ^{112} are scalar products of the dipole vectors $\mathbf{p_1}$ and $\mathbf{p_2}$:

$$\Phi^{110} \propto \mathbf{p_1} \cdot \mathbf{p_2} \tag{4}$$

$$\Phi^{112} \propto 3(\mathbf{p_1} \cdot \mathbf{r_{12}})(\mathbf{p_2} \cdot \mathbf{r_{12}}) - \mathbf{p_1} \cdot \mathbf{p_2} \tag{5}$$

Using the trigonometric relationship

$$\mathbf{p_1} \cdot \mathbf{p_2} = p^2 \cos \gamma_{12} = p^2 [\cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2)] \tag{6}$$

the irreducible invariants, Φ_x^{11}, used below are obtained:

$$\Phi_o^{11} = \Phi^{110} + \Phi^{112} \ \alpha \cos\theta_1 \cos\theta_2 \tag{7}$$

and

$$\Phi_1^{11} + \Phi_{-1}^{11} = \Phi^{112} - 2\,\Phi^{110} \ \alpha \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2) \tag{8}$$

Consider a system of roughly spherical molecules which have, in addition to short range interactions, long ranged electrostatic interactions of the type[8,9]

$$u(1,2) = \frac{1}{r_{12}^3} [\mathbf{p_1} \cdot \mathbf{p_2} - 3(\mathbf{p_1} \cdot \hat{r}_{12})(\mathbf{p_2} \cdot \hat{r}_{12})] \simeq \sqrt{\frac{10}{3}} \frac{p_1 p_2}{r_{12}^3} \Phi^{112} \tag{9}$$

In the notation used here, the vector $\mathbf{r_{12}} \equiv \{r_{12}, \hat{r}_{12}\}$ with magnitude r_{12} has a direction given by the unit vector $\{\hat{r}_{12}\} = \{\theta_{12}, \phi_{12}\}$. The GEMSA approximations require that the direct correlation function satisfies the equation

$$c(1,2) = -\beta u(1,2) \qquad \text{for } r_{12} > A \tag{10}$$

Since the dipole-dipole interaction is long ranged, the u(1, 2) interaction yields a virial coefficient that diverges as the volume of the sample goes to infinity. This is also true for the integrals of both the pair correlation function g(1, 2) and the direct correlation function.[2,11] Therefore, the analysis of the dielectric properties of fluids must include the proper treatment of the long ranged dipolar contributions in the correlation functions.

Consider first the simplest expression for the Kirkwood factor g_K:

$$\frac{\varepsilon_s-1}{\varepsilon_s+2} = \frac{4\pi}{9}\beta\rho_s\left\{p^2 + \frac{\Omega}{\rho_s}\int d(2)\, G_2^{o}(2)\mathbf{p}(1).\mathbf{p}(2)\right\} \tag{11}$$

Using the notation of Nienhuis and Deutch[14], ρ_s is the number density of dipoles, and Ω, a solid angle. The function $G_2^{o}(2) = g(1, 2)$ is the pair correlation function for the system in an external electrostatic test field $\mathbf{E_s}$. The pair correlation function has an angular dependence. One may show that a completely general expansion of this function is

$$G_2^{o}(2) = g(1, 2) = g^{000}(r_{12}) + g^{110}(r_{12})\frac{\mathbf{p_1 \cdot p_2}}{p_1 p_2} + g^{112}(r_{12})\,\Phi^{112} \tag{12}$$

The integral in equation (11) contains all three terms of the expansion. The first term is zero because of the angular integrations. The second term yields the Kirkwood g_K factor:

$$g_K = 1 + 4\pi\rho_s \int_0^\infty dr\, g^{110}(r)\, r^2 \tag{13}$$

In the older literature, the integral containing the last term, g^{112} was neglected or improperly estimated. If the volume of the system were truly infinite, this integral would vanish because of orthogonality in the angular contributions, and diverge because of the radial term.

Using the notation of previous work[2,3,11,12,15], equation (11) may be rewritten as

$$\frac{\varepsilon_s-1}{\varepsilon_s+2} = \frac{y}{3}\left[1 + 4\pi\rho_s\, \mathcal{H}_o^{11}(k=0) + 2(1 + 4\pi\rho_s\, \mathcal{H}_1^{11}(k=0))\right]$$

$$= \frac{y}{3}\left[\frac{1}{1-4\pi\rho_s\, \tilde{\mathbf{C}}_o^{11}(k=0)} + \frac{1}{1-4\pi\rho_s\, \tilde{\mathbf{C}}_1^{11}(k=0)}\right] \tag{14}$$

where

$$y = \frac{4\pi\,\rho\,\beta p^2}{9} \tag{15}$$

This result is incorrect because it does not include the long ranged interactions. When these are included following Wertheim[2-4], the following result is obtained

$$\frac{\varepsilon_s-1}{\varepsilon_s+2} = \frac{y}{3}\left[\frac{1}{y_o^2-2y} + \frac{2}{y_1^2+y}\right] \tag{16}$$

where

$$y_o^2 = 1 - 4\pi\,\rho_s\,\tilde{\mathbf{C}}_o^{11}\,(k=0) \tag{17}$$

and

$$y_1^2 = 1 - 4\pi\,\rho_s\,\tilde{\mathbf{C}}_1^{11}\,(k=0) \tag{18}$$

The closure of the GEMSA is

$$y = \frac{1}{3}\,(y_o^2 - y_1^2) \tag{19}$$

Applying this result to equation (14), the result is

$$\frac{\varepsilon_s-1}{\varepsilon_s+2} = \frac{y_o^2 - y_1^2}{y_o^2 + 2y_1^2} \tag{20}$$

from which one obtains

$$\varepsilon_s = \frac{[1-4\pi\,\rho_s\,\tilde{\mathbf{C}}_o^{11}(k=0)]}{[1-4\pi\,\rho_s\,\tilde{\mathbf{C}}^{11}(k=0)]} = \frac{y_o^2}{y_1^2} \tag{21}$$

This is an extension for our case of Wertheim's result.[2-4]

Now explicit relationships for the anisotropic sticky hard dipole model can be written. These are

$$y_o^2 = 1 - 4\pi\rho_s\,\tilde{\mathbf{C}}_o^{11}\,(k=0) = \frac{\lambda^2(\lambda+2)^2}{9}\left(1 - \frac{t_0}{\lambda}\right)^2 \tag{22}$$

and

$$y_1^2 = 1 - 4\pi\rho_s\,\tilde{\mathbf{C}}_o^{11}\,(k=0) = \frac{16}{\lambda^2(1+\lambda)^4}\;\frac{\lambda^2(\lambda+2)^2}{9} \tag{23}$$

where t_0 is the longitudinal sticky factor defined in our previous work.[1] Equations (21) - (23) immediately lead to the relation

$$\varepsilon_s = \frac{\lambda^2(1+\lambda)^4}{16} \left(1 - \frac{t_0}{\lambda}\right)^2 \tag{24}$$

Furthermore, we note that the closure relation for the sticky MSA is

$$d_p^2 = 3y = \frac{\lambda^2(\lambda+2)^2}{9} (1-t_0/\lambda)^2 (1-1/\varepsilon_s) = y_o^2 - y_1^2 \tag{25}$$

We consider now the polar-polarizable system which was investigated in detail by Wertheim.[3] The added complication for such a system is that the polarization force is a long range many body force and collective effects cannot be ignored. In other words, a simple pairwise additive potential is not adequate. Therefore, a renormalization approximation with an effective dipole moment that depends not only on the polarizability but also on the density and molecular interactions is needed. A simple but powerful method for computing these effects was described by Høye and Stell.[16] It is based on the concept that a system of polar-polarizable molecules is equivalent to a mixture of molecules with permanent dipole moments $\mathbf{m}_\alpha$ where

$$\mathbf{m}_\alpha = \mathbf{p}_\alpha + \mathbf{E_p} \cdot \alpha \tag{26}$$

where α is the polarizability tensor and $\mathbf{E_p}$ is the local (fluctuating) microfield.[17] It can be shown that this yields a random Gaussian distribution of the electric microfield, and therefore, of the instantaneous dipole moment. However, as shown by Adelman and Deutch[18], a random mixture of equal size molecules of diameter σ_s with fluctuating dipoles in the MSA and the GEMSAs is equivalent to a fluid with a single dipole moment given by

$$<p> = \Sigma \rho_i <m_i>^2 / \Sigma \rho_i \tag{27}$$

The result for the MSA approximation is

$$d_p^2 = a^2 \cdot d_2^2 + 4\pi\, a\, \rho_s\, \alpha \tag{28}$$

where

$$a = \frac{1}{1 - \frac{8\alpha}{\sigma_s^3} \left(\frac{\lambda-1}{\lambda+2}\right)} \tag{29}$$

and

$$d_2^2 = \frac{4\pi\ \beta\rho_s\ p^2}{3} \tag{30}$$

This gives different results from our previous analysis because the factor $(1 - t_o / \lambda)^2$ is now included. Finally, the Kirkwood g_K factor can be defined in several different ways, **all of which** are equivalent in the GEMSA type of approximations. Thus, one obtains

$$g_K = 1 + \rho_s \tilde{h}^{110}(0) \tag{31}$$

or

$$g_K = \frac{(\varepsilon_s-1)(2\varepsilon_s+1)}{3\varepsilon_s\ d_p^2} \tag{32}$$

Experimental Data for Polar Solvents

In I, experimental permittivity data at both static and optical frequencies were related to molecular properties of polar solvents using the MSA. In this regard the solvent molecules were assumed to be approximately spherical with diameters estimated from gas phase solubilities.[19] The molecular diameter σ_s together with other molecular properties are given in Table 1 for 20 polar solvents, both protic and aprotic.

The molecular polarizability may be calculated from the optical permittivity using the present model as described in I. The Wertheim equation is then written as

$$\varepsilon_{op} = \lambda_{op}^2\ (\lambda_{op}+1)^4 / 16 \tag{33}$$

where ε_{op} is the square of the refractive index, and λ_{op}, the value of the polarization parameter at optical frequencies. One may then estimate the optical value of the parameter d_p using the relationship

$$d_{op}^2 = \frac{\lambda_{op}^2\,(\lambda_{op}+2)^2}{9}\left(1 - \frac{1}{\varepsilon_{op}}\right) \tag{34}$$

Alternatively, d_{op} can be calculated from equation (28) written in a form applicable at optical frequencies:

$$d_{op}^2 = 4\pi\, a\, \rho_s\, \alpha \tag{35}$$

where

$$a = \frac{1}{1 - \frac{8\alpha}{\sigma_s^3}\left(\frac{\lambda_{op}-1}{\lambda_{op}+2}\right)} \tag{36}$$

The polarizability α is found by solving equation (35) using the value of d_{op} obtained from equation (34).

Values of α found by this route are also recorded in Table 1. These estimates are slightly higher than those obtained from the classical continuum model.[20] Equations (33) - (36) represent an approximate solution of the high frequency problem. However, since there is good agreement between values of α obtained experimentally, from the continuum model and from the MSA model, we believe that the present treatment deals adequately with the contribution to the permittivity from molecular polarizability at static frequencies.

Estimation of the MSA parameters at low frequencies involves solving the following three non-separable equations for λ and t_0:

$$\varepsilon_s = \frac{\lambda^2(1+\lambda)^4}{16}\left(1 - \frac{t_0}{\lambda}\right)^2 \tag{37}$$

$$d_p^2 = \frac{\lambda^2(\lambda+2)^2}{9}\left[\left(1 - \frac{t_0}{\lambda}\right)^2 - \frac{16}{\lambda^2(1+\lambda)^4}\right] \tag{38}$$

and

$$d_p^2 = a^2 d_2^2 + 4\pi\, a\, \rho_s\, \alpha \tag{39}$$

Equation (38) is obtained by subtracting equation (23) from equation (22). In order to obtain a solution, t_0 was initially assumed to be zero. An initial estimate of λ was then obtained from equation (37). Using the solvent's molecular density, dipole moment, and polarizability, the parameter d_p was estimated on the basis of equation (39). Finally, the stickiness parameter t_0 was estimated using equation (38). This process was repeated using the new estimate of t_0 in equation

(37). Eventually by iteration, values of λ and t_0 corresponding to an exact solution of these equations were obtained.

Values of the MSA parameters determined for 22 polar solvents are summarized in Table I. the numerical values of λ and t_0 are different than those obtained earlier[1] but follow the same qualitative trends. In the case of aprotic solvents, t_0 is negative. This indicates that the polarization parameter λ is overestimated when the simpler model based on non-sticky interactions is used. In addition, these interactions result in the break up of structure due to head-to-tail interactions.

Another trend apparent in the data in Table I shows that parameter t_0 increases in magnitude as the length of the alkyl group increases for solvents with the same functional group. Thus, in the nitriles, t_0 increases from -2.53 for acetonitrile to -1.93 for butyronitrile. Similarly, for the alcohols, t_0 increases from 0.81 for methanol to 1.47 for 1-butanol. The positive value of t_0 in these solvents indicates that head-to-tail interactions provide a major contribution to the polarity of the solvent. A similar comment can be made about N-methylformamide, the only other solvent with a positive value of t_0.

As noted earlier[1], the stickiness parameter is linearly related to the strength of dipole-dipole interactions within a given series of solvents. This is illustrated in Figure 1 for the water-alcohol and alkyl nitrile series. As the length of the alkyl chain increases, the parameter t_0 becomes more positive as noted above. This trend accompanies the displacement of the dipolar functional group further from the geometrical center of the molecule. At the same time, the tendency for structure forming interactions in head-to-tail configurations increases.

Values of the Kirkwood structure factor g_K calculated according to the MSA (equation (30)) are also given in Table I. These parameters vary from 1.09 for butyronitrile to 4.52 for N-methylformamide. The latter solvent is known to be highly structured and to form long chains of solvent molecules linked through hydrogen bonding.[21] This results in the very high static permittivity and value of g_K. In the case of water, the value of g_K is 2.79, that is, very close to the value estimated by Kirkwood[22,23] on the basis of the well known tetrahedral structure for surrounding hydrogen bonded water dipoles. The value of g_K for the alcohols is higher, increasing from 2.99 for methanol to 3.26 for n-butanol. This suggests that the tendency to form hydrogen bonded chains in these solvents increases with the length of the alkyl group.

Values of g_K for the aprotic solvents lie between 1 and 2. Acetonitrile is an example of a solvent with very little structure in the bulk.[24] Its value of g_K is close to unity as expected for n-butanol. This suggests that the tendency to form hydrogen bonded chains in these solvents increases with the length of the alkyl group.

Values of g_K for the aprotic solvents lie between 1 and 2. Acetonitrile is an example of a solvent with very little structure in the bulk.[23] Its value of g_K is close to unity as expected. On the other hand, dimethylsulfoxide which is known to be strongly associated as dimers in the bulk[25] has a value of g_K equal to 1.67. In the case of propylene carbonate, g_K is equal to 1.86 suggesting some degree of association in the pure liquid. In fact, dielectric relaxation measurements for this system[26-28] show the existence of two relaxation processes which could be interpreted as evidence of molecular association. More than one relaxation process is observed for several aprotic solvents.[29] When the dipole moment is high, dimer formation may take place in these systems.

The values of g_K reported here are very different from those estimated by Marcus.[30] The latter quantities were calculated on the basis of a revised version of the Kirkwood equation proposed by Cole.[31] Cole's relationship is not consistent with the dielectric theory used here[12] and therefore is not considered to give a good representation of the relative values of the structure factors for the solvents discussed.

Discussion

The revised formulation of the MSA presented here leads to new values of the parameters λ and t_o. However, it is clear that the new parameters follow the same trends as those presented earlier.[1] Thus, the conclusions reached earlier regarding the stickiness parameter t_o are qualitatively correct. The MSA model is both analytical and relatively simple, providing an excellent molecular description of the dielectric properties of the polar solvents considered.

In applying any molecular model one must have accurate values of the molecular parameters involved. In the present case, these are the dipole moment, polarizability, and molecular diameter.

The diameters which are based on gas-phase solubilities[19] correlate well with the cube root of the molar volume and therefore are regarded as giving good estimates within the context of the spherical approximation used. In previous work dipole moments were taken from compilations based largely on liquid solution measurements.[32] The values in Table 1 are mainly those from gas phase measurements[33] and are considered to be more appropriate to the present correlations. This is apparent with the revised dipole moment data for the nitriles. For these solvents, the values of t_o including that for benzonitrile, as linear in the energy parameter p^2/d^3. Obviously, small errors in p can result in large errors in p^2/d^3, so that in the previous correlation, the benzonitrile data did not fit with the results for the alkyl nitriles.

Finally, the present estimates of the structure factor g_K appear to be very reasonable on the basis of what is known about the structure of the solvents considered. More experimental work in this area is definitely needed. Infrared spectroscopy has proven especially effective in the case of aprotic solvents and provides a means of understanding the estimates of g_K obtained in these solvents.[24,25]

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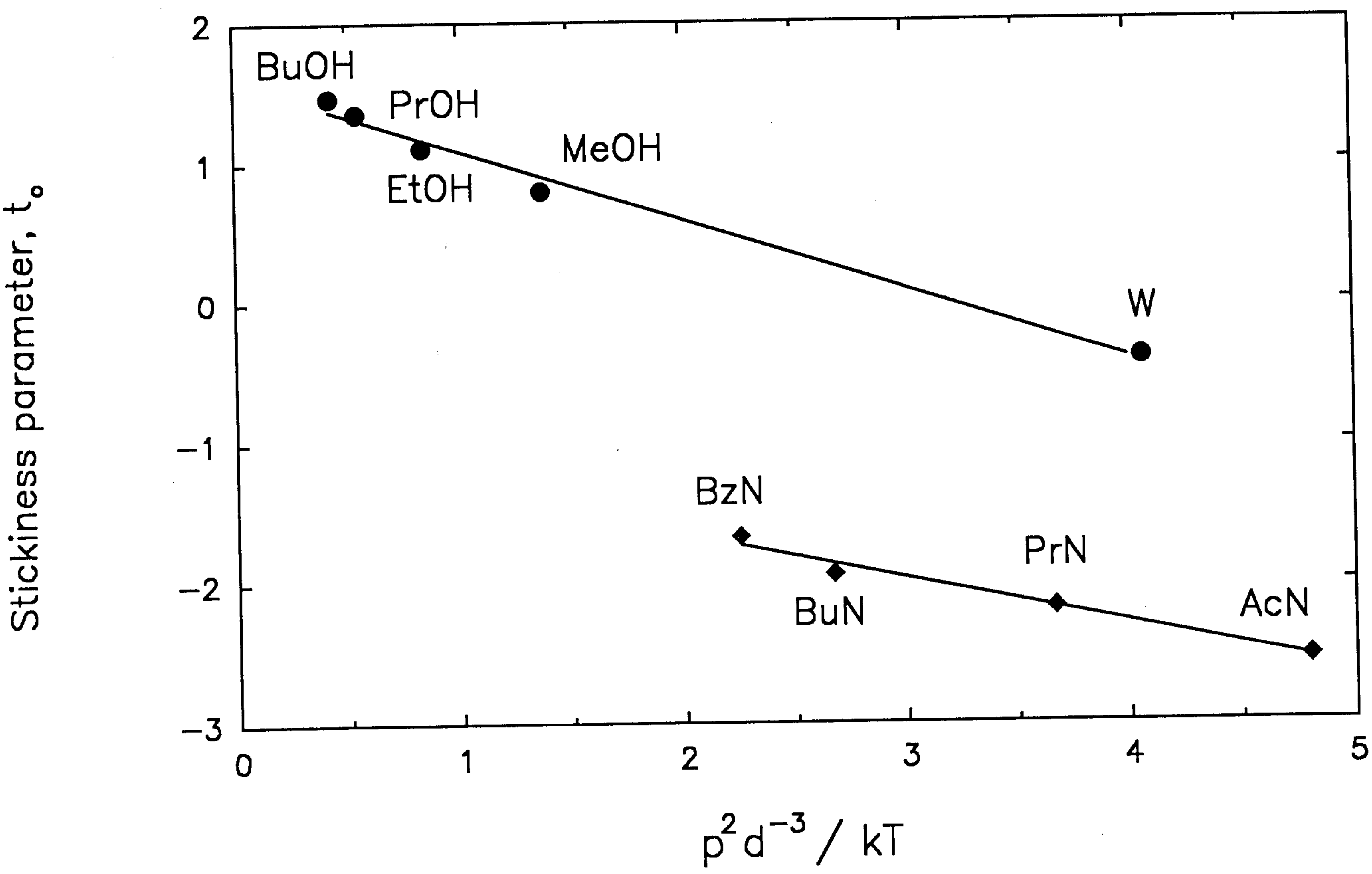
Figure Legend

Figure 1. Plot of the stickiness parameter, t_o versus the dipole-dipole interaction energy factor p^2/d^3 for the lower alcohols and water, and for the nitriles. The abbreviations for the solvents are defined in Table 1.


Stickiness parameter, t_o
$p^2 d^{-3} / kT$
2
1
0
−1
−2
−3
0
1
2
3
4
5
BuOH
PrOH
EtOH
MeOH
W
BzN
BuN
PrN
AcN