The Interactions of Small Chain Solutes in Nematic Solvents

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THE INTERACTIONS OF SMALL CHAIN SOLUTES IN NEMATIC SOLVENTS

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Abstract   We formulate the probability distribution of orientations and conformations of flexible chains by explicitly taking into account short range repulsions and el ectrostatic interactions with the solvent molecules. The theory is used calculate the segmental order parameters associated with proton NMR measurements on n-alkanes and to study the apparent shift of the *gauche-trans* energy in the nematic phase. The foundation of the modular description of chain ordering is investigated in the light of the above developments. Excluded volume and electrostatic effects on the conformation energy of dimethoxyethane are evaluated.

INTRODUCTION

When flexible molecules are dissolved in liquid crystals their segments acquire orientational order and their conformation statistics is modified[1]. The modifications may range from slight shifts of conformation energies to effective suppression of certain internal motions, depending on the structure of the solvent and solute molecules and also on the type and the extent of the ordering exhibited by the solvent. The intermolecular interactions giving rise to these phenomena are primarily short range repulsions (steric or excluded volume) dictated by molecular shape. It has been shown recently[2,3] that electrostatic interactions mäy also contribute significantly in certain cases.

To date, the ordering and conformations of small chain solutes in nematic solvents has been the subject of many experimental studies, mainly by NMR methods[4-6]. They provide sufficiently detailed information to test theoretical models describing the conformations and ordering of simple chain molecules such as n-alkanes[1,5] and α,ω-substituted alkanes[2].

The model most often used to describe the conformations of chain molecules is based on the Rotational Isomeric State (RIS) approximation[7] according to which the conformations are generated by discrete internal rotations. The models that have been proposed for the description of the orientational ordering of chain solutes fall essentially in two categories.   One category is based on the modular development[8,9] of the anisotropic interactions by combining particular contributions from rigid submolecular units. The simplest, and yet very successful, representative of this category is the chord model for

alkanes[1]. The other category of models[10-12] considers each molecular conformation separately and determines its orientability in a nematic continuum from some simple characteristic of its geometry. The ordering of n-alkanes has also been studied using the maximum entropy approach[13].

Here we present the results of a microscopic description of chain solute ordering that takes explicitly into account short range repulsions and electrostatic interactions. We study in detail the effects of these interactions on the conformation statistics and the segmental ordering of certain small chain solutes for which extensive experimental results are available. Particular emphasis is placed on elucidating the variation of the basic RIS parameters of interacting chains and also the role electric dipole interactions in the nematic phase.

THEORY

The essential assumptions underlying the formulation of our model for the distribution function $f(\omega,n)$ of a chain molecule in its n-th conformation and with orientation ω relative to the nematic director, are as follows.

1) The conformations are generated according to the standard RIS scheme with three rotational states $\phi = 0,\ \pm\phi_g$ and two energy parameters E_{tg}^0 and $E_{g^+g^-}^0$. These determine the internal energy $E^0(n)$ of a conformation which in turn determines its probability in the absence of intermolecular interactions (gas phase).

2) Each of the above conformations interacts with the solvent molecules as a rigid object.

3) The flexibility of the solvent molecules is not considered explicitly and thus their shape is approximated by a spherocylinder of diameter d and full length l+d.

4) The distribution $f(\omega,n)$ is related to the internal energy $E^0(n)$ and the effective potential $V(\omega,n)$ of interaction with the solvent according to

$$f(\omega,n) = \zeta^{-1}\exp[-(E^0(n)+V(\omega,n))/kT] \qquad , \qquad (1)$$

where ζ is a normalisation factor. $V(\omega,n)$ is determined from the explicit intermolecular potentials by using the molecular field approximation to treat solvent-solvent interactions and an exact statistical mechanical procedure for solute-solvent interactions. The details of this approach for rigid molecules are given in reference 3 . Here we give the final expressions for the case of a chain molecule that can assume several "rigid" conformations labelled by the index n and interacts only with the solvent molecules (dilute solutions). The respective $V(\omega,n)$ is expressed as an expansion in spherical harmonics of even rank L,

$$V(\omega, n) = (Nv/V) \sum_{L,M} (C_{LM}^{(0)}(n) + C_{LM}^{(ES)}(n)) < P_L > \cdot$$

$$\cdot [1 - \delta_{M,0}/2][Y_M^L(\omega) + Y_M^{L*}(\omega)] \quad , \qquad (2)$$

where v, N/V and $<P_L>$ denote respectively the molecular volume, the number density and the L-th rank order parameters of the solvent. The expansion coefficients are given by

$$C_{LM}^{(0)}(n) = (4\pi v)^{-1} \int d\vec{r}' \, d\Omega' \left[(1 - g(\Omega', r'; n)) \right] \left[Y_M^L(\Omega') + Y_M^{L*}(\Omega') \right] \quad , \qquad (3)$$

and

$$C_{LM}^{(ES)}(n) = (4\pi v)^{-1} \int d\vec{r}' \, d\Omega' \left[1 - \exp(U^{(ES)}(\Omega', r'; n)/kT) \right] \cdot$$

$$\cdot g(\Omega', r'; n) \left[Y_M^L(\Omega') + Y_M^{L*}(\Omega') \right] \qquad (4)$$

Here r' and Ω' denote the position and orientation of a solvent molecule relative to the solute, $g(r', \Omega')$ is a shape function (that vanishes if the molecular volumes of the solvent and the solute intersect, and is equal to one otherwise) and $U^{(ES)}$ is the electrostatic potential. Obviously the coefficients $C_{LM}^{(0)}$ and $C_{LM}^{(ES)}$ represent the contribution of excluded volume and electrostatic interactions respectively. The coefficient of rank $L>4$ have been shown to have a negligible effect on the potential of mean torque for usual nematic solvents.

The coefficients of rank $L=0$ are irrelevant to the ordering of strictly rigid solutes but are important in the case of flexible chains because they determine the "apparent" conformation energy shift resulting from the isotropic part of the interactions with the solvent molecules. This becomes evident by noting that the isotropic part of the exponent in eq. (1) is given according to eq. (2) by the term

$$E(n) = E^0(n) + (Nv/V) (C_{0,0}^{(0)}(n) + C_{0,0}^{(ES)}(n))Y_0^0 \quad , \qquad (5)$$

which therefore describes the effective conformational energy in the presence of intramolecular interactions.

The numerical evaluation of the expressions in the right hand sides of equations (3) and (4) involves in general a six-fold integration for each chain conformation. Applications to systems exhibiting a large number of conformations, combined with low molecular symmetry, become computationally rather lengthy and require the development of efficient algorithms for parallel computation.

EXCLUDED VOLUME INTERACTIONS: n-ALKANES.

The permanent electrostatic moments of n-alkanes are negligible and the effect of induced moments on the orientational ordering is marginal[3]. Therefore only the coefficients $C^{(0)}_{LM}$ pertaining to excluded volume interactions are significant in this case.

The distribution of eq. (1) is applied to the calculation of the segmental order parameters associated with the measurements[5] of proton NMR dipolar couplings $<D_{ij}>$ by M.E. Rosen *et all* for the series of n-alkane solutes C_6H_{14} to $C_{10}H_{22}$ in nematic solvents. The internal energy $E^0(n)$ is obtained using the values $\varphi_g = 112°$, $E^0_{tg} = 0.9$ kcal/mol , and $E^0_{g^+g^-} = 4$ kcal/mol for the gas phase RIS parameters[7,14]. The following values have been used for the parameters involved in the evaluation of the potential $V(\omega,n)$ from equations (2) and (3): $l/d=4$, $d=6$ Å , $Nv/V=2.18$ and $<P_2> =.51\pm.01$ for the principal order parameter of the solvent at the reduced temperature $T/T_c=0.875$. The shape of the alkane conformers is determined using $R_{vdw}=1.77$ Å for the van der Waals radius of the united carbon atoms.

A comparison of the calculated dipolar couplings with the measured values (with reported[5] experimental error ±25 Hz) for octane is presented in table I. Similar agreement is obtained for the other members of the n-alkane series.

TABLE I   Experimental[5] and theoretical dipolar couplings for n-octane.

proton pairs i-j	dipolar couplings $<D_{ij}>$/Hz	
	measured	calculated
1 - 2	1637	1610
4 - 5	3539	3472
6 - 7	4119	4072
8 - 9	4319	4406
1 - 4	-319	-363
1 - 6	-949	-927
1 - 8	-538	-535
1 - 10	-296	-294
1 - 12	-204	-208
1 - 14	-129	-140
1 - 16	-96	-96
4 - 8	-1544	-1602
4 - 9	-976	-980
6 - 10	-1710	-1778
6 - 11	-1088	-1056

The effective conformational energy E(n) relative to the *all-trans* state is evaluated from $E^0(n)$ and the coefficients $C_{0,0}^{(0)}(n)$ according to eq. (5). The results for the statistically significant conformations of the hexane solute at T=330 ° K are shown in table II, where N_g denotes the number of *gauche* rotations, $P^0(n)$ denotes the gas phase probability

$$P^0(n) = \zeta_0^{-1} \exp(-E^{(0)}(n)/kT) \quad , \tag{6}$$

and $\Delta E(n) = E(n) - E^0(n)$ is the energy shift for the n-th conformation.

TABLE II Conformation energies (in kcal/mol) for n-hexane.

conformation (multiplicity)	$E^0(n)$	E(n)	$\Delta E(n)/N_g$	$P^0(n)$
ttt (1)	0.0	0.00	0.00	0.320
ttg (4)	0.9	0.81	0.09	0.083
tgt (2)	0.9	0.81	0.09	0.083
tgg (4)	1.8	1.62	0.09	0.021
gtg (2)	1.8	1.60	0.10	0.021
g⁻tg (2)	1.8	1.64	0.08	0.021
ggg (2)	2.7	2.43	0.09	0.005

It is worth noting in table II that the nearly constant value of $\Delta E(n)/N_g$ for all the conformations suggests that the effective conformational energy E(n) may be obtained to a good approximation by applying directly the RIS scheme (i.e. without using eq. (5)) and using in place of E_{tg}^0 the "corrected" parameter $E_{tg}' = E_{tg}^0 - \Delta_{tg}$, where

$$\Delta_{tg} = \sum_n P^0(n) \, \Delta E(n)/N_g(n) \quad . \tag{7}$$

From this equation and the entries in table II we find for hexane the value $\Delta_{tg}=0.087$ kcal/mol, with a standard deviation of ± 0.005 kcal/mol. Analogous results are found for the longer n-alkane chains ($\Delta_{tg}=0.09$ to 0.11 kcal/mol) indicating that the appropriate value for the effective *gauche-trans* energy difference E_{tg}' in the nematic phase is appreciably lower than the gas phase value. This result is in general accord with optimal E_{tg}' values suggested by conformation studies[5,15] based on the direct application of the RIS scheme without explicit consideration of intermolecular interactions. The present analysis shows the relation of the effective E_{tg} parameter to more basic parameters of the interacting molecules and furthermore clarifies the approximate character and the limitations of the direct use of the RIS methodology to describe the conformation statistics of n-alkanes in nematics.

RELATION TO THE MODULAR APPROACH

To formulate the potential of mean torque, i.e. the anisotropic part of $V(\omega, n)$, using the modular approach one identifies the elementary rigid units of the chain molecule and combines additively their tensor contributions[1,8,9]. Choosing, for example the C-C bonds of the n-alkane molecule as elementary units one has the following representation for the leading (second rank) terms of the potential of mean torque

$$V^{(2)}(\omega,n) = w_0 \sum_{i=1}^{N} (\tfrac{3}{2}(s_i \cdot D)^2 - \tfrac{1}{2}) + w_1 \sum_{i=1}^{N-1} (\tfrac{3}{2}(s_i \cdot D)(s_{i+1} \cdot D) - \tfrac{1}{2}(s_i \cdot s_{i+1}))$$

$$+ w_2 \sum_{i=1}^{N-2} (\tfrac{3}{2}(s_i \cdot D)(s_{i+2} \cdot D) - \tfrac{1}{2}(s_i \cdot s_{i+2})) + ... \quad , \tag{8}$$

where D is the nematic director, s_i are the unit vectors along the C-C bonds i=1,2..N and w_0, w_1, w_2 are the coupling parameters associated respectively with direct segmental ordering, orientational correlations among first neighbour segments, second neighbours ...

The modular potential of eq. (8) gives an accurate description[1] of the segmental order parameters of n-alkane solutes in nematics. It involves, however , a number of assumptions the validity of which has only been confirmed indirectly, i.e form the good agreement with measurement. Such assumptions refer to

(a) the invariance of the couplings w_0, w_1, w_2..with conformation,

(b) the uniformity of the couplings everywhere along the chain (equivalently, the neglect of end effects) which is expressed by using a single set of couplings w_0, w_1, w_2.. to describe the orientability of all the sites i=1,2..N of the chain, and

(c) the ascending magnitude of the couplings with increasing neighbour distance which allows the neglect of correlations terms beyond second neighbours. In actual applications[1] w_1 is found slightly smaller than w_0 and w_2 is found much smaller than w_1.

Here we test the validity of these assumptions by direct evaluation of the couplings from the coefficients $C_{2M}^{(0)}(n)$ of eq. (3) for each conformation of the chain. This is done by equating the second rank component of the potential of eq. (2) to the expression in the right hand side of eq. (8) where, in order to test simultaneously the uniformity assumption, we allow the terminal C- C bonds to have different couplings denoted by w'_0 and w'_1 . Thus, given the coefficients $C_{2M}^{(0)}(n)$, we obtain a set of numerical values $w_0(n)$, $w'_0(n)$, $w_1(n)$, $w'_1(n)$, $w_2(n)$ for each conformation. The average values and the standard deviations of these quantities are computed using the conformation probability distribution of eq. (6) with the value of E'_{tg} set at 0.8kcal/mol and T=330°K. The results are shown in table III.

TABLE III   Calculated average values and ratios of modular coupling parameters.

	w_0/kcal mol^{-1}	w'_0/w_0	w_1/w_0	w'_1/w_0	w_2/w_0
hexane	0.12±0.01	1.08±0.01	0.76±0.01	0.90±0.01	-0.01±0.01
heptane	0.12	1.08	0.81	0.86	0.18
octane	0.12	1.10	0.87	0.82	0.08
nonane	0.12	0.96	0.84	0.80	0.19
decane	0.13	1.00	0.81	0.73	0.15

The above values   confirm to a very good approximation the validity of the assumptions (a), (b), (c) stated above for the modular potential of eq. (8) and they are in satisfactory agreement with the results obtained from the deuterium NMR spectra of n-alkanes[1] by direct optimisation.

ELECTROSTATIC INTERACTIONS: DIMETHOXYETHANE

The permanent electric dipoles ($\mu=1.3D$, see figure 1) of dimethoxyethane (DME) make it a particularly suitable chain solute for the study of the conformational and orientational influence of dipolar interactions in nematics. The solvent molecules are modelled as a spherocylinders with localised transverse and longitudinal dipole moments as shown in figure 1. In common nematogens the magnitude of these moments are in the range of 2 to 4D.
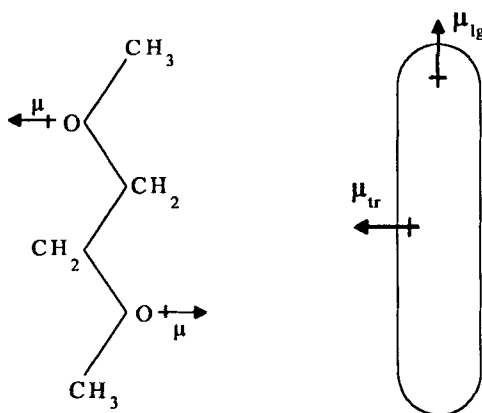

FIGURE 1   Configuration of permanent dipoles in DME and in the solvent molecule.

The description the conformations of DME involves the following RIS parameters: the *gauche* angle ϕ_g for rotations about the C-C bond and the respective energy E_{tg}^0, the angle $\tilde{\phi}_g$ and the energy $\tilde{E}_{tg}^0$ for rotations about the O-C bonds and $E_{g^+g}^0$ the energy associated with the g^+g^- sequences about the O-C-C. The precise values of some of these parameters are still an open question in the literature[6,7,16] and furthermore there are calculations suggesting[16] the necessity of including terms associated with g^+g^- sequences. The values we use in this study are fairly representative, namely $\phi_g = 115°$, $\tilde{\phi}_g = 100°$ for the angles and $E_{tg}^0 = -0.6$, $\tilde{E}_{tg}^0 = 0.9$, $E_{g^+g^-}^0 = 0.5$ for the energies (in kcal/mol).

The expansion coefficients of equations (3) and (4) are evaluated for various combinations of μ_{tr} and μ_{lg}, the other characteristics of the spherocylindrical solvent being as described in the preceding sections. From the values of the isotropic coefficients $C_{00}^{(0)}$ and $C_{00}^{(ES)}$ we find the effective conformational energy $E(n)$ of eq. (5) for all the significant conformations of DME. The results of these calculations for three cases of solvent dipole composition, namely a purely longitudinal dipole moment, a purely transverse dipole moment and no dipole moment at all, are shown in table IV together with the gas phase values $E^0(n)$ of the DME conformational energy at $T = 305$ °K   .

TABLE IV   Gas phase ($E^0(n)$) and effective ($E(n)$) conformation energies (in kcal/mol) of DME for three cases of the solvent molecule dipole:

(A) $\mu_{lg}=0$, $\mu_{tr}=0$. (B) $\mu_{lg}=4$ D, $\mu_{tr}=0$. (C) $\mu_{lg}=0$, $\mu_{tr}=3$ D.

conformation	$E^0(n)$	$E(n)$		
		(A)	(B)	(C)
t t t	0.0	0.00	0.00	0.00
t g t	-0.6	-0.69	-0.68	-0.62
t t g	0.9	0.82	0.84	0.79
t g g⁻	0.8	0.47	0.50	0.53
t g g	0.3	0.12	0.14	0.16
g t g	1.8	1.62	1.65	1.60
g t g⁻	1.8	1.65	1.67	1.65
g g g⁻	1.7	1.25	1.28	1.29
g g⁻ g	1.6	0.93	0.95	0.95
g g g	1.2	0.95	0.98	1.01

It is evident from the comparison of $E^0(n)$ and $E(n)$ in this table that (i) the excluded volume interactions (case A) cause a substantial shift of the energy of nearly all the conformations of DME. The effect is rather marked for tgg', ggg' and gg'g. (ii) The shift does not follow a simple pattern and thus, unlike the case of n-alkanes, it can not be accounted for by using "corrected" values for the RIS energy parameters E^0_{tg}, $\tilde{E}^0_{tg}$, E^0_{tg} . (iii) The inclusion of dipole-dipole interactions (cases B and C) introduces further changes to the energy. These are, however, small compared to the shift introduced by excluded volume interactions alone.

The above considerations suggest that it is not possible to have an accurate description of the conformation statistics of DME in liquid crystals simply in terms of the RIS energy parameters. Accordingly, attempts to determine optimal values for these parameters from the RIS analysis of order parameter measurements, without explicit consideration of solvent-solute interactions, can only provide rough estimates. The electrostatic part of the solvent-solute interaction appears to have a minor effect on the conformation energy. By contrast, it could have quite substantial effects on the segmental order profiles of chain molecules with dipole moments[2.9]. A realistic model of the full distribution function $f(\omega,n)$ for such molecules should, therefore, include the electrostatic interactions.

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