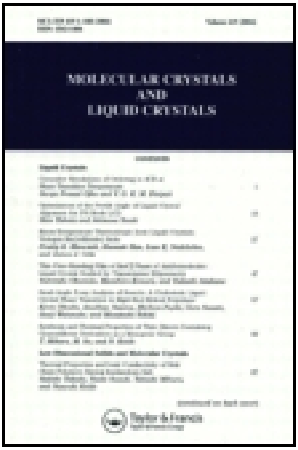

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Order Parameter in Binary Mixture by Monte Carlo Simulation Hybridized with Mean Field Approximation

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Order Parameter in Binary Mixture by Monte Carlo Simulation Hybridized with Mean Field Approximation

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The order parameters of each component in a binary mixture consisting of substances exhibiting a nematic phase and an isotropic phase have been evaluated by Monte Carlo simulation using the method of Vacatello and Iovino based on the Flory-Ronca-Irvine mean field theory. An induction of ordering for an isotropic solute has been obtained in the nematic phase. The degree of induction is dependent not only on the parameters of the interactive orientational potential but also on the anisotropy of the molecular shape of the isotropic solute.

Keywords: Monte Carlo simulation; binary mixture; nematic phase; order parameter

INTRODUCTION

Computer simulations have been expected to evaluate ordering properties in detail for complicated systems composed of some substances and/or phases. Many parameters are required to describe such systems compared with pure

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systems. It is also necessary to treat a large simulation system in order to evaluate the physical properties. These problems hinder the availability of computer simulations for complicated systems. Vacatello and Iovino have proposed a computer-simulation model in which the anisotropy of both the molecular shape and intermolecular force is taken into account for pure systems[1], with the molecular-force-anisotropy incorporated through a mean-field-type potential based on the Flory-Ronca-Irvine (FRI) theory [2]. It is expected that the use of a mean-field type potential is preferred from the point of view of computational load and a clear correspondence between the simulation parameters and physical properties for complicated systems. Recently, we applied Vacatello and Iovino's method to liquid-crystalline binary systems composed of the same shape of molecules with different potential parameters [3]. In the binary system consisting of substances exhibiting the nematic phase with different potential parameters, there is an approximately linear relationship between the order parameter and the composition. When the isotropic molecules are mixed with the nematic substance, the order parameter decreases with increasing mole fraction of the isotropic molecule, and the nematic phase changes into the isotropic phase at a specific composition.

In this study, the order parameters of each component in a binary mixture consisting of nematic and isotropic molecules with the same or different shapes have been evaluated by Monte Carlo simulation using Vacatello and Iovino's method. We discuss the relations between the potential parameter or molecular shape of the isotropic molecules and the ordering property in a nematic phase.

METHOD

The Monte Carlo simulation was carried out using the method of Vacatello and Iovino[1] for the linear chain model composed of four (x_i=4) or two (x_i=2) successive atoms. The flexibility of the molecule was ignored. The energy of molecule *i* is given by

$$E_i = \tfrac{1}{2}\sum_{j \neq i} E_{ij} + E(\theta_i). \tag{1}$$

The energy E_{ij} is the term based on the anisotropy of the molecular shape.

$$\begin{aligned} & E_{ij} = \sum_{k=1}^{x_i} \sum_{l=1}^{x_j} E(r_{kl}) & & \\ & E(r_{kl}) = \infty & & r_{kl} < 0.75\sigma \\ & E(r_{kl}) = \varepsilon\left\{\left(\frac{\sigma}{r_{kl}}\right)^{12} - 2\left(\frac{\sigma}{r_{kl}}\right)^{6} + 1\right\} & & 0.75\sigma \leq r_{kl} \leq \sigma \\ & E(r_{kl}) = 0 & & \sigma < r_{kl} \end{aligned} \tag{2}$$

The interatomic distance in the molecule is fixed to the length of σ. The reported value of 6.91×10^{-22} J was used for the softness parameter of an atom, ε[1]. The orientational energy of molecule *i*, $E(\theta_i)$, is given by

$$E(\theta_i) = -\frac{kx_i\tau_i}{V_r} S \frac{3\cos^2\theta_i - 1}{2}, \tag{3}$$

as a function of angle θ_i between molecule *i* and the director (z axis), where τ_i, V_r and *k* are the characteristic parameter, reduced volume, and the Boltzmann constant, respectively. The characteristic parameter, τ_i, is introduced to express the ordering ability caused by the chemical structure, and the values of τ_i used are shown in Table 1. The order parameter for the whole system is calculated by $S = (3\langle\cos^2\theta\rangle - 1)/2$. The reduced volume, V_r, was fixed at 125 for each molecule [1,3].

TABLE 1 x_i and τ_i parameters used in this study.

molecule	x_i	τ_i/K	molecule	x_i	τ_i/K
4a	4	250	2a	2	250
4b	4	150	2b	2	150
4c	4	0	2c	2	0

The number of molecules, N, was determined to be 4000-6000 and a completely ordered state without a layer structure was used for the initial configuration. We confirmed that the results are independent of the number of molecules and the initial configuration. A physical quantity was obtained from the average of the final 10^8 steps (attempted translations and rotations) after 2×10^8 to 8×10^8 equilibration steps. The ratio of acceptance was kept at 50 percent, but the value of the rotating angle was not higher than 10 degrees [1]. Calculations were performed in a cell with 3-dimensional periodic boundary conditions under an NVT ensemble.

RESULTS AND DISCUSSION

The 4a molecules form a nematic phase at temperatures below 290K (see Figure 4). The simulations were performed for binary mixtures consisting of a nematic solvent 4a and a solute exhibiting an isotropic phase in its pure system. The mole fraction of the isotropic solute, x, is expressed as $C_x = N_x/(N_{4a} + N_x)$. Figure 1 shows the plots of S vs. the mole fraction of an isotropic solute at 240K for systems 4a+4b and 4a+4c. As shown in Figure 1A, the nematic phase is

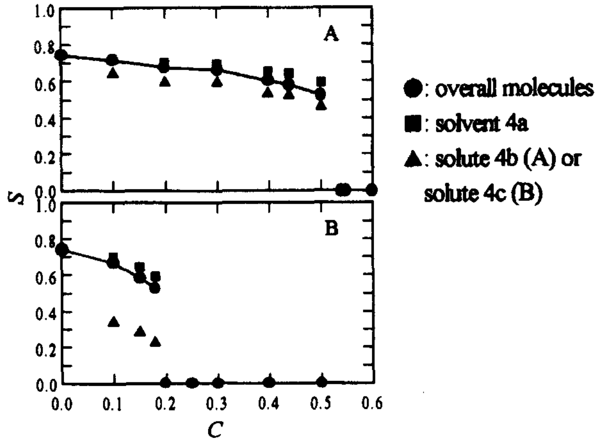

FIGURE 1 Plots of the composition dependence of the order parameter at 240K for the 4a+4b (A) and 4a+4c (B) binary systems.

stable in the region below C_{4b}=0.5. The ordering of solute 4b is consequently induced in the nematic phase. The value of S decreases with increasing C_{4b}, and a transition to the isotropic phase is clearly observed at C_{4b}=0.54. In the isotropic phase, the value of the order parameter is actually obtained to be zero not only for solute 4b but also for solvent 4a. The phase transition is also obtained in the 4a+4c system, but the mole fraction at the transition is much smaller than that in the 4a+4b system. The induction of ordering for solute 4c (τ_{4c}= 0) is caused by the packing effect because the value of orientaional energy $E(\theta_i)$ in eq.(3) is always zero. On the other hand, high induction of ordering for solute 4b (τ_{4b} = 150K) is regarded not only as the packing effect but also as the effect of the orientational energy.

Figure 2 shows the plots of S vs. the mole fraction of an isotropic solute at

240K for systems 4a+2a(A), 4a+2b(B) and 4a+2c(C). The pure systems, 2a, 2b and 2c, exhibit the isotropic phase at 240K. Although the anisotropy of molecular shape is very small, the induction of ordering is also obtained for each solute. The value of S for the isotropic solutes is decreased with decreasing of τ, e.g., $S_{2a} = 0.35$ (τ_{2a} = 250K), $S_{2b} = 0.26$ (τ_{2b} = 150K) and $S_{2c} = 0.09$ (τ_{2c} = 0K). The induction of solute 2c in the 4a+2c system is responsible for the packing effect in analogy with solute 4c in 4a+4c system, but the value of S_{2c} is much smaller than that of S_{4c}.

Figure 3 shows the plots of the angle correlation function $A(|\cos\phi_{ij}|)$ within the intermolecular distance of 3σ.[3] The value of the mole fraction of solute 4c or 2c is chosen to be 0.1. The solid and dotted lines indicate the angle correlation functions for the solvent-solvent and solute-solvent, respectively. In

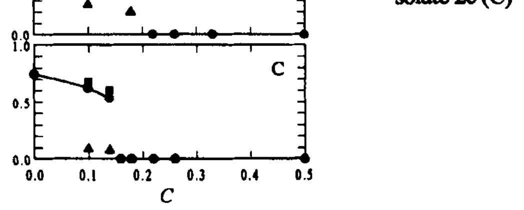

FIGURE 2 Plots of the composition dependence of the order parameter at 240K for the 4a+2a(A), 4a+2b (B) and 4a+2c (C) binary systems.

each system, the nematic phase is stable at 240K. A clear correlation between solute 4c and solvent 4a is observed as shown in Figure 3A, although there appears to be little correlation between 2c and 4a. Figure 4 shows the dependence of the order parameter on temperature for the 4a+4c and 4a+2c systems. The value of the mole fraction of the solute is also 0.1. At temperatures exhibiting the nematic phase, a large induction of ordering for 4c is obtained. The orientational energy based on eq.3 should be zero for the 4c and 2c solutes with τ=0, but the anisotropy of molecular shape for 4c is larger than that of 2c. It is appeared that the effect of shape-anisotropy of the solute is sensitive to the induction of ordering for the isotropic solute. On the other hand, it makes substantially little difference in the transition temperature between the 4a+4c and 4a+2c systems, although these transition temperatures are appreciably lowered by the addition of a solute to the pure 4a system.

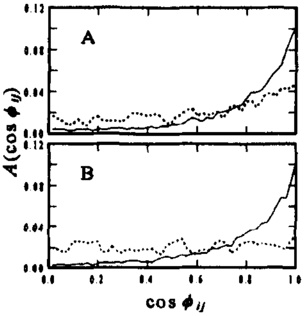

FIGURE 3 Plots of angle correlation function $A(|\cos\phi_{ij}|)$ [3] within the intermolecular distance of 3σ at 240K for the 4a+4c (A) and 4a+2c (B) binary systems. Solid line: 4a-4a ; dotted line: 4a-4c or 2c.

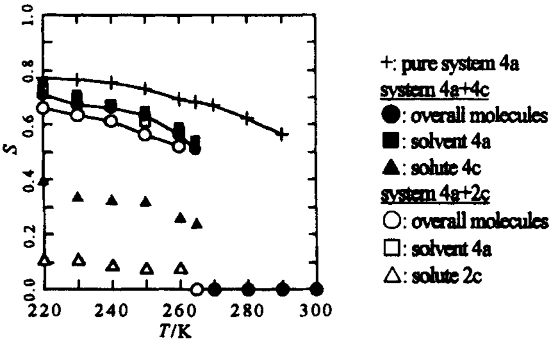

FIGURE 4 Temperature dependence of the order parameter for the 4a+4c and 4a+2c systems at C_{4c}=0.1 and C_{2c}=0.1, respectively.

CONCLUSIONS

The induction of ordering for the isotropic solute in the nematic phase has been evaluated by Monte Carlo simulation using the method of Vacatello and Iovino based on the Flory-Ronca-Irvine mean field theory. It has been demonstrated that the induction is due to the packing effect attributed to the shape-anisotropy. The degree of induction is dependent not only on the shape-anisotropy but also on the characteristic parameter, which is related to the ability to follow the surrounding orientation. This method provides a useful means of studying a complicated system such as liquid crystal mixtures from the viewpoint of the load of computers.

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