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Temperature Effect on the Configurational Properties of an *n*-Decane Chain in Solution

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Equilibrium and dynamical behaviors of an *n*-alkane polymer (decane) in solution have been investigated by a molecular dynamics simulation method. The polymer is assumed to be a chain of elements (CH₂) interconnected by bonds having a fixed bond length and bond angle, but each bond of the polymer is allowed to execute hindered internal rotation. The calculation explicitly considers the molecular nature of solvent by including the intermolecular interactions between solvent-solvent molecules and chain element-solvent molecule. We present the results of calculations on (1) equilibrium properties (the solvent molecule-chain element pair correlation function, chain element-chain element pair correlation function, the mean square end-to-end distance and the mean square radius of gyration of the polymer) and (2) dynamic properties (four different autocorrelation functions, namely, the autocorrelation functions for the end-to-end distance and the radius of gyration, and the velocity autocorrelation functions for the center of mass and the end point of the chain). We found that the physical properties of the polymer chain depend sensitively on temperature. Comparison of the present work with other authors' results is also presented.

1. Introduction

The behavior of chain molecules in solution has been the subject of considerable attention.¹⁻¹² Chandler et al.² have reported the theoretical predictions that condensed-phase environment can shift the equilibrium between the gauche and trans forms of *n*-butane, and that the gauche population increases upon transfer from gas phase to aqueous solution. Jorgensen³ has carried out the Monte Carlo (MC) simulation of *n*-butane in water, and found a similar fact as predicted by Pratt and Chandler.^{2d} In the case of longer chain molecules, many computation results have been reported. Ceperley et al.⁴ developed a dynamic MC technique which simulates the dynamics of a single polymer chain immersed in a solvent. Other MC results for the static and dynamic properties of condensed systems of polymers have been reported.⁵⁻⁸

Molecular dynamics (MD) simulation of chain molecules has been carried out by various authors.⁹⁻¹⁴ Bishop et al.⁹

have simulated polymer chains represented by beads linked by springs. Rapaport¹⁰ simulated a freely linked polymer chain of hard spheres immersed in a solvent represented by hard spheres. Bruns and Bansal¹¹ have carried out a simulation of the dynamics of a nonamer chain immersed in solvent, the solute being nine beads connected by rigid rods. Lee et al.¹² have calculated the static and dynamic properties of a polymer chain immersed in solvent by using the model of beads connected by springs. The chain molecules of the above four groups⁹⁻¹² are freely-jointed chains having intramolecular interaction as well as the intermolecular interaction with solvent molecules.

Calculations using more realistic chain models are carried out by Weber et al.¹³ and Ryckaert et al.¹⁴ The former group simulated the chain molecules by flexible chains having the nature of bond stretching, bond-angle bending and bond rotation, and the latter group simulated by semi-rigid chains with fixed bond-length, fixed bond-angle and hindered

bond-rotation. However, these groups have treated only pure liquid systems without solvent.

Recently we have reported an MD simulation study¹⁵ which examines the role of attractive force on physical properties of an *n*-alkane chain immersed in solvent. The model of the chain was assumed to be semirigid, *i.e.*, the bond length and bond angle are fixed, but the bond rotation is allowed to take place in a restricted manner. Our calculations gave results which are different from those of similar MD studies available in the literature.⁹⁻¹² The difference would be partly caused by the temperature since our temperature (298K) was quite different from other authors'. In this paper, we study the effect of temperature on the behavior of a decane molecule in solution more closely, and compare the results with other similar MD studies.⁹⁻¹⁴

2. Model and Method

A single *n*-decane molecule immersed in 246 solvent particles is considered. This is the same model used in our earlier work.¹⁵ Namely, the chain was represented by a semi-rigid one with a constant bond length ($=0.154$ nm) and bond angle ($=112^\circ$),¹⁶ but with hindered bond rotation. The rotational potential of the bond is given by^{17,18}

$$V(\phi) = \frac{V_m}{2} \{x(1 - \cos \phi) + (1-x)(1 - \cos 3\phi)\} \quad (1)$$

where V_m ($=4.1$ kcal/mole) is the height of the potential barrier, and x ($=0.25$) is the weighting factor of the trans-conformation relative to the gauche.

The interaction potential $V(r)$ between solvent-solvent molecules (SS), between chain element-solvent molecules (CS), and between two chain elements (CC) are represented by an exp-6 potential,

$$V(r) = \frac{\epsilon}{\alpha - 6} \left\{ 6 \exp \left[\alpha \left(1 - \frac{r}{r_m} \right) \right] - \alpha \left(\frac{r_m}{r} \right)^6 \right\} \quad (2)$$

where r_m ($=0.36$ nm) is the distance at which $V(r)$ becomes minimum, ϵ ($=0.3$ kcal/mole) is the depth of the potential, and α ($=14.0$) represents the stiffness of the repulsive part of the potential. The masses m for the chain and solvent particles were set to be identical. All the above mentioned numerical values of the parameters were followed from our previous paper.¹⁵

For the MD simulation we use a system of N ($=10+264$) particles which were placed in a periodic cubic box with side-length L ($=6.703r_m$). The value of L is chosen to satisfy

$$L > r_{\max} + r_c \quad (3)$$

where r_{\max} is the maximum end-to-end distance of the chain molecule, and r_c ($=2.5r_m$) is the distance beyond which the potential (eq 2) is truncated. [This prevents a chain element to interact with an element in the periodic image of the chain molecule] In order to generate an initial configuration, we first place all N particles on the lattice sites of a face-centered cubic structure. Next we choose consecutive ten particles lying in the central portion of the box, and place the solute *n*-decane molecule according to the manner given in the pre-

vious paper.¹⁵ The velocities of individual particles are chosen according to the Maxwell-Boltzmann distribution so that the temperature of the system is identical to the desired temperature. The Newton's equations of motion of the N particles are solved by Verlet's finite difference algorithm,¹⁹ with constraints on the fixed bond length and bond angle of the chain molecule adopting the matrix method of Ryckaert *et al.*^{14a} In order to remove the contribution of the initial distribution from the calculated results, calculations are carried out to sufficient long time-steps. Five thousand time-steps are proved to be sufficient to reach equilibrium [one time-step Δt being equal to 0.005 in the reduced time unit (see below)].

The temperature is computed by^{11a}

$$T^* = \frac{kT}{\epsilon} = \frac{6\alpha}{\alpha-6} \frac{1}{3N_s + N_c + 3} \sum_{i=1}^N v_i^{*2} \quad (4)$$

where T^* is the reduced temperature; v_i^* is the reduced velocity of the i th particle; $N = N_s + N_c$, and N_s and N_c represent the number of solvent particles and of the chain elements, respectively. The temperature variation is made by changing the linear momenta of entire particles. Reduced units have been used throughout this paper: time, in $[m(\alpha-6)/6\epsilon\alpha]^{1/2} r_m$; length in r_m ; velocity in $[6\epsilon\alpha/m(\alpha-6)]$; temperature in ϵ/k , and density in $N/(L/r_m)^3$.

3. Results and Discussion

(1) *Pair Correlation Functions.* Pair correlation function $g(r)$ describes the possibility of finding the particles within the distance r and $r + \Delta r$ from a reference particle:²⁰

$$\rho g(r) = \frac{1}{N} \left\langle \sum_{i \neq j} \delta(r + r_i - r_j) \right\rangle \quad (5)$$

where ρ is the bulk number density (N/V), r_i and r_j are the positions of the i th and j th particles, respectively. We use eq 5 to compute the pair correlation functions for solvent-chain (SC) and chain-chain (CC) pairs. For example, the pair correlation function for solvent-chain $g_{sc}(r)$ is proportional to the probability of finding solvent molecules at distance r from an element in the chain, and it gives the information on the arrangement of solvent molecules around a chain element. The computed result on $g_{sc}(r)$ is shown in Figure 1. The shape of $g_{sc}(r)$ at 298 K resembles the corresponding result in our earlier work,¹⁵ while $g_{sc}(r)$ at 100 K (which was not computed in Ref. 15) is similar to those at 100 K of other workers.^{11,12} Note that the model used in Ref. 15 is identical to the present model, while the model in other work^{11,12} is different from ours. Therefore, we conclude that the shape of $g_{sc}(r)$ is very sensitive to the temperature but is weakly sensitive to the models used to represent the chain. The heights of the first and second peaks at 298 K lie lower than the corresponding peaks at 100 K, which is similar to the case for simple liquid.²¹ This result can be explained as follows: the higher temperature, the higher the velocity of particles; thus, the solvent particles move more freely at higher temperature to form a uniform background rather than staying in a shell making an arrangement of

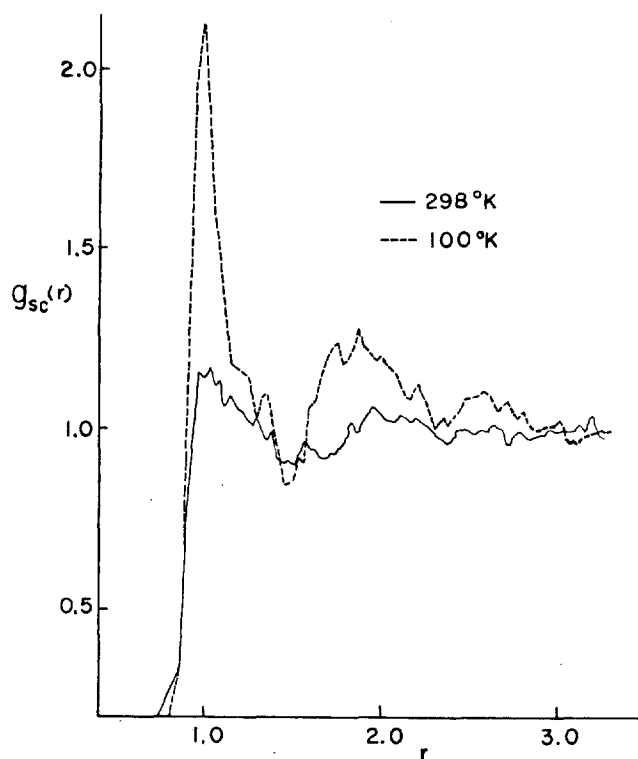


Figure 1. Pair correlation function $g_{sc}(r)$ between solvent molecule and chain element of an *n*-decane molecule vs. reduced distance.

solvent around a chain element.

The $g_{cc}(r)$ is proportional to the probability of finding the chain elements at distance r from a reference chain element, and it is related to the configuration of the chain. Since the bond length and bond angle of the chain are fixed, and the rotation angle varies in our study, the results of $g_{cc}(r)$ are different from other similar MD simulations of chain molecules in solution,⁹⁻¹² which were based on the freely jointed chain elements. [The details of the differences will not be shown here.] The peaks at $r=0.43$ and $r=0.71$ are indicated by perpendicular straightlines in Figure 2. [For the significances for the two peaks reference is made to the previous paper.¹⁵] The first and second maxima in Figure 2 represent the gauche and trans configuration, respectively. The shape of the peaks at 298 K in Figure 2 is similar to that of the previous work (see System 1 in Figure 4 in Ref. 15). Note that at 100 K the gauche peak is significantly higher than that of the trans-form, while the reverse is true at 298 K. A similar fact as above was observed by Weber^{13a} at temperature $T=76$ K, 315 K and 745 K for *n*-butane liquid. Weber^{13b} also found that the gauche peaks are higher than the transpeaks at $T=305$ K, 358 K and 589 K for *n*-octane liquid in agreement with our finding at 100 K for *n*-decane. Thus, the appearance of higher peaks of gauche forms than trans-forms is not unique in our case only. The higher peak at the gauche position (Figure 2) in our case is due to the contraction of the decane chain at lower temperature (see the next section) as well as the interaction between solvent molecules attached to the chain elements (see Figure 1), i.e., although the gauche form generally is

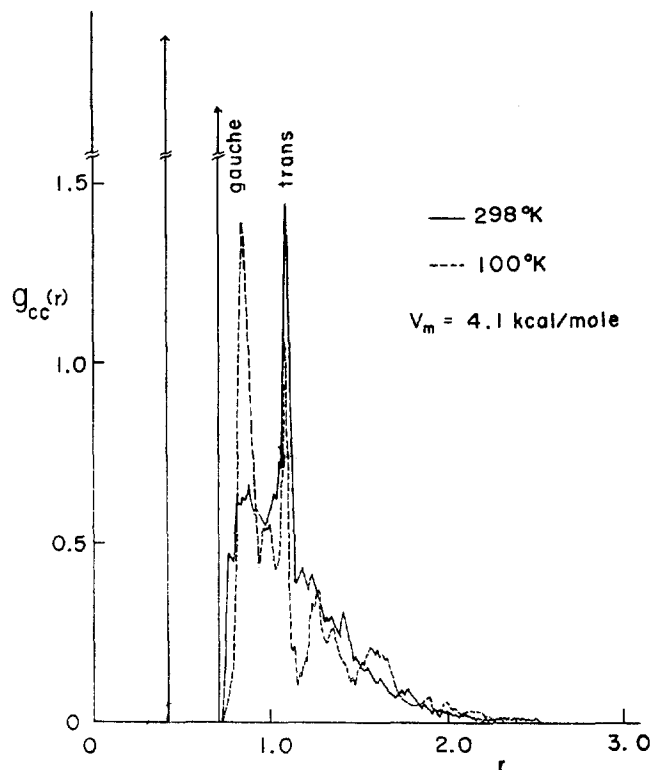


Figure 2. Pair correlation function $g_{cc}(r)$ between two chain elements of an *n*-decane chain immersed in a solvent vs. reduced distance.

energetically less stable than the trans-form, because of the above-mentioned reasons, the gauche peak appears higher than the trans-form at the low temperature.

One also notes that in Figure 2, the gauche peak of $g_{cc}(r)$ appears higher at 100 K than at 298 K. This is also caused by the interaction between chain elements and solvent molecules. As one notes from Figure 1, the SC interaction at 100 K is stronger than at 298 K. Because of the strong interaction more solvent molecules are attached to the chain elements at low temperature, and due to the interactions between the attached solvent molecules, the gauche form becomes more stable at 100 K than at 298 K, thus the $g_{cc}(r)$ appears higher at the lower temperature.

The interaction between solvent molecules attached to the chain elements becomes weak at the trans-position because of the larger separation. Thus the interaction effect of the attached solvent molecules appears feebly in the trans-position, especially at the higher temperature. The trans-peak which is higher at 298 K than at 100 K is thus explained, since the trans form is more stable at the higher temperature. [Note: The fraction of the gauche (or trans) forms is not immediately clear from Figure 2; the problem concerning the fraction of the conformers will be considered in a later publication. The height of the $g_{cc}(r)$ is the main interest in this section.]

Ryckaert and Bellemans^{14c} reported that the percentage of the trans-forms of butane is larger in the gas state than in the liquid state. This result means that the chain molecule has more transconformation in free environment. In our case, the chain molecule at 100 K has much more constraints

than at 298 K because of the reasons mentioned in the above paragraph, thus it is supposed that the gauche form appears favorably than trans-form, *i.e.*, the $g_{cc}(r)$ of the gauche position at 100 K is higher than that of trans-form.

(2) *Dimensional Properties.* Next we present the results of the calculations on the mean square end-to-end distance $\langle R^2 \rangle$ and the mean square radius of gyration $\langle S^2 \rangle$. These quantities are represented by¹⁶

$$\langle R^2 \rangle = \langle |r_i - r_{N_c}|^2 \rangle \quad (6)$$

and

$$\langle S^2 \rangle = \langle \frac{1}{N_c} \sum_{i=1}^{N_c} (r_i - r_{cm})^2 \rangle \quad (7)$$

The computed results on $\langle R^2 \rangle$, $\langle S^2 \rangle$ and ratio $\langle R^2 \rangle / \langle S^2 \rangle$ are tabulated in Table 1. The lower temperature result gives smaller values of $\langle R^2 \rangle$ and $\langle S^2 \rangle$ as would be expected. The chain contraction at lower temperature was also observed in the MD simulation of liquid octane.^{9b}

Note that $\langle R^2 \rangle / \langle S^2 \rangle$ is 6 for random-flight chains or freely rotating chains with very high molecular weights.¹⁶ Our results on $\langle R^2 \rangle / \langle S^2 \rangle$ differ slightly from six, this is due to the low N_c ($N_c = 10$) in our case. The eigenvalue of the moment of inertia tensor, S_i^2 ($i = 1, 2$ or 3), represents the shape of the chain approximately. The deviation of the ratio $\langle S_i^2 \rangle / \langle S^2 \rangle$ from $1/3$ indicates the asphericity of the chain shape. Table 1 shows that the chain has a nearly spherical shape in agreement with our previous paper,¹⁵ but contrarily to other works.^{6c, 9-11} The difference is caused by the fact that the latter authors^{6c, 9-11} assumed free bond rotation while in the present and previous¹⁵ papers a hindered

TABLE 1: Chain Configuration Properties

property	temperature	
	298 k	100 k
$\langle R^2 \rangle$	3.388 ± 0.329	3.191 ± 0.549
$\langle S^2 \rangle$	0.551 ± 0.021	0.493 ± 0.023
$\langle R^2 \rangle / \langle S^2 \rangle$	6.148	6.473
$\langle S_1^2 \rangle / \langle S^2 \rangle$	0.392	0.440
$\langle S_2^2 \rangle / \langle S^2 \rangle$	0.337	0.298
$\langle S_3^2 \rangle / \langle S^2 \rangle$	0.231	0.262

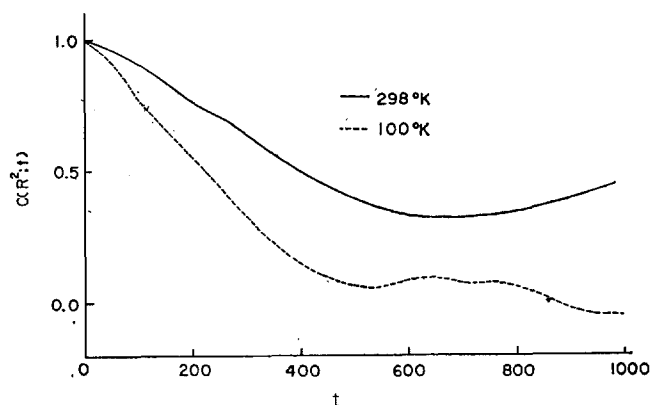


Figure 3. Autocorrelation function of the square end-to-end distance of the *n*-decane chain $C(R^2; t)$ vs. reduced time. The time axis is shown in units of Δt .

bond rotation (ep 1) was assumed. It seems that the molecular shape depends greatly on the rotational potential as will be reported later.

(3) *Dynamic Properties.* We have calculated the autocorrelation function to find out the relaxation phenomena of the chain molecule. The autocorrelation function describes the relation of quantity A at two different times t and $t + k\Delta t$, *i.e.*,

$$C(A; k\Delta t) = \frac{\langle A(t) A(t + k\Delta t) \rangle}{\langle A^2(t) \rangle} \quad (8)$$

When A is a scalar quantity, the autocorrelation function is represented by the following equation:

$$C(A; k\Delta t) = \left\{ (n-k) \sum_{l=1}^{n-k} A(l\Delta t) A[(l+k)\Delta t] - \sum_{l=1}^{n-k} A(l\Delta t) \sum_{l=1}^{n-k} [A(l+k)\Delta t] \right\} \cdot \left\{ (n-k) \sum_{l=1}^{n-k} A^2(l\Delta t) - \left[\sum_{l=1}^{n-k} A(l\Delta t) \right]^2 \right\}^{-1/2} \cdot \left\{ (n-k) \sum_{l=1}^{n-k} A^2[(l+k)\Delta t] - \left[\sum_{l=1}^{n-k} A[(l+k)\Delta t] \right]^2 \right\}^{-1/2} \quad (9)$$

where k and l are integers, n being the total number of time-steps taken for the averaging procedure. We choose $A(l\Delta t)$ to represent either R^2 or S^2 at time $t = l\Delta t$. The computed results on $C(R^2; t)$ and $C(S^2; t)$ are displayed in Figure 3 and 4, respectively. We note that these autocorrelation functions decay faster at the lower temperature. The reason is as follows: $g_{sc}(r)$ at the lower temperature ($= 100$ K) in Figure 1 has higher peaks than at 298 K, *i.e.*, at the lower temperature more solvent molecules are clustered around the solute chain elements than at the higher temperature. Consequently the interaction of the chain with solvent is stronger at the lower temperature. This implies that both $C(R^2; t)$ and $C(S^2; t)$ relax faster at the lower temperature.

We next compute the velocity autocorrelation function (VACF), $C(v; t)$, by using eq 8. The results on the VACF for the center of mass and the end point of the chain are shown in Figure 5 and 6, respectively. We note that the VACF's become similar to $C(R^2; t)$ and $C(S^2; t)$; *i.e.*, $C(v; t)$

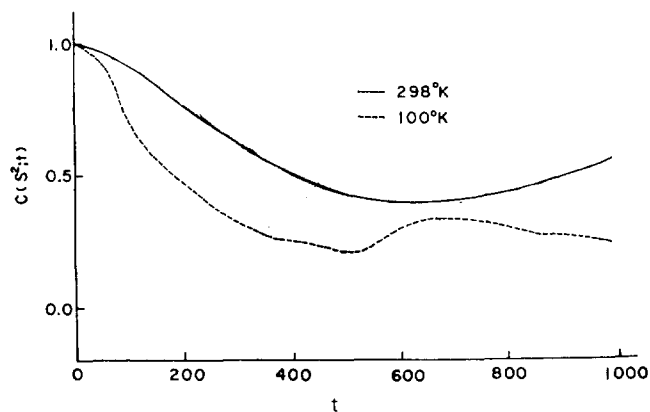


Figure 4. Autocorrelation function of the square of radius of gyration of the *n*-decane chain $C(S^2; t)$ vs. reduced time. The time axis is shown in units of Δt .

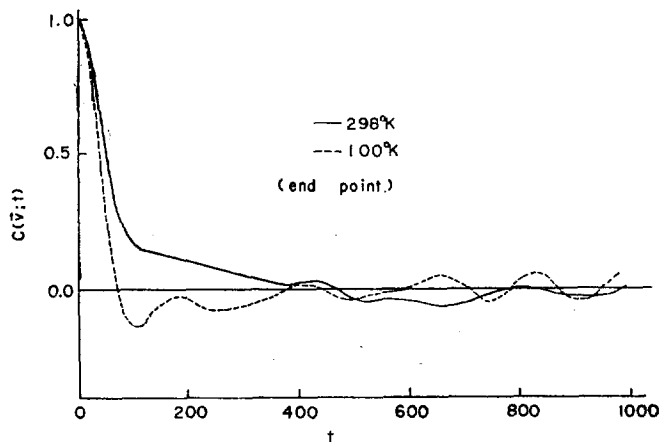


Figure 5. Velocity autocorrelation function of the center of mass of the *n*-decane chain $C(\mathbf{v}; t)$ vs. reduced time. The time axis is shown in units of Δt .

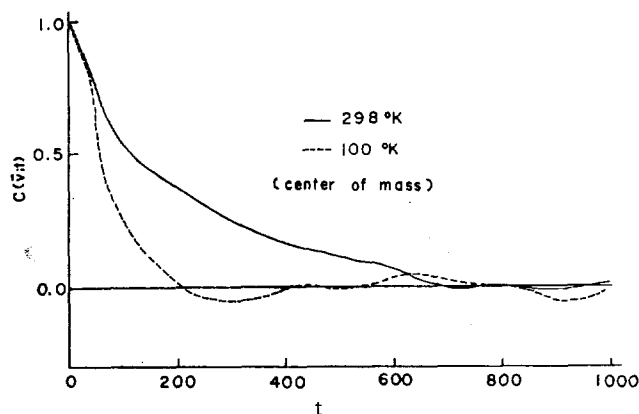


Figure 6. Velocity autocorrelation function of the end point of the *n*-decane chain $C(\mathbf{v}; t)$ vs. reduced time. The time axis is shown in units of Δt .

relaxes faster at the lower temperature. This behavior arises by the same reason as mentioned concerned with the relaxation behavior of the functions $C(R^2; t)$ and $C(S^2; t)$ in the preceding paragraph.

The diffusion coefficient D is expressed by²²

$$D = \frac{1}{3} \int_0^\infty \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle dt \quad (10)$$

and is calculated from the Einstein equation:

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{\langle r^2(t) \rangle}{t} \quad (11)$$

where $\langle r^2(t) \rangle$ is the mean-square displacement of the center of mass. We obtained the following values:

$$D = 1.062 \times 10^{-5} \quad \text{at } 100 \text{ K}$$

and

$$D = 9.035 \times 10^{-5} \quad \text{at } 298 \text{ K}$$

This agrees with the well known fact that D at lower temperatures is smaller than that at higher temperatures.

Figure 5 shows that $C(\mathbf{v}; t)$ at 298 K does not oscillate, this result is similar with that observed by Ryckaert and Bellemans^{14c} who used similar chain model as ours for liquid butane and decane without solvent at higher temperatures.

The VACF of the end point at 100 K (Figure 6) shows a different behavior, *i.e.*, it oscillates more than that of the center of mass (Figure 5). The particle at the end point moves more freely than any other chain elements since it feels less constraints of the intramolecular potential. So it can execute more oscillation than the center of mass, (Compare Figures 5 and 6). Other workers,^{11, 12c} who have considered no internal rotational degree of freedom have reported similar results as ours at 100 K (Figure 6), *i.e.*, the oscillation occurs in the systems with less constraints.

It is generally believed that the negative values in the VACF (*i.e.*, in the oscillation) are due to the cage effect of solvent or backscattering of the solute.²³ We could not find, however, any definite evidence in favor of such a mechanism.

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Evidence for Nitrogen-Bonded Acrylonitrile to Iridium(I) in Acrylonitrilecarbonylbis(triphenylphosphine)iridium(I) perchlorate

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Analyses of ¹H-NMR, infrared and electronic spectral data for [Ir(CH₂=CHCN)(CO)(P(C₆H₅)₃)₂ClO₄] (**1**) prepared by the reaction of Ir(OCIO₃)(CO)(P(C₆H₅)₃)₂ with CH₂=CHCN, agree with the suggestion that **1** is a mixture of the nitrogen-bonded acrylonitrile complex, [(CO)(P(C₆H₅)₃)₂Ir-NCCH=CH₂]ClO₄ and other compound which may be the C=C π-system-bonded acrylonitrile complex, $\left[\text{(CO) (P(C}_6\text{H}_5\text{)}_3\text{)}_2\text{Ir} - \begin{array}{c} \text{CHCN} \\ \parallel \\ \text{CH}_2 \end{array} \right] \text{ClO}_4$.

Introduction

We recently reported the formation of a cationic acrylonitrile-iridium(I) complex, [Ir(CH₂=CHCN)(CO)(P(C₆H₅)₃)₂]ClO₄ (**1**) by the reaction of Ir(OCIO₃)(CO)(P(C₆H₅)₃)₂ (**2**) with CH₂=CHCN.¹ The bonding between iridium and acrylonitrile in **1**, however, has not been unequivocally understood thus far: CH₂=CHCN may coordinate to metal through the nitrogen or through the π-system of the nitrile group or/and through the π-system of the olefinic group.² Vibrational spectral data are known to be very useful in determining the bonding types of unsaturated nitriles to metals. It is well established that ν_{C≡N} increases when the coordination of a nitrile to a metal occurs through the nitrogen.² Coordination of a nitrile through the C≡N π-system should cause a significant decrease in ν_{C≡N} as seen in succinonitrile (NCCH₂CH₂CN) complex of Mn(0).³ To our knowledge, no acrylonitrile complexes where acrylonitrile is coordinated through the π-system of the nitrile group have been observed thus far. It is also well known that both ν_{C=C} and ν_{C≡N} of CH₂=CHCN show considerable decreases (up to -168 cm⁻¹ for ν_{C=C} and up to -55 cm⁻¹ for ν_{C≡N}) upon coordination to metal through the C=C π-system.² In this paper, we wish to report that [Ir(CH₂=CHCN)(CO)(P(C₆H₅)₃)₂]ClO₄ (**1**) prepared by the reaction of Ir(OCIO₃)(CO)(P(C₆H₅)₃)₂ with CH₂=CHCN is a mixture of nitrogen-bonded acrylonitrile complex,

[P(C₆H₅)₃]₂(CO)Ir-NCCH=CH₂]ClO₄ and some amount of other compound which may be the C=C π-system-bonded acrylonitrile complex, $\left[\text{(P(C}_6\text{H}_5\text{)}_3\text{)}_2\text{(CO)Ir} - \begin{array}{c} \text{CH}_2 \\ \parallel \\ \text{CHCN} \end{array} \right] \text{ClO}_4$.

Results and Discussion

Infrared spectrum of **1** (in Nujol) prepared by the reaction of **2** with CH₂=CHCN shows ν_{C≡N} (weak and broad) at 2220~2240 cm⁻¹ and ν_{C=C} (very weak and broad) at 1600~1620 cm⁻¹, while free CH₂=CHCN shows ν_{C≡N} (sharp) and ν_{C=C} (weak) at 2230 and 1609 cm⁻¹, respectively. These infrared spectral data clearly suggest that the acrylonitrile in **1** does not coordinate through the C≡N π-system to iridium, but does not indicate whether the acrylonitrile coordinates through the nitrogen or through the C=C π-system. It should also be mentioned that infrared spectrum of **1** shows two ν_{CO} bands at 2052 cm⁻¹ (medium) and 2047 cm⁻¹ (strong), which may imply that **1** is a mixture of two complexes since the related monocarbonyl iridium complexes always show a single strong ν_{CO} band, respectively.⁴ Then, the broad ν_{C≡N} band at 2220~2240 cm⁻¹ observed for **1** may represent two bands: one at lower and the other at higher frequency than 2230 cm⁻¹ at which free CH₂=CHCN shows ν_{C≡N}. Accordingly, these infrared spectral data for **1** may suggest that **1** is a mixture of the nitrogen-bonded acrylonitrile complex, [(CO)(P(C₆H₅)₃)₂Ir-NCCH=CH₂]ClO₄ and other compound which may