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THERMODYNAMIC STUDY OF A MODEL MONOMER-DIMER SYSTEM BY THE MONTE CARLO METHOD

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Excess molar enthalpies and volumes for a model system, Ar + hypothetical Ar dimer, are calculated by the Monte Carlo method. The excess enthalpies are large and positive, while the excess volumes are large and negative. The distribution of potential energy per molecule and that of orientation between dimers are also calculated in order to describe the thermodynamic behavior of the system from the microscopic point of view. The simulations show that differences of molecular shape and size of the components play an important role in the thermodynamic behavior of the system through the change of the orientational order.

KEY WORDS: Excess enthalpy, excess volume, monomer-dimer system, Monte Carlo method.

INTRODUCTION

Thermodynamic quantities are of interest in the study of aqueous or non-aqueous solutions. Recently, calorimetric and volumetric experiments have been done with high precision, and the results of molar excess enthalpies, H^E , excess volumes, V^E , of various binary systems have been reported [1–3]. Molar excess heat capacities, C_p^E , and excess isothermal compressibilities, κ_T^E , are also measured more easily than before, owing to the development of the experimental instruments [4–7]. It is, however, very difficult to clarify the microscopic feature of the solutions even through combining various kinds of thermodynamic information. The difference of intermolecular forces between the pure and solution states gives, in general, the main contribution to the thermodynamic behavior of the solution and as a result, H^E and V^E tend to take the same sign. This is true for such systems like aromatic hydrocarbon + aliphatic hydrocarbon. It is explained (reasonably) as follows; the attractive π – π interactions between aromatic hydrocarbons would be destroyed by the presence of aliphatic hydrocarbons [8]. The total potential energy of the system would increase to positive H^E , and the space between molecules would be extended to produce positive V^E . On the other hand, we have reported the experimental results of H^E and V^E for the decalin isomers + alkane systems, which showed positive H^E but negative V^E [2, 8–12]. Through the experimental study, we have pointed out that the difference

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of molecular size and shape between the component molecules produces important contributions to thermodynamic properties of these systems.

In this paper, we report the concentration dependence of H^E and V^E for the model monomer-dimer systems at some pressures calculated by the Monte Carlo method. The result is discussed in relation to the microscopic information obtained at the same time.

MODEL AND CALCULATION

The Argon molecule (Ar), is widely used as a model particle in the computer simulation study of simple liquids and their mixtures, including LB model mixtures [13, 14]. In the present work the Ar molecule and a hypothetical Ar dimer have been employed as a model monomer and a model dimer respectively, to make it easy to check and compare the present results with those reported by others. The monomer and each mer of a dimer interact through a Lennard-Jones 12-6 potential function with the same ϵ and σ . The values of (ϵ/k) and σ are 119.8(K), 3.405×10^{-10} (m), respectively [15]. The distance between two atomic centers of a dimer was set to be 0.46σ . Calculations were done in the NTV ensemble with 256 particles in a unit cell at $T = 100$ K. The maximum displacement length of a molecule was automatically changed in every 100 steps to as to keep the acceptance ratio about 0.5. We carried out a usual long run test generating about 2.0×10^7 configurations and ensured the convergence of the potential energy of the system by the generation of less than 1.0×10^6 configurations. We made another test on the pure dimer program, which is made in the condition that a dimer is regarded as a monomer: that is, (ϵ/k) for each mer of a dimer is 29.95(K) and the distance of the atomic center is zero. The result calculated for such the dimer showed very good agreement with that for the pure Ar, especially for the potential energy. The total number of generated configurations is about 5×10^6 , and the various kinds of thermodynamic quantities and the distribution functions were calculated from the second half of the configurations. The concentrations of the solutions calculated are 0.1, 0.3, 0.5, 0.7, and 0.9 in mole fraction. Preliminary MC calculations were made to establish the liquid region of each concentration. Such calculations were done at several densities of a concentration, generating about 1.5×10^6 configurations. The actual calculations were performed at 4 or 5 points of density in the liquid region. The calculated data were treated by the least squares method to determine their pressure dependence, from which the molar enthalpy and volume at a fixed pressure were obtained. The error bars in Figures 1 and 2 show the standard deviations of fit calculated by the least squares method.

RESULTS AND DISCUSSION

Excess thermodynamic function X^E are defined by

$$X^E = X_{\text{mix}} - X_{\text{id}} \quad (1)$$

$$X_{\text{id}} = x_1 X_1 + x_2 X_2 \quad (2)$$

where X_{mix} is the molar enthalpy or the molar volume of mixture, and X_i is the

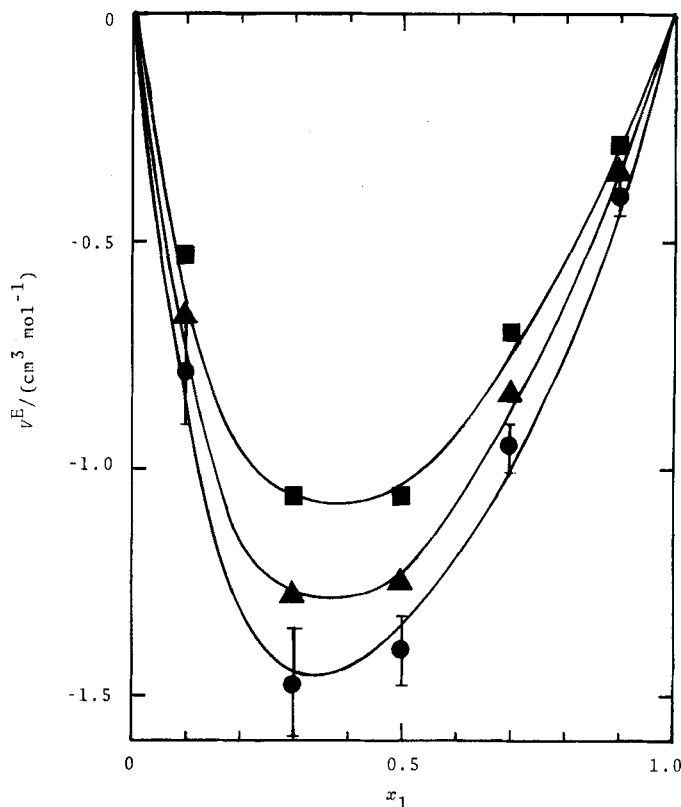


Figure 1 The concentration dependence of H^E for the model dimer (1) + model monomer (2) systems at three pressures for $T = 100$ K. ●: 0 atm; ▲: 100 atm; ■: 200 atm.

corresponding quantities of pure liquid i and x_i is the mole fraction of the component i . In this study, the component 1 is the Ar dimer.

Figure 1 shows the concentration dependence of V^E at different pressures. As shown in this figure, V^E for the present model system is large and negative for the whole concentration range. The magnitude of V^E becomes smaller with increasing in pressure. At a mole fraction of about 0.4 V^E shows a minimum. From the experimental work, V^E is said to show its minimum or maximum value near the equivolume concentration, with which trend the present model system coincides. Figure 2 shows the concentration dependence of H^E at some different pressures. As shown in this figure, H^E is large and positive, contrary to V^E . The maximum value exceeds 200 J/mol near the mole fraction of 0.5. The pressure dependence of H^E is not so large, but it is difficult to discuss in more detail because of the error inherent in H^{SE} .

McDonald has reported the concentration dependence of some kinds of excess thermodynamic quantities for simple systems, calculated by Monte Carlo method in the NTP ensemble [16]. Since the purpose of his study was to simulate real systems, both the Lennard-Jones parameters, ϵ and σ , were changed by the component molecules. In such a study, it is difficult to extract the influence on thermodynamic quantities only from ϵ or σ and to compare his results with the present one.

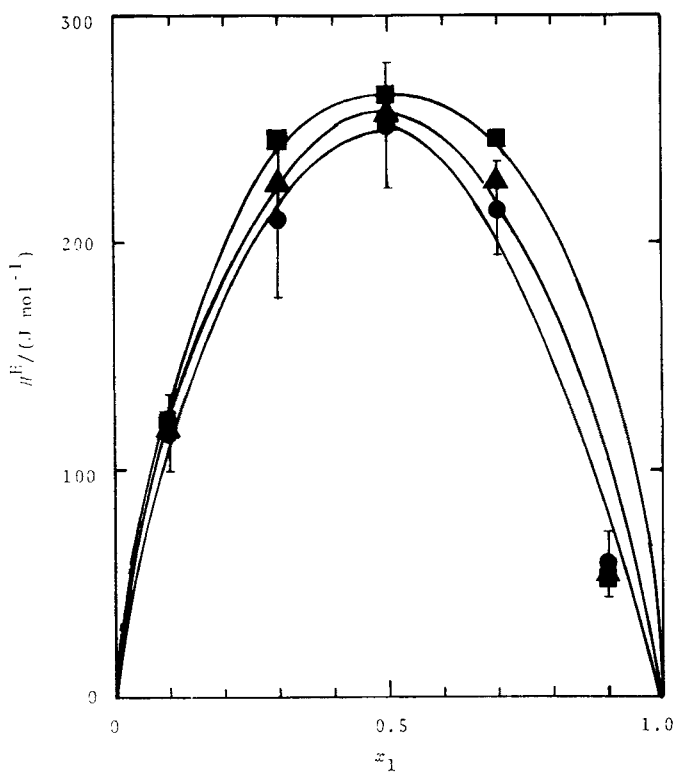


Figure 2 The concentration dependence of fH^E for the model dimer (1) + model monomer (2) systems at three pressures for $T = 100\text{K}$. \bullet : 0 atm; \blacktriangle : 100 atm; \blacksquare : 200 atm.

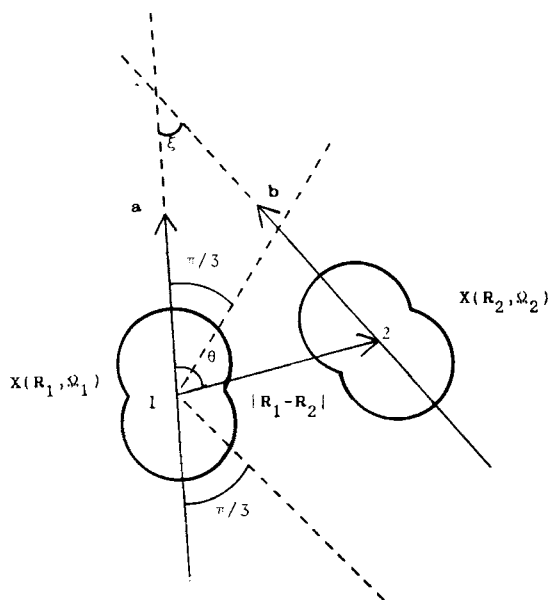


Figure 3 Schematic illustration of the calculation of the orientational distribution between dimers.

The general feature of the excess thermodynamic functions for the present model systems coincides qualitatively with those of real systems such as alkane + alkane [8, 12, 17]. This suggests the microscopic study of the model systems will give us important information on solution structure of real systems. Some distribution functions were calculated for this purpose. Among them, the usual potential energy distribution function, and the orientational distribution function between dimers were of special interest. The method calculating the latter one is illustrated in Figure 3. First, picking one of dimers, the configuration of which is specified by $\mathbf{X}(\mathbf{R}, \Omega)$, where \mathbf{R} designates the location of molecular center, and Ω the orientation of molecule. Vector \mathbf{a} is a unit vector from an atomic center to another. The distribution was calculated with the dimers, the molecular centers of which are located in the lateral

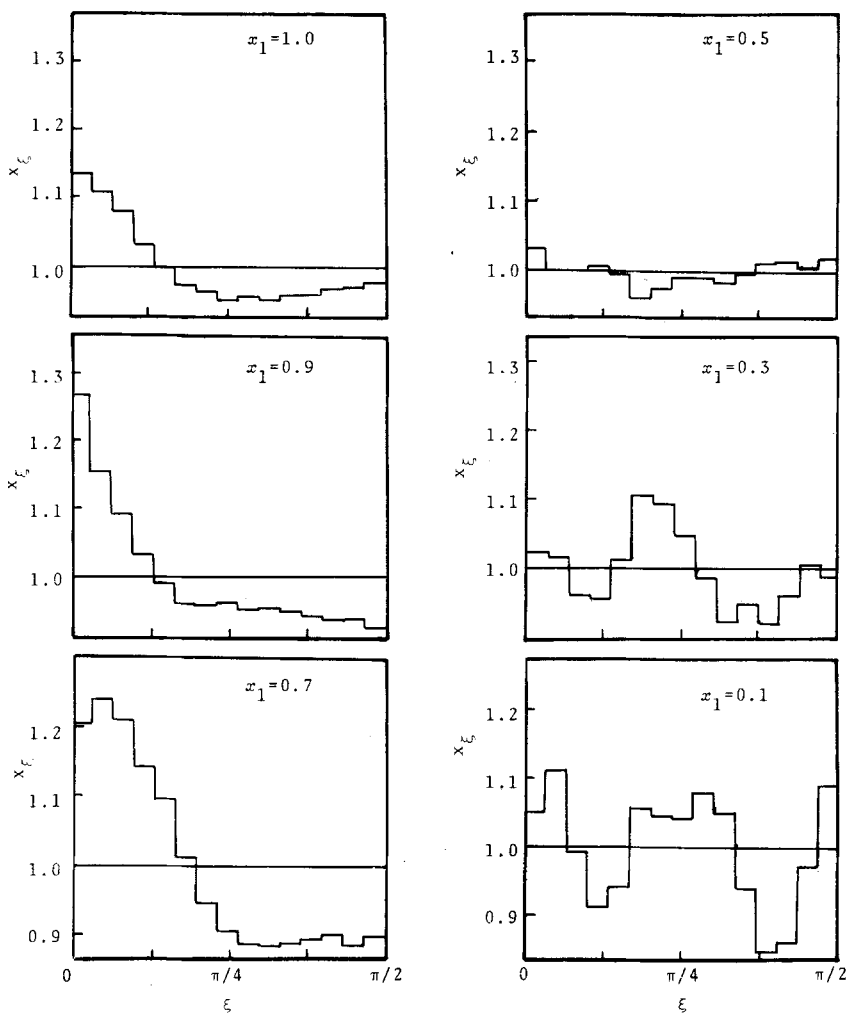


Figure 4 The dimer-dimer orientational distribution function, x_{ξ} , for each concentration near zero pressure.

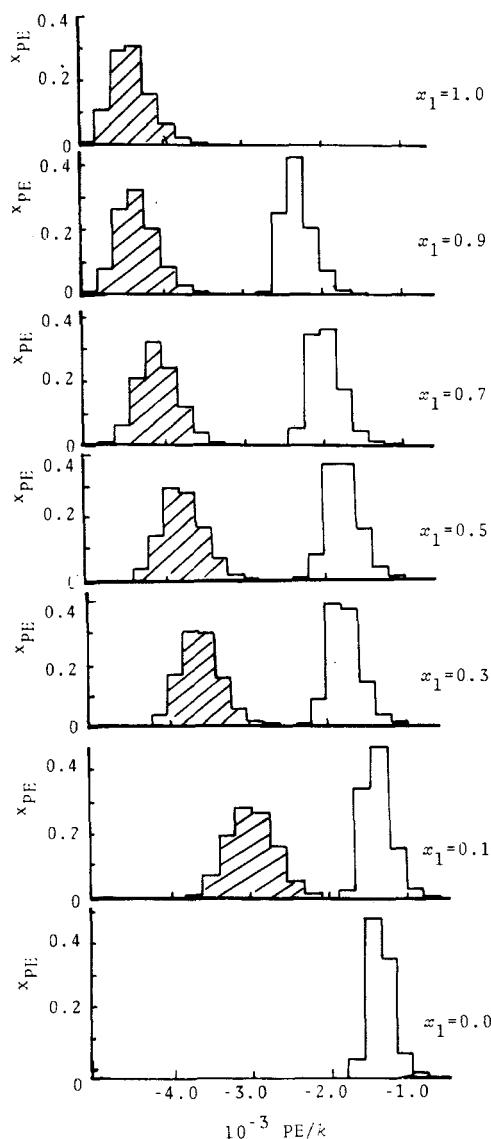


Figure 5 The distribution function of potential energy, x_{PE} , for each concentration near zero pressure. PE is the potential energy per a molecule. \square ; monomer \blacksquare ; dimer.

space of the molecule 1, specified by $\pi/3 \leq \theta \leq 2\pi/3$ and $|\mathbf{R}_1 - \mathbf{R}_2| < 2\sigma$. The angle ξ , between \mathbf{a} and \mathbf{b} was determined from the inner product \mathbf{a} and \mathbf{b} . Figure 4 shows the orientational distribution functions, x_i , for each concentration near zero pressure. They are normalized so that the average is unity. As seen in this figure, the parallel orientation, i.e. $\xi \simeq 0$, is slightly predominant in the pure state. On mixing with the spherical monomers, such a biased distribution may be expected to disappear. Contrary to this expectation, the parallel orientation between dimers increases up to

$x_1 = 0.7$, and is not found below $x_1 = 0.5$. The increase of the parallel orientation of dimer and the negative V^E suggest a possible molecular packing mode including molecular orientation, preferable to that of random mixing in the solution state. Such packing mode may be impossible if the size and shape of component molecules are the same.

Patterson *et al.* have pointed out that the difference of molecular shape between component molecules gives a great influence on the orientational order in mixtures, especially cycloalkane + alkane systems [18]. The present results suggest the possibility of this kind of orientational order even in simpler systems.

Figure 5 shows the distribution function of potential energy, x_{PE} , at different concentrations. They are also calculated near zero pressure. As shown in this figure, the potential energy distribution for the dimer shifts to the positive side when mixed with monomers, while that for monomer shows negative shift. This means that the restraint imposed on the dimer is weakened by introducing the monomer. On the other hand, that on monomer is strengthened, when the monomer is surrounded by the larger dimers. The shift to the positive side in the distribution for the dimer is larger than that to the negative side in that for the monomer, resulting in the positive H^E for the present model system.

In conclusion, some of the thermodynamic features of real systems (for example, the cyclohexane + decalin systems [19]) can be reproduced by the present MC calculations in spite of the simplicity of the model. The simulations give very important information on the microscopic structure which is strongly correlated with macroscopic properties of the solution.

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