

Figure 3a and 3b. The plane of the cholesteryl group is parallel to the *ac* plane with the entire molecule orientated parallel to the $[\bar{1}02]$ direction.

The most interesting feature is the close proximity of the cholesteryl ring group of one molecule to its translation-related neighbor along the *b* axis. The shortest distance (3.601 Å) is C(6)---C(19). As a result of this packing mode, d_{010} is only 6.073 Å, shortest of all cholesterol esters.

The crystal structure of cholesteryl formate contains antiparallel molecules packed to form monolayers which are parallel to the crystal (100) planes with a thickness $d_{100} = 15.757$ Å. Such monolayers are similar to those of cholesteryl hexanoate,⁶ octanoate,⁷ oleate⁸ and chloroformate.⁵ They are called monolayers of type II,⁹ so as to distinguish them from the monolayers of type I which occur in cholesteryl nonanoate,⁹ laurate¹⁰ and decanoate.¹¹ At the center of the monolayers of type II there is an efficient packing of antiparallel cholesteryl groups which are related by 2_1 screw axis.

In the cholesteryl formate, the molecules are centered between four screw axes and there is no overlap of the cholesteryl rings within one unit cell as shown in Figure 3a. The cholesteryl tails are loosely packed to form the layer interface region. The formate atoms are closely packed along the 2_1 screw axis and there are four intermolecular contacts less than 3.9 Å, of which shortest (3.237 Å) is C(28)---O(3).

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Thermodynamic Properties of the Polymer Solutions

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A statistical mechanical approach to elucidate the solvent effects on the high polymer solutions has been carried out on the basis of the simple model of liquids improved by Pak. In our works, the partition function of the polymer solutions is formulated by the lattice model and our simple treatment of liquid structures. For the ideal polymer solutions proposed by Flory, thermodynamic functions of the polymer solutions are obtained and equations of mixing properties and partial molar quantities are derived from the presented partition function of the polymer solutions. Partial molar quantities are calculated for the rubber solutions in carbon disulfide, benzene and carbon tetrachloride. Comparisons have been made between our equations and those of Flory's original paper for partial molar properties of the rubber-benzene system. Comparing the experimental data of the osmotic pressure of polystyrene-cyclohexane system with our calculated values and those of Flory's, our values fit to the agreeable degrees better than those of Flory's.

Introduction

The polymer solutions show thermodynamically abnormal behaviors compared to the ideal binary liquid mixtures. It has been found that partial molar entropy of dilution for solutions of long chain compounds dissolved in simple solvents is much greater than in ideal binary mixtures.¹

Meyer² has provided a plausible explanation for deviation from the ideal behaviors of liquid mixtures. He has suggested an idealized model for solutions, which consists of a "quasi-solid" lattice. Due to many calorimetric experiments and numerous semi-quantitative approaches, there was development of a theory of high polymer solutions by Flory³ and Huggins⁴. They calculated the number of possible lattice configurations for a mixture of polymer molecules occupying x -sites each and solvent molecules occupying single sites. They evaluated the number of configurations for a lattice of coordination number z by simple mathematical process of computation of the number of available sites for the polymer molecules. From the idealized model, that is, "Flory-Huggins" model, Flory^{3,5} obtained the equations of thermodynamic properties of dilution.

But, a little consideration of the effects of solvent properties in polymer solutions was taken in the above treatments. The partial molar entropy of the polymer solution under consideration seems to be dependent only on the volume fractions of solvent and polymer, independent of other properties of solvent and polymer molecules in the Flory's original paper.³ And, he improved the original equations for partial molar properties of polymer solutions by the lattice solution model. In his improved works, he considered the interaction energy parameters between solvent-solvent, solute-solute and solvent-solute molecular pairs.⁵ But, no account was taken in "quasi-solid" model that there are many vacant cells in polymer solutions, equivalent to the "holes" in simple liquids.³

As the results of the continuous researches of Eyring and coworkers,⁶⁻⁹ the theory of simple liquids was established by introducing the concept of the "fluidized vacancies or holes". In this model of the liquid state, it is assumed that $N(V-V_s)/V_s$ of molecular size holes are introduced at random in one mole of liquid, where N is the Avogadro's number, V and V_s are the molar volume of the liquid at a given temperature and that of the solid at triple point, respectively. All the liquid molecules should not exist in the same energy state because of holes introduced among the molecules. If the holes are distributed at random, $N(V-V_s)/V_s$ molecules have gas-like degrees of freedom and $N(V_s/V)$ may have solid-like degrees of freedom. In this model, the partition function of the simple liquids has been presented and many applications to thermodynamic properties of the liquids have been made by the above authors.

In polymer solution systems, the extension of "hole" concept in simple liquids is possible. Since the holes in present system nearly depend on the solvent molecules at moderate concentrations, it can be assumed that $N_1(V-V_s)/V_s$ of holes are introduced at random into the total volume, where the system contains N_1 solvent molecules and N_2 polymer molecules. The size of each hole is assumed to be equal to the molecular size of the solvent molecules. Also, this involves one of the basic assumption of Flory³ that the size of each polymer segment is

equal to that of a solvent molecule.

In the present paper, the partition function of the polymer solutions is formulated according to the simple statistical process of the lattice solution theory and the simple model of liquids improved by Pak⁹ for the solvent part without any modification. The polymer part is formulated by the assumption that each segment has only solid-like degree of freedom at moderate concentrations. In addition, for the ideal polymer solutions, Flory-Huggins lattice model⁵ is used. But, some modification is reasonable, because the number of holes should be introduced in the calculation of the total number of configurations. Consequently, thermodynamic functions of the polymer solutions are presented and dilution properties are calculated in various polymer solutions.

Theory

1. *Formulation of the Partition Function.* In the ideal binary mixtures, N_1 solvent molecules and N_2 solute molecules in total volume V at temperature T under consideration constitute a canonical ensemble of the system. According to the non-electrolyte solution theory,¹⁰ the general partition function of the binary mixtures can be expressed as

$$Q(N, V, T) = q_1(N_1, V, T)^{N_1} \cdot q_2(N_2, V, T)^{N_2} \cdot \sum g(N_1, N_1 + N_2, N_{12}) e^{-W/kT} \quad (1)$$

where q_1 is the molecular partition function of the solvent, q_2 is that of the solute, W is the total interaction energy in this system and g is the number of configurations with given N_1 and N_2 , respectively. In lattice statistics,¹⁰ the convenient method was provided, which can cover the entire concentration range. It is particularly appropriate to give only a brief introductory treatment of the non-electrolyte solution system. Roughly speaking about this model, the system is condensed, incompressible solution containing N_1 and N_2 molecules which occupy a regular and rigid lattice which has a fixed volume; there are no vacant sites. Each site has z nearest-neighbor sites. Taking into account nearest-neighbor interactions, Eq.(1) is rearranged as Eq.(2).¹⁰

$$Q = (q_1 e^{\chi_1})^{N_1} \cdot (q_2 e^{\chi_2})^{N_2} \cdot \sum_{N_{12}} g \xi^{N_{12}} \quad (2)$$

where $\chi_1 = -\frac{z\omega_{11}}{2kT}$, $\chi_2 = -\frac{z\omega_{22}}{2kT}$, $\xi = e^{w/2kT}$ and

z being the coordination number, respectively.

In the polymer solution systems, since there are x -segments in each chain, the number of lattice sites are $N_1 + xN_2$ according to the lattice solution model. Thus, the partition function of the polymer molecules may be expressed as that of the segment for the ideal linear polymers. If the end effect of each chain can be neglected for the long chain compounds, the partition function of the segment can be treated to be the same in the entire system. Therefore, the general canonical ensemble partition function of the polymer solutions can be expressed as

$$Q = (q_1 e^{\chi_1})^{N_1} \cdot (q_2 e^{\chi_2})^{xN_2} \cdot \sum_{N_{12}} g \xi^{N_{12}} \quad (3)$$

where q_1 is the molecular partition function of the solvent and q_2 is the segment partition function of the polymer, respectively.

But, Eq.(3) is not enough to apply to the actual polymer solu-

tion systems directly. As mentioned previously, the major assumption in our work is that there are $N_1(V-V_s)/V_s$ holes introduced at random in the polymer solution system. Thus, the solvent molecules should not be in the same energy state because of existence of the holes. Here, $N_1(V-V_s)/V$ of the solvent molecules have gas-like degrees of freedom and $N_1(V_s/V)$ of the solvent molecules have solid-like degrees of freedom. Therefore, there is a combination factor in the solvent partition function because of the two different microscopic energy states.

Thus, the partition function q_1 of the solvent part is used as the form presented by Pak⁹ without any modification. The nearest-neighbor interaction energy terms in the solvent partition function can be treated as equal to the average molar interaction energy terms E_s and E_g in his treatment. The partition function of the solvent part is given as

$$Q_1(N_1, V, T) = n_{1T} C_{N_{1S}} q_{1S}^{N_{1S}} \cdot q_{1g}^{N_{1g}} \cdot \frac{1}{N_{1g}!} \quad (4)$$

$$\text{where } q_{1s} = \frac{e^{E_s/RT}}{(1 - e^{-\theta_1/T})^3} \cdot b_s,$$

$$q_{1g} = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot (V - V_s) \cdot b_g \cdot e^{E_g/RT},$$

$$N_{1T} = N_1(V/V_s), \quad N_{1S} = N_1(V_s/V),$$

$$N_{1g} = N_1(V - V_s)/V \text{ and } E_g = \epsilon(V_s/V)^2$$

respectively.

Additionally, the degeneracy factor g for the polymer solutions in Eq.(3) is different from that of the ideal binary mixtures. For the ideal polymer solution system, the expectation number of the configurations Ω in Flory-Huggins lattice model⁸ can be introduced as the degeneracy factor. But, the total sites in this model are $N_1(V/V_s) + xN_2$ rather than $N_1 + xN_2$ because of holes. By the simple calculation, the degeneracy factor is obtained as

$$\Omega = \left(\frac{z-1}{e}\right)^{(x-1)n_2} \cdot \frac{(N_1t + xN_2)^{(N_1t + N_2)}}{N_2^{N_2} \cdot (N_1t)^{N_1t}} \quad (5)$$

where $t = \bar{V}/V_s$.

In order to simplify this work, it is assumed that the polymer segment has only solid-like degree of freedom. Since the chain of the polymer molecules is long enough, the polymer segments are not in a free motion even they are in solution state. Thus, this assumption is more reasonable for the high polymer solutions. And, there are various different vibrational modes per each chain. Here, an average θ_2 is used.¹¹ It resembles the Einstein characteristic temperature of the solid-like partition function of the theory of liquids. The optical vibrations are designated as the internal degrees of freedom b_2 . Therefore, the partition function of the polymer segment can be expressed as

$$q_2 = \frac{b_2}{(1 - e^{-\theta_2/kT})^3} \quad (6)$$

where θ_2 is the average Einstein characteristic temperature of the polymer segment and b_2 are the internal degrees of freedom, respectively.

Consequently, from the Pak's treatment,⁹ Eqns.(5) and (6), the total partition function of the polymer solutions is formulated as

$$Q = n_{1T} C_{N_{1S}} \cdot q_{1S}^{N_{1S}} \cdot q_{1g}^{N_{1g}} \cdot \frac{1}{N_{1g}!} \cdot (q_2 e^{\chi_2}) \cdot \Omega \cdot e^{-\bar{N}_{12}\chi} \quad (7)$$

$$\text{where } \chi = -z\omega/2kT, \quad \bar{N}_{12} = \frac{zxN_1N_2}{N_1t + xN_2}.$$

And, taking the logarithm of the partition function, $\ln Q$ is obtained as

$$\ln Q = (N_1/t) \cdot \{t^2 \ln t^2 - (t^2 - 1) \cdot \ln(t^2 - 1)\} + \sigma + (t-1) \cdot [\gamma + \epsilon/(t^2RT) + \ln t] + xN_2 \cdot (\ln q_2 + \chi_2) + \ln \Omega - N_{12} \cdot \chi \quad (8)$$

$$\text{where } \sigma = E_s/RT - 3 \ln(1 - e^{-\theta_1/T}) + \ln b_s$$

$$\gamma = \ln \left[\frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{V_s e}{N_1} \right] + \ln b_g$$

2. Derivation of the Thermodynamic Functions of the Polymer Solutions. Various equations of the thermodynamic properties are obtainable from the following relation.

$$A = -kT \ln Q$$

From the above relation and Eq.(8), Helmholtz free energy is obtained as

$$\begin{aligned} -A/RT = & (n_1/t) \cdot \{t^2 \ln t^2 - (t^2 - 1) \cdot \ln(t^2 - 1)\} \\ & + \sigma + (t-1) \cdot [\ln t + \gamma + \epsilon/(t^2RT)] \\ & + xn_2 \cdot (\ln q_2 + \chi_2) + (x-1)n_2 \cdot \ln\left(\frac{z-1}{e}\right) \\ & + (n_1t + n_2) \cdot \ln(n_1t + xn_2) \\ & - xn_2n_2/(n_1t + xn_2) \cdot \chi \end{aligned} \quad (9)$$

where n_1 is the number of moles of the solvent and n_2 is that of the polymer, respectively.

Entropy and vapor pressure of the polymer solutions are obtained as Eqns.(10) and (11) using the relations

$$S = -\left(\frac{\partial A}{\partial T}\right)_{n, v}, \quad p = -\left(\frac{\partial A}{\partial V}\right)_{n, T},$$

$$\begin{aligned} S/R = & (n_1/t) \cdot \{t^2 \ln t^2 - (t^2 - 1) \cdot \ln(t^2 - 1)\} \\ & + C + (t-1) \cdot (\ln t + \gamma + \ln b_s + T \frac{\partial \ln b_g}{\partial T} + 3/2) \\ & + xn_2 D + (x-1)n_2 \cdot \ln\left(\frac{z-1}{e}\right) \\ & + (n_1t + n_2) \cdot \ln(n_1t + xn_2) \\ & - n_2 \ln n_2 - n_1t \cdot \ln(n_1t) \end{aligned} \quad (10)$$

$$\text{where } C = -3 \ln(1 - e^{-\theta_1/T}) + 3(\theta_1/T) \cdot \frac{e^{-\theta_1/T}}{(1 - e^{-\theta_1/T})} + \ln b_s + T \frac{\partial \ln b_s}{\partial T},$$

$$D = -3 \ln(1 - e^{-\theta_2/T}) + 3(\theta_2/T) \cdot \frac{e^{-\theta_2/T}}{(1 - e^{-\theta_2/T})} + \ln b_2 + T \frac{\partial \ln b_2}{\partial T},$$

$$\begin{aligned} pV_s/RT = & (n_1/t^2) \cdot \{t^2 \ln t^2 - (t^2 + 1) \cdot \ln(t^2 - 1)\} \\ & + \gamma - \sigma + \epsilon/(t^2RT) + \ln t \\ & + (t-1) \cdot [1 - 2\epsilon/(t^2RT)] \\ & - n_1 \ln \phi_{1,e} - n_1(1-1/x) \phi_{2,e} \\ & + n_1 \chi \phi_{1,e} \phi_{2,e}/t \end{aligned} \quad (11)$$

where $\phi_{1,e}$ being the effective volume fraction of the solvent and $\phi_{2,e}$ being that of the polymer such that

$$\phi_{1,e} = \frac{N_1t}{N_1t + xN_2}$$

$$\phi_{2,e} = \frac{xN_2}{N_1t + xN_2}$$

respectively. The "effective volume fraction" means the volume fraction containing "fluidized vacancies or holes".

And, from the usual thermodynamic relations, the equations of the chemical potentials of the solvent and the polymer are obtained as

$$-\mu_1/kT = (1/t) \cdot \{t^2 \ln t^2 - (t^2 - 1) \cdot \ln(t^2 - 1)\} + \sigma + (t-1) \cdot \{\gamma + \epsilon/(t^2 RT) + \ln t - 1\} - t \ln \phi_{1,e} - t(1-1/x) \phi_{2,e} - \chi \phi_{2,e}^2 \quad (12)$$

$$-\mu_2/kT = x(\ln q_2 + \chi_2) + (x-1) \cdot \ln\left(\frac{z-1}{e}\right) - \ln(\phi_{2,e}/x) + (x-1) \phi_{1,e} - (t/x) \cdot \chi \phi_{1,e}^2 \quad (13)$$

3. *Mixing Properties.* From the thermodynamic functions of the polymer solutions given previously, the equations of the mixing properties are derived. According to Eq.(10), the equation of entropy of dilution is obtained as

$$\Delta S_M/R = -(n_1 t \ln \phi_{1,e} + n_2 \ln \phi_{2,e}) \quad (14)$$

The free energy of mixing is obtained as

$$\Delta A_M/RT = n_1 t \ln \phi_{1,e} + n_2 \ln \phi_{2,e} + n_1 \chi \phi_{2,e} \quad (15)$$

And, from Eqns.(14) and (15), the energy of mixing is given as

$$\Delta E_M/RT = n_1 \chi \phi_{2,e} \quad (16)$$

4. *Partial Molar Quantities.* Differentiating Eqns.(14), (15) and (16) with respect to N_1 , we obtain for the partial molar quantities of the solvent as

$$\Delta S_1/R = -t \cdot \{\ln(1 - \phi_{2,e}) + (1-1/x) \phi_{2,e}\} \quad (17)$$

$$\Delta A_1/RT = t \cdot \{\ln(1 - \phi_{2,e}) + (1-1/x) \phi_{2,e}\} + \chi \phi_{2,e}^2 \quad (18)$$

$$\Delta E_1/RT = \chi \phi_{2,e}^2 \quad (19)$$

respectively.

With the partial molar free energy of the solvent available, the vapor pressure of the solvent and osmotic pressure are obtained as

$$\ln \frac{p_1}{p_1^0} = t \cdot \{\ln(1 - \phi_{2,e}) + (1-1/x) \phi_{2,e}\} + \chi \phi_{2,e}^2 \quad (20)$$

$$\pi = -(RT/V_o) \cdot \{t \ln(1 - \phi_{2,e}) + t(1-1/x) \phi_{2,e} + \chi \phi_{2,e}^2\} \quad (21)$$

5. *Phase Equilibria.* Using the critical point conditions,

$$\left(\frac{\partial \mu_1}{\partial \phi_{2,e}}\right) = \left(\frac{\partial^2 \mu_1}{\partial \phi_{2,e}^2}\right) = 0$$

we obtain the following conditions

$$\phi_2^c = t / (t + x^{1/2}) \quad (22)$$

$$\chi^c = t(1 + x^{1/2})^2 / (2x) \quad (23)$$

respectively.

Results and Discussion

The parameters of various solvents in our work which are E_s , V_s , ϵ and θ are calculated by the method provided by Pak.⁹ These values are given in Table 1.

The total interaction energy parameter χ can be obtained easi-

ly from the second virial coefficient of the osmotic pressure at given temperature.¹ The values of V/V_s at given volume fraction of the polymer and temperature under consideration may be evaluated from the condition that free energy of the polymer solutions is minimum. The calculated curves of V/V_s vs. volume fraction of the natural rubber in carbon disulfide, benzene and carbon tetrachloride at 25°C assuming $x=1000$ is presented in Figure 1. As shown in Figure 1, the different polymer solution systems give different curves of V/V_s . Hence, we can conclude that the free volume of the polymer solutions is governed by the properties of the solvent and the interactions in solutions. These factors may alter the polymer solution properties in various polymer solution systems.

Partial molar properties of the rubber solutions in our used solvents are calculated and given in Figure 2-4. These can be calculated at given volume fraction of the polymer using the calculated values of V/V_s . At the limiting case that V/V_s is equal to one, the equations for partial molar properties as in Eqns.(17), (18) and (19) are equal to those of Flory's paper.⁵ But, even for the ideal polymer solutions proposed by Flory,³ the values of V/V_s at the given condition slightly greater

TABLE 1: Parameters of Liquids

	C ₆ H ₆	CCl ₄	CS ₂	C ₆ H ₁₂
θ (°K)	46.57	27.31	34.11	35.68
E_s (cal/mole)	9627	9262	8105	9450
ϵ (cal/mole)	2797	1696	4397	1869
V_s (ml/mole)	80.02	89.39	49.00	100.2

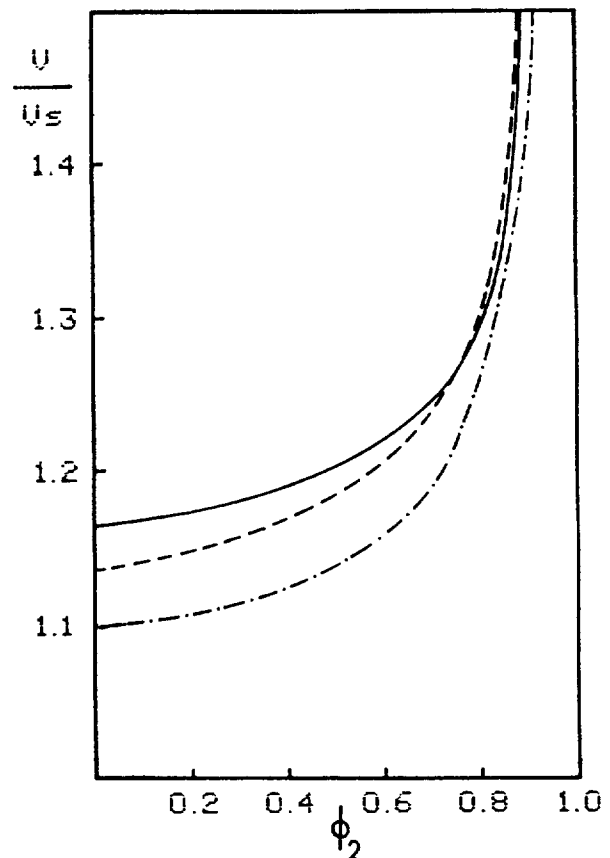


Figure 1. Calculated values of V/V_s of natural rubber solutions ($x=1000$) at 25°C: solid line, CS₂ solution; broken line, C₆H₆ solution; dotted line, CCl₄ solution.

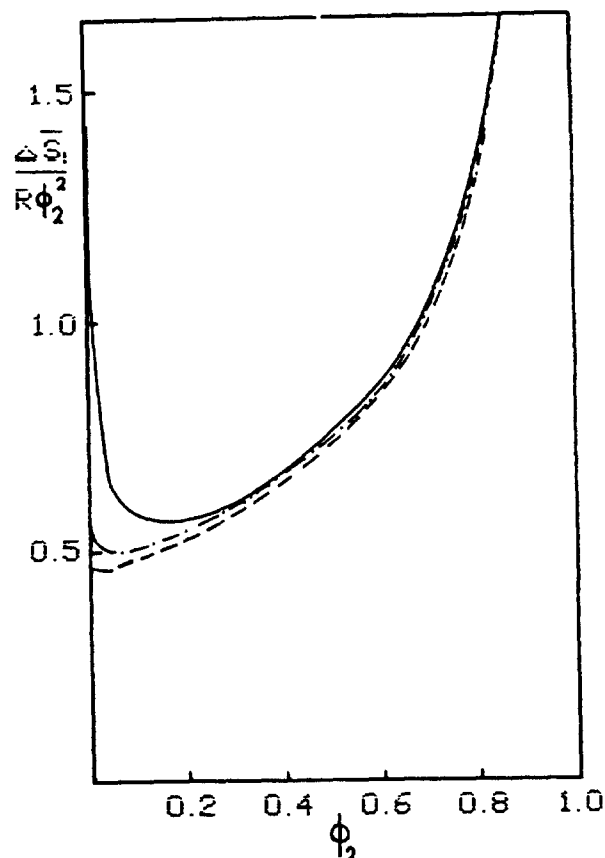


Figure 2. Calculated values of partial molar entropy of natural rubber solutions at 25°C: solid line, CS₂ solution (x=100); dotted line, CCl₄ solution (x=1000); broken line, C₆H₆ solution (x=5000).

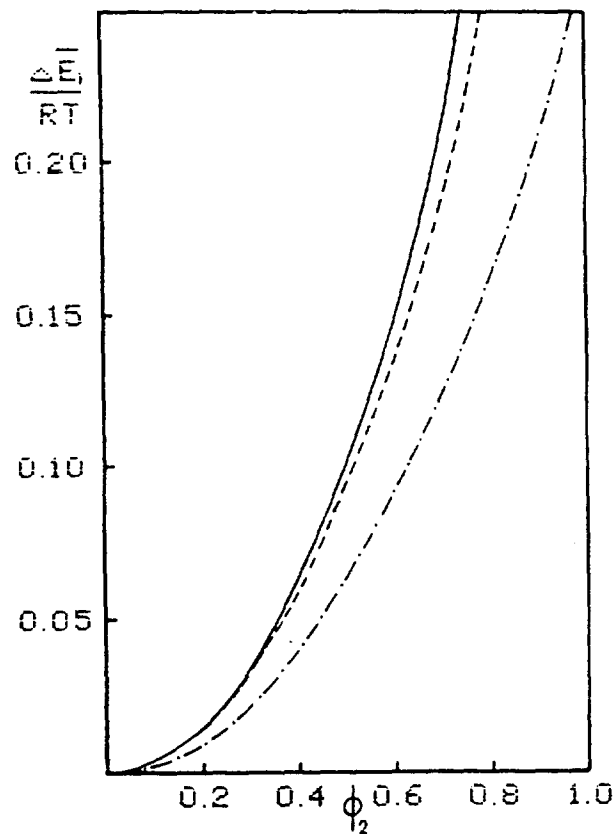


Figure 4. Calculated values of partial molar energy of rubber solutions (x=1000) at 25°C: solid line, CS₂ solution; broken line, C₆H₆ solution; dotted line, CCl₄ solution.

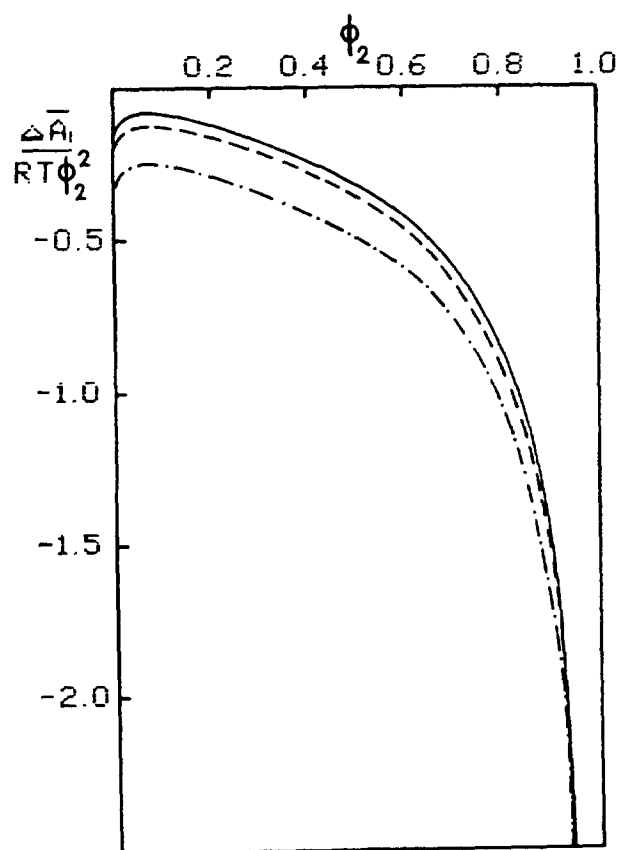


Figure 3. Calculated values of partial molar free energy of rubber solutions at 25°C assuming x=1000: solid line, CS₂ solution; broken line, C₆H₆ solution; dotted line, CCl₄ solution.

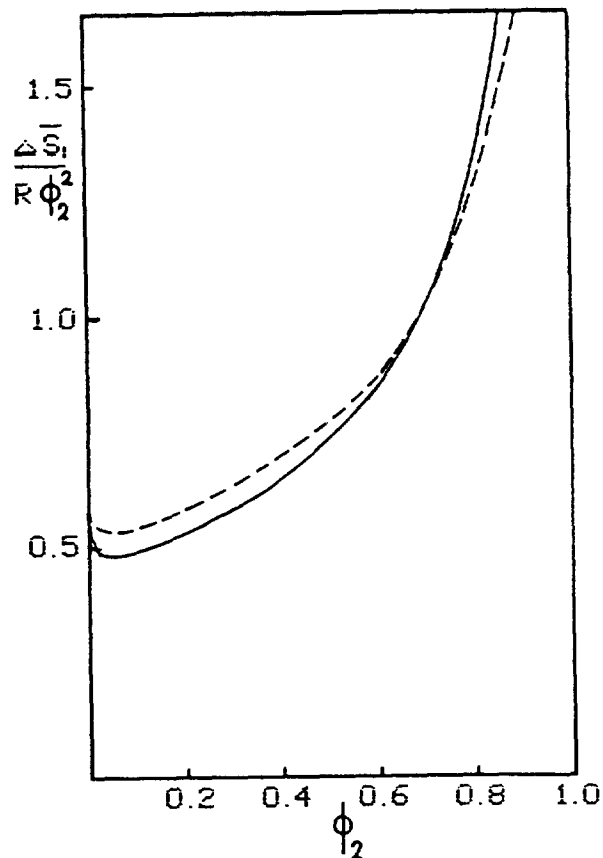


Figure 5. Comparison of partial molar entropy between our calculated values and those of Flory's in rubber-benzene at 25°C assuming x=1000: solid curve indicates our values; broken curve indicates those of Flory's original equation.

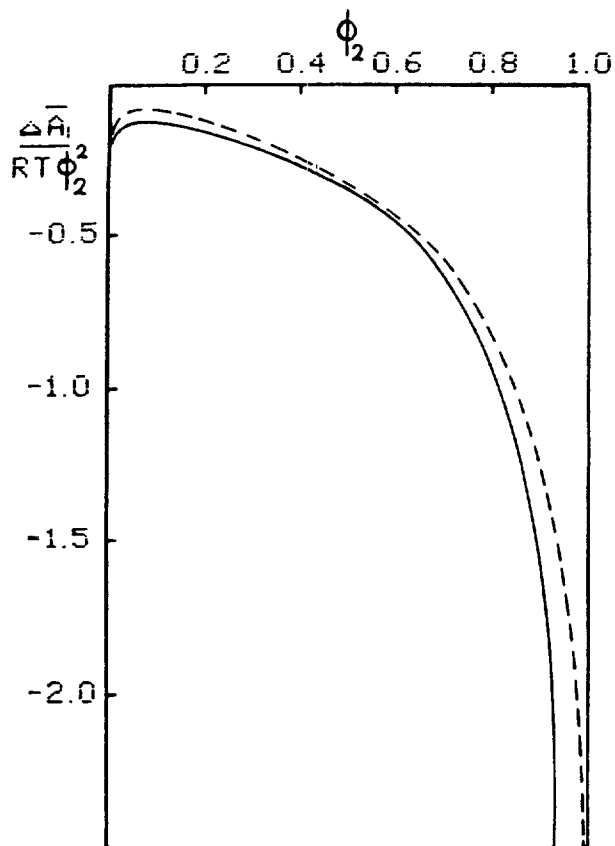


Figure 6. Comparison of partial molar free energy between ours and those of Flory's in rubber-benzene at 25 °C assuming $x = 1000$: solid line, our values; broken line, those of Flory's.

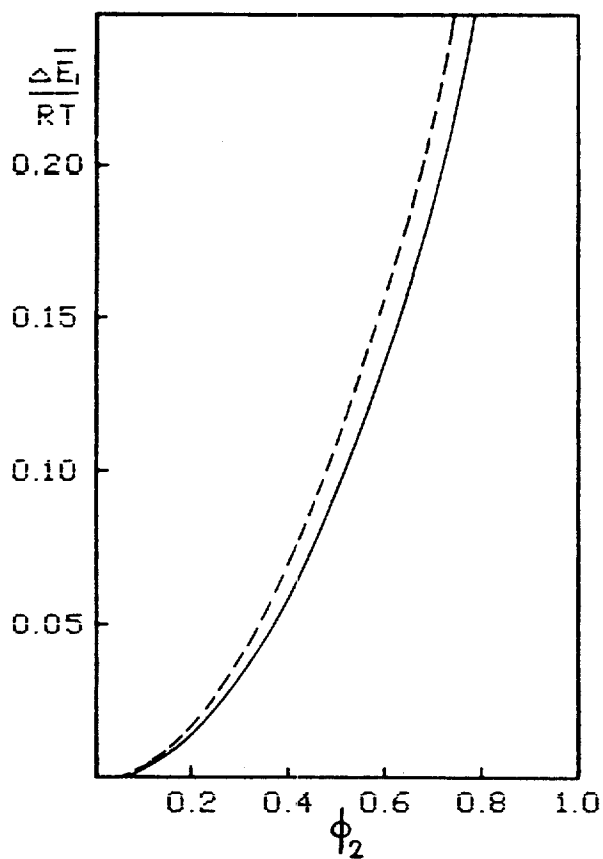


Figure 7. Comparison of partial molar energy in rubber-benzene at 25 °C assuming $x = 1000$: solid line, our calculated values; broken line, those of Flory's equation.

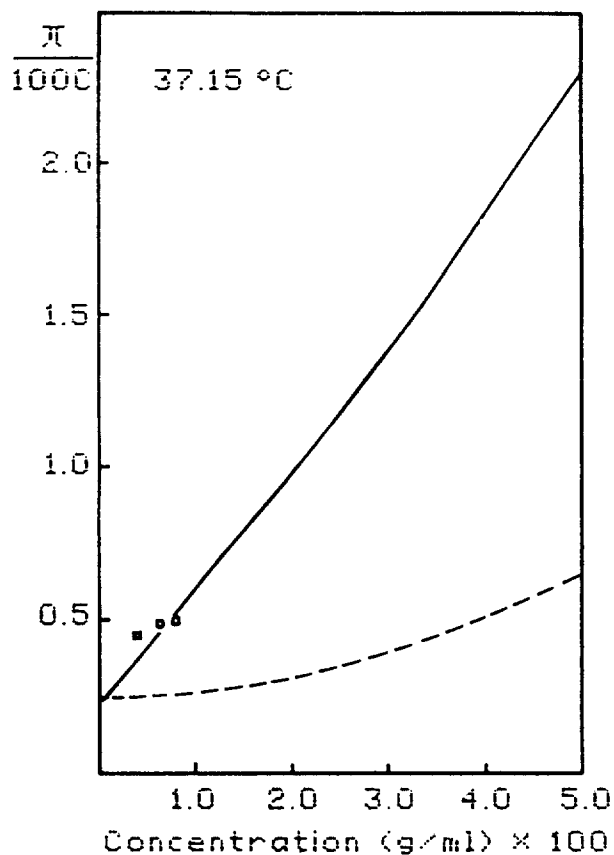


Figure 8. Comparison of osmotic pressure in polystyrene-cyclohexane at 37.15 °C: solid line, our values; broken line, those of Flory's equation; squares, experimental data.¹²

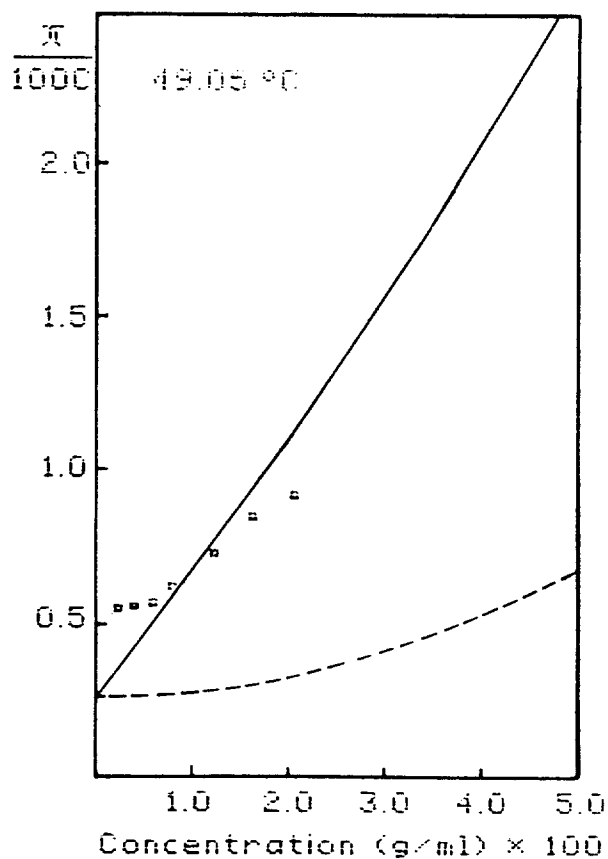


Figure 9. Comparison of osmotic pressure in polystyrene-cyclohexane at 49.05 °C: solid line, our values; broken line, those of Flory's equation; squares, experimental data.¹²

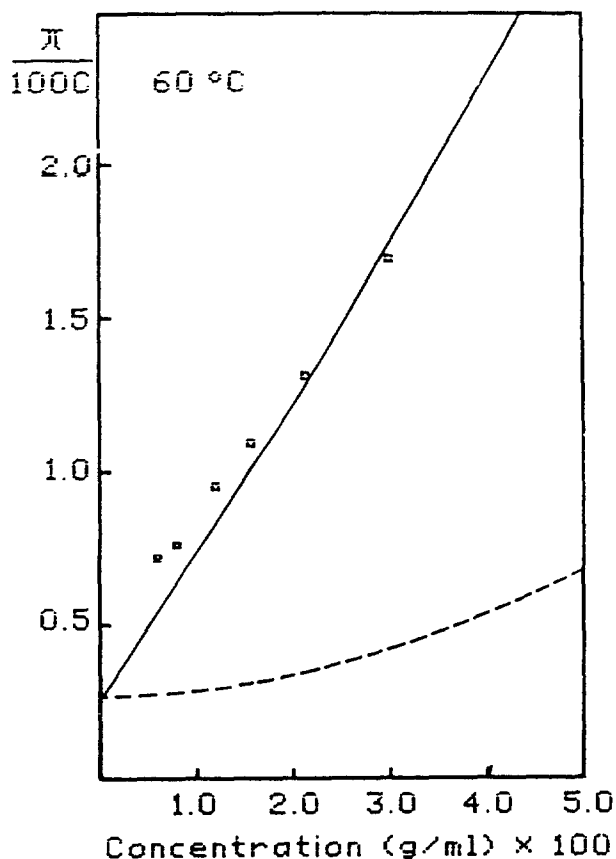


Figure 10. Comparison of osmotic pressure in polystyrene-cyclohexane at 60.0°C: solid line, our calculated values; broken line, those of Flory's equation; squares, experimental data.¹²

than one even in the very dilute solution as Figure 1 shows. This behavior results from the solvent properties and the interactions in polymer solutions. Considering our partition function of the polymer solutions as in Eq.(7), the limiting case that V/V_0 is equal to one can be considered that it is simply composed of the solid-like solvent and polymer molecules.

Next, comparisons of our equations for partial molar properties of the rubber-benzene system with those of Flory are made in Figures 5-7 assuming $\chi=1000$. As shown in these figures, our calculated curves (solid lines) show lower values slightly than those of Flory (broken lines) except for partial molar entropy at the range that volume fraction of the polymer is greater than 0.7. Thus, we may say that the partial molar properties of the polymer solutions in non-polar solvents are not very sensitive to the values of V/V_0 .

Finally, we have made comparisons of our equation for osmotic pressure with that of Flory and experimental data from paper¹² in polystyrene-cyclohexane system at three different temperatures as in Figures 8-10. At 37.15°C as shown in Figure 8, we can not compare our values with experimental data to the agreeable degrees. But, at 49.05°C and 60.0°C as in Figures 9 and 10, our equation for osmotic pressure agrees with experimental data better than Flory's original equation for osmotic pressure of the polymer solutions.

Consequently, we can conclude that our equations can make much account of the solvent effects in the polymer solutions, because our theoretical model is reasonable that it includes the contributions by the solvent to the partition function of the polymer solutions. For the actual systems, which contain non-ideal polymers, our partition function can be applicable if more development of Flory-Huggins lattice model to the actual systems will be made.

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