A Hole Theory of Polymer Liquids and Glasses.
VI. Mixtures

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ABSTRACT: The hole theory of pure polymer liquid previously developed by the
author is extended to be applicable to polymer mixtures. The theory is applied to
some mixture systems, and close agreement with experimental observations is obtained
in the thermal pressure coefficients of mixtures of low-molecular weight substances,
surface tensions of molten ethylene-vinylacetate copolymers with different compositions,
and diluent effects on the glass transition temperatures of polystyrene and poly(methyl
methacrylate).
KEY WORDS   Hole Theory / Polymer / Mixture / Thermal Pressure
Coefficient / Surface Tension / Glass Transition /

In the previous papers of this series[1-3] the
hole theory was applied to polymeric systems
along the line of the theories of polymer liquids
developed recently by Prigogine,[4] and Flory, *et
al.*[5] The partition function, the equation of
state, internal pressure, and surface tension have
been derived for pure polymers. The differences
in the equation of state and internal pressure
between the liquid and glassy states and the
glass transition were also discussed.

In this paper, in order to apply our treat-
ments to mixtures, we reform the partition func-
tion to be applicable for mixture systems. As
a result, it is found that the formulas for pure
systems also hold for mixtures without modify-
ing the original forms only by transforming the
characteristic parameters. The results of the
theory are applied to some properties which
were discussed in previous papers,[1-3] *i.e.*, ther-
mal pressure coefficient or internal pressure of
liquid mixtures, surface tension of copolymers,
and the glass transition temperature of diluted
polymers are discussed.

THEORY

Formulation

In considering the mixture system by a lattice
theory, we encounter some difficult problems;
e.g., (1) how the lattice sites are set for the
mixture of molecules or segments with differ-
ent sizes, or how the coordination number must
be counted, (2) how far the segments of differ-
ent sizes are separated from each other and
how the intersegmental interactions vary with
the separation, and (3) how to calculate the
number of contact pairs between segments of
the same and different kinds. The problems of
(2) and (3) are not peculiar to a lattice theory,
but are general in the treatment of liquid mix-
tures.

In the present theory, for the problems (1)
and (2), a certain average cell volume v^* is
considered, and the coordination number, inter-
segmental interactions, and free volume are
defined as those against the average volume v^*
of segment. Namely, the coordination number
z_i is defined as the number of sites around a
segment of the i-th component whose volume
is $v,^*$ and it is assumed that the interaction
potential energy $\varphi_{ij}(0)$ per volume v^* between
the segments of the i-th and the j-th com-
ponents, when they are located at the centers
of nearest neighbor lattice sites, is expressed as
the form:

$$\varphi_{ij}(0) = \varepsilon_{ij}^* f(\sigma^3/v^*) \qquad (1)$$

where ε_{ij}^* represents the magnitude of interac-
tion energy between the segments of the i-th
and the j-th components, σ^3 is an average char-

acteristic volume of a segment, and $f(\sigma^3/v^*)$ is a function of σ^3/v^*. As for the problem (3), random mixing is assumed for simplicity.

The mixture system of the molecules of n different kinds and holes is now considered. The number of molecules of the i-th component, each molecule comprising r_i segments, is N_i/r_i $(r=1, 2, \cdots n)$, where N_i is the number of sites having the volume v_i^* which are occupied by the segments of the i-th component. The zero-th component is taken as the hole or empty site. Thus there are N_0 holes, and $N_0 = \sum_{i=0}^{n} N_i - \sum_{i=0}^{n} N_i = M - N$, where M and N are the total numbers of lattice sites and segments respectively. The volume of hole v_0^* is assumed to be an average cell volume, v^*, equal to V/M where V is the volume of the system. Then we have

$$v^* = V/M = \sum_{i=0}^{n} N_i v_i^* / \sum_{i=0}^{n} N_i = \sum_{i=1}^{n} N_i v_i^* / N = V^* / N \tag{2}$$

The partition function for this system may be written

$$Z = \prod_{i=1}^{n} j_i(T)^{N_i} \prod_{i=1}^{n} q_i^{c_i N_i} \prod_{i=1}^{n} \bar{v}_f^{(i)c_i N_i}$$
$$\times \exp(-\bar{U}_0/kT) \sum_{\lambda} g_{\lambda} \tag{3}$$

under zero-th approximation (Bragg—Williams),[6] just as the same form as in the pure system. Here, $j_i(T)$ is the partition function associated with intrasegmental interactions, q_i the kinetic part of the partition function associated with the external degrees of freedom, and c_i one third of the external degrees of freedom, which are all those of the segment of the i-th component. The symbol $\bar{v}_f^{(i)}$ denotes the free volume of a segment of the i-th component, $\bar{U}_0$ the potential energy of the system when all of the segments are at the centers of lattice sites, and $\sum_{\lambda} g_{\lambda}$ the combinatory factor associated with the mixing of molecules and holes.

If Guggenheim's theory for mixtures is used,[7] the quantity $\bar{U}_0$ can be written

$$\bar{U}_0 = \sum_{i=1}^{n} \sum_{j=1}^{n} z_i N_i z_j N_j \varphi_{ij}(0)/(2 \sum_{i=0}^{n} z_i N_i) \tag{4}$$

Using the form of the Lennard-Jones 12-6 po-

tential, as in a previous treatment,[1] we can write $\varphi_{ij}(0)$ with the aforementioned assumption of eq 1,

$$\varphi_{ij}(0) = \varepsilon_{ij}^* \{1.0109(\sigma^3 N/V^*)^4 - 2.409(\sigma^3/V^*)^2\} \tag{5}$$

where

$$\sigma^3 N = \sum_{i=1}^{n} \sigma_i^3 N_i \tag{6}$$

Here, ε_{ij}^* is the minimum value of potential energy between the segments of the i-th and the j-th components in the Lennard-Jones 12-6 potential, and σ_i is the distance between segment centers of the i-th components at which pairwise potential energy is zero in the Lennard-Jones 12-6 potential. Therefore we can derive from eq 4 and 5,

$$\bar{U}_0 = -K\varepsilon^*\bar{z}^2 N^2 / \sum_{i=0}^{n} z_i N_i \tag{7}$$

Here

$$K = -\{1.0109(\sigma^3 N/V^*)^4 - 2.409(\sigma^3 N/V^*)^2\}/2 \tag{8}$$

$$\varepsilon^* = \sum_{i=1}^{n} \sum_{j=1}^{n} z_i N_i z_j N_j \varepsilon_{ij}/\bar{z}^2 N^2 \tag{9}$$

and

$$\bar{z} = \sum_{i=1}^{n} z_i N_i / N \tag{10}$$

On the other hand, analogous to the approximate expression of $\bar{v}_f$ used for a pure system previously,[1] the quantity $\bar{v}_f^{(i)}$ may be expressed as

$$\ln \bar{v}_f^{(i)} = \sum_{k=0}^{n} \bar{\omega}_k^{(i)} \ln v_{fk}^{(i)}$$

where $\bar{\omega}_k^{(i)}$ is the most probable value of the segment fraction of the k-th component in the nearest neighbor sites of a segment of the i-th component, and $\bar{v}_{fk}^{(i)}$ is an adjustable parameter, usually taken as the free volume for a segment of the i-th component when all of its nearest neighbor sites are occupied by segments of the k-th component. Since $\bar{\omega}_k^{(i)}$ is equal to $z_k N_k / \sum_{i=0}^{n} z_i N_i$ in the zero-th approximation, the quantity $\bar{v}_f^{(i)}$ can be written

$$\ln \bar{v}_f^{(i)} = \{\sum_{k=0}^{n} z_k N_k \ln v_{fk}^{(i)}\}/\sum_{i=0}^{n} z_i N_i \tag{11}$$

For simplicity, $v_{fk}^{(i)}$ is taken here as $\bar{v}_f^{(i)}$ when

$\bar{\omega}_k{}^{(i)} = 1$. Then, $v_{\mathrm{f}k}^{(i)}(=\bar{v}_{\mathrm{f}}{}^{(i)}(\bar{\omega}_k{}^{(i)}=1))$ for $k \neq 0$ is assumed to be expressed as $v_{\mathrm{f}k}^{(i)} = v_i{}^* h(\sigma^3/v^*)$, analogous to eq 1, where h is the function of σ^3/v^* independent of i and k. On the other hand when $\bar{\omega}_0{}^{(i)} = 1$, i.e., when there is no segment at the nearest neighbor sites, the free volume $\bar{v}_{\mathrm{f}}{}^{(i)}$ may be taken as the cell volume $v_i{}^*$ as in a previous paper.[1] Accordingly we assume here

$$v_{\mathrm{f}k}^{(i)} = v_{\mathrm{f}m} v_i{}^*/v^* \quad (k \neq 0) \tag{12}$$

$$v_{\mathrm{f}0}^{(i)} = \bar{v}_{\mathrm{f}}{}^{(i)}(\bar{\omega}_0{}^{(i)}=1) = v_i{}^* \tag{13}$$

where $v_{\mathrm{f}m}$, equal to $v^* h(\sigma^3/v^*)$, is a mean free volume independent of the components, and $v_i{}^*/v^*$ is assumed to be independent of temperature and volume. Here, $v_{\mathrm{f}m}/v^* = h(\sigma^3/v^*)$ is assumed to be expressed in the same form as in a pure system;

$$v_{\mathrm{f}m}/v^* = (4\pi 2^{1/2}/3)\{1 - 2^{-1/6}(\sigma^3 N/V^*)^{1/3}\}^3 \tag{14}$$

where the square well potential and hexagonal packing were assumed.[1] Then, we obtain from eq 11, 12, and 13

$$\prod_{i=1}^{n} \bar{v}_{\mathrm{f}}{}^{(i)c_i N_i}$$

$$= \prod_{i=1}^{n} (v_{\mathrm{f}m} v_i{}^*/v)^{c_i N_i \sum_{i=1}^{n} z_i N_i / \sum_{i=0}^{n} z_i N_i}$$

$$\times v_i{}^{* c_i N_i z_0 N_0 / \sum_{i=0}^{n} z_i N_i}$$

$$= v_{\mathrm{f}m}^{cN}(v^*/v_{\mathrm{f}m})^{z_0 N_0 / \sum_{i=0}^{n} z_i N_i} \prod_{i=1}^{n} (v_i{}^*/v^*)^{c_i N_i} \tag{15}$$

where

$$cN = \sum_{i=1}^{n} c_i N_i \tag{16}$$

As for $\sum_{\lambda} g_{\lambda}$, Flory's expression is adopted,[8] i.e.,

$$\sum_{\lambda} g_{\lambda} = \frac{M!}{\prod_{i=0}^{n} (N_i/r_i)!} \{(z_0-1)/M\}^{\sum_{i=1}^{n}(r_i-1)N_i/r_i}$$

$$= \frac{(M/N)^{M-N+\sum_{i=1}^{n} N_i/r_i}}{(M/N-1)^{M-N}} \cdot \frac{N^{\sum_{i=1}^{n} N_i/r_i}}{\prod_{i=1}^{n} N_i^{N_i r_i}} (\prod_{i=1}^{n} r_i^{-N_i/r_i})$$

$$\times \{(z_0-1)/e\}^{\sum_{i=1}^{n}(N_i-N_i/r_i)} \tag{17}$$

If $\tilde{V}$ is defined as $\tilde{V} = M/N = V/V^*$, then we have

$$z_0 N_0 / \sum_{i=0}^{n} z_i N_i = z_0 N_0 / (z_0 N_0 + \sum_{i=1}^{n} z_i N_i)$$

$$= (M-N)/\{(M-N) + \bar{z} N z_0\}$$

$$= (\tilde{V}-1)/(\tilde{V}-1+\bar{z}/z_0) \tag{18}$$

Finally, using eq 2, 7, 14, 17, and 18, we have

$$Z = Z_{\mathrm{v}} \prod_{i=1}^{n} j_i(T)^{N_i} \prod_{i=1}^{n} q_i{}^{c_i N_i} \prod_{i=1}^{n} (v_i{}^*/v^*)^{c_i N_i}$$

$$\times \{(z_0-1)/e\}^{N-N/r} \prod_{i=1}^{n} (N_i r_i)^{-N_i/r_i} N^{N/r} \tag{19}$$

$$Z_{\mathrm{v}} = \tilde{V}^{N(\tilde{V}-1)+N/r}(\tilde{V}-1)^{-N(\tilde{V}-1)}$$

$$\times v_{\mathrm{f}m}^{cN}(v^*/v_{\mathrm{f}m})^{cN(\tilde{V}-1)/(\tilde{V}-1+\bar{z}/z_0)}$$

$$\times \exp\left\{ \frac{(\bar{z}/z_0)\bar{z} N K \varepsilon^*}{kT(\tilde{V}-1+\bar{z}/z_0)} \right\} \tag{20}$$

where $N/r = \sum_{i=1}^{n} N_i/r_i$, the total number of polymer molecules in the system.

The form of the volume dependent part of the partition function, Z_{v} (eq 20), is identical with that for a pure system derived previously.[1] Therefore, if the expressions for parameters of eq 6, 9, 10, and 16 are used, the arguments made in previous papers[1-3] of this series for pure systems are valid for mixtures. (This identity in the formula between pure and mixture systems is assumed also in the treatments of Prigogine[4] and Flory.[9]) The examples of the results obtained previously, which will be used in this paper, are shown in the following.

Internal pressure $P_i \equiv (\partial U/\partial V)_T$, ($U$, internal energy) or thermal pressure coefficient $\mu \equiv (\partial P/\partial T)_V$ at atmospheric pressure is given, in the case where the cell volume is constant, $v^* = \sigma^3$, by[1]

$$T\mu \cong P_i = E^*(\bar{z}/z_0)^2(\tilde{V}'-1+\bar{z}/z_0)^{-2} \tag{21}$$

where $\tilde{V}' = V/\sigma^3 N$ and $E^* = K^0 \varepsilon^* z_0/\sigma^3$. Here K^0 is the value of K at $V^* = \sigma^3 N$, i.e., $K^0 = 0.699$ from eq 8, and E^* represents a characteristic cohesive energy density. The equation 21 reproduces the experimental observations fairly well.[1]

The surface tension derived is written[3]

$$\gamma = (\varepsilon^* \bar{z}/\sigma^3)(\sigma^3/c)^{1/3}(\bar{z}/z_0)\tilde{V}'^{-1}(\tilde{V}'-1+\bar{z}/z_0)^{-1}$$

$$\times (0.160 - 0917 f\tilde{T}) \tag{22}$$

where $\tilde{T}$ is the reduced temperature defined as $\tilde{T} = T/T^* = ckT/\varepsilon^* \bar{z}$, and f is the parameter which

represents the difference in the free volume between the surface and bulk phases.

Transforming eq 9, 10, and 16 into alternative forms in terms of $E_{ij}^* \equiv K^0 \varepsilon_{ij}^* z_0 / \sigma^3$ and $\theta_i = N_i \sigma_i^3 / N \sigma^3$, we have

$$E^* \equiv K^0 \varepsilon^* z_0 / \sigma^3$$

$$= \sum_{i=1}^{n} \sum_{j=1}^{n} z_i^0 z_j^0 / z_0^2) \theta_i \theta_j E_{ij}^* \qquad (23)$$

$$\bar{z} = \sum_{i=1}^{n} z_i^0 \theta_i \qquad (24)$$

$$c / \sigma^3 = \sum_{i=1}^{n} (c_i / \sigma_i^3) \theta_i \qquad (25)$$

where

$$z_i^0 = z_i v^* / v_i^* = z_i \sigma^3 / \sigma_i^3 \qquad (26)$$

The quantity θ_i defined above may be almost equal to the volume fraction. The coordination number z_i^0 defined by eq 26 should be dependent on shapes and volumes of molecules or segments in the system. If the segment or molecule is spherical, the following relation may hold; $z_i^0 / z^{(i)} = (z_i / z^{(i)})(z_i^0 / z_i) = (v_i^* / v^*)^{2/3} (v^* / v_i^*)^{1/3}$ where $z^{(i)}$ is the coordination number of a segment of the i-th component in the pure system. On the other hand, if the segments of the different kinds in the system are composed of the atomic groups having almost identical volume, for examples, $-CH_2-CH_2-$ and $-CH_2-CH(COOCH_3)-$, the $z_i / z^{(i)}$ is rather equal to v_i^* / v^*, therefore $z_i^0 / z^{(i)} \cong (v_i^* / v^*)(v^* / v^* / v_i^*) = 1$. The evaluation described here is close to Flory's estimation[9] based on the concept of the surface contact sites.

The present theory may be also valid for a copolymer, if the parameters for the components in the copolymer are used, though these may not be always equal to those in corresponding homopolymers. Furthermore the parameter ε^* of a complex molecule or segment may be also estimated by eq 9 from the parameters of the atomic groups composing the molecule or segment.

E^* and T^* Binary Systems

For a binary system (i.e., $n=2$), if the Berthelot relation, $\varepsilon_{ij}^* = {}_{ii}^{*1/2} \varepsilon_{jj}^{*1/2}$, for intermolecular dispersion force is assumed, the quantity E^* is given from eq 23 as

$$E^* = \{(z_1^0 / z_0) \theta_1 E_{11}^{*1/2} + (z_2^0 / z_0) \theta_2 E_{22}^{*1/2}\}^2 \qquad (27)$$

Here the quantity E_{ii}^* is related to E_i^* of the pure system of the i-th component by the equation $E_{ii}^* / E_i^* = z^{(i)} / z_i^0$ because $E_i^* = K^0 \varepsilon_i^* z_0 / \sigma_i^3$, $\varepsilon_i^* = \varepsilon_{ii}^* z_i / z^{(i)}$, and $E_{ii}^* = K^0 \varepsilon_{ii}^* z_0 / \sigma^3$ with eq 26, where ε_i^* is ε_{ii}^* in the pure system. The characteristic temperature T^* for a binary system can be derived from eq 24, 25, and 27 as

$$T^* = \varepsilon^* \bar{z} / ck$$

$$= E^* \sigma^3 \bar{z} / K^0 z_0 ck$$

$$= (z_1^0 / z_0) \{\theta_1 T_1^{*-1} + \theta_2 A (z^{(2)} / z^{(1)}) T_2^{*-1}\}^{-1}$$

$$\times \{\theta_1 + (z_2^0 z^{(2)} / z_1^0 z^{(1)})^{1/2} A^{1/2} \theta_2\}^2 \qquad (28)$$

where $A \equiv E_2^* / E_1^*$ and $T_i^* \equiv \varepsilon_i^* z^{(i)} / c_i k$.

Internal Pressure and Thermal Pressure Coefficient for Binary Systems

For a binary system, using eq 21 and 27, we obtain

$$v\{1 - (1 - \bar{z} / z_0) \tilde{V}'^{-1}\} \mu^{1/2}$$

$$= x_1 v_1 (z_1^0 / z^{(1)})^{1/2} \{1 - (1 - z^{(1)} / z_0) \tilde{V}_1'^{-1}\} \mu_1^{1/2}$$

$$+ x_2 v_2 (z_2^0 / z^{(2)})^{1/2} \{1 - (1 - z^{(2)} / z_0) \tilde{V}_2^{-1}\} \mu_2^{1/2} \qquad (29)$$

where the subscripts 1 and 2 refer to components 1 and 2, respectively, x_i is the segment fraction N_i / N, v is the mean molar volume of segment in the mixture, $V N_A / (N_1 + N_2)$ (N_A, Avogadro's number), and v_i is the molar volume of segment in the pure system of the i-th component. When the terms in the braces $\{\ \}$ in eq 29, which are all very close to unity, are approximated to be equal to each other, and when $z_i^0 = z^{(i)}$, eq 29 reduces to

$$v \mu^{1/2} = x_1 v_1 \mu_1^{1/2} + x_2 v_2 \mu_2^{1/2} \qquad (30)$$

With the use of eq 30, excess thermal pressure coefficient μ^E at atmospheric pressure is written

$$\mu^E = \mu - (x_1 \mu_1 + x_2 \mu_2)$$

$$= -x_1 x_2 (\mu_1^{1/2} - \mu_2^{1/2})^2 + x_1^2 (\phi_1^2 - 1) \mu_1$$

$$+ x_2^2 (\phi_2^2 - 1) \mu_2 + 2 x_1 x_2 (\phi_1 \phi_2 - 1)(\mu_1 \mu_2)^{1/2} \qquad (31)$$

where $\phi_i = v_i / v$.

Since $P_i \cong T \mu$ at atmospheric pressure (eq 21), μ in eq 29, 30, and 31 can be replaced by internal pressure P_i.

Glass Transition Temperature of Binary Mixtures

In a previous paper,[2] we have shown that the value of $\tilde{T}_g$, the reduced temperature T_g / T^*, is almost constant for any polymer and that this constancy of $\tilde{T}_g$ gives a rough measure to

estimate the glass transition temperature. If the above condition, i.e., T_g=constant, is satisfied, T^* in eq 28 can be replaced by T_g:

$$T_g=(z_1{}^0/z_0)(\theta_1 T_{g1}^{-1}+\theta_2 A(z^{(2)}/z^{(1)})T_{g2}^{-1})^{-1}$$
$$\times\{\theta_1+(z_2{}^0 z^{(2)}/z_1{}^0 z^{(1)})^{1/2}A^{1/2}\theta_2\}^2 \qquad (32)$$

Then, from eq 32 with the assumption of $z_i{}^0=z^{(1)}$, the change in T_g of component 2 when a small amount of component 1 is added, can be derived as

$$(\partial T_g/\partial W_1)_{W_1=0}=-T_{g2}(z_1{}^0\sigma_1{}^3/M_{w1})(z_0{}^2\sigma_2{}^3/M_{w2})^{-1}$$
$$\times\{T_{g2}/T_{g1}-1+(A^{1/2}-1)^2\} \qquad (33)$$

where W_1 is the weight fraction of the component 1, the diluent, and M_{wi} is the molecular weight of segment of the i-th component. Deviation from the simple additivity law of T_g is expressed by the quantity

$$-\{(\partial T_g/\partial W_1)_{W_1=0}+\Delta T_g\}\Delta T_g$$
$$=(z_1{}^0\sigma_1{}^3/M_{w1})(z_2{}^0\sigma_2{}^3/M_{w2})^{-1}T_{g2}A^{-1}$$

$$\times\{T_{g1}^{-1}+(A^{1/2}-1)^2/\Delta T_g\}-1 \qquad (34)$$

where $\Delta T_g=T_{g2}-T_{g1}$.

COMPARISON WITH EXPERIMENTALS AND DISCUSSION

Thermal Pressure Coefficient and Internal Pressure

According to Flory's theory[9] with the Berthelot relation, we have

$$v\mu^{1/2}=x_1 v_1\mu_1{}^{1/2}(s_1/s)^{1/2}+x_2 v_2\mu_2{}^{1/2}(s_2/s)^{1/2} \qquad (35)$$

where s is the number of external contact sites. The difference between eq 29 and 35 arises from the difference in expression for P_i, i.e., $P_i\propto\bar{z}/z_0(\tilde{V}'-1+\bar{z}_0)^{-2}$ in the present theory whereas $P_i\propto V^{-1}$ in Flory's one. When $(s_1/s)^{1/2}$ and $(s_2/s)^{1/2}$ can be regarded as unity, eq 35 reduces to eq 30. Equation 30 shows the additivity of $\mu^{1/2}v$, whereas Hildebrand, et al.,[10] presented the empirical equation, $v\mu=x_1 v_1\mu_1+x_2 v_2\mu_2$, which

Table I. Comparison of observed and calculated values of excess thermal pressure coefficient μ^E for mixtures (50%—50% mol fraction) at 25°C[10]

Mixture	V_1, cc/mol	V_2, cc/mol	μ_1	μ_2, atm/deg	μ	$-\mu^E$	$-\mu^E$, Calcd		$x_1 x_2 \times(\mu_1{}^{1/2}-\mu_2{}^{1/2})^2$
							$(\mu v)^*$	$(\mu^{1/2}v)^{**}$	
Heptane Acetone	147.57	73.85	8.41	11.00	9.00	0.71	0.44	0.46	0.043
Heptane Carbontetrachloride	147.57	97.07	8.41	11.15	9.38	0.40	0.28	0.38	0.048
Heptane Benzene	147.57	89.34	8.41	12.23	9.59	0.73	0.44	0.55	0.089
Heptane Carbon disulfide	147.57	60.63	8.41	12.31	9.55	0.81	0.81	0.88	0.093
Heptane Ethylene bromide	147.57	86.51	8.41	14.80	10.35	1.26	0.84	1.05	0.226
Heptane Bromform	147.57	87.91	8.41	14.92	10.60	1.07	0.83	1.13	0.230
Benzene Carbontetrachloride	89.34	97.07	12.23	11.15	11.73	−0.04	0.02	0.03	0.006
Benzene Carbon disulfide	89.34	60.63	12.23	12.31	12.00	0.27	0.01	−0.01	6×10^{-5}
Benzene Ethylchloride	89.34	78.86	12.23	13.88	12.64	0.42	0.06	0.05	0.013
Benzene Bromform	89.34	87.91	12.23	14.92	13.70	−0.12	0.02	0.07	0.035
Carbon disulfide Acetone	60.63	73.85	12.31	11.00	11.42	0.24	0.07	0.06	0.01
Carbon disulfide Ethylene bromide	60.63	86.51	12.31	14.80	13.58	−0.02	−0.21	−0.20	0.029

* (μv), $-\mu^E$ calculated with $\mu^E=\mu-(x_1\mu_1 v_1+x_2\mu_2 v_2)$.
** $(\mu^{1/2}v)$, $-\mu^E$ calculated with $\mu^E=\mu-(x_1\mu_1{}^{1/2}v_1+x_2\mu_2{}^{1/2}v_2)$.

Table II. Comparison of calculated and observed various quantities for ethylene—vinyl acetate copolymers and pure components at 150°C[a]

| | Vinyl acetate, wt% | V, cc/g | | $\sigma^3 N$ cc/g | $\tilde{V}' = V/\sigma^3 N$ | | $\tilde{T}$ $\times 10^2$ | | E^*, cal/cc | $N\sigma^3/c$, cc/mol | | γ, dyn/cm² | | |
		Obsd	Calcd		Obsd	Calcd	Obsd	Calcd		a	b	Obsd	Calcd c	d
Polyethylene	0	1.268	—	1.091	1.161	—	5.34	—	96.8	136.4	—	27.7_6	27.4_5	—
Copolymer	17.6_7	1.210	1.210	1.030	1.174	1.174	5.60	5.60	102.3	123.2	123.2	27.0	27.0_5	27.1_0
	26.5_8	1.181	1.178	0.998	1.183	1.180	5.78	5.73	106.1	115.1	116.0	26.5	26.7_5	27.0_0
	30.9_2	1.169	1.163	0.982	1.190	1.184	5.92	5.80	107.9	110.5	112.9	26.4	26.3_0	26.9_5
	38.7_1	1.140	1.137	0.955	1.193	1.190	5.98	5.91	111.2	106.2	107.6	26.9	26.6_0	26.9_0
Poly(vinyl acetate)	100	0.905	—	0.740	1.222	—	6.56	—	149.2	71.9	—	28.7_2	28.9_0	—

[a] a, calculated from the observed $\tilde{T}$ with E^*. b, calculated from the calculated $\tilde{T}$ with E^*. c, calculated from the observed $\tilde{V}'$ and $\tilde{T}$ with E^* and $N\sigma^3/c$ in column a. d, calculated from the parameters of pure components alone, i.e., from the calculated $\tilde{V}'$ and $\tilde{T}$ with E^* and $N\sigma^3/c$ in column b. The $\tilde{V}'$—$\tilde{T}$ relation used is the curve of $\tilde{V}'$—$\tilde{T}$ obtained experimentally with the theorem of corresponding states in the previous paper.[1]

shows the additivity of μv. In eq 31 the molar volume of mixture v can be regarded as $x_1 v_1 + x_2 v_2$, when the absolute value of $(v_1 - v_2) x_i$ is much larger than that of the excess volume $v^E (= v - x_1 v_1 - x_2 v_2)$ because $\phi_i - 1 = \{(v_j - v_i) x_j - v^E\}/v$. In such a case, therefore, μ^E is insensitive to volume change on mixing. For the mixtures (50—50 mol%) of low molecular weight liquids,[10] the comparisons of the above two additivity properties with experimental results are shown in Table I. The two additivity properties give almost the same values and that of $\mu^{1/2} v$ presented here gives a slightly better value, provided that the approximation, $v = x_1 v_1 + x_2 v_2$, was used in the calculation. The first term of eq 31 is usually very small compared with the other terms as shown in Table I, and μ^E is dominated by the difference in molar volume between the pure components from which the terms involving ϕ_1 and ϕ_2 in eq 31 arise. The agreement with experimentals is fairly satisfactory. In some cases, e.g., benzene mixtures with carbodisulfide and ethylchloride, however, considerable discrepancies are found, some of which may arise from the molecular orientation and invalidity of $P_i \infty V^{-2}$ due to peculiar interactions, and some may arise from the use of the Berthelot relation and the neglect of the coordination number.
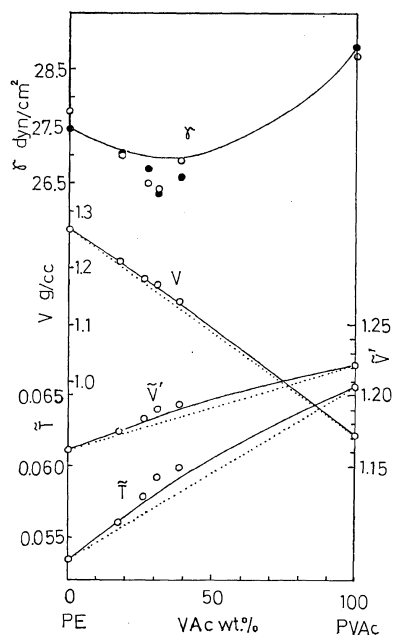

Figure 1. Weight per cent dependence of reduced temperature $\tilde{T}$, reduced volume $\tilde{V}'$ volume V and surface tension γ for ethylene—vinylacetate copolymers: ◯, experiments; —, calculated curves; ●, γ calculated with $\tilde{T}_{\text{obs}}$ and $\tilde{V}'_{\text{obs}}$. The dotted straight lines indicate the values expected from the simple additivity law.

Specific Volume and Surface Tension of Ethylene—Vinyl Acetate Copolymers

In Table II and Figure 1, theoretical and experimental values of specific volumes, reduced volumes $\tilde{V}'$, reduced temperatures $\tilde{T}(\equiv T/T^*)$, and surface tensions γ for ethylene—vinyl acetate copolymers[11] (ELVAX) of different compositions at 150°C are shown for comparison. The observed values of reduced temperature for copolymers were determined from volume—temperature measurements by a method previously described,[1] where at first the values of $N\sigma^3$ were evaluated with eq 5. The calculated values of $\sigma^3 N/c$, E^*, and T^* were obtained from eq 25, 27, and 28 with those for pure components, polyethylene, and poly(vinyl acetate), which were estimated in the first paper,[1] assuming that the coordination number z_i^0 in the mixture system is equal to that in the pure one, $z^{(i)}$, accordingly, $E_{ii}^*=E_i^*$ because $E_{ii}^*/E_i^*=z^{(i)}/z_i^0$. The calculated values of $\tilde{V}'_{cal}$ and V_{cal} were evaluated from the calculated $\tilde{T}_{cal}$ with the experimental curve[1] of $\tilde{V}'$—$\tilde{T}$ relation. The surface tensions γ for the homo- and co-polymers were computed with these values of $\tilde{T}$, $\tilde{V}'$ by eq 22 with $f=0.64$ which is available for polymers as mentioned previously. Figure 1 shows fairly close agreement between the theoretical and experimental values. The observed values of V, $\tilde{V}'$, and $\tilde{T}$ for copolymers are larger than those expected from the simple additivity law, in accordance with the theoretical prediction. Examining in detail, however, we find that the observed values of V(or $\tilde{V}'$) and $\tilde{T}$ abnormally deviate from the calculated smooth curves in the vicinity of 30 wt% of vinyl acetate. The reason for this abnormality is not clear, and experimental errors may not be responsible alone because the same tendency is found in surface tension as shown in Figure 1. The values of surface tension (indicated by closed circles) calculated from $\tilde{V}'_{obs}$ and $\tilde{T}_{obs}$ show better agreement with experimental values (indicated by open circles) than those from $\tilde{V}'_{cal}$ and $\tilde{T}_{cal}$ (indicated by a solid line). The theory well explains the fact that the weight fraction dependence of γ has a minimum. Qualitatively speaking, the minimum arises from the fact that the introduction of a little vinyl acetate having a large number of external degrees of freedom causes the increase in the value of $\tilde{V}$, $\tilde{T}$, and c/σ^3; hence it induces the decrease in the value of γ, whereas it does not cause a comparable increase in the characteristic interaction energy E^*.

Glass Transition Temperatures of Mixtures

According to eq 28, the characteristic temperature of a binary system is usually less than that expected from the simple additivity law when plotted against volume fraction as shown in Figure 2. The calculated curves of eq 32 for T_g are also represented by these curves for T^* in Figure 1. The equation 32 may be also
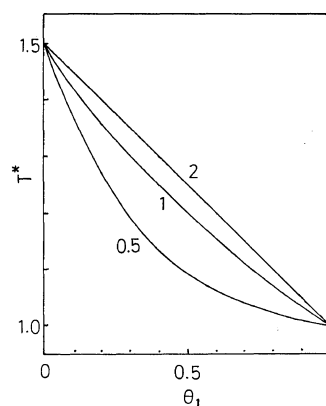
Figure 2. Characteristic temperature T^* vs. occupied volume fraction θ_1 when $T_2^*=1.5$, $T_1^*=1$ and $z_1^0=z_2^0$ with various values of $A(=E_2^*/E_1^*)$ which are indicated by the numers in the figure.

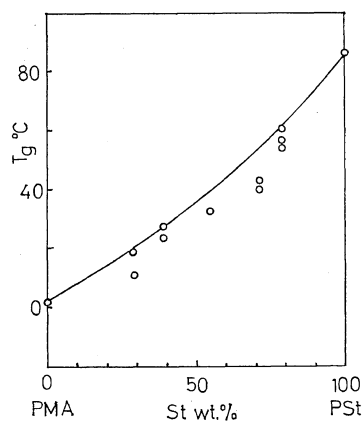**Figure 3.** Glass transition temperatures of styrene-methylacrylate copolymers: ◯, experiments[12]; —, calculated curve.

Table III. Molecular parameters used in the calculation of the glass transition temperatures of binary systems

Substance	$\sigma^3 N/M_w$, cc/g	$\dfrac{0.699\sigma^* z}{\sigma^3 N}$, cal/mol	$T_{g1\ hyp}$, °K[a]	$T_{g1\ exp}$, °K	$z_i{}^0$
Polystyrene	0.884	112.2	—	359[obsd]	10
Poly(methyl acrylate)	0.740	149.2	—	275[obsd]	10
Poly(methyl methacrylate)	0.809	138.2	—	358[obsd]	10
Benzene	0.980	164	217	174[b]	12
Toluene	0.997	150	226	112[b]	12
Methyl chloride	0.620	147	187	110[b]	12
Chloroform	0.563	126	194	133[b]	12
Carbon tetrachloride	0.528	105	197	162[b]	12
Acetone	1.018	145	183	110[b]	11
Methyl acetate	0.861	(160)	171	109[b]	11
Ethyl acetate	0.896	149.2	179	109[b]	10.5
n-Propyl acetate	0.924	138.2	186	101[b]	10.25
n-Butyl acetate	0.945	130.9	190	125[b]	10

[a] hypothetical glass transition temperatures $T_{g1\ hyp}$ of diluents are determined by the equation $T_g = \tilde{T}_g$ $T^* = 0.0397T^*$ with the values of T^* listed in a preceding paper.[3]

[b] estimated with the experimental equation proposed by Jenckel,[14] $i.e.$, $T_g/T_m = 0.6 + 3 \times 10^{-4} M_w$, where T_m and M_w are melting point and molecular weight, respectively.

valid for random copolymers. As an example of the applications, the comparisons of the calculated values with the observed ones are shown in Figure 3 for styrene—methyl methacrylate copolymers.[12] The parameters are obtained by a method adopted previously[1] and shown in Table III. The theoretical predication is satisfied in the shape of the T_g $vs.$ weight fraction relation, but not so well quantitatively. One of the possible reasons for the disagreements is that the quantity c_i in a copolymer is not always equal to the one in the homopolymer of of the i-th component because of the short range interaction between segments of different kinds.

Next, the effect of a diluent on the glass transition temperature will be considered with eq 33 and 34 derived from eq 32, on the assumption that the value of $\tilde{T}_g$ does not change by adding a diluent. This assumption may not be so valid for polymer—diluent systems because $\tilde{T}_g$ may decrease with increasing the diluent fraction. This is suggested by the fact that $\tilde{T}_g$ in a pure system decreases with decreasing chain length as shown previously.[2] It is expected, however, that the diluent-effect on T_g will be qualitatively estimated by the condition $\tilde{T}_g =$

constant. Therefore we examine with eq 33 and 34 the validity of the above assumption for the diluent-effect.

In Figures 4 and 5, calculated and observed values of the two quantities, $(\partial T_g/\partial W_1)_{W_1=0}$ and $-\{(\partial T_g/\partial W_1)_{W_1=0} + \Delta T_g\}/T_g$, are shown for diluted polystyrenes and poly(methyl methacrylate)s with
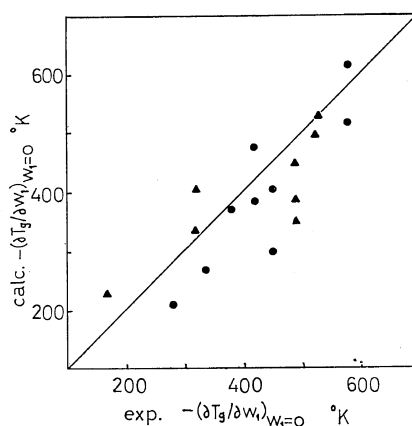

Figure 4. Comparison of calculated and experimental values of $-(\partial T_g/\partial W_1)_{W_1=0}$: ●, diluted polystyrenes; ▲, diluted poly(methyl methacrylate)s.
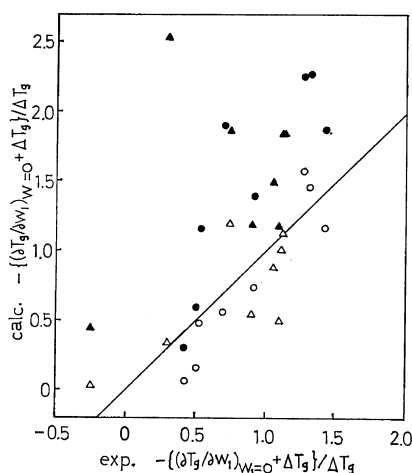
Figure 5. Comparison of calculated and experimental values for the deviation from the simple additivity law of T_g: ● and ○, diluted polystyrenes; ▲ and △, diluted poly(methyl methacrylate)s. Filled points (●, ▲) and open points refer to the two different calculations described in the text, respectively.

the use of Jenckel's data.[13] The parameters used are shown in Table III, which were obtained by the preceding method.[1] Considering the shape of the molecules, appropriate values were given to z_i^0. In the calculation of eq 33 and 34, the hypothetical glass transition temperatures of diluents $T_{g1\,hyp}$ were used as T_{g1}, which were evaluated by the relation $T_{g1\,hyp}=\tilde{T}_g\cdot T_1^*$ with $\tilde{T}_g=0.0396$; this value of $\tilde{T}_g$ is an average for some polymers.[2] Some of the values of $T_{g1\,exp}$ are those estimated with the empirical equation presented by Jenckel.[14]

Figure 4 shows that the calculated values of $-(\partial T_g/\partial W_1)_{W_1=0}$ agree fairly well with the observed ones. The calculated values, however, tend to be slightly smaller than the observed ones. This may arise from the decrease in $\tilde{T}_g$ with increasing the diluent fraction. As can be seen in Figure 5, the observed deviation from the simple additivity accords qualitatively with the theoretical prediction. The negative deviation becomes larger as specific (occupied) volume and cohesive energy density of the diluent become larger and as the characteristic temperature becomes smaller. The fact that the calculated values (indicated by ● and ▲),

in general, are larger than the observed ones as shown in Figure 5 may arise from the underestimation of ΔT_g, i.e., the overestimation of T_{g1} owing to the assumption of $\tilde{T}_g=$constant, since $\tilde{T}_g$ of a diluent may be smaller than that of a polymer, in other words, $T_{g1\,hyp}$ is much larger than $T_{g1\,exp}$ as shown in Table III, and $T_{g1\,exp}$ is closer to the actual glass transition temperature of a diluent than $T_{g1\,hyp}$. In fact, if the calculated deviation is taken to be $-\{(\partial T_g/\partial W_1)_{W_1=0\,cal}+\Delta T_{g\,exp}\}/\Delta T_{g\,exp}$, the calculated values (indicated by ○ and △) become much closer to the observed ones as shown in Figure 5, where $\Delta T_{g\,exp}=T_{g2\,obs}-T_{g1\,exp}$.

LIST OF SYMBOLS

A,	defined as E_2^*/E_1^*.
c,	parameter associated with external degrees of freedom defined by eq 16.
c_i,	one third of external degrees of freedom per segment of i-th component.
E^*,	characteristic cohesive energy density defined by eq 23.
E_i^*,	E^* of the pure system of i-th component, defined by $E_i^*=K^0\varepsilon_i^* z_0/\sigma_i^3$.
E_{ij}^*,	parameter associated with interaction energy between i-th and j-th components, defined as $K^0\varepsilon_{ij}^* z_0/\sigma^3$.
f,	parameter in the expression for surface tension of eq 22.
$\sum_\lambda g_\lambda$,	combinatory factor associated with the mixing of molecules and holes.
$j_i(T)$,	partition function per segment associated with the intrasegmental interactions of i-th component.
K,	function defined by eq 8.
K^0,	K when $V^*=\sigma^3 N$, i.e., $K^0=0.699$.
k,	Boltzmann's constant.
M,	total number of lattice sites in the system, $M=\sum_{i=1}^{n} N_i$.
M_{wi},	molecular weight of segment of i-th component.
N,	total number of segments in the system, $N=\sum_{i=1}^{n} N_i$.
N_i,	number of segments of i-th component in the system.
N_0,	number of holes in the system.

n,   number of components in the system.

P,   pressure.

P_i,   internal pressure defined as $(\partial U/\partial V)_T$ (U, internal energy).

q_i,   kinetic part of partition function associated with the external degrees of freedom of an i-th component segment.

N/r,   total number of molecules in the system.

r_i,   number of segments of i-th component.

s,   mean number of external contact sites per segment of mixture, used in Flory's theory[9].

s_i,   number of external contact sites of an i-th component segment involved in Flory's theory[9].

T,   temperature.

T^*,   characteristic temperature defined by $\varepsilon^* \bar{z}/ck$.

T_i^*,   characteristic temperature of the i-th component defined as $\varepsilon_i^* z^{(i)}/c_i k$.

T_g,   glass transition temperature.

T_{gi}, T_g of pure i-th component.

$T_{g1\,exp}$, T_g of diluent estimated with the empirical equation presented by Jenckel[14].

$T_{g1\,hyp}$,   hypothetical T_g of diluent determined by $T_{g1\,hyp} = \tilde{T}_g T_1^* = 00396 T_1^*$.

ΔT_g,   difference of T_g, $T_{g2} - T_{g1}$.

$\Delta T_{g\,exp}$, T_{g2}(observed) $- T_{g1\,exp}$.

$\bar{U}_0$ potential energy of the system when all of the segments are at the centers of lattice sites, as given by eq 4.

V,   volume of the system.

v,   volume per mole of segment, $V N_A/N$ (N_A, Avogadro's number).

v_i,   volume per mole of segment of the i-th component in the pure system.

V^*,   cell volumes occupied with segments, $N v^*$.

$\tilde{V}$,   reduced volume defined by $\tilde{V} = M/N = V/V^*$.

$\tilde{V}'$,   reduced volume defined by $\tilde{V}' = V/\sigma^3 N$.

v^*,   average volume of cell defined by eq 2.

v_i^*,   cell volume of the i-th component.

$\bar{v}_f^{(i)}$,   free volume of a segment of the i-th component.

$\bar{v}_{fk}^{(i)}$,   parameter in eq 11, usually taken as $\bar{v}_f^{(i)}$ when the nearest neighbor sites are all occupied with segments of the k-th component.

v_{fm},   mean free volume in eq 12.

W_1,   weight fraction of the component 1, the diluent.

$\bar{w}_k^{(i)}$,   most probable value of segment fraction of the k-th component in the nearest neighbor sites of an i-th component segment.

x_i,   segment fraction of the i-th component, N_i/N.

Z,   partition function of the system.

Z_v,   volume dependent part of partition function of the system.

z_i,   coordination number of an segment of the i-th component, defined as the number of sites around a segment of i-th component whose volume is average cell volume v^*.

$\bar{z}$,   mean coordination number of the system defined by eq 10.

z_i^0,   coordination number defined by eq 26, $z_i^0 = z_i v^*/v_i^*$.

$z^{(i)}$,   coordination number of a segment of i-th component in the pure system.

γ,   surface tension.

ε^*,   parameter of intersegmental interaction energy defined by eq 9.

ε_i^*,   intersegmental interaction energy parameter of pure system of i-th component, representing the minimum potential energy in the Lennard-Jones 12-6 potential.

ε_{ij}^*,   parameter of interaction energy between the segments of i-th and j-th components, in eq 5.

θ_i,   characteristic volume fraction, defined as $\theta_i = N_i \sigma_i^3/N \sigma^3$.

μ,   thermal pressure coefficient, $(\partial P/\partial T)_V$.

μ^E,   excess thermal pressure coefficient, $\mu - (x_1 \mu_1 + x_2 \mu_2)$.

σ^3,   average characteristic volume of a segment, defined by eq 6.

σ_i^3,   characteristic volume of an i-th component segment (σ represents the distance of the zero potential energy in the Lennard-Jones 12-6 potential).

$\varphi_{ij}(0)$,   interaction potential energy per volume v^* between the segments of i-th and j-th components when they are located at the centers of nearest neighbor sites.

ϕ_i,   ratio of molar volume of the i-th component to average molar volume, v_i/v.

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