Thermodynamic Interactions of Branched Polyethylene in Polar and Nonpolar Systems

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Synopsis

The thermodynamic properties of polymer solutions are frequently described in terms of the Flory-Huggins equation. This equation includes a parameter χ, which depends upon the intermolecular forces acting between the molecules in a solution. The experimental determination of χ was performed by an improved microtechnique and extended to a wide range of polar and nonpolar diluents of polyethylene. Careful correlations are prescribed for calculating χ from pure-component properties; they are based on an extension of the Hildebrand-Scatchard theory of solutions and on the theory of intermolecular forces. Polar (τ) and nonpolar (δ) solubility parameters are presented for a variety of solvents. For polyethylene–nonpolar solvent systems we have emphasized the factor deciding the sign of heat of mixing, while for polyethylene–polar solvent systems we have determined the contribution of dipole-induced dipole interactions $\psi(\delta\tau)$ in interchange-energy density B and, hence, χ.

INTRODUCTION

The determination of polymer–diluent interactions is a problem of considerable theoretical, besides practical, interest, since knowledge of these interactions is a key to understanding the properties of polymer solutions. The thermodynamic properties of polymer solutions are frequently described in terms of the Flory-Huggins equation, which was first proposed more than twenty years ago; its use for data reduction was pointed out by Gee,[1] Scott and Magat[2] and numerous other workers.[3] This equation gives the free-energy change which occurs when a noncrystalline polymer is mixed with a solvent; for any given polymer–solvent pair it contains a characteristic parameter χ, called the Flory interaction parameter, which reflects the intermolecular forces between the molecules in the solution. The Flory-Huggins equation is

$$\Delta G_M/RT = n_1 \ln v_1 + n_2 \ln v_2 + \chi v_1 v_2 (n_1 + x n_2) \qquad (1)$$

where ΔG_M is the free energy of mixing the liquidlike, disoriented polymer with the solvent, n_1 and n_2 are the number of moles of solvent and polymer, respectively, v_1 and v_2 are the volume fractions of solvent and polymer, respectively, x is the ratio of molar volume of the polymer and solvent, and χ is a dimensionless quantity which is a function of the interaction energy

characteristic of a given solvent–solute pair.   If the free energy of mixing is negative, the polymer and solvent may mix spontaneously to form a solution.   If it is positive, two phases form, and the polymer does not dissolve appreciably in the solvent.   The first two terms of eq. (1) account for the configurational entropy of mixing and are always negative.   Therefore, for the polymer to be soluble in a solvent, the third term in this equation must be small (if positive) or it must be negative.   For polymer solubility, therefore, the Flory interaction parameter must be either negative or a small positive number.

If eq. (1) is used for describing the thermodynamic properties of polymer solutions, then the problem of predicting polymer solubility is equivalent to that of determining reasonably accurate values of the Flory interaction parameter.   Much effort, therefore, has been directed toward the development of methods of determining the degree of these interactions.   The majority of the reported methods, however, require rather troublesome measurements.[4-9]

Some years ago[10] there was reported a fast and simple method of determining the degree of interactions in polymer–diluent systems based on Flory's statistical thermodynamic treatment of the effect of diluent on the melting point of pure polymer.   The method, as a matter of fact, involves microdetermination of the depressed melting point of a polymer particle in its mixtures with a diluent.   The satisfactory results obtained in the PVC–diluent systems investigated[10] have encouraged extension of the method to linear polyethylene–diluent systems for evaluation of solvency by the χ parameter and to correlate solvency with the structure.[11]

Of the solvents reported on so far little attention has been devoted to the low members of the paraffinic and olefinic series and to the chlorinated hydrocarbons.   Besides extending investigation to these solvents this work aims at evaluating the agreement between the experimental and calculated χ values, so to control the reliability of a more general method of estimating the χ parameter, starting from the properties of pure components.   Therefore, by an improved technique a wide investigation has been made and extended to the polar solvents, which until now have not been the object of many investigations.

EXPERIMENTAL

Melting Point of Polymer

The melting point of pure polyethylene samples was determined microscopically, as previously reported.[11]   A few particles of powdered sample were placed between two flat little glasses and then placed on a Kofler hot stage (20–230°C., Reichert Co., Wien, Austria).   Over the assembly was placed the usual buffer plate associated with the Kofler hot stage and then the large cover plate.   The specimen was observed by a microscope capable of 100 magnification between crossed polaroids with through illumination. The specimen was then heated at an optimum rate of 1°C./min., starting

from a temperature 20 C.° below its melting point. Before being heated the specimen appeared as well-defined and roughly spherical particles but upon being heated its outlines slowly degenerated and $T_M°$ was taken as the temperature at which degeneration was complete.

The samples used present quite definite and reproducible melting points, which well agree with dilatometric ones.[12]

Determination of Depressed Melting Point of Polyethylene with Diluents

Because of the high volatility of the majority of the hydrocarbons employed the measurements for determining T_M in a closed system were carried out with a particular holder. The apparatus was a small, brass cylinder, about 5.0 mm. deep and 20 mm. in diameter, provided with a brass collar, which can be screwed on the side surface of cylinder. The collar and cylinder held thin glasses (about 0.5 mm. in thickness and 20 mm. in diameter), which were held firmly against a polytetrafluoroethylene gasket, providing a closed cell.

A few granules of powdered polymer sample were placed on the bottom glass, and then the liquid was accurately poured in until the space was filled.

The cell was then closed and placed on the Kofler hot stage. Thereafter the procedure for determining T_M was the same as that previously described.

At first, as the temperature was raised, the polyethylene particle did not change appreciably. Then it began to imbibe the diluent without much increase in volume. This imbibition caused the particle to lose its appearance and become translucent. As heating continued, the particle swelled more and more, retaining, however, its distinct outlines, until a temperature was reached at which it completely lost its distinguishable contours. This temperature was taken as T_M.

Calculation of Flory Interaction Parameter from Experimental Measurements

According to the well-known relation proposed by Flory,[3,12]

$$1/T_M = 1/T_M^0 + (R/\Delta H_u)(V_u/V_s)(v_1 - \chi v_1^2) \qquad (2)$$

where T_M is the depressed melting point (°K.), $T_M°$ is the melting point of pure polymer (°K.), V_u and V_s are the molar volumes of the polymer repeating unit and the diluent at T_M, respectively, R is the gas constant, ΔH_u is the heat of fusion per mole of repeating unit, v_1 is the volume fraction of the diluent, and χ is the Flory interaction parameter.

The high degree of dilution permitted the approximation $v_1 = 1.0$; however, it did not eliminate the gel or network character of the mixture. Accordingly, the eq. (2) becomes

$$1/T_M = 1/T_M^0 + (R/\Delta H_u)(V_u/V_s)(1 - \chi) \qquad (3)$$

which is the simplified Flory equation used for same purposes in other work.[10,11]

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The molar volume V_s of diluent was taken as M/d, where M is the molecular weight of the diluent and d is its density at the depressed melting point. When T_M was higher than the boiling point of the diluent, values of V_s were obtained by extrapolation of an assumed linear relation between liquid density and temperature. The V_u values were obtained by multiplying the molecular weight of a methylene unit by the value of the specific volume of melted polyethylene at T_M.[13] A value of 922 cal. for the heat of fusion, ΔH_u, was taken from the literature.[14]

By substituting these values in eq. (3) we obtain for χ the values listed in Tables I and II.

<div align="center">TABLE I</div>
<div align="center">Thermodynamic Parameters of Branched Polyethylene–Nonpolar Diluent Systems[a]</div>

Diluent	T_M, °C.	V_s at T_M, cm.³/ mole	χ	B, cal./ cm.³	δ, (cal./ cm.³)$^{1/2}$	K
Eicosene 1	98	378.0	−0.13	−0.25	7.83	1.005
n-Tetracosane	101	454.2	−0.09	−0.15	7.42	1.002
n-Esadecane	95	313.0	−0.06	−0.14	7.27	1.001
1-Vinylcyclohexene-3	76	138.0	−0.06	−0.30	7.76	1.005
Cyclohexene	68	107.5	−0.03	−0.19	8.36	1.012
2,4,4-Trimethylpentene-1	85	169.9	0.04	0.17	6.56	1.002
2-Ethylhexene-1	85	166.9	0.05	0.23	6.93	0.999
Decene-1	91	204.4	0.10	0.35	7.93	0.997
3-Methylhexane	85	158.4	0.10	0.55	6.87	0.998
1-Methylcyclopentene-1	75	112.7	0.11	0.67	7.92	0.998
n-Heptane	86	159.6	0.13	0.85	7.12	0.992
Octene-1	88	170.0	0.14	0.59	7.24	0.996
Heptene-1	86	153.4	0.17	0.79	7.10	0.992
n-Octane	88	176.3	0.18	0.73	7.09	0.996
3-Methylpentane	86	142.6	0.22	1.06	6.28	0.998
n-Hexane	86	140.5	0.23	1.17	6.09	1.001
Pentene-1	88	123.0	0.25	1.46	6.33	0.993
n-Pentane	88	128.8	0.35	1.96	6.12	0.995

[a] T_M = depressed melting point, V_s = molar volume of diluent at T_M, χ = Flory interaction parameter, B = interchange energy density = $RT\chi/V_s$, δ = solubility parameter of solvent, and K = factor connected with diluent solvency.

CORRELATION BETWEEN THEORETICAL APPROACH AND EXPERIMENTAL DATA

If it is assumed, according to the Flory's original derivation,[15] that the entropy of mixing in any solution can be put equal to the entropy of mixing of the corresponding athermal solution (i.e., any possible influence of the energies of interaction on the entropy of mixing is neglected), it is found that the heat of mixing of a polymer–solvent system is given by

$$\Delta H_M/RT = \chi v_1 v_2 (n_1 + x n_2) \qquad (4)$$

which is the third term of eq. (1).

TABLE II

Thermodynamic Parameters of Branched Polyethylene–Polar Diluent Systems[a]

Diluent	T_M, °C.	V_s, cm.³/mole	χ	$\Delta E^v_{(np)}$, kcal./mole	$\Delta E^v_{(p)}$, kcal./mole	δ, (cal./cm.³)$^{1/2}$	τ, (cal./cm.³)$^{1/2}$	ψ, cal./cm.³
Methylene chloride	86	72.9	0.60	3.29	2.49	6.72	5.84	14.27
Chloroform	77	87.5	0.25	5.35	1.52	7.82	4.17	7.88
Carbon tetrachloride	73	103.9	0.01	5.42	1.50	7.22	3.80	7.19
Trichloroethylene	72	95.6	0.08	4.78	2.84	7.07	5.45	14.59
Tetrachloroethylene	72	108.4	−0.05	6.09	2.95	7.67	4.96	12.51
1,2-Dichloropropane	93	107.1	0.57	4.93	2.64	6.78	4.97	10.52
Chlorobenzene	75	107.6	0.04	8.45	0.69	8.86	2.53	4.40
o-Dichlorobenzene	88	119.4	0.41	9.89	1.08	9.10	3.01	5.05

[a] T_M, V_s, and χ as in Table I, $\Delta E^v_{(np)}$ = nonpolar contribution to the energy of vaporization, $\Delta E^v_{(p)}$ = polar contribution to the energy of vaporization, δ = nonpolar solubility parameter, τ = polar solubility parameter, ψ = induction energy parameter.

To compute the heat of mixing, a suitable modification of the Hildebrand-Scatchard theory of solution[16-18] can be used. In its most general form this theory is not limited to nonpolar species, but it considers only configurational contributions and neglects contributions from internal degrees of freedom such as rotation and vibration.

The Hildebrand-Scatchard regular solution theory equation for the heat of mixing may be written

$$\Delta H_M = V_s B v_1 v_2 (n_1 + x n_2) \qquad (5)$$

where B is the interchange energy density for the solvent–solute pair. The use of eq. (5) together with the Flory-Huggins expression for the athermal configurational entropy of mixing gives

$$\chi = V_s B / RT \qquad (6)$$

The interchange-energy density B is given by

$$B = (c_{11} + c_{22} - 2c_{12}) \qquad (7)$$

where the c_{ij}'s characterize the intermolecular forces acting between molecules (or molecular segments) i and j. For the pure components c_{11} and c_{22} are the cohesive-energy densities of components 1 (solvent) and 2 (polymer):

$$c_{11} = \Delta E_1^v / V_1 = \delta_1^2 + \tau_1^2 \qquad (8)$$

$$c_{22} = \Delta E_2^v / V_2 = \delta_2^2 = \tau_2^2 \qquad (8\ bis)$$

In these equations ΔE_i^v is the energy of vaporization of substance i to a gas at zero pressure, and δ_i and τ_i are defined, respectively, as the nonpolar and the polar solubility parameters of substance i.

The quantity c_{12} represents the intermolecular forces acting between solvent molecules 1 and molecular segments of polymer 2 in solution. It may include dispersion forces, dipole–dipole forces, dipole-induced dipole forces, and specific interactions (solvation) between solute and solvent:

$$c_{12} = F_{disp}(\delta_1, \delta_2) + F_{di\text{-}di}(\tau_1, \tau_2) + F_{ind}(\delta_1, \tau_1; \delta_2, \tau_2)$$
$$+ F_{spec.\ int.} \qquad (9)$$

where the F's stand for unspecified functions. The terms in eq. (9) have the following meanings.

$F_{disp}(\delta_1, \delta_2)$ represents the (nonpolar) dispersion forces acting between dissimilar molecules. On the basis of the London theory it may be approximately represented by the geometric mean of the nonpolar forces present in the pure components:

$$F_{disp}(\delta_1, \delta_2) \approx K\delta_1\delta_2$$

where K is directly connected with the diluent solvency.[19]

$F_{di\text{-}di}(\tau_1, \tau_2)$ represents the interactions between permanent dipoles in the solute and solvent. If no specific forces (such as hydrogen bonding) are present, it is a function of the pure-component polar solubility parameters

τ_1 and τ_2. For polar molecules or molecular segments, which may be represented by spherical force fields with small, ideal dipoles at their center,[20]

$$F_{\text{di-di}}(\tau_1, \tau_2) = \tau_1 \tau_2$$

$F_{\text{ind}}(\delta_1, \tau_1; \delta_2, \tau_2)$ represents dipole-induced dipole interactions between solute and solvent and may be represented by $\psi(\delta_1 \tau_1, \delta_2 \tau_2)$, where ψ is an unspecified function.

$F_{\text{spec. int.}}$ represents the contribution to the pair-interaction energy from any solvation that may occur in solution. Very little theoretical knowledge is available for characterizing this interaction.

For the polyethylene–diluent systems of our investigation, in which no dipole–dipole forces are present and specific interactions are negligible, eq. (9) becomes

$$c_{12} = F_{\text{disp}}(\delta_1, \delta_2) + F_{\text{ind}}(\delta_1, \tau_{1v}; \delta_2, \tau_2) \tag{10}$$

Polyethylene–Nonpolar Diluent Systems

Since $\tau = 0$ for systems in which the solvent is nonpolar, eq. (7) becomes

$$B = \delta_1^2 + \delta_2^2 - 2K\delta_1\delta_2 \tag{11}$$

In this relation K is the factor deciding the sign of the heat of mixing for the nonpolar–nonpolar systems. As a matter of fact, it is evident that B (and, hence, χ) becomes negative only for $K > 1$. This would imply the likelihood of the existence of an interaction between unlike molecules. The existence of this factor K, which seems to have been overlooked in previous theoretical work, has been only recently pointed out by some authors.[21] In the opinion of the present writers this factor should be connected with the change in the end-to-end distance, which takes place when a molecule leaves the polymer and enters the solution.

In spite of the fact that several papers have been concerned with the thermodynamic properties of polymer, little attention until now has been devoted to the thermal dependence of the solubility parameter of the polymer; the available data are reported for room temperature.[22] With the aim of reaching a better approach, we decided to introduce the δ value of the polymer at the melting point, taking into account that mixing follows polymer melting.

To estimate the δ of a polymer, we used the conclusion of Allen et al.[23] on the empirical correlation between the internal pressure P_i and the c.e.d. (cohesive-energy density):

$$P_i/\text{c.e.d.} = n, \qquad 1.1 \leqslant n \leqslant 1.2 \tag{12}$$

Now, according to Mandelkern's suggestion,[24] the P_i at melting may be found[25] by means of the equation that relates the total entropy of melting with the configurational entropy change and the volume change on melting per mole of crystalline repeat unit:

$$\Delta S_m = (\Delta S_m)_c + (\partial P/\partial T)_v \Delta V_m \tag{13}$$

If we assume[23] that the relationship c.e.d. $= \delta^2$ holds also for polymer, a value of 7.23 (cal./cm.^{3})$^{1/2}$ for the δ of polyethylene is given.

The second unknown amount to determine is the solubility parameter of the nonpolar solvents, which was calculated as follows.

For when the depressed melting point is above the boiling point of the solvent the generalized charts of Hougen and Watson[26] were used. As one knows, to apply the reduced-variables method in addition to the trends of vapor pressure per temperature,[27] the critical values of temperature and pressure must be known. Now, for several of the diluents studied the critical data are still undetermined. The employment of the Lydersen method,[28,29] based on the atomic and group contributions, allowed us to calculate the unknown critical values with a satisfactory accuracy.

When the depressed melting point is below the boiling point of the diluent, δ was calculated at the different temperatures by the conventional square-root ratio of energy of vaporization and molar volume. For many of the solvents investigated, the data on energy of vaporization and their changes with temperature are not available; in this work they were evaluated by means of the Riedel and Watson equations, respectively. Riedel[30] developed the following empirical equation for the heat of vaporization, ΔE^v, at the normal boiling point T_b, which is very accurate[31] for nonpolar or slightly polar substances:

$$\Delta E^v = T_b(5 \log P_c - 2.17)/(0.930 - T_b/T_c) \qquad (14)$$

Having evaluated the latent heat of vaporization at normal boiling point, ΔE^v at different temperatures may be determined anywhere in the liquid range by means of the Watson equation:[32]

$$\Delta E_T{}^v/\Delta E_{T'}{}^v = (T_c - T)/(T_c - T')^{0.38} \qquad (15)$$

The reliability and accuracy of the aforementioned relations are satisfactory, as may be emphasized by a comparison with some of the available data.[33,34]

By means of reported equations it was possible to evaluate the solubility parameters of various solvents under different thermal conditions. The δ values are listed in Table I.

By substituting in eq. (11) the values of B, obtained from experimental results [eqs. (6) and (3)] and the calculated solubility parameters of polymer and solvent at the depressed melting point, we obtained for K the values listed in Table I.

Polyethylene–Polar Diluent Systems

In nonpolar–polar systems the forces between solute and solvent include not only dispersion forces but also dipole-induced dipole forces, aside from specific interactions between the molecules. In considering fluids whose molecules possess permanent dipoles it has been found useful to separate the cohesive-energy densities into polar and nonpolar parts. Splitting the

energy of vaporization of a polar fluid into nonpolar and polar parts permits the following definitions of the solubility parameters to be made:

$$\text{Nonpolar solubility parameter:} \qquad \delta_i = (\Delta E^v_{i(\text{np})}/V_i)^{1/2} \qquad (16)$$

$$\text{Polar solubility parameter:} \qquad \tau_i = (\Delta E^v_{i(\text{p})}/V_i)^{1/2} \qquad (16\text{ bis})$$

where $\Delta E^v_{i(\text{np})}$ and $\Delta E^v_{i(\text{p})}$ are the nonpolar and polar contributions to the energy of vaporization of fluid i; that is,

$$\Delta E^v_{i(\text{total})} = \Delta E^v_{i(\text{np})} + \Delta E^v_{i(\text{p})} \qquad (17)$$

Bondi and Simkin[35] have shown how the energies of vaporization of polar liquids can be divided into polar and nonpolar contributions by using the homomorph idea of Brown et al.[36] The homomorph of a polar molecule is a nonpolar molecule having very nearly the same size and shape as those of the polar molecule. The homomorph concept is relatively easy to apply. The polar energy of vaporization is simply the difference between the experimentally determined total energy of vaporization and the energy of vaporization of the homomorph at the same reduced temperature.

If the polar molecule has a straight-chain structure, a normal paraffin may be used as a homomorph. In that case the energy of vaporization of the homomorph (which is equal to the nonpolar energy of vaporization of the polar molecule) may be estimated from Figure 1. The size of the homomorph may be considered to be a continuous, rather than a discontinuous, variable. This makes it convenient to use the molar volume of the polar liquid as the independent variable, as shown in Figure 1. This step follows from the basic idea that the molar volume of the polar component is equal to that of its homomorph, as long as the comparison is made at the same reduced temperature.
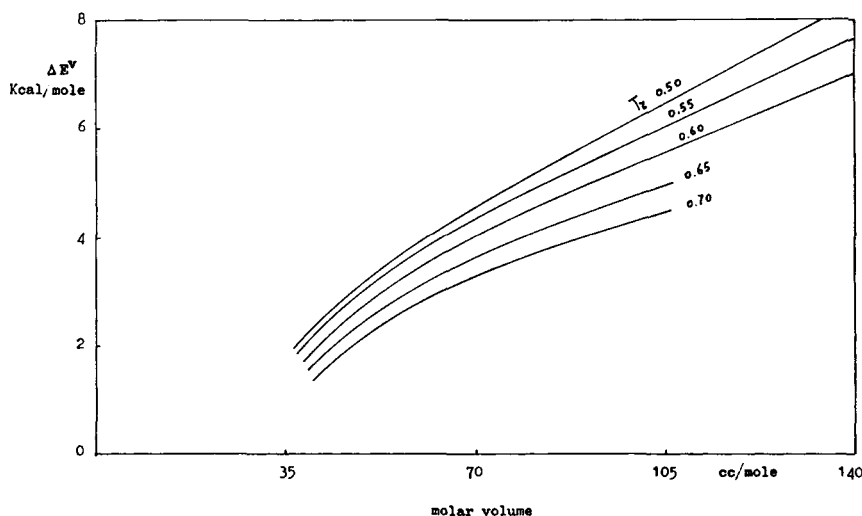

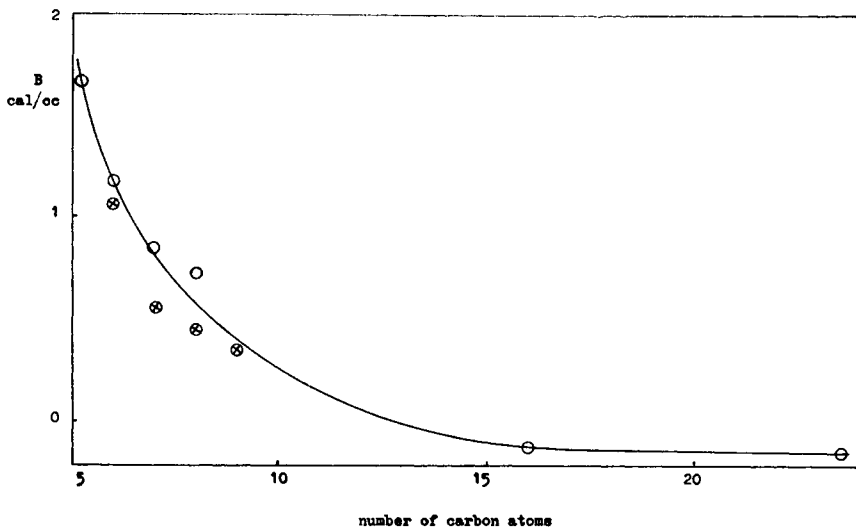Fig. 1. Energy of vaporization for straight-chain hydrocarbons.

Fig. 2. Relation between B and diluent molecular size: (O) normal alkanes; (⊗) isomers.

For a polar molecule whose homomorph is not a linear hydrocarbon the homomorph is chosen as the nonpolar molecule most closely resembling the polar one in shape and molar volume, when they are compared at the same reduced temperature. One must remember to find the energy of vaporization of the homomorph at the same reduced temperature as that of the polar molecule and to compare molar volumes at this temperature, too.

For the solvents of our investigation the molar volumes and the energies of vaporization were taken from the latest literature.[37-39]

From these are evaluated the nonpolar and polar contributions to the solubility parameter, whose values are listed in Table II.

In a nonpolar–polar system, in which $\tau_2 = 0$, we have, from eqs. (7), (8), (8 bis), and (10),

$$B = (\delta_1 - \delta_2)^2 + \tau_1{}^2 - 2\psi \tag{18}$$

where ψ is an unknown empirical term which accounts for inductive effects. By substituting in eq. (18) the values of B, obtained from experimental results [eqs. (6) and (3)] and from the calculated solubility parameter of the polymer and the polar and nonpolar parts of the solubility parameter of the solvent, at the depressed melting point, we found the ψ values, which are reported in Table II.

Plotting ψ against the product $\delta\tau$ (induction-energy density function) we obtained the curve shown in Figure 2, whose trend agrees with the theoretical expectations.

Since the values are relative to the T_M at equilibrium temperature, the plot may be used for predicting, for every solvent characterized by a $\delta\tau$ value, the contribution of the induction forces to the interaction parameter of the binary systems.

RESULTS AND DISCUSSION

The relations between thermodynamic interactions and solvent structure are shown in Figures 3 and 4, where the influence of diluent (nonpolar) molecular size on the interchange-energy density is plotted.

The diagrams show, both for the alkane and the alkene series, a decrease of the B parameter (increasing solvency) with increasing number of carbon atoms, until a nearly constant value is reached for the higher members.
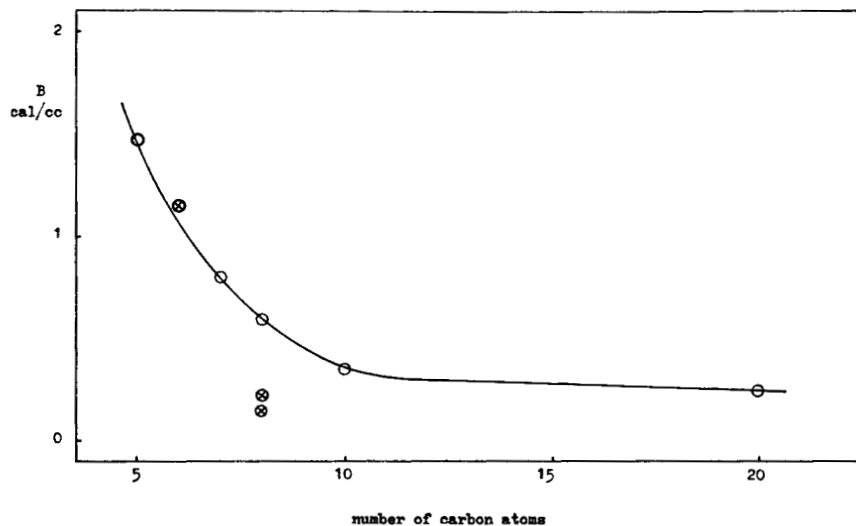

number of carbon atoms

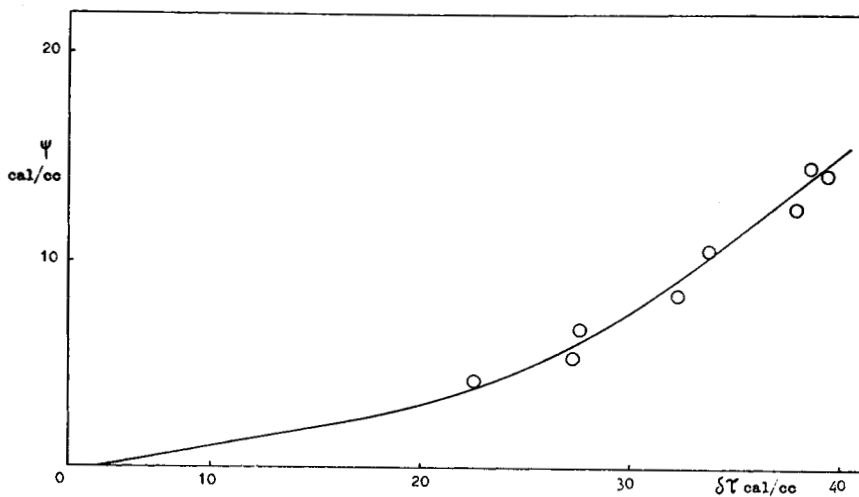Fig. 3. Relation between B and diluent molecular size: (O) normal alkenes; (⊗) isomers.

Fig. 4. Relation between dipole-induced dipole interactions and nonpolar and polar solubility parameters of solvents at $T = T_M$.

The straight-chain members, are poorer solvents than the isomer ones. By comparison with the B trend in the olefinic and paraffinic series the low, unsaturated members present a higher solvent power; with an increasing number of carbon atoms the solvency of the saturated liquids increases more rapidly than the solvency of the unsaturated ones.

Cyclic hydrocarbons, as reported in Table I, have very low values of B and so may be considered very good solvents both for linear[11] and branched polyethylene. Chlorinated paraffinic hydrocarbons have a solvent power which increases with the chlorine content. The same behavior was previously qualitatively noted in the carrying out of different measurements.[40] As may be noticed, the behavior of chlorinated aromatic hydrocarbons does not seem very regular; a definite explanation of this phenomenon is not known, but steric hindrance and conformational differences may
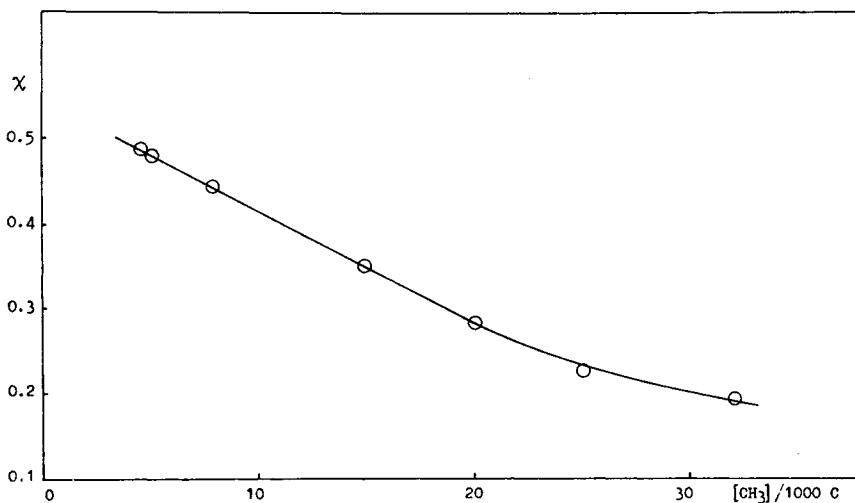

Fig. 5. Correlation between χ and short-chain branching frequency of polyethylene.

influence the interactions between the polymer and these diluents. A wider investigation is, however, required.

To examine the relation between thermodynamic interactions and polyethylene structure, the depressed melting-point measurement was extended to samples that have a different short-chain branching frequency in mixtures with a nonpolar solvent (n-hexane). The short-chain branching frequency was valuated by infrared spectroscopy.[41] We have noticed that the degree of interaction between solute and solvent increases (χ decreases) with increasing chain branching (Fig. 5).

The extension of the depressed melting-point measurements to the lower members of the solvent series examined has required the setup of an improved experimental technique, which has given satisfactory results.

The attempt to find a relation between experimental data and the theoretical approach, so as to have a more reliable general method of estimating the thermodynamic interactions, was made by means of a suitable modification of the Hildebrand-Scatchard theory of solution. It was, therefore, necessary to attain a considerable accuracy in the evaluation of the solubility parameters of the polymer and of the solvent, whether by means of the calculations connected with this evaluation or by taking into account the thermal influence. A till now overlooked evaluation of thermal influence is herein given: if the reliability of the assumption of the thermal independence of χ is quite unknown, without doubt that of B is a rough approximation, it being well known that the thermal decrease of the solvent's δ is very rapid and the decrease of δ for the polymer is slow.[42]

In the polyethylene–nonpolar solvent systems the negative values of χ emphasize a factor K, which decides the sign of the heat of mixing. This factor is directly connected with the dispersion forces acting between unlike molecules. Although it is close to unity, it is very significant from a theoretical standpoint, representing a state of preference for the existence of interactions between unlike molecules.

In the polyethylene–polar solvent systems the K factor tends to vanish compared with the dipole-induced dipole interaction forces represented by the ψ function. For an evaluation of this function in addition to the solubility parameter of the polymer the polar and nonpolar contributions to the solubility parameter of the solvent must be known. These two contributions derive by the retaining the idea of homomorph, applied both to the straight-chain and the nonlinear solvents. The ψ values, obtained from the experimental results, are strictly dependent and well related to the solubility parameters (polar and nonpolar) of the solvents. Moreover, the plot ψ/δ_T may be generalized to every binary system, the ψ values being determined at the equilibrium temperature, so that the contribution of the dipole-induced dipole forces for every system in which the solvent has a definite value of δ_T is valuable.

In conclusion, the extent of the thermodynamic interactions in polyethylene–diluent systems may be accurately evaluated by starting from the pure-component properties both for nonpolar and for polar solvents. For polyethylene–nonpolar systems the factor K must be determined, which, although very significant, does not extensively invalidate the heat of mixing, owing to its small size; in the polyethylene–polar systems, where K can be neglected compared to the contribution of the dipole-induced dipole forces, which, now more accessible, may be quantitatively evaluated.

In both cases, to examine exhaustively the solubility behavior it is convenient to appraise the free energy of mixing, so to cancel the several errors which are connected with the separate calculation of the heat or the entropy of mixing, and which are introduced by the oversimplified models adopted. We have found satisfactory agreement between experimental evidence[43] and the theoretical approach[44] to the phase equilibria of poly-

ethylene–ethylene systems at high pressure by applying the basic relations of the Flory-Huggins polymer solution theory, which still provides the most realistic and reliable representation of the phenomenon.[45,46]

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