

Thermodynamic Properties of Liquids Including Solutions. XV. Intramolecular Contacts and Their Effects on Excess Enthalpies of Solutions of Chain Molecules, Especially Benzene Solutions of Normal Alkanes and Polymethylenes

Maurice L. HUGGINS* and John W. KENNEDY**

*135 Northridge Lane, Woodside, California 96062, U.S.A.

**Institute of Polymer Science, University of Essex, Colchester C04 3SQ, England.

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ABSTRACT: The theory of excess enthalpy (H^E) and enthalpic component of the interaction parameter (χ_h), dealt with in previous papers of this series, is extended to allow for the effects of intramolecular contacts in chain molecule solutes. The number of these contacts, as a function of the number of mers in the chain molecules and their concentration in the solution, is estimated from enumerations over a class of self-avoiding walks (paths) in a lattice-graph. Applied to solutions of polymethylenes in benzene, for which the equilibrium constant parameter (K) has been previously estimated to be unity, we find intramolecular contacts to have little effect on the excess enthalpy at 25°C even for long chains. The enthalpic part of the interaction function is predicted to depend strongly on the extent of intramolecular contacting. Extensions of the theory to solutions for which $K \neq 1$ are briefly considered.

KEY WORDS Thermodynamics of Solutions / Enthalpy / Interaction Function / Benzene / Alkanes / Polymethylene / Oligomer / Polymer Solutions / Intramolecular Contacts / Self-Avoiding Walks / Lattice Graphs / Graph Theory /

The statistical mechanical theory of the thermodynamic properties of liquids, which is the subject of this series of papers,¹⁻⁴ was recently applied⁵ to the published excess enthalpy data for solutions of normal alkanes in benzene at 25°C. This theory leads to an expression for the excess enthalpy of mixing (H^E) in terms of the mole fractions x_1 (benzene) and x_2 (alkane) of the two components

$$H^E = \varepsilon_d x_1 x_2 g_K \quad (1)$$

$$z_2 = 1 - z_1 = \frac{r_\sigma x_2}{x_1 + r_\sigma x_2} \quad (2)$$

$$g_K = 2[(1 + K' z_1 z_2)^{1/2} - 1]/K' z_1 z_2 \quad (3)$$

$$K' = 4(K^{-1} - 1) \quad (4)$$

Here, ε_d is an "exchange energy" for replacing contacts (1-1, 2-2) between like molecules by contacts (1-2) between unlike molecules. The parameter r_σ is the ratio of the numbers of contact sites per molecule in each of the two types

$$r_\sigma = \sigma_2^0 / \sigma_1^0 \quad (5)$$

K is an equilibrium constant, measuring the relative probabilities of contacts of the three types. $K=1$ signifies that the contacts are random in the sense that their relative numbers depend only on the relative numbers of contact sites of the two kinds (hence, on the concentration). If $K=1$, then $g_K=1$ and eq 1 to 4 simplify to

$$H^E = \frac{\varepsilon_d r_\sigma x_1 x_2}{x_1 + r_\sigma x_2} \quad (6)$$

By fitting three points on each of the empirical smoothing curves reported⁶⁻¹⁰ for excess enthalpies of mixing benzene with various n -alkanes, Huggins⁵ obtained values for the three statistical mechanical parameters (K , ε_d , r_σ).

Comparison of the calculated parameters for the ten systems showed that the set

$$K=1; \varepsilon_d = 3068 \text{ J mol}^{-1}; r_\sigma = 0.2 (n+1) \quad (7)$$

represents the data within the rather large experi-

mental uncertainty, (as judged by the standard deviations of data points from their smoothing curves and the differences between data reported for the same system by different investigators).

In this way, the 30 to 40 empirical parameters required by the experimenters' smoothing curves are replaced by just three theoretically meaningful global parameters that can also be used to predict excess enthalpies for benzene solutions of *n*-alkanes for which measurements are not yet available.

The excess enthalpy is defined as the excess of the enthalpy of one mole (Avogadro's number of molecules) of the mixture over what it would be if each molecule contributed the same amount of enthalpy as in its pure liquid. In a pure *n*-alkane liquid, with *n* greater than 5, there must be some intramolecular contacts. In a solution for which the parameter *K* equals 1, there should be the same average number of such contacts per alkane molecule as in the pure alkane liquid. The excess enthalpy therefore measures only the intermolecular contacts. The actual values of σ_{alkane}^0 and r_o derived from excess enthalpy measurements, should not show a rectilinear dependence on the number of carbon atoms in the molecule, as implied by eq 7. Since the number of intramolecular contacts is likely to be relatively small for the alkanes for which H^E data have been published, the deviation from rectilinearity for these solutions would be expected to be very small. The published data are not accurate enough to enable the extent of these deviations to be determined.

In this paper we employ enumerations over a class of walks in a lattice-graph, together with the excess enthalpy data just discussed, to estimate the chain length and concentration dependence of the intra- and intermolecular contacts, and also the excess enthalpy and the enthalpic contribution to the interaction parameter of benzene solutions of polymethylene oligomers (normal alkanes) and higher polymers.

STATISTICAL ANALYSIS OF THE EXCESS ENTHALPY DATA

As a first step, we have re-estimated the three parameters (*K*, ϵ_A , and r_o) for the benzene solutions of *n*-alkanes with *n* equal to 5 through 17, for which excess enthalpy data have been published.

Direct-global least-squares fits to eq 1, with all data points equally weighted (regardless of differences in reliability at different concentrations and by different experimenters using different apparatus), suggest that the parameters of eq 7 be refined to the optimal set

$$K=1; \epsilon_A=3170 \text{ J mol}^{-1}; r=0.192(n+1) \quad (8)$$

The standard deviation, based on the (computed—experimental) residuals of H^E , is 27 J mol^{-1} , for 263 data points whose mean is 885 J mol^{-1} .

Future experiments of greater accuracy will doubtless lead to further refinements of the parameters. (For other comparable systems, H^E data of considerably greater accuracy have been published; see for example Huggins²). Extension of the range of *n*-alkanes studied to larger *n* values will also be useful in estimating departures from the rectilinear dependence of r_o on *n*.

ESTIMATION OF INTRAMOLECULAR CONTACTS BY LATTICE WALK ENUMERATIONS

In previous papers of this series dealing with polymer solutions,^{3,4} the distinction between intra- and intermolecular contacts has been neglected. This neglect, which affects the concentration and chain-length dependence of the thermodynamic properties of polymer solutions, we now explore.

Experimental data appropriate for the calculation of the numbers of intramolecular and intermolecular contacts in a solution as functions of concentration and the number (*n*) of mers in the polymer, are not available. However, combinatorial problems relating to chain configurations can be usefully approximated by appropriate enumerative results defined on walks in a tetrahedral (diamond) lattice-graph.¹¹ For the case at hand, we expect the mean number of intramolecular contacts to be proportional to the mean number (per walk) of first-neighbour approaches¹² $\langle J \rangle$, taken over all (*n*−1)-step self-avoiding walks (called "paths" in graph theory¹³) in the diamond lattice-graph.

Such walks have been categorised in great detail¹⁴ for *n*=2 to 20, using a fast exact enumeration program developed from the "list method" of Martin¹⁵ for the Essex University Computer

System. Each walk is categorised as having n points, i self-intersections, j first-neighbour approaches, and t *trans* steps. For each category the number of walks, $W(n, i, j, t)$ and some statistical measures, such as the mean square end-to-end distance, are tabulated.

For paths (self-avoiding walks), $i=0$. Disregarding the possibility of *trans/gauche* weighting, we write

$$W(n, j) \equiv \sum_t W(n, 0, j, t) \quad (9)$$

and then

$$\langle J \rangle_n^0 = \frac{\sum_j j W(n, j) e^{-\alpha(j)}}{\sum_j W(n, j) e^{-\alpha(j)}} \quad (10)$$

where $\alpha(j)$ is a weighting function for j first-neighbour approaches. If $K=1$, it is appropriate to set $\alpha(j)=0$. This gives us the unbiased mean for n -point paths, $\langle J \rangle_n^0$. The number of contact sites per n -alkane chain used in intramolecular contacts is then proportional to $2\langle J \rangle_n^0$. The total number of contact sites per n -alkane chain is proportional⁵ to $2(n+1)$. Hence, the fraction of chain contact sites used in intramolecular contacts is

$$f_n = \langle J \rangle_n^0 / (n+1) \quad (11)$$

The mean numbers $\langle J \rangle_n^0$ derived from our lattice walks tables and the fractions f_n are listed in Table I.

Jain and Pruitt,¹⁶ working from Theorem 1 of Dvoretzky and Erdős,¹⁷ showed that the number of self-intersections made by an (unbiased) walk of N steps in a (diamond) lattice-graph is an asymptotically normally distributed variable with mean $\langle I \rangle_N^0$ and variance $\text{Var}(I_N^0)$ given by

$$\langle I \rangle_N^0 = c_1 N + c_2 N^{1/2} \quad (12)$$

$$\text{Var}(I_N^0) = c_3 N \ln N \quad (13)$$

where c_1, c_2, c_3 are constants related to the asymptotic return probability. Exploiting the apparent parallelism¹⁸ between walks of N steps and paths of $N-1$ steps, we conjecture a similar asymptotic behaviour for the mean number $\langle J \rangle_n^0$. Consequently,

$$\langle J \rangle_n^0 = k_1 n + k_2 n^{1/2} \quad (14)$$

It is stressed by Fisher and Sykes¹⁹ that convergence to asymptotic behaviour is rapid (especially for paths), so that data from exact enumeration on relatively short walks furnish highly reliable

Table I. Mean numbers $\langle J \rangle_n^0$ of intramolecular contacts per molecule and fractions (f_n) of sites making intramolecular contacts

n	Exact values from tabulated walks		Calculated from eq 15 and 16
	$\langle J \rangle_n^0$	f_n	f_n
6	0.07407	0.01058	0.00892
7	0.10127	0.01266	0.01355
8	0.15451	0.01717	0.01741
9	0.19912	0.01991	0.02068
10	0.26135	0.02376	0.02350
11	0.30638	0.02553	0.02596
12	0.36769	0.02828	0.02813
13	0.41828	0.02988	0.03006
14	0.47952	0.03197	0.03179
15	0.53245	0.03328	0.03336
16	0.59397	0.03494	0.03479
17	0.64855	0.03603	0.03609
18	0.71020	0.03738	0.03729
19	0.76615	0.03831	0.03839
20	0.82781	0.03942	0.03942
30			0.04654
50			0.05410
100			0.06152
500			0.07126
10 ³			0.07354
10 ⁴			0.07875
∞			0.07892

estimates of the parameters in asymptotic expressions of this sort. Accordingly, we use the results for $n=10$ through 20 from Table I to determine the least-squares optimum values.

$$k_1 = 0.07891; \quad k_2 = -0.1678 \quad (15)$$

with a correlation coefficient of 0.998. From eq 11 and 14 it follows that for longer chains

$$f_n = \frac{k_1 n + k_2 n^{1/2}}{n+1} \quad (16)$$

and approaches 0.07891 as n tends to infinity. Values of f_n calculated from this equation are given in Table I for comparison with the exact values for the shorter paths.

It is worth emphasising that the foregoing analysis is not altered in essential details by varying the choice of lattice-graph in which self-avoiding walks are constructed. Our results are not at all dependent on any geometric features that may be associated with an embedding of the lattice-graph in space.²⁰

The analysis can clearly be extended to cover cases with K not equal to unity by employing an appropriate weighting function $\alpha(j)$ in eq 10, thereby obtaining a suitably biased mean $\langle J \rangle_n$. Equations 12 to 14 apply to the unbiased distribution of walks (for which $\alpha(j)=0$). From the parallelism mentioned above, the unbiased distribution is expected to be asymptotically normal with mean $\langle J \rangle_n^0$ and variance $\text{Var}(J_n^0)$. If the set of paths is now biased by a weighting factor β per first-neighbour approach, *i.e.*,

$$\alpha(j)=\beta^j \quad (17)$$

then the new (biased) asymptotic mean is given approximately (see Gordon, *et al.*¹⁸) by

$$\langle J \rangle_n = \langle J \rangle_n^0 - \text{Var}(J_n^0) \quad (18)$$

Hence, when $K \neq 1$

$$\langle J \rangle_n = k_1 n + k_2 n^{1/2} - k_3 n \ln n \quad (19)$$

We hope to return to this relation in future papers. For the remainder of this paper we restrict ourselves to the case $K=1$.

CORRELATION OF LATTICE WALK RESULTS WITH EXCESS ENTHALPY DATA

According to the theory being applied the parameter r_σ determines the skewness of the excess enthalpy *vs.* concentration curve.^{2,4,5} Assuming the number of contact sites per mer to be independent of the chain length and in the absence of intramolecular polymer—polymer contacts, r_σ is a rectilinear function of n as assumed in eq 7 and 8. Since, as has been explained, the excess enthalpy is, by definition, a function of the ratio (r_σ) of the number of polymer sites making intermolecular contacts to the number of solvent sites making (intermolecular) contacts, the observed r_σ values are expected to depart from a rectilinear relation as the chain length increases.

Assuming that the fraction (f_n) of polymer contact sites making intramolecular contacts is given by eq 15 and 16,

$$r_\sigma = \frac{\sigma_{2, \text{intermolecular}}^0}{\sigma_1^0} = \frac{\sigma_{2, \text{total}}^0}{\sigma_1^0} (1 - f_n) \quad (20)$$

a fit of the published H^E data for benzene solutions of the lower n -alkanes furnishes the globally

optimal parameter values (*cf.* eq 8).

$$K=1; \varepsilon_A=3175 \text{ J mol}^{-1}; r_\sigma=0.196(n+1)(1-f_n) \quad (21)$$

Table II compares the values of r_σ computed from eq 8 with those from eq 21. (For $n>6$, differences in r_σ resulting from use of the asymptotic result for f_n in place of the exact values given in Table I are insignificant). Both sets agree, to within the probable limits of certainty, with values obtained by individually fitting each n -alkane—benzene system over the range ($n=5$ through 17) for which experimental data are available.

Table II. Calculated contact ratios

n	$r_\sigma=0.192(n+1)$ (eq 8)	$r_\sigma=0.196(n+1)(1-f_n)$	
		Using exact f_n (Table I)	f_n from eq 15 and 16
5	1.152	1.152	1.172
6	1.344	1.357	1.360
7	1.536	1.548	1.546
8	1.728	1.734	1.733
9	1.920	1.921	1.919
10	2.112	2.105	2.105
11	2.304	2.292	2.291
12	2.496	2.476	2.476
13	2.688	2.662	2.661
14	2.880	2.846	2.846
15	3.072	3.032	3.031
16	3.264	3.216	3.215
17	3.456	3.401	3.400
18	3.648	3.585	3.584
19	3.840	3.770	3.769
20	4.032	3.952	3.953
30	5.952		5.793
50	9.792		9.453
100	19.39		18.58
500	96.20		91.20
10 ³	192.2		181.8
10 ⁶	1.92 × 10 ⁵		1.81 × 10 ⁵

Figure 1 displays representative plots of H^E as a function of x_2 , calculated from eq 6. The dashed lines were drawn for parameters from eq 8 (assuming a rectilinear dependence of r_σ on n , with no intramolecular contacts). The full lines are for the parameters of eq 21. Clearly, the differences are negligible relative to the scatter of the experimental points (also shown). The differences between the two curves for $n=50$ and

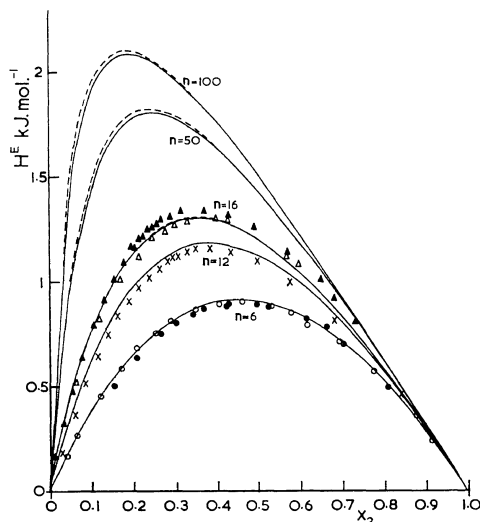


Figure 1. Representative excess enthalpy curves for normal alkanes in benzene at 25°C, calculated from eq 6. The dashed lines are calculated using the parameters from eq 8 which were inferred on the assumption that all contacts are intermolecular. The full lines are calculated using the parameters of eq 21 obtained on the assumption that both intermolecular and intramolecular contacts participate, the extent of the latter having been estimated from enumerations over paths in a lattice-graph. Comparison with the data points:

for $n=6$, (●) Romani and Paz-Andrade⁷ and (○) Harris and Dunlop⁹

for $n=12$, (×) Diaz Pena and Menduina⁸

for $n=16$, (▲) Diaz Pena and Menduina⁸ and (△) Lundberg and Grolier.¹⁰

suggests that even for large n (polymethylene) the contribution from intramolecular contacts will be difficult to detect by directly analysing H^E data at fixed temperature.

between the two curves for $n=100$ suggest that, even for long alkanes, the effect of intramolecular contacting on H^E is not large. It seems unlikely, therefore, that measurements of the concentration dependence of H^E for n -alkanes in benzene (even if much more accurate than those that have been made) will be useful in estimating the extent of intramolecular contacting. We shall now discuss, however, a much more powerful way of studying this effect.

THE ENTHALPY COMPONENT OF THE INTERACTION FUNCTION

In treating the thermodynamic properties of solutions of linear polymers,^{3,4} it is usual to express concentrations as volume fractions (φ_1 , φ_2) rather than mole fractions (x_1 , x_2). It is also useful to examine the magnitude and concentration dependence of the interaction function (χ) and its enthalpic and entropic components (χ_h , χ_s). The enthalpic component is closely related to the excess enthalpy. For mixtures with $K=1$ it is given by the relation³

$$\chi_h = \left(\frac{\varepsilon_A}{RT} \right) \left[\frac{r_{\sigma/v}}{1 + (r_{\sigma/v} - 1)\varphi_2} \right]^2 \quad (22)$$

with

$$r_{\sigma/v} \equiv \left(\frac{V_1}{V_2} \right) r_{\sigma} \quad (23)$$

At 25°C,

$$RT = 8.3144 \times 298.15 = 2478.94 \text{ J mol}^{-1} \quad (24)$$

$$V_1 = 89.406 \text{ cm}^3 \text{ mol}^{-1} \quad (25)$$

and

$$V_2 = (16.39n + 31.75 - 6/n + 90/n^2) \text{ cm}^3 \text{ mol}^{-1} \quad (26)$$

where eq 26 agrees with the molar volumes published by Rossini, *et al.*,²¹ for $n=4$ through 8, with an average deviation of less than 0.005.

For the purposes of the ensuing discussion we shall use the values for ε_A and r_{σ} as furnished by eq 8 when we neglect the effect of intramolecular contacts or eq 21 when we account for them. We are not here proposing to debate the question of whether or not chains exhibit intramolecular contacts, but rather to use the extreme case where there are no intramolecular contacts to assess the strength of the dependence of χ_h on the extent of intramolecular contacting. Plots of χ_h (Figures 2 and 3) for the two cases show surprisingly large differences, especially for small φ_2 and large n . Although the quantitative detail of these curves is something of an artifact of the parameter values (eq 8, 21, 26), the marked qualitative differences between the two cases do allow contributions from the various parameters to be resolved so that the extent of intramolecular contacting can be meaningfully probed in some depth from experiments aimed at measuring χ_h directly. For example, one can calculate χ_h from the temperature coeffi-

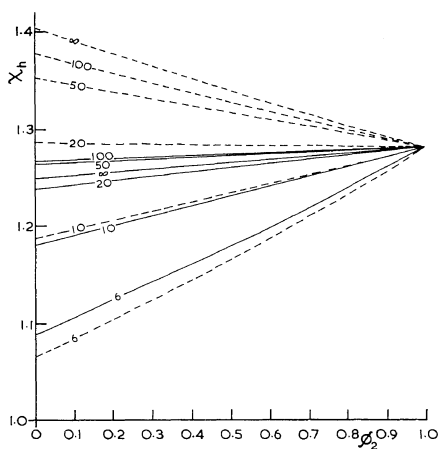


Figure 2. Enthalpic part of the interaction function, χ_h vs. φ_2 , calculated for representative n -alkanes in benzene show a marked dependence on the extent of intramolecular contacting. Dashed curves assume no intramolecular contacts, solid curves assume intramolecular contacts to an extent estimated from enumerating walks on lattice-graphs. Differences between the two sets of curves cannot be entirely attributed to uncertain parameter values obtained from fitting crude data for small n -alkanes, but represent significant dependence on the extent of intramolecular contacts. Compare also Figure 3.

cient of the interaction function χ , using

$$\chi_h = -T^2 \frac{\partial}{\partial T} (\chi/T) \quad (27)$$

The parameter ε_A merely serves to ordinate-scale χ_h (eq 22) and has the same effect whether intramolecular contacts are neglected or not. At $\varphi_2=1$ (see eq 22), χ_h ($=\varepsilon_A/RT$) is independent of n and the influence of intramolecular contacts vanishes. Since for the two cases $\chi_h=1.279$ and 1.281 , respectively (when $\varphi_2=1$), the small difference in ε_A resulting from reoptimisation (compare eq 8 with eq 21) has an insignificant effect even in scaling χ_h .

For all n , the effect of intramolecular contacts on χ_h increases with decreasing φ_2 , attaining its maximum as $\varphi_2 \rightarrow 0$, when

$$\chi_h = \left(\frac{\varepsilon_A}{RT} \right) r_{\sigma/v}^2 \quad (28)$$

In the limit $n \rightarrow \infty$ we have, from eq 26, $V_2 \sim 16.39 n$, while

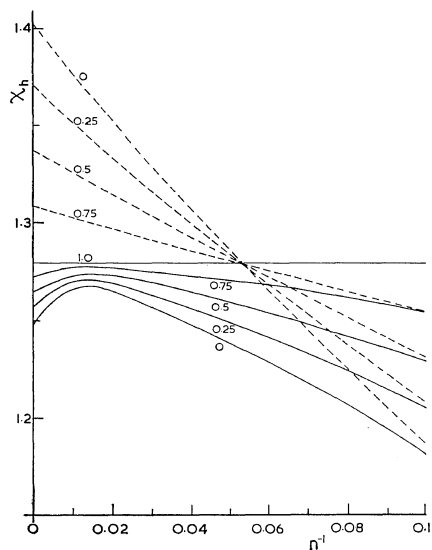


Figure 3. Enthalpic interaction function χ_h vs. n for various volume fractions φ_2 as shown on figure. Dashed and solid lines have the same significance as in Figures 1 and 2. The marked differences between the two sets of curves make χ_h a sensitive probe for the extent of intramolecular contacts (see text) since it separates the roles played by various parameters lifted from optimisation sets.

$$r_{\sigma} = 0.192(n+1) \sim 0.192n \quad (29)$$

$$r_{\sigma/v} \sim 1.04734 \quad (30)$$

$$\chi_h \sim \frac{1.40271}{(1+0.04734\varphi_2)^2} \quad (31)$$

when intramolecular contacts are absent; or

$$r_{\sigma} = 0.196(n+1)(1-f_n) \sim 0.196(1-k_1)_n \quad (32)$$

$$r_{\sigma/v} \sim 0.98461 \quad (33)$$

$$\chi_h \sim \frac{1.24161}{(1-0.01539\varphi_2)^2} \quad (34)$$

when intramolecular contacts are counted. Comparison of eq 29 to 31 with eq 32 to 34 shows how the rather small effect of intramolecular interactions on r_{σ} (or $r_{\sigma/v}$) is amplified in χ_h . Were this merely an amplification of small differences in parameters obtained by optimisation over scattered data (eq 8, 21, 26), it would have dubious value. However, V_2 plays an identical role in both cases and the major contribution stems from the better determined value of the parameter k_1 (see eq 15, 16).

The same point is even more forcefully demonstrated in relation to the existence of maxima displayed by χ_h in Figure 3. Using the case $\varphi_2=0$ as an example, it follows from eq 28 that $\partial\chi_h/\partial n=0$ when

$$V_2 \frac{\partial r_\sigma}{\partial n} - r_\sigma \frac{\partial V_2}{\partial n} = 0 \quad (35)$$

When intramolecular contacts are neglected let $r=p(n+1)$ for some parameter p ($=0.192$ in eq 8). Equation 35 then requires that

$$V_2 - (n+1) \frac{\partial V_2}{\partial n} = 0 \quad (36)$$

Substitution from eq 26 yields a cubic equation in n which has no real positive solution. Thus the maximum in χ_h is not an artifact of either the expression (eq 26) for V_2 or the parameter p which does not even feature in eq 36. When we allow for intramolecular contacts, let

$$r = p(n+1)(1-f_n) = p\{1 + (1-k_1)n - k_2n^{1/2}\}$$

Then eq 35 requires that

$$V_2 \left\{ 1 - k_1 - \frac{1}{2} k_2 n^{-1/2} \right\} - \{ 1 + (1 - k_1)n - k_2 n^{1/2} \} \left(\frac{\partial V_2}{\partial n} \right) = 0 \quad (37)$$

in which, again, the parameter p does not appear, but which now suggests the existence of a maximum in χ_h at $n \approx 90$.

DISCUSSION

Quantitative models for the dependence of thermodynamic functions on concentration and molecular chain length are important for our understanding of the behaviour of polymer solutions.²² A model which is already proven² to describe the excess enthalpy of mixing H^E at fixed temperature of solutions of short chain molecules is not expected to apply to longer chain (polymer) molecules because of the occurrence of intramolecular contacts. The work reported here attempts to remedy this by estimating the extent of intramolecular contacting from enumerations over the class of self-avoiding walks in a tetrahedral lattice-graph.

When, as for solutions of n -alkanes in benzene, the contact distribution parameter K is unity, we find that the extent of intramolecular contacting

(as adduced from the unbiased distribution of self-avoiding walks) has only a small effect on the enthalpy of mixing even for long chain molecules.

On the other hand, for the same systems, our analysis predicts a very sensitive dependence of the enthalpic component of the interaction function χ_h on the extent of intramolecular contacting. Regrettably, direct measurements of this quantity for benzene— n -alkane (polymethylene) solutions are not yet available. Clearly such data would be of considerable theoretical importance in interpreting the extent of intramolecular contacts and the use of lattice-graph models for this phenomenon. Certainly this is an essential step toward better understanding the higher derivatives of the Gibbs free energy of mixing function to which so much of polymer technology is related.²²

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