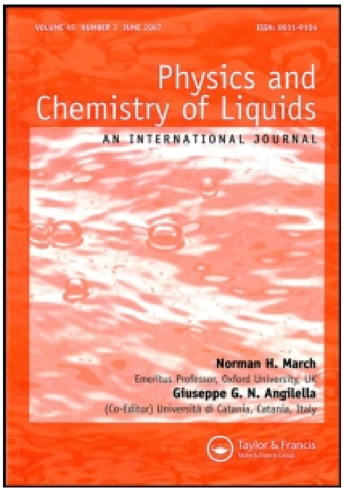

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Properties of Mixtures of Alkane Chains Predicted without Combining Rules

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Methods of predicting excess functions of liquid *n*-alkane mixtures from properties of pure components only are discussed. Some calculations of excess volumes on the basis of the formalism proposed earlier[13] in terms of interactions of walks on graphs are reported. Values of excess volumes at 293.15 K calculated from various approaches are compared among themselves and with the respective experimental data. The theories are evaluated in terms of the assumptions made, application ranges, kinds of data necessary for the calculations and predictive powers.

1 INTRODUCTION

Understanding and prediction of properties of alkanes is important for a number of fields. In polymer industry we have, apart from huge production of polyethylene, various uses of liquid alkanes such as plasticizer of PVC or as flame retardants in plastics, coatings and paints. Other industrial uses include production of biodegradable detergents and lubricant additives. Of course, alkanes—with our without branches—are probably the best model molecules for polymeric chains. Last but not least, alkanes continue to attract attention of liquid state theorists. Monoatomic liquids with spherical force fields are supposedly (although not quite...) understood. A natural next step consists in the study of chain molecules without branches and without specific interactions, that is of normal alkanes.

In the present paper we concentrate on prediction of volumetric properties of liquid *n*-alkane mixture in terms of properties of pure components. A new approach is not proposed; the existing approaches are analysed in terms of the assumptions made, application ranges, kinds of data necessary for the calculation and predictive powers.

2 PREDICTION OF PROPERTIES OF MIXTURES

Typically, properties of mixture are calculated from properties of pure components by using some combining rules. We shall not discuss such rules in any detail here. A detailed revise of the rules has been provided by Kreglewski.[1] Moreover, the most frequently used rules, as well as some promising ones, are discussed in a recent textbook.[2] The conclusion reached[2] is that a single combining rule may work outstandingly well for a particular class of systems, but not necessarily for other systems. Thus, instead of considering relative merits of, say, the geometric vs. the harmonic rule for interaction energies we shall now study only those approaches where the combining rules for *n*-alkane mixtures are *not* necessary.

We shall first consider the theory of the liquid state developed by Flory.[3,4] It is based on the partition function

$$Q = \Omega Q^{fv} Q^{c} \tag{1}$$

where Ω represents the combinatorial contribution; Q^{fv} represents free volume, and is obtainable from experimental values of molar volume V, of isobaric expansitivity $\alpha = V^{-1}(\partial V/\partial T)_P$, where T is the thermodynamic temperature and P pressure, and of isothermal compressibility $\kappa_T = -V^{-1}(\partial V/\partial P)_T$ of pure components; Q^c represents the configurational contribution and for a binary mixtures $i + j$ is expressed in terms of the exchange interaction energy density X_{ij}. The Flory theory has been singularly successful in its applications to organic systems,[3,5] polymer solutions,[4] mixtures of condensed gases,[5,6] extension to liquid metals and alloys,[7] and extension to ternary mixtures of various kinds.[8] In view of the extensive literature on the theory including reviews[4,9] we only quote here the equation for the excess volume

$$V^E = \tilde{v}^E(x_i V_i^* + x_j V_j^*) \tag{2}$$

where

$$\tilde{v}^E = \tilde{v} - \phi_i \tilde{v}_1 - \phi_j \tilde{v}_j, \tag{3}$$

the segment fractions are

$$\phi_i = \frac{x_i V_i^*}{x_i V_i^* + x_j V_j^*}, \tag{4}$$

the quantities with subscripts refer to pure components, those without indices to mixtures, V^* is the hard-core volume, and the reduced volume—whether for a pure component or for a mixture—is

$$\tilde{v} = \frac{V^*}{V} \tag{5}$$

and can be obtained from the isobaric expansivity via

$$\tilde{v} = \left(\frac{\alpha T}{3(1 + \alpha T)} + 1\right)^3 \tag{6}$$

The reduced volume of the mixture $\tilde{v}$ depends on X_{ij}. As discussed by Orwoll and Flory,[10] X_{ij} can be calculated from properties of pure components in terms of interaction energies of end (methyl) and middle (methylene) segments and of the ratio of surfaces s_e/s_m of these two kinds of segments. It turns out, however, that experimental volumetric parameters (V, α and κ_T) of pure hydrocàrbons are not accurate enough for a meaningful prediction of X_{ij}. As noted by Orwoll and Flory[10] "the discrepancies are of no significance except insofar as they serve to call attention to the inadequacy of equation-of-state data, at the level of accuracy attainable, for the specification of these parameters." Therefore, X_{ij} has been obtained from the experimental values of the excess enthalpy H^E and used in a successful prediction of V^E. We observe here an important advantage of the Flory theory of liquids: in absence of sufficiently accurate values for pure components, the energetic parameter X_{ij} has been extracted from calorimetric data, and used to predict functions of mixing of an entirely different kind. In a similar vein, excess enthalpies of binary liquid alloys were used[7] to predict excess volumes; incidentally, in one case, Sn + Ag at 1280 K, the prediction of a s-shaped V^E curve has yet to be tested experimentally.

Another possibility of predicting properties of n-alkane mixtures is based on counting walks on graphs. The one-to-one correspondence between molecules and graphs has been known already in the middle of the XIXth century.[11] Some walks on graphs are redundant from the point of view of molecular properties, therefore interesting walks on graphs have been defined[12] and procedures for counting numbers of such walks derived in terms of adjacency matrices. Then an approach was developed[13] enabling the calculation of properties of components and mixtures in terms of interactions of walks on corresponding graphs. For two kinds, y and y', of interacting units (that is, walks) the molar volume is[13]

$$V = \frac{1}{6NkT} \sum_{y} \sum_{y'} N_y N_{y'} \int R \frac{\mathrm{d}u_{yy'}}{\mathrm{d}R} g_{yy'}(R) 4\pi R^2 \, \mathrm{d}R \tag{7}$$

where N is the total number of interacting units, k is the Boltzmann constant, R the distance between units y and y', $u(R)$ the pair interaction potential and $g(R)$ the pair radial distribution function.

For n-alkanes and for any given length l of walks, two kinds of walks have been taken into consideration, namely the middle and end. For $l = 0$ the walks reduce to single segments, the same as considered by Orwoll and Flory.[10] Since graphs representing n-alkanes are trees without branches (also called snakes), counting interesting walks here is particularly easy. For instance for $l = 2$ Eq. (7) turns here into[13]

$$V = \frac{(r-4)^2}{2(r-2)} V_{mm} + \frac{2}{r-2} V_{ee} + \frac{2(r-4)}{r-2} V_{em} \tag{8}$$

where r is the number of carbon atoms in the molecular while V_{mm}, V_{ee} and V_{em} are characteristic parameters independent of concentration but dependent on temperature. The capability to predict properties of mixtures without using combining rules rests here on the following fact: when mixtures of any number of components are formed, the only kinds of interactions that take place are those already present in pure alkanes. The excess volume is obtainable directly from the definition

$$V^E = V - x_i V_i - x_j V_j \tag{9}$$

Still a different approach to the same problem has been devised by Liebermann and described by him in a paper published nearly simultaneously in two different journals.[14,15] In contrast to the theories characterized above, no statistical mechanics is used and the behaviour at molecular or segmental level is not taken into account; the treatment is purely macroscopic and phenomenological. Liebermann stresses[14,15] that "... it appears desirable to investigate the possibility of deriving a formalism that would allow to express the volume change on mixing in terms of the pure component data." The fact that the problem has been solved at least twice before is not mentioned.

There is one common element in all three approaches under consideration: the use of the Frank[16] formula

$$U_c = -\frac{\varepsilon}{V^n} \tag{10}$$

where U^c is the configurational energy, ε a constant, and n another constant characteristic for a given material. Flory[3] notes that the value of n is usually in the range of 1.0 to 1.5 for non-polar liquids; a formula for n more accurate than those used before has been derived in[13] and applied in some subsequent papers.[17,18] Liebermann[14,15] attributes the present Eq. (10) to Flory (this is inexplicable, since Flory and collaborators[3,19] provide repeatedly references to Frank) and assumes $n = 1$ throughout. This is done for entire molecules, which are anything but spherical. However, this is one assumption of Liebermann such that its validity can be assessed easily. His other assumptions are made for mathematical convenience and their physical significance is obscure. For instance, α/κ_T for the mixture is represented by a Taylor series expansion around the additive (that is ideal) mixture volume V^{id} and terms in powers of V^E higher than the first neglected. Another mathematical assumption is introduced[14,15] "in default of a better approximation.... " At least one assumption seems to involve a contradiction: a parameter m is first characterized as an adjustable one, then its value evaluated for an ideal system, and finally the ideal value adopted for real systems to calculate deviations from ideality. In our notation, the total result of the treatment seems to be

$$\frac{V^E}{V^{id}} = \phi'_i \phi'_j \cdot \frac{\gamma_i - \gamma_j}{4\gamma^{id}} \left[\frac{2(\alpha_i - \alpha_j)}{\alpha_a} - \frac{\kappa_{T_i} - \kappa_{T_j}}{\kappa_{T_a}} \right] \tag{11}$$

where the volume fractions ϕ'_i are defined analogously to segment fractions in Eq. (4) but in terms of molar volumes of pure components instead of hard-core volumes, $\gamma = \alpha/\kappa_T$, $\alpha_a = \phi'_i\alpha_i + \phi'_g\alpha_g$, and κ_{T_a} is defined in the same way as α_a. We have written Eq. (11) in the form given in Ref. 14, as there seem to be some problems with the use of fraction signs in the same equation as spelled out in Ref. 15.

As with any theoretical approaches other than the exact ones, "the proof of the pudding is in the eating." In the following section we provide numerical data enabling us to judge relative merits of various approaches.

3 NUMERICAL CALCULATIONS

In Table I we present experimental V^E values for equimolar binary mixtures of n-alkanes at 293.15 K together with those calculated by various approaches. Numbers of carbon atoms r_i and r_j refer to components.

The values in the table have been grouped into three sets. The first set comprises the alkane pairs for which Liebermann[14,15] has made calculations according to his procedure. We have simply included here for comparison values calculated from interactions of walks for $l = 2$ given in the last column of Table III[13]—something Liebermann could have done easily.

The second set comprises three pairs (6 + 11, 6 + 12 and 7 + 16) for which experimental data are available in sources quoted by Liebermann. Inexplicably, Liebermann has not tested his procedure for these systems. In additions to experiments, for two of these systems (6 + 12 and 7 + 16) values calculated from the Flory theory[10] and from the walk interaction

TABLE I

Excess volumes of equimolar binary *n*-alkane mixtures at 293.15 K

$$\frac{-V^E}{\text{cm}^3\ \text{mol}^{-1}}$$

r_i	r_j	Calc. Orwoll and Flory[10]	Calc. Liebermann[14,15]	Calc. walk interactions[13] $l = 2$	Experim.	Ref. experim.
5	10	—	0.39	0.473	0.418	20
5	16	—	0.77	0.846	0.827	20
					0.82	21
6	10	—	0.21	0.208	0.200	20
6	16	0.56	0.51	0.496	0.493	22
					0.487	23, 24
8	16	0.24	0.18	0.191	0.19	21
10	16	0.10	0.07	0.073	0.073	20
					0.070	21
6	11	—	—	0.268	0.280	25
6	12	0.34	—	0.320	0.31	21
7	16	0.40	—	0.304	0.31	21
5	12	—	—	0.611	—	—
5	15	—	—	0.800	—	—
6	14	—	—	0.416	—	—
7	12	—	—	0.166	—	—
7	15	—	—	0.273	—	—
8	14	—	—	0.139	—	—
9	16	—	—	0.120	—	—
10	15	—	—	0.058	—	—

formalism[13] have been available. The datum for the 6 + 11 pair has been reported[25] later than the paper of Orwoll and Flory[10] and after the publication of the walk interaction formalism.[13] We have now used the V_{ij} parameters given in Ref. 13, to obtain for this pair the value given in column 5 of the table.

The third set of pairs comprises eight systems for which experimental data are not yet available. We have again used here the walk interaction formalism, with the V_{ij} parameters for $l = 2$ given,[13] to predict V^E values for these systems. We hope that somebody will make appropriate experiments to test the present predictions.

4 DISCUSSION

As noted before, the Flory theory of the liquid state[3,4] has been used by Orwoll and Flory[10] to predict V^E of equimolar alkanes, with the interaction parameter X_{ij} obtained from experimental excess enthalpies H_E. Thus, data of a different kind have been used to predict excess volumes, and the agreement between calculation (column 3 in the table) and experiment (column 6) is satisfactory. The capability to predict, in this case, V^E from H^E represents an important advantage of the Flory theory. In this respect, we disagree entirely with Liebermann. Commenting on his final equation (our Eq. (11)) Liebermann says[14,15] that "perhaps, the most important advantage... is that it furnishes V^E independently of other excess functions."

Let us compare now the two approaches in which volumetric properties only are used to predict excess volumes. First, we note that in the walk interaction formalism we have molar volumes of pure components as the only kind of data needed. By constrast, from Eq. (11) we see that the Liebermann procedure requires the use of three kinds of data for pure components: molar volumes V, isobaric expansivities α and isothermal compressibilities κ_T; values of parameters γ are featured also in (11), but these are obtainable from α and κ_T.

Second, we note that the V^E values calculated from interactions of walks agree with the experiments better than those calculated from the Liebermann procedure. There is only one exception to this, namely the 5 + 10 pair. We know, however, that *n*-pentane at room temperature is not far from its boiling point, and therefore quite volatile and relatively difficult to handle. Thus, the experimental value for this system is expected to be less reliable. In principle, the interval of r values for *n*-alkanes which are liquids at room temperature extends from 5 to 16. Significantly, however, the already classic work of McGlashan and collaborators on *n*-alkane pairs,[20,23,26] crowned with finding the change of sign of H_E at elevated temperatures,[27] has been done for the 6 + 16 pair.

We can only conclude that the procedure proposed by Liebermann[14,15] represents a step backwards. Unlike the two other approaches discussed in this paper, it is unrelated to statistical mechanics and does not explain anything at the molecular level. Unlike the Flory theory of liquids, it does not provide any connection to quantities other than volumetric. Physical significance of assumptions and approximations made by Liebermann is obscure. Three kinds of quantities for pure components are needed to calculate excess volumes, while only one kind is required in the walk interaction formalism. As for agreement between calculations and experiment, the Liebermann formula produces no improvement over earlier approaches; the agreement is generally worse than for the walk interaction formalism.

The story based on counting walks on graphs developed in Ref. 13 has then been tested numerically for *n*-alkanes at 293.15 K only. We have now made calculations of liquid state properties at other temperatures too, and these will be reported in a separate paper;[28] among other things, equations representing temperature dependencies of V_{yy}, parameters will be provided.

The same theory has been also successfully used to predict at least one property of *gas* systems, namely the pressure second virial coefficients of hydrocarbons, fluorocarbons and their mixtures.[29]

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