A simple thermodynamic analysis of solid–solution formation in binary systems of homologous extended-chain alkanes

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Binary mixtures of n-alkane chains of comparable length are treated within the Bragg–Williams approximation. A simple model is developed to explain which pairs will form a continuous series of solid solutions (close to their respective melting points). Results are fit very well by the empirical rule that $c_t \leqslant 1.22\,c_s$ ensures such a continuous, mutual solubility. Here, c_t is the number of carbon atoms in the longer alkane and c_s the smaller number. Close analogies are found to the well known Hume–Rothery and Vegard's Law generalizations for metallic systems. The issue of crystal similarity as a requirement for solid solubility is successfully treated as a minor, possibly spurious complication.

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INTRODUCTION

Fractionation during crystallization of polymers is certainly important in determining the solid-state morphology. Qualitative understanding of the factors that control fractionation of mixtures of homologous paraffinic molecules is apparently common[1]; however, quantitative descriptions are lacking. Because of the central importance of the fractionation process, this situation is very unsatisfactory. The elementary case of two-component mixtures of normal alkanes is an attractive one to consider in order to develop this desirable, quantitative understanding.

The qualitative understanding of fractionation, in hydrocarbon systems alluded to above, is largely identical to that for metallic substitutional solid solutions. In metals, pairs of atoms with compatible crystal symmetries will form continuous series of solid solutions if their atomic sizes are comparable and their chemical characters (electronegativity, valence, etc.) similar[2]. Analogously, homologous pairs of alkanes are expected to form continuous series of solid solutions if their chain lengths are comparable and their high-temperature crystal symmetries are compatible. If only the latter requirement is not fulfilled, then at least two series of solid solutions will form: one when the composition is rich in one component and based on its crystal lattice; the other forming from compositions rich in the second component and based on the second, different lattice. Our principal concern in this paper, will be to quantify the critical difference in chain lengths for a binary n-alkane system that will prohibit solid–solution formation. The symmetry-based issue of which systems form continuous solid–solution series and which exhibit a discontinuity due to crystal form incompatibility will be examined less rigorously. The latter point has already been clearly expounded by Mnyukh[3].

The essence of our results is that molecular size and shape dominate the behaviour of condensed phases so completely that only these features need to be carefully modelled. This viewpoint is, of course, not new[4]. However, application of this principle to the solid phases of normal alkanes has been generally neglected in favour of treatments based on surface energies, end effects or similar ideas[1,3,5]. Thus, the present approach has significant conceptual differences from earlier studies. In the next section a rather formal development of the model will be presented. The subsequent discussion endeavours to justify that model.

THEORY

Consider a binary mixture of normal alkanes. Let us distinguish the two types with subscripts s and t that may be construed to stand for 'short' and 'tall', respectively. Let n_i denote the number of molecules of species i, X_i the fractional occurrence of species i, c_i its number of carbon atoms and L_i its length. We shall focus on the solid state of such a system very close to its melting temperature T_M. Thus, we may plausibly and conveniently idealize the molecules to be impenetrable, right-circular cylinders of radius r_i.

Consider the perfect crystal state of one alkane species. We may define this crystal as an array of singly occupied lattice cells; each with volume V_i and coordination number Z_i. Similarly, a lattice denoted with the subscript m will be presumed to define the (possible unstable) solid solution of every binary mixture. By specifying the rules for construction and parameterization of this solution lattice, we shall define a model of the solid state and subsequently deduce its thermodynamic properties.

We shall begin with the well-known Bragg–Williams approximation[6] for the solid–solution lattice. Consequently, we postulate random occupation of the n_m

lattice sites by n_s short and n_t tall molecules without voids $(n_m = n_s + n_t)$. On average this produces $n_s Z_m \dfrac{n_t}{n_m} = Z_m n_m X_s X_t$ unsymmetrical, neighbour–neighbour pairs. To each of these we assign an interaction energy, w, to be specified below. The partition function for the solid solution is therefore

$$\mathscr{Z} = q_s^n q_t^n \frac{n_m!}{n_s! n_t!} e^{-Z_m n_m X_s X_t w / kT} \qquad (1)$$

where q_s and q_t are the single molecule partition functions for the s and t species, respectively, in the m-lattice. The Gibbs free energy per site follows in the usual way from equation (1)

$$G/n_m kT = \frac{-1}{n_m} \ln \mathscr{Z}$$
$$\qquad (2)$$
$$= X_s \ln q_s + X_t \ln q_t + X_s \ln X_s + X_t \ln X_t$$
$$+ X_s X_t (Z_m w / kT)$$

The chemical potential of the ith species obtained from equation (2) is

$$\mu_i / kT = \frac{\partial G}{\partial n_i} = \ln q_i + \ln X_i + (1 - X_i)^2 \frac{Z_m w}{kT} \qquad (3)$$

Let us take the pure crystalline materials at temperature T to be our reference states, and denote these with superscripts, $^\circ$. Then

$$\frac{\mu_i - \mu_i^\circ}{kT} = \ln X_i + (1 - X_i)^2 \frac{Z_m w}{kT} \qquad (4)$$

and the critical conditions of phase stability follow

$$\frac{\partial (\mu_i - \mu_i^\circ / kT)}{\partial X_i} = \frac{1}{X_i} - 2(1 - X_i) \left(\frac{Z_m w}{kT} \right) = 0 \qquad (5a)$$

$$\frac{\partial^2 (\mu_i - \mu_i^\circ / kT)}{\partial X_i^2} = \frac{-1}{X_i^2} + 2 \frac{Z_m w}{kT} = 0 \qquad (5b)$$

Eliminating w from equations (5a) and (5b) yields the familiar critical conditions for solid solution stability in binary regular solutions, viz. $X_i = 1/2$ and

$$w \leqslant 2kT / Z_m \qquad (6)$$

This result depends only on the form of equation (1) which assumes random occupation of lattice sites and pairwise-additive, neighbour–neighbour interaction energy. The task remaining is only to supply a recipe for computing w that is consistent with these assumptions. The following recipe considers size and shape effects to be dominant.

The molecules of interest differ only in the number of methylene groups, $c_i - 2$. If this difference is small, then we may guess $V_s \approx V_m \approx V_t$. In such a situation the difference between like and unlike neighbour–neighbour interactions will be very small; and we shall neglect it entirely. Formally restated then, we shall postulate that there exists a critical number of methylene groups, v, such that for any pair of normal alkanes if $c_t - c_s \leqslant v(c_s, c_t)$, then $w = 0$. The

number v will depend on c_s and c_t, and we shall calculate it as follows. With each alkane there is associated a Van der Waal's volume, a_i. According to Bondi[7]

$$a_i = 6.88 + 10.23 c_i \qquad (a_i \text{ in cm}^3 \text{ mol}^{-1}) \qquad (7)$$

and it follows from this and the projected length per CH_2 group, $p = 1.27 \times 10^{-8}$ cm that

$$L_i = 0.86 + 1.27 C_i \qquad (L_i \text{ in Å/molecule}) \qquad (8)$$

Also, with each alkane we may associate a particular volume per molecule at its melting point. This quantity, taken as equal to V_i at T_M will be computed from

$$V_i(T_M) \equiv V_{Li}(T_M) + \Delta V_{fi} \qquad (9)$$

where V_{Li} is the molar volume of the liquid extrapolated to its melting point and ΔV_{fi} is the volume change on fusion. Values for V_{Li} and ΔV_{fi} are readily available for many n-alkanes[8,9]. We shall define an expansion factor, α_i, by

$$\alpha_i \equiv V_i(T_M) / a_i \qquad (10)$$

The shape of a lattice site is a rather nebulous quantity and we do not wish to specify it explicitly. However, we shall assume that it maintains the same ratio of length to cross-section as the cylindrical Van der Waal's envelope, so that if K_i is the effective length of a site we may write

$$K_i = \alpha_i^{1/3} L_i \qquad (11)$$

The important quantity v will be taken as

$$v \equiv \frac{K_s - L_s}{p} \qquad (12)$$

where $p = 1.27 \times 10^{-8}$ cm; the same value used to arrive at equation (8). Combining equations (8), (10), (11) and (12) gives an expression for the maximum number of carbon atoms in the longer partner that can mix ideally $(w = 0)$ with an alkane possessing c_s carbon atoms:

$$c_t^* = 0.677(\alpha_s^{1/3} - 1) + \alpha_s^{1/3} c_s \qquad (13)$$

Table 1 collects together some of the important parameters of equations (9)–(13) for n-alkanes of modest molecular weight.

If $c_t > c_t^*$ then the Van der Waal's 'length' of the longer alkane partner exceeds the lattice cell 'length' of the smaller partner, and ideal mixing becomes very improbable. Then w must be computed. We shall estimate the energy required to distort the m-lattice just sufficiently to maintain random mixing and identify this as w. Physical justification will be reserved for the Discussion section (see below).

Suppose that $c_t > c_t^*$ and consider a pair of adjacent lattice cells, one with a molecule of species s and the other occupied by t. If the lattice framework is to be continuous, then this juxtaposition requires that the s cell stretch in order to smoothly bound the cell occupied by t. This 'stretching' process is not to be interpreted too literally. One should not imagine a locally expanded lattice along an s–t boundary. The geometrical deformation of the s-lattice site will be delocalized (see Discussion) over an

Table 1 Important parameters for the calculation of w described in the text. Tabulated against the number of carbon atoms of each n-alkane, c, are: T_M, melting point in degrees K; $V(T_M)$ the molar volume at T_M in cm³ mole⁻¹; $\alpha^{1/3}$, the cube root of the expansion factor defined in equation (8); ν, the number of additional carbon atoms tolerable without necessary lattice distortion; and Δ, the maximum ($f = 1$) correction factor to $\alpha^{1/3}$ defined in equation (18)

c	T_M	$V(T_M)$	$\alpha^{1/3}$	ν	$\Delta (f = 1)$
8	216	130	1.14	1.18	1.05
10	244	160	1.13	1.44	1.06
12	264	191	1.14	1.74	1.07
13	268	216	1.16	2.13	1.07
14	279	221	1.14	2.02	1.07
16	291	249	1.14	2.25	1.07
17	295	278	1.15	2.74	1.07
18	301	279	1.14	2.52	1.08
19	305	308	1.15	2.99	1.08
22	318	355	1.15	3.47	1.08
24	324	388	1.15	3.80	1.08
28	335	450	1.15	4.42	1.08
32	343	515	1.15	5.06	1.09

Table 2 Values of c_t, Δ and the parameters necessary for its computation according to equations 16, 17 and 18 in the text. Expansion data was taken from the polyethylene study of Davis et al.[17] with the crystalline long period, l_2 in Å, obtained in each case from equation 8. The tabulated values of Δ and c_t were computed with $f = 1/2$. Differences between the computed values of $V(T_M)$ in Column 2 and the experimental values appearing in column 3 of Table 1 are discussed in the text (see Discussion)

c	$L = l_2$	$V(T_M)$	$\dfrac{dV}{dT} \cdot 10^2$	$\dfrac{1}{3V}\dfrac{(dV)}{dT} \cdot 10^4$	$\Delta (f = 1/2)$	$c_t \ (f = 1/2)$
8	11.0	113	4.15	1.22	1.03	9.5
10	13.6	142	5.41	1.27	1.03	11.7
12	16.1	171	6.60	1.29	1.03	14.2
13	17.4	185	7.06	1.27	1.03	15.7
14	18.6	200	7.74	1.29	1.04	16.7
16	21.2	229	8.85	1.29	1.04	19.3
17	22.4	243	9.35	1.28	1.04	20.5
18	23.7	258	9.94	1.29	1.04	21.5
19	25.0	272	10.5	1.28	1.04	22.9
22	28.8	316	12.1	1.28	1.04	26.4
24	31.3	345	13.2	1.28	1.04	28.8
28	36.4	402	15.4	1.27	1.04	33.6
32	41.5	460	17.5	1.27	1.04	38.4

appreciable volume. However, our model postulates that in the hypothetical, step-wise process of (1) random mixing of s and t species on the s-lattice, (2) local lattice deformation to maintain continuity, (3) delocalization of the deformation to produce the final m-lattice, that only the second step makes an appreciable energy contribution to the total free energy. Because the geometrical change is imagined to be delocalized in the final m-lattice the same energy contribution is made by each s–t pair irrespective of the occupancy of other neighbouring sites. Furthermore, the energy that accompanies the initial local distribution will be viewed as a thermal effect that eventually reequilibrates over the entire lattice and raises its internal energy. Thus

$$w = \frac{k\varepsilon}{Z_m}\left(\frac{d\varepsilon}{dT}\right)_s^{-1} \tag{14}$$

where ε is the initial, local strain ($\Delta K_s/K_s$), T is the absolute temperature, $(d\varepsilon/dT)_s$ is the linear thermal expansion coefficient of the s-lattice and k is Boltzmann's constant. The minimum strain required is given by

$$\varepsilon = \frac{L_t - K_s}{K_s} \tag{15}$$

An *upper bound* on $(d\varepsilon/dT)_s$ is one-third of the volume

thermal expansion coefficient at the melting point of the pure s-alkane. It is an upper bound, since most of the requisite initial distortion will be in the direction of the extended, alkane axis and this crystal axis is known[10] to be far less sensitive to temperature than the perpendicular axes. For lack of better data, and in view of the simple model in hand, we shall set

$$\left(\frac{d\varepsilon}{dT}\right)_s = f\left[\frac{1}{3}\left(\frac{dV}{VdT}\right)_s\right]_{T = T_M} \tag{16}$$

where f is an adjustable parameter obeying $0 \leqslant f \leqslant 1$. It follows from equations (6), (8), (11), (14) and (15) that solid solutions are expected when

$$c_t \leqslant 0.677[\alpha_s^{1/3}(1 + 2T(d\varepsilon/dT)_s) - 1] + \alpha_s^{1/3}c_s(1 + 2T(d\varepsilon/dT)_s) \tag{17}$$

The form is directly comparable to equation (13); with the only change being the appearance of a new factor

$$\Delta \equiv 1 + 2T(d\varepsilon/dT)_s \tag{18}$$

that multiplies each appearance of $\alpha_s^{1/3}$. Parameters required by equation (16) are collected in *Table 2*[17], and values for Δ are also reported in *Table 1*. The loci of solutions to equations (13) and (17) are plotted in *Figure 1*.
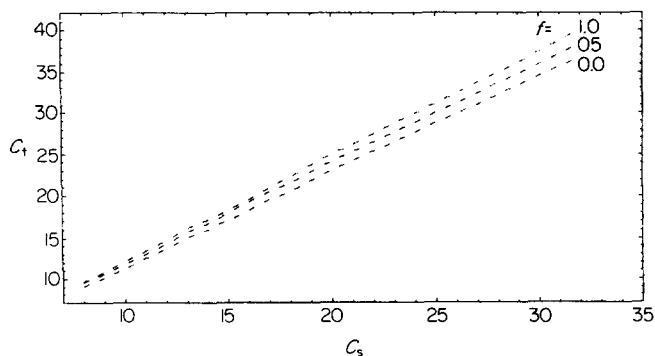
Figure 1 Loci of solutions to equation (17) are displayed for various assumed values of the parameter f. The locus with $f=0$ is, of course, the set of solutions for equation (13)
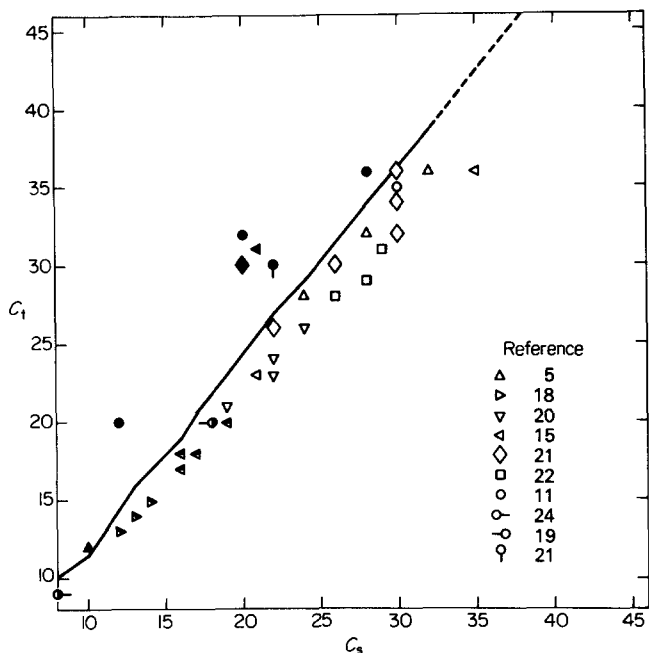
Figure 2 Loci of solutions to equation (17) using the parameters tabulated in *Table 2* ($f=1/2$) is compared to some available data. Filled symbols denote systems that show crystal–crystal phase separation; open symbols correspond to continuous solid solution behaviour; and half-filled symbols represent systems with discontinuous solid solutions

RESULTS AND DISCUSSION

One criterion for the acceptability of the model at hand is its success in correlating experimental results. Some of the available literature data is compared to the theoretical line using $\Delta(f=1/2)$ in *Figure 2*. There can be no question that the predicted demarcation between miscible and immiscible solid phases is consistent with the data presented. However, the tabulation is incomplete. An exhaustive comparison to both previously published work and some new experimental results is being prepared[11]. That comparison reinforces the good agreement sketched in *Figure 2*.

Other aspects of the current model are similarly attractive. The empirically observed values of $\alpha^{1/3}$ (see column 4 of *Table 1*) are sensibly constant and $c_i^* \equiv \alpha_s^{1/3} c_s \approx 1.15 c_s$. This is gratifying because it recapitulates the empirical rule of Hume–Rothery[12] that limits the atomic size disparity of metals which form solid solutions. In our model, the fully extended molecular length of the n-alkanes is the characteristic length that

plays the same role as atomic diameter in metallic solutions. Less quantitatively, our model possesses a close relationship to Vegard's Law[13]. This empirical observation asserts that a characteristic lattice dimension should increase linearly with the mole fraction of the larger species in a binary solid solution. Although this is not explicitly incorporated in our model, it is certainly suggested by and consistent with our picture of the necessary, delocalized distortion of the *m*-lattice as it accommodates more of the *t*-species. Thus, the methods of parameterizing and calculating model-required quantities possess striking similarities to simple empirically established rules for metallic systems.

Also, it may be observed (see *Figure 1*) that the only 'adjustable' parameter in our model, f, does not have a large, quantitative role to play. The very loose, indeed, it is arguably a ludicrously weak upper bound of $f=1$ only changes the correction factor, Δ, by 10% from its value at $f=0$ (see column 6 of *Table 1*). Evidently, a careful estimate of Δ, hence w, is not required.

It was mentioned in the Introduction that the necessity of matching the symmetries of the respective crystal lattices is a complicating feature of binary n-alkane solid solutions. It is a rather uninteresting complication for most of the chain lengths analysed here; and certainly so for larger molecular weights. The facts[14] are that for $c_i \geqslant 44$ all alkanes melt from an orthorhombic crystal. Consequently, the question of crystal compatability is moot for these chains. For n-alkanes defined by a number of carbon atoms in the range $9 \leqslant c_i \leqslant 43$, all melt from a closely related, hexagonal, 'rotator' phase except those with even numbers in the range $10 \leqslant c_i \leqslant 32$. The dozen alkanes in this latter group exhibit high temperature crystal symmetries of the triclinic $(10 \leqslant c_i \leqslant 22)$, monoclinic (28, 30) or undefined (24, 26) variety. Thus, only for binary mixtures in which at least one of the components falls into this latter group is the question of crystal-symmetry even relevant. Moreover, for all of the n-alkanes $(c_i \gtrsim 8)$ the high temperature crystal phase exhibits an orthorhombic sub-cell similar to that found in polyethylene[1]. Thus, in a crude but suggestive approximation, one might consider all of the n-alkane solids very close to their respective melting points to be crystals with rather high densities of thermal and chain-end defects. From this point of view, it is obvious that the occasional failure to observe continuous solid–solutions for symmetry reasons[3,15] is an inconclusive result. Kinetic factors and details such as material purity and homogeneity will assume major importance. These issues are addressed more fully in the accompanying paper. Here, we wish only to justify passing over the complication of crystal compatibility. It is not important for large molecular weight alkanes $(c_i \geqslant 33)$, to which we now direct attention.

The critical curve displayed in *Figure 2* is very nearly linear. Let us extrapolate this line to longer alkanes and inquire about its predictive power. An empirical fit gives

$$c_N^{max} = 1.224 c_N^{min} - 0.411$$

with a correlation coefficient of 0.9999. Disregarding the trivial constant, we conclude that our extrapolation suggests that continuous solid solubility is assured for binary extended-chain polyethylene systems in which the molecular weights differ by less than about 22% of the smaller chain.

The physical rationale for our model rests on the

dominant role played by the repulsive side of inter-molecular potentials in determining the structure of condensed phases. The same rationale appears in some of the recent, successful approaches to liquid structure[4,16]. Particularly in the method used to estimate w, this viewpoint permits us to keep calculations simple. Under the presumption that expansion of the lattice is much less expensive in free-energy terms than compression of molecular Van der Waal's envelopes, it suffices to estimate only the former in order to account for the energetic effects of excessive molecular crowding. Similarly, the presumption of rather weak and reasonably nondirectional attractive forces between molecules results in a consistent picture of delocalized crystal-defects for the ill-matched solid solutions. Of course, these approximations are extreme; almost caricatures of the physical situation. Nevertheless, they are justified as expedient and semi-quantitatively successful simplifications.

In conclusion, we have found that a very simple scheme can successfully predict which pairs of n-alkanes will form a series of solid solutions. The scheme focuses solely on geometrical factors and presupposes regular solution behaviour. The single adjustable parameter in the model, f, is bounded in the range between 0 and 1; and the results are very insensitive to the fractional value chosen. We have used $f = 1/2$. It is apparently unnecessary to invoke surface energies, or the like, although one could obviously generate a parameterized form for the quantity w by doing so. Application of the concepts introduced here to the problems of fractionation and morphology in truly polymeric n-alkane systems is a topic for future work.

REFERENCES

1   Wunderlich, B. Macromolecular Physics, Vol. 3, Academic Press, New York, 1976
2   Darken, L. S. and Gury, R. W. Physical Chemistry of Metals, McGraw-Hill, New York, 1953, Ch. 4
3   Mnyukh, Yu. V. *J. Struct. Chem. (USSR)* 1960, **1**, 346
4   Longuet-Higgins, H. C. and Widom, B. *Mol. Phys.* 1964, **8**, 549
5   Asbach, G. I. and Kilian, H. G. *Ber. Bunsen. Gesel.* 1970, **74**, 814
6   Bragg, W. L. and Williams, E. J. *Proc. Roy. Soc.* 1934, **A145**, 699
7   Bondi, A. *J. Phys. Chem.* 1964, **68**, 441
8   Dreisbach, R. R. Physical Properties of Chemical Compounds, Adv. in Chemistry Series No. 22, 11, 1959
9   Bondi, A. Physical Properties of Molecular Crystals, Liquids and Glasses, John Wiley and Sons, Inc., New York, 1968
10   Vand, V. *Acta Crystallogr.* 1953, **6**, 797
11   Smith, P. and Matheson, Jr., R. R. manuscript in preparation
12   Hume-Rothery, W., Mabbott, G. W. and Channel Evans, K. M. *Phil. Trans. Roy. Soc.* 1934, **A233**, 1
13   Vegard, L. *Z. Physik.* 1921, **5**, 17
14   Flory, P. J. and Vrij, A. *J. Am. Chem. Soc.* 1963, **85**, 3548
15   Mazee, W. M. *Anal. Chim. Acta* 1957, **17**, 97
16   Anderson, H. C., Chandler, D. and Weeks, J. D. *Adv. Chem. Phys.* 1976, **34**, 105
17   Davis, G. T., Eby, R. K. and Martin, G. M. *J. Appl. Phys.* 1968, **39**, 4973
18   Sobzgeber, R. *Compt. Rend.* 1955, **240**, 1642
19   Kitaigorodskii, A. I., Mnyukh, Yu. V. and Nechitailo, N. A. *Kristallografiya* 1958, **3**, 298
20   Mazee, W. M. *Erd. u. Kohle* 1960, **13**, 88
21   Nechitailo, N. A., Topchiev, A. V., Rozenberg, L. C. and Terenteva, E. M. *Z. Fiz. Khim.* 1960, **34**, 2694
22   Mazee, W. M. *Anal. Chem.* 1970, **74**, 814