

Solid-liquid equilibrium of n-alkanes using the Chain Delta Lattice Parameter model

João A. P. Coutinho, Simon I. Andersen and Erling H. Stenby

Engineering Research Center, IVC-SEP, Department of Chemical Engineering, Bldg. 229
Technical University of Denmark, 2800 Lyngby, Denmark

ABSTRACT

The formation of a solid phase in liquid mixtures with large paraffinic molecules is a phenomenon of interest in the petroleum, pharmaceutical, and biotechnological industries among others. Efforts to model the solid-liquid equilibrium in these systems have been mainly empirical and with different degrees of success.

An attempt to describe the equilibrium between the high temperature form of a paraffinic solid solution, commonly known as rotator phase, and the liquid phase is performed. The Chain Delta Lattice Parameter model (CDLP) is developed allowing a successful description of the solid-liquid equilibrium of n-alkanes ranging from n-C₂₀ to n-C₄₀.

The model is further modified to achieve a more correct temperature dependence because it severely underestimates the excess enthalpy. It is shown that the ratio of excess enthalpy and entropy for n-alkane solid solutions, as happens for other solid mixtures, is related with the values of the melting temperatures by a function common to the entire homologous series. When applied to systems with a symmetric behavior, this yields a correct description of both the enthalpic and entropic parts of the excess Gibbs free energy with the CDLP model.

Further considerations about the pressure dependence of the model are also made showing that the model presented can be applied to pressures as high as 100 bar.

1. INTRODUCTION

The ability to describe the solid-liquid equilibrium (SLE) in mixtures of large paraffinic molecules is of immense importance in fields like petroleum technology, pharmacy and biotechnology both in a direct approach like for the study of wax formation in petroleum fluids as for understanding the behavior of molecules with large alkyl groups like components of cellular membranes and fatty acids.

The n-alkanes larger than n-C₂₀ experience a phase transition in the solid phase. The high temperature solid phase, known as rotator phase due to the capacity of the chain molecules to rotate around their axis, has a hexagonal crystalline structure and exists within a few degrees below the freezing point. Upon further cooling, the molecules will rearrange themselves in other, more stable, crystalline structures, developing the low temperature solid phase. A true thermodynamical equilibrium exists between the two solid phases.

The thermodynamic modeling of solid-liquid equilibrium is based on Eq. (1) [1].

$$\ln \frac{s \gamma^s}{x \gamma^l} = \frac{h_m}{RT_m} \left(\frac{T_m}{T} - 1 \right) + \frac{h_r}{RT_r} \left(\frac{T_r}{T} - 1 \right) - \frac{\Delta C p_m}{R} \left(\ln \frac{T}{T_m} + \frac{T_m}{T} - 1 \right) \quad (1)$$

This equation relates the composition in both solid and liquid phases, *s* and *x*, with the nonideality of these phases, γ^l and γ^s , and the thermophysical properties of the pure components present in solution. These

last properties are known for most compounds and can be easily found in the literature. The challenge in the description of SLE lies in the capacity to describe the nonideality of the phases in presence. Coutinho et al. [2] found the Flory-free volume to be a good model for the description of a liquid mixture of saturated hydrocarbons in equilibrium with a solid phase. They showed that it can describe the phase behavior of mixtures of branched and linear alkanes even for large differences in molecular size. In systems of saturated molecules only the nonideality of the solid phase remains to be modeled.

This work will focus on the development of a model that can describe the nonideality of the high temperature solid phase of alkanes ranging from about n-C₂₀ to n-C₄₀. Its ability to represent the equilibrium between the liquid and the rotator phases in n-alkane systems is demonstrated. The temperature and pressure dependence of this model are also studied and an alternative form with a more correct temperature dependence is presented.

2. MODEL

The data available for excess enthalpies in solid solutions [3-5] indicate that these have a symmetric behavior. This is not unexpected attending the crystallographical description of the rotator phase and it can be understood if a statistical thermodynamical description is attempted.

Crystallographical analyses show that the rotator phase can be roughly described as a layered structure formed by a hexagonal packing of aliphatic chains rotating as rigid rods around their long axis [6]. Recent studies picture a somewhat more complex behavior but the idea of the hexagonally packed rods remains accurate enough for the purposes of this work [7-8].

A solid solution lattice can be used to describe this system. In short and following the Bragg-Williams approximation [9] a random occupation of n_m sites in a lattice by n_s short and n_l long molecules is considered. An interaction energy, w , is assigned to each neighbor-neighbor interaction. The partition function for the solid solution is

$$Z = q_s^{n_s} q_l^{n_l} \frac{n_m!}{n_s! n_l!} \exp\left(\frac{-Z_m n_m X_s X_l w}{kT}\right) \quad (2)$$

Where q_s and q_l are the single molecule partition functions, Z_m the coordination number and X_i the fractional occurrence of species i . Using standard thermodynamics the excess Gibbs free energy is derived.

$$g^E = Z_m N w x_l x_s = \Omega x_l x_s \quad (3)$$

where N is the Avogadro number, and x_l and x_s are the molar fractions of the long and short alkane respectively. If the interaction energy, w , is considered to be temperature independent the model will be an enthalpic model with a zero excess entropy.

This simple symmetric model seems to be able to describe the experimental phase diagrams for mixtures of long chain n-alkanes. The parameter Ω , however, would be system dependent.

Molecules of n-alkanes differ only in the chain length, therefore the interaction energy for the different pairs should only be dependent on their differences in size. A method to equate the variation of interaction energy with molecular size is used in the Delta Lattice Parameter model. This model first presented by Stringfellow [10] for inorganic compounds like alloys and semiconductors relates the interaction energy with the crystal lattice parameters. A similar procedure, but applied to long chain molecules, will be followed here.

2.1. Chain Delta Lattice Parameter

The temperatures and heats of melting of n-alkanes are asymptotic functions of the chain length. Let us assume that the heat of melting can be related with the molecular size l by an equation with the form:

$$h_m = \frac{k l}{l + b} \quad (4)$$

The excess enthalpy of the solid phase is related to the heats of melting by:

$$h^E = x_1 h_{ml}^o(l_1) + x_2 h_{ms}^o(l_2) - h_m^{mix}(l^{mix}) \quad (5)$$

and should be equivalent to Eq. (3) if the symmetric behavior and zero excess entropy previously assumed are valid.

The cell length parameter for the mixture is presumed to follow the Vegard's law

$$l^{mix} = x_1 l_1 + x_2 l_2 \quad (6)$$

Notice that the use of Vegard's law presupposes a zero excess molar volume for the mixture.

The parameter Ω may be obtained comparing the results from Eqs. (4)–(6) with Eq. (3) for $x=0.5$,

$$\Omega = \frac{2kl_1}{l_1 + b} + \frac{2kl_2}{l_2 + b} - \frac{4k(l_1 + l_2)}{(l_1 + l_2) + 2b} \quad (7)$$

meaning that Ω is only a function of the pure components chain length. Expanding Eq. (7) in series around l_s and neglecting the terms of higher order yields for l_s larger than b :

$$\Omega = \Theta \frac{(l_1 - l_2)^2}{l_s^3} = \Theta \Psi \quad (8)$$

Introducing this result in Eq. (3) a model for excess enthalpies and/or Gibbs free energies for n-alkane mixtures is obtained.

$$g^E = h^E = \Theta \frac{(l_1 - l_2)^2}{l_s^3} x_1 x_2 \quad (9)$$

Using just one parameter, Θ , it should then be possible, according to this model, to describe the non ideality of the high temperature solid phase in the entire range of chain lengths for n-alkane molecules.

A similar result based on the same assumptions of zero excess volume and entropy was achieved through a completely different procedure by Williamson and Scott [11]. In their work the authors, using as departure points either the van der Waals equation or the zeroth approximation of Guggenheim's lattice model, arrive to U^E equations in which the Ω parameter has a similar molecular size dependence.

3. RESULTS

The conclusions of the previous section suggest that it should be possible to describe the solid-liquid equilibrium in n-alkane systems by using the excess Gibbs energy model described by Eq. (9). To test the model capacities and to calculate the parameter Θ , a data base of SLE for n-alkane systems ranging from about n-C₂₀ to n-C₄₀ was collected. After a preliminary quality analysis of the data the systems considered reliable were correlated using Eq. (1). The thermophysical properties used were obtained from Broadhurst [12]. The Flory-free volume model [2] was used for the description of the liquid phase and the proposed model for the solid phase. The parameter Ω was estimated using a modified Marquardt optimization procedure where the objective function

$$F_{obj} = \sum (T_{calc} - T_{exp})_{solidus}^2 + \sum (T_{calc} - T_{exp})_{liquidus}^2 \quad (10)$$

was minimized. Solidus refers to the melting point and liquidus to the freezing point lines.

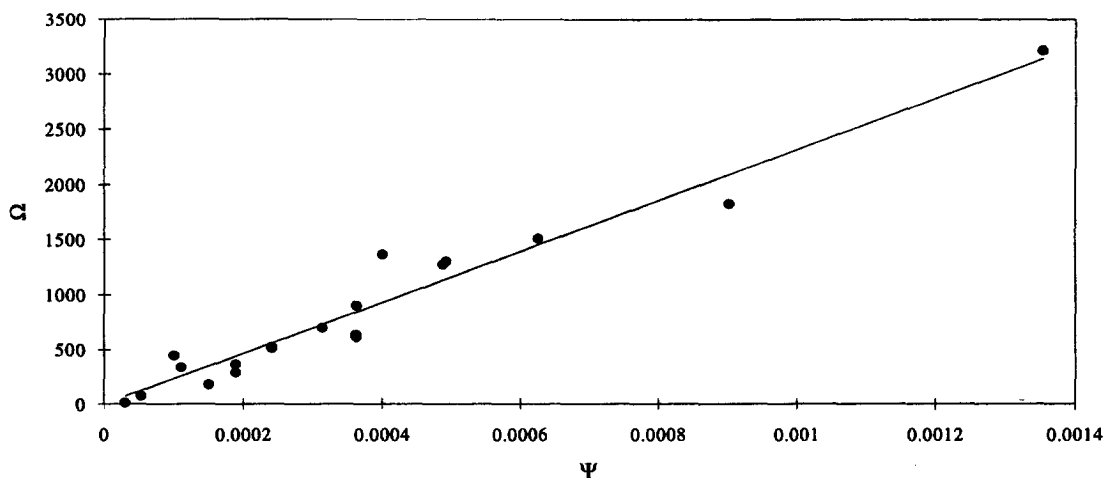


Fig. 1. Correlation of the parameter Ω [J/mol] with the size dependence function Ψ [\AA^{-1}].

The lengths of the crystalline cell (l) were obtained from Broadhurst [12]. The Θ parameter is assessed by a linear correlation of the data also presented in the figure. A value of $\Theta = 2317$ kJ \AA^{-1} /mol was obtained.

The ability of the model to provide a good description of the equilibrium between a liquid and a rotator phase is shown in Figs. 2a-b. Here experimental data are compared with the results obtained using the CDLP model and the ideal solution approximation in the solid phase. Considering the solid solution as ideal clearly results in a very poor description of the SLE behavior.

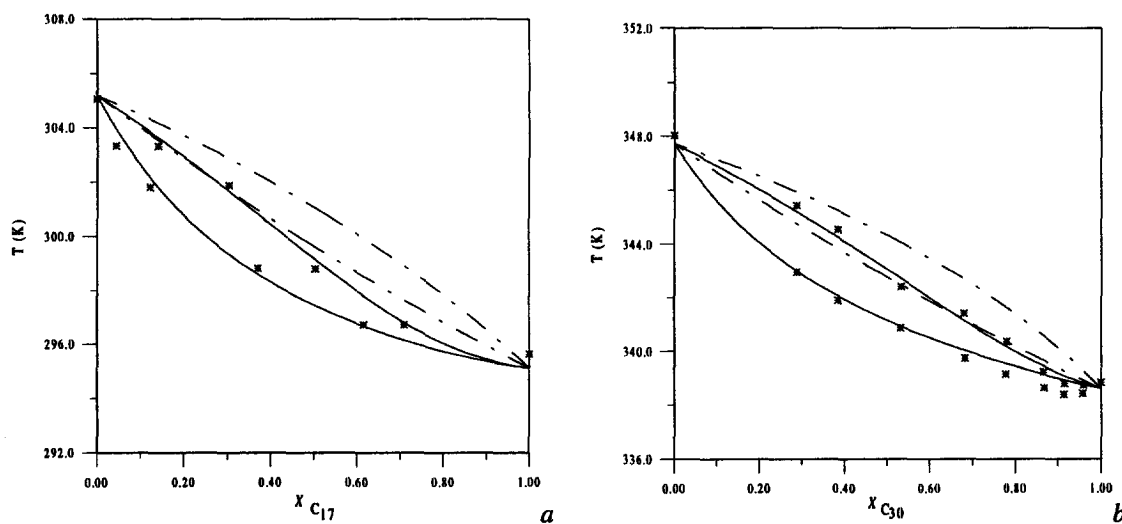


Fig. 2. Experimental and calculated phase equilibria for the systems: a) $n\text{-C}_{17}\text{H}_{36}/n\text{-C}_{19}\text{H}_{40}$ [13] and b) $n\text{-C}_{30}\text{H}_{62}/n\text{-C}_{35}\text{H}_{72}$ [14]. The CDLP results in solid line and the ideal solid solution approximation in dashed line.

4. TEMPERATURE DEPENDENCE

The CDLP model presented can successfully describe the excess Gibbs free energy for solid solutions of n-alkanes. Eq. (9) is, however, based in the hypothesis of a negligible excess entropy. If the hypothesis about s^E does not hold, both the s^E and h^E will be wrongly estimated in spite of the capacity of the model in what relates to g^E . A wrong value for h^E leads to a poor temperature dependence. In the liquid phase an incorrect excess enthalpy is not usually a difficulty because generally its value is not very large and thus a model can be used within a fair temperature range without problems. The solid phase models have to be able to cover large temperature ranges. As a result a model with a poor temperature dependence will perform poorly at temperatures removed from its validity domain.

The available experimental data for excess enthalpies of n-alkanes solid solutions are scarce. Only the data on the systems n-C₁₉/n-C₂₁ [3-4] and n-C₂₄/n-C₂₆ [5] will be considered here. The remaining data available in the literature are of poor accuracy.

A comparison between the experimental values of h^E and the values predicted by the CDLP model was performed to evaluate the accuracy of the temperature dependence. The results presented in Table 1 denote experimental values that are up to 30 times larger than the predicted! The effect of such an excess enthalpy difference on the activity coefficients at different temperatures is presented in Table 2 for the system n-C₁₉/n-C₂₁. Within a temperature range as narrow as 20 K, the activity coefficients calculated using the experimental h^E values show a variation that cannot be matched by the CDLP model. These results show that the hypothesis of negligible s^E is not valid and assert the importance of a correct h^E description in the alkane solid phase. The proper description of the excess Gibbs free energy, as the comparison of the calculations with experimental data suggests, does not imply that $s^E=0$ and $g^E=h^E$ as was assumed but that $Ts^E=h^E$. This indicates that an equation similar to Eq. (9) can be used to describe the solid-liquid equilibrium but cannot be applied to temperatures different from those around the melting point of the pure components being therefore of limited interest.

Table 1
Experimental and calculated h^E for $x=0.5$

System	h_{exp}^E (J/mol)	h_{calc}^E (J/mol)
n-C ₁₉ /n-C ₂₁	6700	222
n-C ₂₄ /n-C ₂₆	2234	110

Table 2

$\ln \gamma^{\infty}$ (T) for n-C₁₉/n-C₂₁

T (K)	$\ln \gamma^{\infty} (h_{\text{calc}}^E)$	$\ln \gamma^{\infty} (h_{\text{exp}}^E)$
305	0.3668	0.3668
285	0.3925	1.108

Nevertheless, keeping the use of a simple symmetric model, there seems to be a way to describe accurately g^E , h^E , and s^E simultaneously.

The experimental data show a symmetric behavior for h^E . The phase equilibrium data require a similar trend for g^E implying that s^E should also be approximately symmetrical given the narrow temperature range in these phase diagrams. It should thus be possible to represent the three excess properties by Margules type equations. Tanaka et al. [15] have, based on statistical thermodynamical considerations, shown that for solids:

$$\frac{h^E}{s^E} = \alpha \frac{T_{ml} T_{ms}}{T_{ml} + T_{ms}} = \alpha \phi \quad (11)$$

where α should be approximately constant for similar systems. Later Tanaka [16] extended the validity of this relation to solids. This relation was first applied to liquid to alloys but Oonk and co-workers [17] have shown that it can be used with organic solids with each family of compounds presenting a characteristic value of α . If it holds also for n-alkanes it should then be possible to represent g^E , s^E and h^E simultaneously by:

$$g^E = \Theta \frac{(l_l - l_s)^2}{l_s^3} \left(1 - \frac{T}{\alpha \phi} \right) x_l x_s \quad (12)$$

where ϕ represents the melting temperature function.

There are two approaches that can be followed in the calculation of α , the first relies on h^E experimental data and on the experimental phase diagram, the other uses Eq. (12) and estimates the parameters α and Θ' through a procedure similar to the previously described using the new model for the solid phase.

The first approach was applied to the two systems for which experimental excess enthalpy data were available. Using the experimental data, assuming h^E to be temperature independent, and using the CDLP model to obtain g^E , the value of s^E at the melting point of the light component was calculated for each system and from this the corresponding values of α were obtained as presented in Table 3.

Table 3
Values of α from experimental h^E

System	α
n-C ₁₉ /n-C ₂₁	2.05
n-C ₂₄ /n-C ₂₆	2.08

Table 4
Estimated values for the parameters in Eq. (12)

α	2.055
Θ' [KJ Å/mol]	67614

The second method was also applied to the SLE data available. Through an optimization procedure similar to that previously described, the parameters α and Θ' were estimated and are presented in Table 4. The value of α obtained by the two methods is remarkably similar. Since the two procedures use different properties to estimate the value of α this similarity is a good indication that the excess enthalpy is correctly described.

The introduction of a temperature dependence in the model (Eq. (12)) improves the temperature independent version (Eq. (9)) but in consequence of the small temperature range present in the phase diagrams the improvement is not always very important. The temperature dependent version should provide a much better description of the phase equilibria at temperatures far from the melting temperatures of the pure components as happens in ternary or multicomponent mixtures where the solvent is a low molecular weight alkane or in the description of the solid-solid equilibrium between the rotator phase and the solid phase present below the solid phase transition point.

5. PRESSURE DEPENDENCE

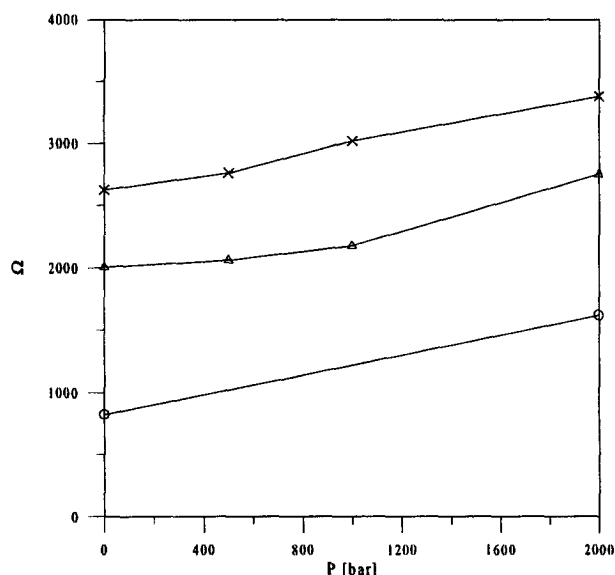


Fig. 3. Pressure dependence of Ω [J/mol] for the systems n-C₂₄/n-C₂₈ (o), n-C₂₄/n-C₃₀(Δ), and n-C₂₆/n-C₃₂(x).

The thermophysical properties of n-alkanes have been measured up to 3000 bar [3,18]. These authors have also measured the phase equilibrium for a few systems at high pressures. The data indicate that the effect of pressure on both the thermophysical properties and nonideality of solid phase is small at moderate pressures: The enthalpies of phase transition have a variation of only 10% up to 3000 bar and the melting and transition temperatures increase only about 2K within 100 bar. The phase behavior data by Hohne and Blankenhorn [18] were correlated using Eq. (3) at several pressures and the pressure dependence of Ω is shown in Fig. 3. The nonideality of the solid phase shows a slight and approximately linear increase with pressure. Ω changes less than 15% up to 1000 bar thus the variation between 1 and 100 bar

will be inferior to 2%. It seems then reasonable to conclude that the model can be applied without further corrections at moderate pressures up to 100 bar and that Vegard's law used in the derivation of the Delta Lattice Parameter model holds for n-alkane solid solutions.

6. CONCLUSIONS

The Chain Delta Lattice Parameter model is proposed for n-alkane systems. The model is able to describe the solid-liquid equilibria in paraffins mixtures, with molecules in the solid phase ranging from about n-C₂₀ to n-C₄₀, with only one parameter.

The capacity of the model to describe the influence of temperature and pressure was evaluated. The former was found to be rather poor. A temperature dependent version of the CDLP model was developed based on a ratio of the excess enthalpy and entropy characteristic of the homologous series. An analysis of solid-liquid phase behavior shows that it is almost pressure independent and thus the model is expected to be valid up to 100 bar.

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LIST OF SYMBOLS

C _p	heat capacity
g	Gibbs free energy
h	enthalpy
l	molecular chain length
N	Avogadro number
s	entropy
s	solid phase molar fraction
T	temperature
x	liquid phase molar fraction
Z	coordination number

Greek letters

α	parameter in Eq. (11)
γ	activity coefficient
Θ	binary parameter in Eq. (9)
Ω	binary parameter in Eq. (3)

Indices

cal	calculated
E	excess property
exp	experimental
l	liquid phase
l	long molecule
m	melting point
o	pure component

s	solid phase
s	short molecule
tr	transition point

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