



Molecular structure stability of short-chain chlorinated paraffins (SCCPs): Evidence from lattice compatibility and Simha–Somcynsky theories



A. Yumak^{a,*}, K. Boubaker^b, P. Petkova^c, U. Yahsi^a

^a Physics Department, Faculty of Arts and Sciences, Marmara University, 34722 Göztepe, Istanbul, Turkey

^b Unité de physique des dispositifs à semi-conducteurs, Tunis EL MANAR University, Tunisia

^c Shumen University “Konstantin Preslavsky”, 115 Universitetska street, 9712 Shumen, Bulgaria

ARTICLE INFO

Article history:

Received 16 April 2015

Received in revised form

1 June 2015

Accepted 2 June 2015

Available online 4 June 2015

Keywords:

Short-chain chlorinated paraffins

LCT

Simha–Somcynsky theory

Free volume

Hole fraction

Thermo-occupancy function

ABSTRACT

In is known that short-chain chlorinated paraffins (SCCPs) are highly complex technical mixtures of polychlorinated n-alkanes with single chlorine content. Due to their physical properties (viscosity, flame resistance) they are used in many different applications, such as lubricant additives, metal processing, leather fat-liquoring, plastics softening, PVC plasticizing and flame retardants in paints, adhesives and sealants. SCCPs are studied here in terms of processing-linked molecular structure stability, under Simha and Somcynsky-EOS theory calculations and elements from Simha-Somcynsky-related Lattice Compatibility Theory. Analyses were carried out on 1-chloropropane, 2-chloropropane, 1-chlorobutane, 2-chlorobutane, 1-chloro 2-methylane, and 2-chloro 2-methylane as (SCCPs) universal representatives. This paper gives evidence to this stability and reviews the current state of knowledge and highlights the need for further research in order to improve future (SCCPs) monitoring efforts.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

n-Paraffin (kerosine) is a chemical mixture of hydrocarbons containing from a few to 16 carbon atoms per molecule. This mixture has a relative density and a boiling temperature in [0.76–0.85] and [140–320 °C] range, respectively [1–5]. n-Paraffin compounds are obtained from crude oil by distillation and are used as a fuel for heating and aircraft. They can be mainly classified either in straight chains (normal paraffin) or branched chains (iso-paraffin).

Most paraffin chains are natural, but iso-paraffins are mostly synthetic. The latter is a good engine-combustion initiator. Longer-chain paraffins constitute waxes and are used for a wide range of applications as solvents, basic material for surfactants manufacturing, oils for aluminum cold rolling, lube oil components, carrier for olefin polymerization and plasticizers [6,7].

Short-chain chlorinated paraffins (SCCPs) are highly complex technical mixtures of polychlorinated n-alkanes with carbon-chain lengths in the range of <10–13> and chlorine content between 49 and 70%. They are produced by chlorination of n-alkanes and do not occur naturally. Their interesting physical properties (viscosity, flame resistance) enabled their use in many different applications, such as lubricant additives, PVC plasticizers and flame retardants in paints, adhesives and sealants.

For example, chlorinated high purity molecular sieved n-paraffins (Polychlorinated n-alkanes (PCAs)) as chlorinated waxes are good plasticizers for polyvinyl chloride (PVC) with light colors, low viscosity and good thermally stability. Their properties depend on both chlorine content and carbon chain length [8].

In this paper, the controversial chlorination-induced molecular structure stability is discussed in terms of Simha and Somcynsky-EOS theory calculations and elements from Simha-Somcynsky-related Lattice Compatibility Theory. Analyses were carried out on pentane, butane, 1-chloropropane, 2-chloropropane, 1-chlorobutane, 2-chlorobutane, 1-chloro 2-methylane, and 2-chloro 2-methylane as (SCCPs) universal representatives.

* Corresponding author.

E-mail address: ayumak@marmara.edu.tr (A. Yumak).

2. Simha and Somcynsky-EOS theory

2.1. Preliminary fundamentals

Simha and Somcynsky (SS) [9] proposed an equation of state (EOS) based on the lattice-hole model. EOS has been applied to low and high molecular weight systems to describe their thermodynamic properties and extended to the interpretation of the non-equilibrium properties, visco-elasticity, physical aging, etc. The theory makes it possible to compute the hole fraction, $h = h(T,P)$, of the model lattice—a measure of the free volume [9]. The hole fraction has been utilized to express a variety of equilibrium and kinetic processes such as viscosity.

In the SS theory the temperature and pressure dependent occupied site fraction, $y(T,P) = 1 - h$, is assumed to be:

$$y = \frac{sN}{sN + N_h} \quad (1)$$

where h is the hole fraction and s , N , N_h are the number of segments in a molecule, of molecules, and of holes respectively. The EOS based on the lattice-hole model providing $\tilde{P} = \tilde{P}(\tilde{V}, \tilde{T}, h(\tilde{V}, \tilde{T}))$ derived from the configurational Helmholtz energy:

$$\tilde{P}\tilde{V}/\tilde{T} = (1 - Q)^{-1} + (2y/\tilde{T})(y\tilde{V})^{-2} \left[1.011 (y\tilde{V})^{-2} - 1.2045 \right] \quad (2)$$

which is formulated in terms of volume, temperature and pressure in scaled forms, viz. $V = V/V^*$, $T = T/T^*$ and $P = P/P^*$. For an s -mer, V^* is defined by $N_A v^*/m_0$, where N_A is the Avagadro's number, m_0 is the molar mass of the segment, and characteristic molar volume v^* of a segment given by the segmental location r^* of the potential minimum. T^* equals to $q_z \epsilon^*/ck$ as a balance between attraction and thermal energy contributed by the external degrees of freedom (3c) where attractive interaction parameter ϵ^* of a segment corresponds to the potential minimum. Accordingly, P^* is defined by the ratio between chain attraction energy $q_z \epsilon^*$ and chain hard core volume sv^* , where q_z is the number of the first neighbor intermolecular pairs of the s -mer (chain length of a polymer), viz., $s(z - 2) + 2$ with the coordination number z . SS-EOS is defined in terms of occupied site fraction, y , to be computable by minimization of Helmholtz energy of an ensemble, $\partial F/\partial y|_{\tilde{V}, \tilde{T}, c/s} = 0$:

$$(s/3c) \left[(s - 1)/s + y^{-1} \ln(1 - y) \right] = (Q - 1/3)/(1 - Q) + (y/6\tilde{T})(y\tilde{V})^{-2} \left[2.409 - 3.033 (y\tilde{V})^{-2} \right] \quad (3)$$

where $Q = 2^{-1/6} y (y\tilde{V})^{-1/3}$. The SS-EOS has been applied to low and high-molecular-weight systems to describe their thermodynamical properties and extended to interpret the non-equilibrium properties, viz. viscoelasticity, physical aging, etc. The hole fraction has been also utilized to express a variety of equilibrium and kinetic process such as viscosity, ionic conductivity, etc.

2.2. Thermo-occupancy function

The thermo-occupancy function defined and responsible for the transport phenomena is given by

$$E_h = \frac{1 - h}{h} \frac{1}{\tilde{T}} \quad (4)$$

here the quantity, E_h , is a ratio of a number of occupied sites to unoccupied sites (holes) divided by the absolute temperature; it can be interpreted as the number of occupied sites for each empty site per unit temperature. Thus, E_h contributes to the calculation of transportation of segmental molecules in two folds: First, it depends on the structural occupancy; second, it is inversely related to temperature which is also correlated with vibrational energy. Because of such importance of this contribution to our calculations, we name E_h as “thermo-occupancy function”.

3. Calculations

3.1. Scaling parameters of the SS theory

PVT behavior of short-chain chlorinated paraffins such as 1-chloropropane, 2-chloropropane, 1-chlorobutane, 2-chlorobutane, 1-chloro 2-methylane, and 2-chloro 2-methylane has been studied in the temperature range 10–55 °C and the pressure range 0.1–65 MPa. For the comparison of corresponding chain length, we have included pentane and butane in this work.

Using the specific volumes of these polymers in terms of temperature and pressure, the scaling parameters P^* , V^* , T^* with 3c have been computed from Eqs. (1) and (2). The values of chain lengths set to the number of C and Cl on the backbone of the molecule. The scaling parameters P^* , V^* , T^* are computed by superimposing the experimental PVT data on the theoretical $\tilde{P}\tilde{V}\tilde{T}$ surface. To do this, first, the parameter c is assumed as an adjustable parameter, and then the set of the experimental data is projected on the theory to get an equation in terms of V^* and T^* including P^* . Second, expanding each up to the first power in V^* and T^* , N equations are obtained from the N PVT data and solved for two unknowns V^* and T^* using the Pseudo Inverse Matrix Technique. The best c values with the scaling parameters P^* , V^* , T^* are taken by the least mean percentage error in specific volume defined by

$$\Delta V(\%) = \frac{100}{N} \sum_i \frac{|V_i^{\text{exp}} - V_i^{\text{calc}}|}{V_i^{\text{exp}}} \quad (5)$$

The obtained parameters with the mean and maximum percentage error in specific volume are reported in Table 1 for the polymers. The mean percentage deviation ranges from 0.15 to 0.0010 % and the maximum percentage error is 0.59% for butane and less for the chlorinated alkanes. These parameters are ready to

be used to compute the temperature and pressure dependent hole fraction, and then applied to the variety of problems such as ionic conductivity [10], viscosity [11], etc.

The mean characteristic repulsive molar volume, $\langle v^* \rangle$, and the mean attractive interaction energy $\langle \epsilon^* \rangle$ of a segment for each alkane and chlorinated alkanes are tabulated in Table 1. These parameters are candidate to compare their role in Chlorine additive to the backbone of an alkane. Butane with segment length 4 can be compared with 1-chloro propane and 2-chloro propane since Cl is replaced instead of C in the backbone. The mean segmental molar repulsive volume for Butane with 20.288 cm³/mol has a relative deviation of about 5.5% and 3.5% higher than those for 1-chloro propane and 2-chloro propane with 19.226 and 19.598,

Download English Version:

<https://daneshyari.com/en/article/1409214>

Download Persian Version:

<https://daneshyari.com/article/1409214>

[Daneshyari.com](https://daneshyari.com)