



# Solid-liquid equilibria of eicosane, tetracosane or biphenyl + 1-octadecanol, or + 1-eicosanol mixtures

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## ABSTRACT

A differential scanning calorimetric (DSC) technique has been used to obtain solid-liquid equilibrium temperatures for *n*-C<sub>20</sub>, or *n*-C<sub>24</sub>, or biphenyl + 1-octadecanol, or + 1-eicosanol mixtures. All the systems show a simple eutectic point. The final composition of these points is determined on the basis of the Tamman plots using values of the eutectic heat and of the heat of melting, which are also reported. Deviations of activity coefficients ( $\gamma$ ) from unity for the mentioned mixtures and for the systems *n*-C<sub>24</sub> or *n*-C<sub>28</sub> + cyclododecane, or + cyclododecanol and for dodecane + cyclohexanol are discussed in terms of the alcohol self-association and size effects. Mixtures with alkanols show positive ( $\gamma - 1$ ) values. Such differences are larger for the cyclohexanol system, as this is the most self-associated alcohol considered. Size effects lead to slightly negative ( $\gamma - 1$ ) values for cyclododecane solutions. Using the regressed parameters, DISQUAC provides a good description of the phase diagrams for the mixtures under consideration and improves results from the UNIFAC (Dortmund) model. The influence of size effects on the DISQUAC interaction parameters is discussed.

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## 1. Introduction

There are a number of effects which must be taken into account when determining interaction parameters in the framework of any theoretical model. The different positions of a polar group within a linear chain (steric effects), or in a cyclic ring (cyclization), or regarding an aromatic ring (aromaticity), or the relative separation of two equal or different polar groups within the same molecule (proximity effects), or large differences in size between the mixture compounds are all of them effects which can drastically change the interaction parameters. For example, in the Dortmund UNIFAC model [1], specific main groups are defined for aniline or pyridine, and a main group is also defined in order to improve predictions on thermodynamic properties of mixtures including cyclic molecules. It has been shown that proximity effects between the – OH and –

O– groups in alkoxyethanols [2] lead to DISQUAC [3] interaction parameters for the (OH/O) contacts which are very different to those corresponding to 1-alkanol + linear ether systems [2,4]. In this work, we examine the dependence of the DISQUAC interaction parameters with the molecular structure for the contacts (aliphatic/hydroxyl) and (aromatic/hydroxyl) in the following binary systems: *n*-C<sub>20</sub>, *n*-C<sub>24</sub>, or biphenyl + 1-octadecanol, or + 1-eicosanol. With this idea, we report here solid-liquid equilibrium (SLE) temperatures, obtained by means of a differential scanning calorimetric (DSC) technique, for the mentioned systems. In addition, cyclization is also investigated in similar terms using SLE data available in the literature for the cyclohexanol + dodecane [5] and cyclododecanol + *n*-C<sub>24</sub>, or + *n*-C<sub>28</sub> [6] mixtures. Systems of the type 1-alkanol + *n*-alkane [7,8], or + cyclohexane [9], or + benzene, or + toluene [10] and cycloalkanol + alkane [11] have been extensively studied by one of us using DISQUAC. In the case of long chain 1-alkanol ( $\geq 1$ -octadecanol) + *n*-alkane mixtures, values of the first dispersive interaction parameter for the (CH<sub>2</sub>/OH) contacts were determined using SLE data for solutions including shorter *n*-alkanes. Calculations show that these parameters are not useful for systems with long *n*-alkanes (e.g. *n*-C<sub>20</sub>, or *n*-C<sub>24</sub>), and that new

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parameters are required. Results obtained from DISQUAC are compared to those determined using UNIFAC, with interaction parameters from the literature (see below). From a practical point of view, solubility of a solid in pure or mixed solvents are of great importance in chemical process design, particularly when process conditions have to be specified to prevent the precipitation of a solid. SLE data for systems containing alkanols with a large number of C atoms are relevant in fat, cosmetic and oil technology. Biphenyl is a polycyclic aromatic hydrocarbon which can be considered built by blocks of benzene. The study of biphenyl systems is needed for a better understanding of aromatic-aromatic interactions which are commonly encountered in very complex systems [12]. Due to its stability and inertness, biphenyl is employed as heat-storage material [13], and the eutectic mixture diphenyl ether + biphenyl is used as heat transfer agent [14].

## 2. Experimental

### 2.1. Materials

All the chemicals were used as delivered without any further purification. Information about the source and purity of the pure compounds is collected in Table 1. Table 2 lists physical properties determined in this work (see below), together with values from the literature, of the pure compounds used along the experimental research:  $T_m$ , melting temperature,  $\Delta H_m$  molar enthalpy of fusion,  $\Delta C_{pm}$ , change of the molar heat capacity during the melting process of the compound,  $T_{tr}$ , transition temperature and  $\Delta H_{tr}$ , the molar enthalpy of transition. These properties are in fair agreement with values reported in the literature. We have not observed a solid-solid phase transition for  $n$ -C<sub>20</sub> or for 1-eicosanol. Nevertheless, transition temperatures, very close to the corresponding melting points have been reported for these chemicals. Thus, for  $n$ -C<sub>20</sub>,  $T_{tr}/K = 309.2$  and  $T_m/K = 310.05$  [15,16] and for 1-icosanol,  $T_{tr}/K = 337.65$ ;  $T_m/K = 338.05$  [17].

### 2.2. Procedure and experimental results

1-Octadecanol or 1-eicosanol and  $n$ -alkanes or biphenyl are completely miscible in the liquid state. Details on the experimental methodology applied to determine the solid-liquid phase diagrams have been given previously [18–20]. Mixtures were heated under constant agitation until complete melting of the least volatile compound and the sample was heated very slowly inside a glass cell. After melting, the cell was immersed rapidly in a liquid nitrogen bath to obtain a homogeneous solid mixture. Then, a small amount of solid (5–10 mg) was sealed in the aluminium pan of the DSC (204F1 Phoenix ASC). The solubility measurements were conducted under an inert atmosphere (20 ml min<sup>-1</sup>). The heating rate was 0.8 K min<sup>-1</sup>. The equipment was calibrated using 99.99% pure Indium ( $T_m = 429.70$  K;  $\Delta H_m = 28.45$  J g<sup>-1</sup>). Mole fractions were calculated on the basis of the relative atomic mass table of 2015 issued by the Commission on Isotopic Abundances and Atomic

Weights (IUPAC) [21]. The standard uncertainty in the final mole fraction is estimated to be 0.0005.

For the investigated systems, the DSC curves show several peaks (see Fig. S1 of supplementary material for the tetracosane (1) + 1-eicosanol (2) mixture). One of them occurs at the same temperature and is found at any composition (except for the pure compounds) and corresponds to a simple eutectic point. For the mentioned mixture, the solid-solid transition of pure alkane is also observed (Fig. S1, supplementary material). The determination of the liquidus temperature is more difficult as one can have several effects superimposed on the DSC curves. For simplicity, as in other previous applications [22,23], we have selected the maximum peak temperature of the broadest peak as the liquidus temperature. Regarding to data acquisition of  $\Delta H_m$  of pure compounds and onsets of the SLE temperatures and processing were done with Perkin Elmer's Pyris software [24]. The standard uncertainty of the equilibrium temperatures is 0.1 K and the relative standard uncertainty for the heats of fusion and solid-solid transitions (Table 2) is estimated to be 0.03. Results for the solid-liquid equilibrium temperatures vs. composition are given in Tables 3 and 4 (see Figs. 1–3). Our results for the biphenyl + 1-octadecanol mixture compare well with those available in the literature [25] (Fig. 2). Values of the eutectic heat and of the heat of melting needed to determine the final composition of the eutectic points on the basis of the Tamman plots [24,26,27] are listed in Tables 5 and 6 (see Fig. 4).

## 3. Models

### 3.1. DISQUAC

Some important features of the model are briefly summarized. (i) The group contribution model DISQUAC is based on the rigid lattice theory developed by Guggenheim [28]. (ii) The total molecular volumes,  $r_i$ , surfaces,  $q_i$ , and the molecular surface fractions,  $\alpha_i$ , of the system compounds are calculated additively on the basis of the group volumes  $R_G$  and surfaces  $Q_G$  recommended by Bondi [29]. As volume and surface units, the volume  $R_{CH_4}$  and surface  $Q_{CH_4}$  of methane are taken arbitrarily [30]. The geometrical parameters for the groups considered along the work are listed in Table 7. (iii) The molar excess functions, as Gibbs energy,  $G_m^E$ , or enthalpy,  $H_m^E$ , are the result of two contributions: a dispersive (DIS) term due to the contribution from the dispersive interactions; and a quasi-chemical (QUAC) term arising from the anisotropy of the field forces created by the solution molecules. For  $G_m^E$  a combinatorial term,  $G_m^{E,COMB}$ , given by the Flory-Huggins equation [30,31] must be considered. Thus,

$$G_m^E = G_m^{E,COMB} + G_m^{E,DIS} + G_m^{E,QUAC} \quad (1)$$

$$H_m^E = H_m^{E,DIS} + H_m^{E,QUAC} \quad (2)$$

(iv) The interaction parameters are dependent on the molecular structure; (v) the value  $z = 4$  for the coordination number is used for all the polar contacts. This is one of the more important shortcomings of the model, partially removed via the hypothesis of considering structure dependent interaction parameters.

The equations used to calculate the DIS and QUAC contributions to  $G_m^E$  and  $H_m^E$  are given elsewhere [32]. The temperature dependence of the interaction parameters is expressed in terms of the DIS and QUAC interchange coefficients [32],  $C_{st,l}^{DIS}$ ,  $C_{st,l}^{QUAC}$  where  $s \neq t$  and  $l = 1$  (Gibbs energy;  $C_{st,l}^{DIS/QUAC} = g_{st}^{DIS/QUAC}(T_0)/RT_0$ );  $l = 2$  (enthalpy;  $C_{st,l}^{DIS/QUAC} = h_{st}^{DIS/QUAC}(T_0)/RT_0$ ),  $l = 3$  (heat capacity;

**Table 1**  
Sample description.

Chemical	CAS number	$M^a/g \cdot mol^{-1}$	Source	Purity <sup>b</sup>
Eicosane	112-95-8	282.547	Avocado	0.99
Tetracosane	646-31-1	338.653	Avocado	0.99
Biphenyl	92-52-4	154.208	Acros	0.99
1-octadecanol	112-92-5	270.494	Fluka	>0.98
1-eicosanol	629-96-9	298.547	Fluka	>98

<sup>a</sup> Molar mass.

<sup>b</sup> In mole fraction.

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