Thermochimica Acta 575 (2014) 122–128

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Mesophase behavior of binary and ternary mixtures of benzoic acids bearing terminal substituents of different polarity and chain-lengths

H.A. Ahmed*, M.M. Naoum

Department of Chemistry, Faculty of Science, Cairo University, Egypt

ARTICLE INFO

Article history:
Received 2 July 2013
Received in revised form 18 October 2013
Accepted 27 October 2013
Available online 4 November 2013

Keywords:
4-Alkoxybenzoic acid
Supramolecular hydrogen-bonded carboxylic acid
Phase transition
Binary phase diagram

ABSTRACT

The thermal and mesophase behavior of all possible 1:1 mixtures (**I***m*/**I***n*) formed from any two derivatives of 4-n-alkoxy benzoic acids bearing different alkoxy chains (*m* and *n* vary between 6 and 16 carbons), were investigated by differential scanning calorimetry (DSC) and phases identified by polarized light microscopy (PLM). Phase transitions were investigated as a function of the average alkoxy-chain length ($\bar{n} = (m + n)/2$) of the mixed acids. In order to investigate whether a supramolecular complex is formed between the mixed acids, phase diagrams were constructed for the binary mixtures of 4-n-hexyloxy benzoic acid (**I***6*) with the two homologues bearing extreme alkoxy-chain lengths, namely, *8* and *16* carbons. Investigation of the mesophase behavior of ternary mixtures, made from the two eutectic mixtures (**I***6*/**I***8* or **I***6*/**I***16*) with 4-methoxy or 4-cyano-benzoic acids revealed that the stability of the SmC and N mesophases of the eutectic mixtures is affected in a way that is dependent on both the polarity of the substituent and the difference in the alkoxy-chain lengths.

1. Introduction

Intermolecular hydrogen-bond interactions have shown great potential in the preparation of new liquid crystalline systems, especially in thermotropic liquid crystals [1–3]. Following the examples of liquid crystal formation through the interaction of aromatic carboxylic acids [4], several classes of compounds have been prepared by the interaction of complementary molecules, the liquid crystalline behavior of which is crucially dependent on the structure of the resulting supramolecular systems. Typical examples of the acids are 4-n-alkoxybenzoic [1,2] and 4-n-alkoxycinnamic [5] acids, as well as other 4-substituted benzoic acids [6]; these compounds form dimers through H-bonding that exhibit stable nematic and smectic mesophases. Generally, hydrogen bonds are used as links connecting two independent molecular species [1–6]. Such hydrogen-bonded dimers are optically anisotropic that complies with the main characteristics of liquid crystal molecules. Other hydrogen-bonded binary systems are based on pyridine as hydrogen acceptors and carboxylic acid derivatives as the hydrogen donors [7]. A number of such systems have been investigated following the reports of Kato and Fréchet [1] and later are reviewed extensively [8–10].

Liquid crystal materials for device applications are mostly mixtures, because no single compound fulfills all the required criteria. So, the study of mixtures of liquid crystalline compounds is a subject of considerable interest [11]. Benzoic acid derivatives are the most frequently employed components for the formation of LC materials through such hydrogen bonding interaction [10]. The higher members of 4-alkoxybenzoic acid homologues are well known mesogenes. 4-Methoxy- and 4-ethoxy benzoic acids, individually, do not exhibit liquid crystalline phase, yet, their mixtures are reported to exhibit mesomorphism [12]. A detailed study of the binary system of 4-methoxybenzoic acid with 4-ethoxybenzoic acid revealed that they exhibit extremely small nematic mesophase region [12].

Usually, wing polar groups are used in the modification of a liquid crystal material. Since a calamitic molecule has two ends, the wing groups may be similar or different. Many terminal units have been employed in the generation of liquid crystals, but the most successful route [13] is to use either a fairly long, straight hydrocarbon (usually alkyl or alkoxy), or a small polar substituent (e.g. CH_3O, NO_2). The role of these groups is to act either as a flexible extension to the core (in the former case) or as a dipolar moiety to introduce anisotropy in physical properties (in the latter case). The option to choose dissimilar wing groups in the case of 4-substituted benzoic acids, were previously investigated [6] as binary mixtures of two types of 4-substituted benzoic acids. The first type of the acid was substituted with a small compact polar group that covers a wide range of polarity, while the other type of the acids were 4-alkoxy benzoic acids bearing an alkoxy group with varying chain length. The authors found that, irrespective of the type of the polar substituent, X, the stability of the SmC phases decreases slightly with

* Corresponding author. Tel.: +20 1007994973.
E-mail address: hadyelrahman@yahoo.com (H.A. Ahmed).

0040-6031/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tca.2013.10.027

the increase of the alkoxy-chain length. Meanwhile, the nematic phase appears only with the shorter homologues and remains up to the homologue ($n = 10$) with 4-methyl benzoic acid.

The present work aims to investigate the possible formation of supramolcular hydrogen-bonded complexes (**I***m*/**I***n*) formed between pairs of benzoic acid derivatives bearing different alkoxy chain (m and n), where m and n individually varies from 6 to 16 carbons. The study is directed to investigate the phase characteristics of the binary mixtures of 1:1 molar ratio of any two complimentary components. In addition, binary phase diagrams will be constructed to follow the homogeneity of mixture throughout the whole composition range.

The study expands further to include the mesophase behavior of ternary mixtures made from eutectic mixtures of two homologues of extreme chain-length difference, namely **I***6*/**I***8* and **I***6*/**I***16*. The third components are going to be 4-substituted benzoic acids bearing substituents of extreme polarity, namely, the strong electron-withdrawing CN and electron-donating CH_3O groups.

2. Experimental

2.1. Preparation of 4-n-alkoxybenzoic acids (*I*m & *I*n)

These were prepared from ethyl 4-hydroxybenzoate (Aldrich (Wisconsin, USA), 99%) according to the method described previously [13]. The prepared acids have transition temperatures as reported in the literature [13].

4-Cyanobenzoic acid and 4-methoxybenzoic acid (99%) were of pure grades and purchased from the following companies: Buchs (Switzerland), Aldrich (Wisconsin, USA), E. Merck (New Jersey, USA).

Calorimetric measurements were carried out using a PL-DSC of Polymer Laboratories, England. The instrument was calibrated for temperature, heat and heat flow according to the method recommended by Cammenga et al. [14]; the measurements were carried out for small samples (2–3 mg) placed in sealed aluminum pans. All measurements were conducted at a heating rate of 10 °C/min in an inert atmosphere of nitrogen gas (10 mL/min).

Transition temperatures for the individual components (**I***m* & **I***n*), the 1:1 associated complexes (**I***m*/**I***n*), and the binary and ternary mixtures of the acids were checked, and the types of the mesophase were identified using a standard polarized-light microscope PLM (Wild, Germany), attached to a homemade hot-stage. The temperature is measured by thermocouple attached to a Brookfield temperature controller, England. Measurements were made twice and the results have accuracy in transition temperature within ±0.2

2.2. Preparation of supramolecular hydrogen-bonded complexes

For the preparation of supramolecular complexes (**I***m*/**I***n*), binary mixtures of any two complimentary acids were prepared in 1:1 molar ratio of sample, by melting the appropriated amounts of each component, stirring to give an intimate blend, and then cooling with stirring to room temperature (Scheme 1).

For the construction of binary phase diagrams, the mixtures of the two components (**I***m* & **I***n*) were made to cover the whole range of composition. While for the construction of the ternary phase diagrams, we start with the eutectic mixtures of the binary systems (**I***6*/**I***8* or **I***6*/**I***16*), and the third component **I**x (**I**a, X = CH_3O or **I**b, X = CN) is added to cover a composition range of **I**x from 0 to 100 mol%.

Transition temperatures obtained for all prepared blends, as measured by both DSC and PLM, agreed within 2–3 °C. In the phase diagrams, constructed by plotting transition temperatures versus mixture mole fraction (X) or average alkoxy-chain length ($\bar{n} = X_{\mathbf{I}m} n_{\mathbf{I}m} + X_{\mathbf{I}n} n_{\mathbf{I}n}$), the symbol "○" denotes crystal-mesophase, "□" mesophase–isotropic transitions, "●" smectic C-to-nematic mesophase, and, "▲" eutectic temperature.

3. Results and discussion

3.1. Mesophase behavior of binary mixtures

Fig. 1 represents the two binary phase diagrams of the 4-n-hexyloxy benzoic acid (**I***6*) with the two homologues bearing extreme alkoxy-chain lengths, i.e., with $n = 8$ and *16* carbon atoms, respectively. The examples chosen in Fig. 1 represent extreme in the difference of the alkoxy-chain lengths (m & n), where in the first system (Fig. 1a) the difference is only 2 carbons, $m = 6$ and $n = 8$ carbons, whereas in the second (Fig. 1b) there is a big difference in length, i.e., 6 and 16 carbons, were tested. As can be seen from these diagrams, although both components, in each binary mixture, are of similar polarity, the individual components exhibit different solid crystalline structure that pass through a eutectic composition. With respect to their mixed mesophase behavior, whether it is nematic or smectic C, the first system varied linearly upon mixing, since the difference in the length of the terminal alkoxy-chain is only two carbon atoms and, consequently, the average alkoxy-chain length ($\bar{n}$) varies between 6 and 8 carbons. This is consistent with pervious findings [15]. The SmC phase starts to appear early upon addition of ≈0.30 mol **I***8*, while the nematic stability decreases slightly and linearly from 153.2 °C for **I***6* to 149.0 for **I***8*. Conversely, in the second system **I***6*/**I***16* (Fig. 1b), the big difference in the length of the two terminal alkoxy groups, m and n, is associated with a great variation in the average alkoxy-chain length, $\bar{n}$, of the mixture that varies between 6 and 16 carbons. This system seems to obey the conventional dependence of transition temperatures on the wing-chain length [4]. That is, the tendency of the compound to be nematic is decreased as the alkoxy chain (n) is lengthened, and at the same time, its tendency to exhibit smectic properties is increased and there would be a stage at which no nematic properties are shown and the system becomes purely smectogenic. This is exactly observed in our case (Fig. 1b). In this system, the SmC phase starts to show up from average alkoxy-chain length $\bar{n} = 8$ with SmC stability = 124.4 °C and nematic stability = 141.5 °C. The smectic C stability increases with $\bar{n}$ to be the only mesophase for the mixture with $\bar{n} = 14$. The nematic phase decreases gradually with $\bar{n}$ and disappeared completely at $\bar{n} = 14$.

These results indicated that there is no possibility of supramolecular complex formation since the stability of both mesophases, SmC or N, varies linearly with composition. Even in the solid state no complex was detected since one eutectic composition was observed.

3.2. Effect of alkoxy chain length on the mesophase behavior of 1:1 molar mixtures with dissimilar alkoxy chains

All possible 1:1 molar mixtures, made alternatively from the six homologues of 4-n-alkoxybenzoic acid, were prepared and their mesophase behavior characterized by DSC and PLM. Transition temperatures are represented graphically, as a function of the average alkoxy-chain length ($\bar{n} = (m + n)/2$) for m & n varying between 6 and 16 carbons, in Fig. 2a–f, respectively. As can be seen from these diagrams, there is, as usual, no systematic change of melting temperatures with the increase of $\bar{n}$. As for the first two series, **I***6*/**I***n* and **I***8*/**I***n* (Fig. 2a and b), except for the pure, nematogenic, homologue **I***6* (represented in Fig. 2a as **I***6*/**I***6*), all other mixtures