Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Preface

Version of record first published: 03 Jan 2007.

To cite this article: (1984): Preface, Molecular Crystals and Liquid Crystals, 115:1-4, xi-xiii

To link to this article: http://dx.doi.org/10.1080/00268948408073734

PREFACE

Practically a whole century has passed since the first observation of liquid crystals with scientific consequences (on some cholesteryl esters by Reinitzer[1]). Some lists of mesogens are given in the earlier papers and books, for example 21 compounds by Schenck[2] in 1905, for other references see reference 3. To the best of our knowledge the first table dates from 1923[4]: melting, clearing and possibly other transitions temperatures for 109 compounds. Three years later another similar table[5] appeared with over 250 compounds. In 1957, a large review[6] with 475 references was published. A recent edition of the Landolt-Börnstein collection contains tables of the dielectric properties[7], transition temperatures for 1400 substances[8] and optical constants.[9] In 1974 a table appeared with transition temperatures of more over 5000 calamatic mesogens.[10] This list of compounds can be completed by a more recent compilation (ref.3, p. 69).

Knowledge of the temperature ranges for the mesophases is often insufficient. Other data are necessary. For example, the enthalpy changes are meant to obtain information about the orders of the mesophases. Earlier measurements are obtained from cryoscopy, pressure influence on transition temperature (ref. 2, p. 88), or by conventional calorimetry (ref. 2, p. 117 and 11 to 13). Fortunately, the differential thermal analysis and, more recently, the differential scanning calorimetry (DSC) are good tests for purity control.[14] DSC is now a routine technique in synthesis laboratories. With these measurements it is possible to distinguish structure changes from texture changes.[15] Many phase changes are detected in this manner, including solid polymorphisms. Also obtained by these measurements are temperature and enthalpy changes at the phase transitions. With these last data it is possible to calculate a priori the phase diagrams for mixtures.[16,17]

From a systematic study of entropy changes Timmermans[18] established the existence of the plastic crystalline phases for compounds having globular molecules. More recently calorimetric measurements have proved to be a good experimental means to study the blue phases[19,20] and permit the

distinction for the first time of different smectic A sorts.[21] At transition temperatures the partial molar solution enthalpies differences are correlated to the enthalpies of transition of solvent.[22] In 1905, Schenck[2] (p. 88) reported enthalpy changes for only six compounds. In 1969, a review paper[23] mentioned measurements for 139 transitions. In a current larger table[10] the available calorimetric data for some calamitic mesogens are indicated (all references followed by the number 3 contain calorimetric data). A table for temperatures and molar enthalpy changes of 198 compounds appeared in 1974.[24] References for 391 calamitic mesogens are quoted in a paper published one year later.[25] In 1972, one of the authors here began collecting calorimetric data. With the encouragement of P. G. de Gennes, a group interested in this project formed and progressively grew. Here we present in part one data sources of enthalpy changes for over 1500 mesogens including 37 discogens and 97 compounds exhibiting plastic crystalline mesophases.

No pertinent method exists to detect in small samples the phase transitions between two highly organized phases. The barometric method[26] is convenient for these cases. Different thermodynamic data are necessary to develop an apparatus. We think the values collected during this work are useful in many cases. In the second part we present collected data on volume changes at the transitions; some characteristics for the phases: density and some second derivatives of the thermodynamic potentials: thermal expansion, isothermal and adiabatic compressibilities. The first determinations of the density and thermal expansion of mesophases date from 1898.[27] In 1905, Schenck reported data for six compounds[2] (p. 48). If the transition enthalpy change is known the pressure dependence of the transition temperature gives also the volume change at this transition. Since 1899, some volume change measurements have been made[28-30] (for review papers see references 31 and 32). Measurements of these various quantities are not common and we report data for only 235 compounds including 5 discogens and 25 chemicals exhibiting plastic crystalline mesophases.

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