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Melting properties of molten salts and ionic liquids. Chemical homology, correlation, and prediction

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ABSTRACT

The application of the concept of chemical homology to describe melting properties of molten salts and ionic liquids (ILs) is analyzed. This concept was used several years ago to correlate and predict properties of solids and more recently to correlate melting temperatures of ILs. To analyze the characteristics of the extended method, this is first applied to melting properties of organic substances for which abundant data are available. The method is extended to analyze its applicability for properties of molten salts and ILs such as glass transition temperature, heat of melting, and entropy of melting. The foundation of the chemical homology concept is revised, and the difficulties for extending the method to correlate and predict melting properties of ILs are presented. Despite the difficulties, the homology concept can still be used with some conditions and limitations that are analyzed in this article. Several correlations are proposed.

1. Introduction

Room temperature ionic liquids (ILs), also called simply ILs, are substances formed only by ions and having melting temperatures less than 100 °C [1]. ILs have been a matter of studies for the past 25 years and new aspects and applications appear every day in the open literature. The main interest has been on their unique characteristics as liquids, and therefore solid–liquid transition properties have been a matter of several studies, mainly the melting temperature. Other melting properties such as glass transition temperature, enthalpy of fusion, and entropy of fusion have received less attention. These melting properties, the errors in the published data, the difficulties for their experimental determination, and mainly the possibilities of correlating and predicting melting properties are analyzed in this article.

There are difficulties for accurately measuring melting properties, difficulties that have been recognized and discussed by several authors. Holbrey and Rogers [2] presented a good summary of the main problems that present the experimental determination of melting properties of ILs. These are some of them: (1) Usually, cooling from the liquid state causes glass formation at low temperatures, because solidification kinetics are slow; (2) on cooling from the liquid, the low-temperature region is not usually bounded by the phase diagram liquidus line. It is extended down to a lower temperature limit imposed by the glass transition temperature; and (3) in some cases, there is evidence of multiple solid–solid transitions, either crystal–-crystal polymorphism or formation of plastic crystal phases. The authors also give some recommendations on how to obtain good data: (1) The most efficient method for measuring the transition temperatures is differential scanning calorimetry; (2) thermodynamic data must be collected in heating mode to obtain reproducible results; and (3) long equilibration times, with small samples that

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allow rapid cooling, are needed to quench nonequilibrium states in mixtures and to obtain reliable transition data. It must also be considered that melting properties are influenced by the charge distribution on the ions, hydrogen-bonding ability, symmetry of the ions, and van der Waals interactions, but the presence of impurities in the samples and even confusion between melting and glass transition produce wrong data and add more difficulties to the development of correlating and predicting methods for estimating melting properties [3].

Also Preiss et al. [4] discuss the general reliability and reproducibility of the experimental data published. Aspects such as purity, phase behavior, disorder, and thermal history of a given substance, experimental mistakes, systematic errors, and lack of conventions to define melting properties are well analyzed. In particular, the authors discussed the presence of polymorphism (existence of more than one form or crystal structure) and conclude that "*we think that the existence of polymorphs poses the most serious limitation on developing a prediction model*." In fact, melting properties might be influenced by the presence of solid–solid phase transitions, but more accurate data are needed to obtain a final conclusive answer to this phenomenon.

Data on melting properties have been presented by several authors, but in many cases agreement between values is poor. It seems that the difficulties mentioned above have surpassed the recommendations given by Holbrey and Rogers [2] and other authors. In fact, an approximate estimate of data indicates that for ILs there must be 1600 data for melting temperature, 800 data for glass transition temperature, 200 data for enthalpy of melting, and 50 data for entropy of melting available in the open literature. For some ILs several values of a melting property have been reported. For some cases, these values tremendously differ from one source to another. Aparicio et al. [5] analyzed published thermophysical properties data for ILs until 2010, including melting temperature, and concluded that it was necessary to perform further systematic thermophysical studies for the development of reference data sets. In a study, Valderrama [6] discussed several aspects related to available data and models presented in the literature to estimate the melting temperature of ILs.

The modeling of melting properties of ILs is perhaps one of the most challenging tasks. There are so many factors and phenomena occurring during transition from solid to liquid or vice versa that taking into account all factors in a single model is almost impossible. There are many studies explaining why a given IL or a group of ILs behave in a certain manner to find immediately several exceptions to such explanations. Preiss et al. [7] indicate that a group contribution method to estimate melting properties is not easy to adapt for ILs in which charges, ambiguous bonding situations, and the presence of inorganic elements affect the transition process in many different ways. In fact, there are much more than grouping groups as simply done for organic substances.

Despite all the problems mentioned previously, some proposals are found in the literature to estimate melting properties, mainly the melting temperature. A good review on the different methods for estimating thermophysical properties of ILs has been performed by Coutinho et al. [8]. The authors dedicate an important section of the article to the different attempts made by several authors presented in the literature to estimate melting properties. The authors discuss the different modeling approaches and make suggestions about what are the best methodologies for the prediction of each property. They state that because most of the literature analyzed is from about 2007 until 2011, this field of modeling and predicting IL properties is still in its infancy. After 5 years from that review, no major progress has been made, but several researchers are attempting different approaches to estimate phase transition properties of ILs. Molecular dynamics simulation has been used by Zhang and Maginn [9], Aguirre et al. [10] used group contribution methods, and Eike et al. [11] and Farahani et al. [12] used computational chemistry. In other reports, Zhu et al. [13] and Bai et al. [14] used quantitative structure–activity relationship models to estimate heat of fusion of several types of ILs, and Adamova et al. [15] analyzed the alternation effect in chemically homologous series.

Homology, homologous series, and homologous compounds are concepts derived from the word homologue, a term "*used to describe a compound belonging to a series of compounds differing from each other by a repeating unit*" [16]. This concept of chemical homology has been used by Valderrama and Rojas [17] for data selection and estimation of the normal melting temperature of ILs. According to the authors, the estimation method gives reasonable values of the normal melting temperature for engineering calculations. However, despite that most of the existing data published until 2012 was used, the method gave positive results for a reduced number of IL families only.

2. Data on melting properties

Data on melting properties of ILs are scarcer than for other physical and physicochemical properties, melting temperature being the most studied of these melting properties. In general, data are ambiguous, not very well defined and, as mentioned previously, values may tremendously differ from one another. Most reports including correlations with the use of literature data do not explain the reasons for choosing one value or another, although the literature sources are provided. Differences up to 70 K for the melting temperature (25% with respect to the lowest reported value), 20 K for glass transition temperatures, and 10 kcal mol^{-1} for the heat of fusion (100% with respect to the lowest reported value) are found for some ILs, which are not acceptable for producing good and general correlating and predicting models for these properties [6].

It should also be mentioned that data compilations and databases of melting properties are not clear enough about the accuracy of the values that are reported. In some cases, uncertain values are given [18–21]. Valderrama [6] analyzed the information provided by the NIST database for the melting temperature of ILs concluding that the huge differences between reported melting temperature values are not acceptable for producing good and general correlating and predicting models for the melting temperature. The same can be said about other melting properties such as glass transition temperature, heat of melting, and