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Selection of Normal Melting Temperature Data of Imidazolium-type Ionic Liquids by Chemical Homology

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Abstract. A simple method based on homologous series for determining the best available data for the normal melting temperature (Tm) of ionic liquids (ILs) proposed by the authors (Valderrama and Rojas, 2012) is revised and extended. The selection of melting temperature data of ionic liquids is necessary because of the great differences in the values reported in the literature for the same ionic liquid, differences that produce a major problem when such data are used for design, simulation or for developing correlation and estimation methods. The extension of the homology method proposed in this paper considers doing homology between all ionic liquids for which experimental data are available instead of using data for ionic liquids that contains one reference fluid only (hexaflurophosphate ionic liquids), as previously proposed by the authors. The method shows to be effective to detect outliers among the data available. A database for the melting temperature of imidazolium -type ionic liquids is proposed.

Keywords: chemical homology, ionic liquids, melting temperature

1. Introduction

Room temperature ionic liquids, also called simply ionic liquids, are substances formed only by ions and having melting temperatures below 100 ℃ [1]. Of the several physicochemical properties of a substance, the melting temperature is the most characteristic property that is used for defining the so-called room temperature ionic liquids [2]. Experimental values of melting temperature reported in the literature for the same ionic liquid, however, may show great differences, originating a major problem when experimental data are needed. Therefore, selection of accurate data of melting temperature of ionic liquids data is necessary before using such data in design, simulation or for developing correlation and estimation methods.

Most reports including correlations with the use of literature data do not explain the reasons for choosing one or another value, although the literature sources are provided. Differences up to 70 K are found for some ionic liquids, a difference that is not acceptable for producing good and general correlating and predicting models for the melting temperature [3]. Even chemical families of ionic liquids present erratic values of the melting temperature, which cannot be explained from any physical or chemical point of view. Additionally, data compilations and databases are not clear about the accuracy of the reported values, although in some cases uncertainty values are given. It is also known that values of physicochemical properties of compounds having either homologous cations or anions follow a regular smooth pattern, a characteristic that facilitates the calculation of properties of a given substance by knowing the same property for another substance that has similar structural characteristics [4]. In organic chemistry, for instance, the n-alkanes and the n-alkanols form homologous series, as detailed later in this paper.

In the case of ionic liquids families of these compounds, for example, [xmim][PF6] and [xmim][BF4], form a chemical family and the melting temperature of these types of compounds must be somehow related, as previously demonstrated by the authors. The hypothesis and concept here is that a value of the chosen property of a compound that does not follow a certain pattern and is far away from the other observations

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must be in error and constitute an outlier.The authors have previously used the homology concept defining ionic liquids that contains the [PF6] anion (hexaflurophosphate) as reference fluids and proposed estimating the melting temperature of other ionic liquids based on the values of Tm for [X][PF6].

The extension proposed in this paper considers doing homology between all ionic liquids for which experimental data are available and selecting those that follow a certain pattern in all possible combinations. That means for instance, that ionic liquids of the type [X][BF4] are not only compared to [X][PF6] but compared to any other ionic liquid of the type [X][Y].All melting temperature data of imidazolium-type ionic liquids available in the literature were collected and thoroughly analyzed using the homology concept, between all possible pairs of ionic liquids, as proposed in this paper. After analysis and selection, a database formed by those ionic liquids that homologated was constructed and is proposed for future use.

2. Properties of Homologous Series

In chemistry, a homologous series is a series compounds with similar general formula, with similar functional groups, only differing in some structural characteristics. As written above, the n-alkanes and the n-alkanols form homologous series. One –H in an alkane is replaced by an –OH, forming the n-alkanol. The properties of the compounds of a series present in many cases a regular and smooth change as the molecular size, molecular mass or other basic properties, change. The Fig. 1 shows the homology concept applied to the melting temperature of n-alkane and n-alkanol families while the Fig. 2 shows the smooth regular change of the melting temperature in the n-alkanes and n-alkanol chains as the number of carbon in the chain increases.

What is interesting to observe in Fig. 2 is that the melting temperature decreases as the length of the chain increases to then increase again. This characteristic is also observed in ionic liquids although the decreasing is more notorious [2]

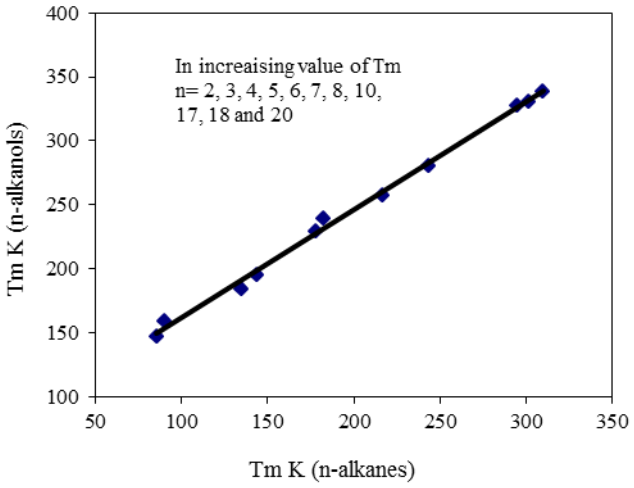


Fig. 1:Melting temperature of homologous organic compounds, n-alkanols v/s alkanes.

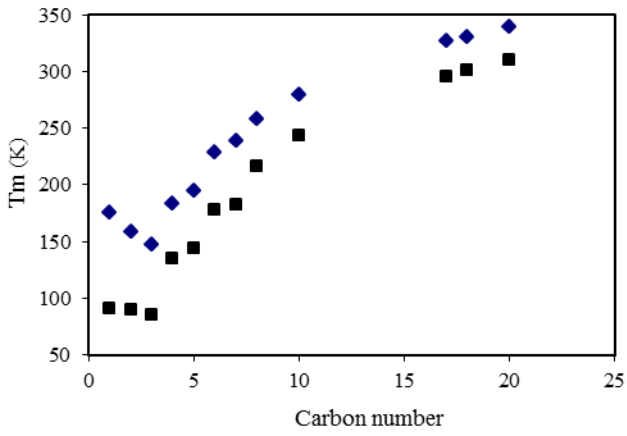


Fig. 2: Melting temperature of n-alkanes (■) and n-alkanols (♦) –vs- the number of carbons in the chain

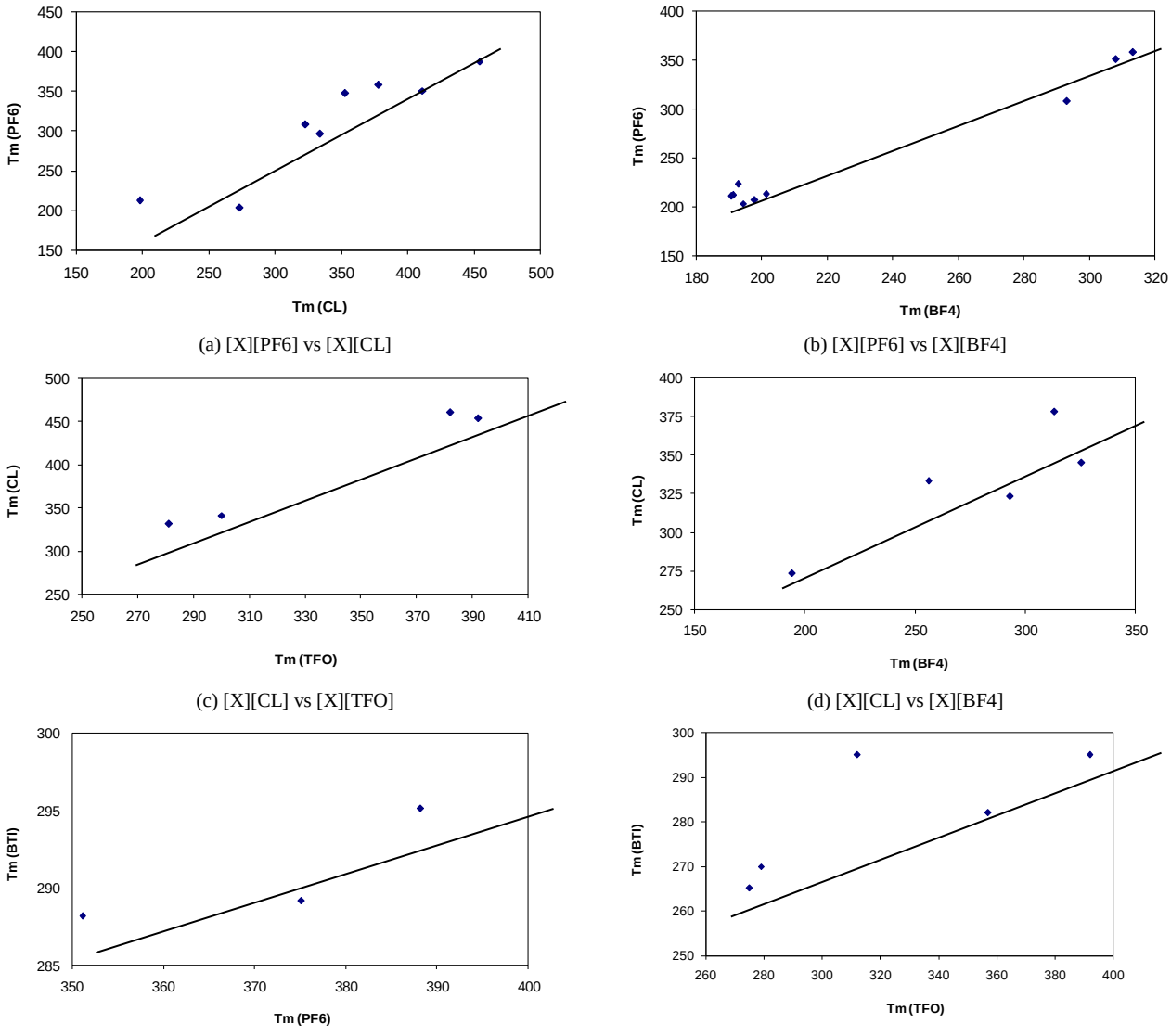
Based on this same concept of homologous series, the concept of homologous compounds seems more interesting in some applications. Karapetyants [5] used this concept in what he called "comparative calculations" to determine several properties of solids and liquids. What the author actually did was relating a given property of compounds that have either the same cation or the same anion. He gave examples for the entropy of formation and the Gibbs free energy of formation. What is interesting about this approach is its extension to estimate the melting temperature of organic compounds and then exploring its application to ionic liquids.This concept can be extended to correlate the melting temperature of ionic liquids and determine inaccurate data that do not follow a regular tendency or pattern. According to the homology concept, a point not following such a pattern may be in error.To apply the concept of homology, several factors and conditions were set and imposed:i) More than two points must be available to perform homology; ii) If there point were available and a tendency (line) is not found the cases is dismissed; iii) If several points are available and the majority of the number of points following a clear tendency those data were considered as valid data; iv) If the difference in melting temperatures of all ionic liquids in the family is below

experimental uncertainty (say 20K) then the groups are accepted as homologated ;v) After one data is accepted that value is considered correct for all other homology cases.

There are several sources where compilation of melting temperature data are available such as a study of Zhang et al.[6] (445 data points), the Dortmund Data Bank [7] (more than 400 values), the Ionic Liquids Database [8] (86 data points), the Merck data base (192 values) and the handbook by Zhang et al. [9] (975 data points). Several other values are reported in papers published in different journals. All data reported in the literature has been collected to form a database of 1500 values of melting temperature for 953 ionic liquids. Of all the data collected, 189 melting temperature data belonged to imidazolium-type ionic liquids. This was the starting set of data used in this paper.

3. Results

The first finding was that the best homologation of the data available were those belonging to the ionic liquids[X] [BTI] and [X] [CL]. These gave a relation close to a straight line (with four points and R^2=0.994) so homology is fulfilled very accurately and all data is considered to be consistent and correct.



(a) [X][PF6] vs [X][CL]

(b) [X][PF6] vs [X][BF4]

(c) [X][CL] vs [X][TFO]

(d) [X][CL] vs [X][BF4]

(e) [X][BTI] vs [X][PF6]

(f) [X][BTI] vs [X][TFO]

Fig. 3: Homology applied to different types of imidazolium ionic liquids

Table 1. Ionic liquids for which Tm data are accepted as consistent and accurate, based on the homology concept.

N º	Cation [X]	Anion [Y]	T_m(K)	Homology with

1	[mim]	[BF4]	325.55	[X][CL]	[X][TA]	
2	[C3mim]	[BF4]	256.15	[X][CL]		
3	[hmim]	[BF4]	191.15	[X][PF6]	[X][BTI]	
4	[omim]	[BF4]	194.15	[X][CL]	[X][PF6]	
5	[C1CNmim]	[BF4]	308.15	[X][PF6]		
6	[C2CNmim]	[BF4]	293.15	[X][CL]	[X][PF6]	
7	[C4CNmim]	[BF4]	201.25	[X][PF6]		
8	[C3CNdmim]	[BF4]	313.15	[X][CL]	[X][PF6]	
9	[DPPHIM	[BF4]	197.65	[X][PF6]		
10	[DPEHIM	[BF4]	190.55	[X][PF6]		
11	[DPEBIM	[BF4]	192.65	[X][PF6]		
12	[hmim]	[BTI]	266.00	[X][CL]		
13	[C4C2im]	[BTI]	265.15	[X][TFO]		
14	[dmprim]	[BTI]	288.15	[X][CL]	[X][PF6]	
15	[E1M3,5im]	[BTI]	270.00	[X][TFO]		
16	[i-C3mim]	[BTI]	289.15	[X][PF6]		
17	[Dmim]	[BTI]	295.15	[X][CL]	[X][TFO]	[X][PF6]
18	[mim]	[BTI]	282.15	[X][CL]	[X][TFO]	
19	[mim]	[CL]	345.15	[X][BTI]		
20	[C3mim]	[CL]	333.15	[X][BTI]		
21	[e'mim]	[CL]	451.15	[X][NO3]	[X][CL]	
22	[hmim]	[CL]	198.15	[X][PF6]	[X][BTI]	
23	[omim]	[CL]	273.15	[X][BF4]		
24	[dmprim]	[CL]	411.15	[X][PF6]	[X][BTI]	
25	[M1,2E3im]	[CL]	461.15	[X][TFO]		
26	[Dmim]	[CL]	454.15	[X][PF6]	[X][BTI]	[X][TFO]
27	[eim]	[CL]	331.15	[X][TFO]	[X][NO3]	
28	[C2OHmim]	[CL]	333.95	[X][PF6]		
29	[C2CNmim]	[CL]	323.15	[X][PF6]	[X][BF4]	
30	[C3CNdmim]	[CL]	378.15	[X][PF6]	[X][BF4]	
31	[C3CNmim]	[CL]	353.15	[X][PF6]		
32	[e'mim]	[NO3]	348.15	[X][CL]		
33	[eim]	[NO3]	304.15	[X][CL]		
34	[Dmim]	[NO3]	357.15	[X][CL]		
35	[hmim]	[PF6]	212.15	[X][CL]	[X][BF4]	
36	[dmprim]	[PF6]	351.15	[X][CL]		
37	[i-C3mim]	[PF6]	375.15	[X][BTI]		
38	[Dmim]	[PF6]	388.15	[X][CL]	[X][BTI]	
39	[C2OHmim]	[PF6]	296.15	[X][CL]		
40	[C1CNmim]	[PF6]	351.15	[X][BF4]		
41	[C2CNmim]	[PF6]	308.15	[X][CL]	[X][BF4]	
42	[C3CNdmim]	[PF6]	358.15	[X][CL]	[X][BF4]	
43	[C3CNmim]	[PF6]	348.15	[X][CL]		
44	[C4CNmim]	[PF6]	212.85	[X][BF4]		
45	[DPPHIM	[PF6]	206.95	[X][BF4]		
46	[DPEHIM	[PF6]	210.85	[X][BF4]		
47	[DPEBIM	[PF6]	222.95	[X][BF4]		
48	[omim]	[PF6]	203.15	[X][BF4]		
49	[Bemim]	[TFO]	300.15	[X][CL]		
50	[C4C2im]	[TFO]	275.15	[X][BTI]		
51	[M1,2E3im]	[TFO]	382.15	[X][CL]		
52	[E1M3,5im]	[TFO]	279.00	[X][BTI]		
53	[Dmim]	[TFO]	392.15	[X][CL]	[X][BTI]	
54	[mmim]	[TFO]	312.15	[X][BTI]		
55	[eim]	[TFO]	281.15	[X][CL]		
56	[mim]	[TFO]	357.15	[X][BTI]		

After doing homology between these groups (all having at least three homologous points), values for the melting temperature of 37 ionic liquids are considered to be consistent and accurate enough data. Selected results for six pairs of different types of imidazolium ionic liquids are presented in Fig. 3. Of all the original data (189 ionic liquids) 133 values were not homologated. This does not mean that data are inconsistent, because they have been no subjected to any test. This must be defined when additional values become available and homologation can be done.

4. Conclusion

The homology concept applied to families of ionic liquids seems to be a reasonable method for detecting erroneous data of melting temperature of ionic liquids. The main problem of the method is that to be applied, melting temperature data for several ionic liquids are needed and such data in many cases are not available. The values of the melting temperature for the 56 ionic liquids listed in Table 1 are believed to be consistent from the point of view of homology and are therefore acceptable as the "true" melting temperature.

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