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Group contribution and parachor analysis of experimental data on density and surface tension for members of the homologous series of 1-C_n-3-methylimidazolium chlorides

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ABSTRACT

The density and surface tension values are presented that represent the best current knowledge of these properties for members of the homologous series of 1-C_n-3-methylimidazolium chlorides. To identify these values, a method was used based on the consistency requirement between selected background experimental data and group contribution models of known best achievable accuracy. The models have been developed using our own and other authors' data. For this purpose 64 and 119 new experimental data on the density and surface tension, respectively, have been measured for [C_1IM][Cl] and [C_nMIM][Cl] with $n = 2, 3, 4, 6$, and 10 at temperatures from (263 to 365) K and at the pressure of 0.1 MPa. The density was measured using the buoyancy method while the surface tension was measured by the Wilhelmy plate and du Noüy ring method in parallel. The respective expanded combined uncertainties at the 0.95 confidence level of the resultant means of sets of individual measurements performed at a given temperature do not exceed 1 kg·m^{-3}, 0.07 mN·m^{-1} and 1 mN·m^{-1}. The estimated maximum deviations of the obtained recommended values from the true density and surface tension values are 0.1 kg·m^{-3} and 0.15 mN·m^{-1}, respectively.

1. Introduction

Chlorides, like acetate or dimethylphosphate anions, are good hydrogen-bond acceptors. In combination with imidazolium- or pyridinium-based cations, they form ionic liquids exhibiting some exceptional features on which their special applications are based. Owing to their hydrogen-bonding ability, they are capable of dissolving cellulose and thus converting waste biomass into clean, sustainable bio fuels [1]. Dialkyl-imidazolium chlorides are among the most common ILs. They are sufficiently stable, relatively inexpensive, and can be easily synthesized. They are commercially available in large quantities. Over the past three decades, many promising applications of them have been developed. Besides the use as solvent for biopolymers, imidazolium-based chlorides can be used as an absorbent in working pairs absorbent/refrigerant for absorption chillers and absorption heat pumps [2–5] and in combination with metal chlorides, as aprotic electrolytes for electrolytic deposition of metals. The use of the dialkyl-imidazolium chlorides for absorption chillers and absorption heat pumps is made more difficult by their relatively high melting point, which results in elevated process temperatures required in the liquid state and in an increase in energy consumption.

The chloride anion comes into consideration as one of the anions for the multi-ion ionic liquids. Ning et al. [6] have studied three-ion ionic liquids composed of one type of imidazolium-based cations and the tetrafluoroborate and chloride anions. In still more complex four-ion ionic liquids containing the chloride anion and approached as binary mixtures of simple two-ion ionic liquids, the non-ideal behavior may occur due to newly appearing additional hydrogen bonds, which are not present in the mixture components.

Chloride anions, originating from an incomplete anion exchange in the preparation process, rank among the most common impurities in ionic liquids. Since the paper by Seddon et al. [7], chloride impurities present in the ionic liquid sample are generally believed to have a very significant impact on all the properties of ionic liquids. However, the effect of the chloride anions on the density and surface tension can be described quantitatively with sufficient accuracy. Knowing the chloride content in the sample, it is possible to introduce the corresponding correction for chloride content,

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accurate to the extent to which the model used is valid.

Table 1 shows the melting temperature decreasing along the homologous series of 1-C_n-3-methylimidazolium chlorides from C1 to C3 and slightly then increasing to C4. There is no crystallization in C6 and C8, but only glass transition occurs, with melting temperature rising again for C10 and C12 [8–12]. The viscosity of IL grows with the chain length [13,14]. Well dried samples of imidazolium-based chlorides can be significantly supercooled, which considerably extends the liquid range available for measurements. This is important because data covering a wider temperature range provide more favorable conditions to create a property description that would provide values of the property as close as possible to its actual values. The presence of hydrogen bonding in 1-alkyl-3-methylimidazolium chlorides results in their higher melting points and viscosities, what causes their property measurements to be more difficult compared to ILs with other anions. Consequently, the data on density and surface tension for [C_nMIM][Cl] available in the literature are less accurate and with exception of $n = 4$, 6, and 8 are rare or completely absent.

Tables 2 and 3 provide an overview of the literature sources for the data on the 0.1 MPa density and surface tension of the ionic liquids of interest. There are 26 experimental studies [6,11,15–38] available in the literature on the density of [C_nMIM][Cl] with $n = 1$ to 4, 6, 8, and 10 containing a total of 230 data points. For $n > 3$ no density data are available in the literature for the odd values of n. There are 5 studies, [11,37,38,44,45] available in the literature on the surface tension of [C_nMIM][Cl] for $n = 4$, 6, 8, and 10, reporting 72 data points while no surface tension data are available for other values of n. In this situation, to determine the most reliable values of the properties of the investigated ionic liquids, there is no choice but to find a way to make the best use of existing sparse data even with the help of an expansion of the existing database by additional measurements.

[C_8MIM][Cl] is the most thoroughly studied member of its homologous series. There exist 16 studies in the literature containing a total of 78 data points for density of [C_8MIM][Cl] and five studies containing 31 data points on its surface tension. Additional data seemed to be superfluous, which has also been confirmed in subsequent primary data selection and the recommended data generation.

Property values of different authors are often spread over a much wider interval than it would correspond to the uncertainties reported by the authors. So, recently it has become obvious that the identification and selection of accurate and reliable data from all data available is absolutely crucial in the development of an accurate property model [39]. The principle of this approach lies in formulation of an additional data requirement where it can reasonably be assumed that only sufficiently accurate data meet such a requirement. Data can be tested for consistency with assumptions of a model for which the best achievable accuracy is known [40–43]. To select the most accurate subcollection of data sets from all available data sets, we use a requirement in Subsection 3.3 of approximate consistency of the data with the GC model that they define by the least-squares fitting.

The objective of the present study was: (i) to acquire new accurate experimental data for the temperature dependence of the 0.1 MPa density and the surface tension of pure 1-methylimidazolium chloride and five 1-C_n-3-methylimidazolium chlorides with $n = 2$, 3, 4, 6, and 10, for which samples are commercially available, (ii) for the members of the studied homologous series, to develop empirical models capable of generating values for their 0.1 MPa density and surface tension with well-reasoned accuracy, which could be regarded as representing the best current knowledge.

2. Experimental section

2.1. Materials

Commercially supplied samples of pure ionic liquids were used in the present measurements. Table 4 shows their main characteristic including results of the purity analysis of the samples certified by the manufacturer's certificate. The water mass fraction in the samples was measured in our laboratory with the Karl Fischer Mettler Toledo C30 coulometric titrator. The starting water content limits in the samples before measurements reported in Table 4 were achieved by intensive stirring and evaporation under vacuum at temperature 363 K. The absence of any systematic directional change of the obtained values of the measured quantities with time during the one-day measurements suggests that the absorption of the moisture and air in the sample, regardless of their possible amount, does not cause an observable change in the measured properties.

2.2. Measurements of density at 0.1 MPa

The density data reported here were obtained by the single-sinker buoyancy method implemented using the Krűss K100 Mk2 tensiometer. Ref. [46] describes in detail the apparatus, and the experimental and data evaluation procedures used in the measurements. Both in the density and in surface tension measurements, the temperature of the measuring vessel containing the sample was stabilized within ±0.02 K by the Lauda ECO RE1050 G thermostat and measured using a platinum resistance thermometer with a standard uncertainty of 0.02 K as stated by the manufacturer. The pressure, which was not controlled during the measurement, was within the interval of (0.1±0.002) MPa given by the annual variations in the atmospheric pressure in Prague.

The combined standard uncertainty u_C in density measurements consists of the type-A and type-B standard uncertainties [47] u_A and u_B, respectively; $u_C^2 = u_A^2 + u_B^2$. The type-A uncertainty, estimated as the standard deviation of the mean of a set of repeated density measurements at a given set point temperature, do not exceed 0.52 kg·m^{-3}, that is, 0.050% of the measured density. The contributions from the density of the sinker material and the air density form the type-B uncertainty, which is, however, in this case, considerably smaller [48] than the type-A uncertainty, so that the expanded combined uncertainty U_c at the 0.95 confidence level ($k = 2$) do not exceed 1 kg·m^{-3}, that is, 0.1% relatively to the measured density.

Table 1
Temperatures of fusion T_f, that is, temperatures of melting or of glass transition available in literature for the members of the homologous series of 1-C_n-3-methylimidazolium chlorides.

n	1	2	3	4	6	8	10	12
Reference	[9]	[8]	[9]	[10]	[11]	[11]	[12]	[12]
T_f/K	399.45^m	369.75^m	335.05^m	341.95^m	198.05^g	186.05^g	311.15^m	369.75^m

^{m} melting, ^{g} glass transition.