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Odd-even effect on the formation of aqueous biphasic systems formed by 1-alkyl-3-methylimidazolium chloride ionic liquids and salts

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Abstract

This work provides a comprehensive evaluation of the effect of the cation alkyl side chain length of the 1-alkyl-3-methylimidazolium chloride series ($[C_nC_1im]Cl$, $n = 2-14$) of ionic liquids (ILs) on their capability to form aqueous biphasic systems (ABSs) with salts and self-aggregation derived properties. The liquid-liquid phase behavior of ternary systems composed of $[C_nC_1im]Cl$, water, and K_3PO_4 or K_2CO_3 and the respective Setschenow salting-out coefficients (k_s), a quantitative measure of the two-phase formation ability, were determined. An odd-even effect in the k_s values along the number of methylene groups of the longest IL cation alkyl side chain was identified for the ABS formed by K_2CO_3 , a weaker salting-out agent where the phenomenon is clearly identified. In general, cations with even alkyl side chains, being likely to display higher molar volumes, are more easily salted-out and thus more prone to undergo phase separation. The odd-even effect in the k_s values is, however, more significant in ILs up to $n = 6$, where the nanostructuration/nanosegregation of ILs plays a less relevant role. Still, with the $[C_nC_1im]Cl$ ($n = 7-14$) series of ILs, an odd-even effect was also identified in the ILs' ionization degree, molar conductivity, and conductivity at infinite dilution. In summary, it is shown here that the ILs' odd-even effect occurs in IL aqueous solutions and not just in neat ILs, an already well-established phenomenon occurring in a series of ILs' properties described as a result of the orientation of the terminal methyl groups to the imidazolium ring cation and consequent effect in the ILs' cohesive energy.

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I Introduction

Aqueous biphasic systems (ABSs) were originally proposed by Albertsson.¹ They are composed of two immiscible aqueous-rich phases and are formed when two distinct substances, yet both miscible with water, e.g., polymer/polymer, polymer/salt, or salt/salt combinations, are mixed at given concentrations. Mainly due to their high water content, ABSs constitute a more biocompatible alternative in liquid–liquid extractions and have thus been applied in the separation and fractionation of several biological compounds.² In addition to the more conventional polymer-based ABS, Rogers and co-workers³ demonstrated that ionic liquids (ILs) can also be employed as phase-forming components of ABSs.³ Since then, IL-based ABSs have been widely investigated as powerful alternatives to conventional systems due to the possibility of easily tuning the properties of the coexisting phases, such as the phase's hydrophobicity and solvation ability. Furthermore, their biodegradability and toxicity features can be adjusted through the judicious choice of the chemical structure of the IL ions.^{4,5}

Several studies aimed at better understanding the interactions occurring between water and ILs and between ILs and salts in aqueous solutions,^{6–9} are essential to understand the molecular-level phenomena governing the IL-based ABS formation. Within this field, after the work of Bridges *et al.*,¹⁰ a large number of publications arose addressing the influence of the ILs' cation/anion nature on the formation of ABSs.^{11–26} The authors¹⁰ evaluated the phase behavior of imidazolium-, pyridinium-, quaternary ammonium-, and phosphonium-based chloride ILs salted-out by K_3PO_4 , K_2HPO_4 , K_2CO_3 , KOH, and $(NH_4)_2SO_4$, concluding that the higher the hydrophobicity of the IL, the higher the ability of the IL to be salted-out and to phase separate. The effect of the IL alkyl side chain length on the formation of ABSs has also been investigated by several researchers, with the imidazolium class of ILs being the most studied.¹⁷ In general, the longer the IL cation alkyl side chain, the easier it is to form an ABS.¹⁷ Aiming to address this phenomenon more deeply, a systematic investigation on the influence of the cation alkyl side chain length of 1-alkyl-3-methylimidazolium chloride ILs ($[C_nC_1im]Cl$ with $n = 1–14$) had been previously carried out by us.¹⁵ We demonstrated that the increase of the cation alkyl chain length enhances the formation ability of ABSs, yet only for cations with alkyl chain sizes up to hexyl. ILs with longer alkyl side chains showed a more complex behavior in which the capacity of the IL to self-aggregate was shown to have a significant influence on the phase separation ability.¹⁵ The ABS formation ability also depends on the anion alkyl side chain length, in which ILs with longer aliphatic moieties are more easily salted-out by inorganic salts; yet, no major conclusions on the self-aggregation phenomenon have been drawn since only alkyl side chains up to heptyl have been evaluated.²⁶

Although the impact of numerous structural changes on the ABS formation has been extensively studied, particularly regarding the effect of the cation alkyl side chain length,¹⁵ differences between cations with even and odd alkyl side chains have never been addressed. Most results reported up to date were obtained with ILs composed of cations with even alkyl side chains due to their commercial availability. To address this aspect, this work provides a comprehensive evaluation of the odd-even effect of the IL cation alkyl side chain on ABS formation and self-aggregation/nanostructuration phenomena in aqueous media. For this

purpose, the phase diagrams and respective equilibrium compositions of the ternary systems composed of ILs of the 1-alkyl-3-methylimidazolium chloride series, water, and two salts (K_3PO_4 and K_2CO_3) were determined. Subsequently, the Setschenow coefficients were estimated, a parameter that characterizes the salting-out strength and the two-phase forming capability. The critical micellar concentration (CMC), ionization degree, molar conductivity, and conductivity at infinite dilution of the surface-active ILs ($[\text{C}_n\text{C}_1\text{im}]\text{Cl}$, $n = 7-14$) were additionally determined to appraise the odd-even effect on the ILs' self-aggregation phenomenon.

II Experimental Section

A Materials

The ABSs studied in this work were prepared using tribasic potassium phosphate, K_3PO_4 , 98 wt. % pure from Acros Organics, and potassium carbonate, K_2CO_3 , 99 wt. % pure from Sigma-Aldrich. These two salts were chosen due to their different salting-out capability, in which K_3PO_4 is a stronger salting-out species according to the Hofmeister series.²⁷ The ILs studied belong to the 1-alkyl-3-methylimidazolium chloride series, namely, 1-ethyl-3-methylimidazolium chloride ($[\text{C}_2\text{C}_1\text{im}]\text{Cl}$, >98 wt. %), 1-methyl-3-propylimidazolium chloride ($[\text{C}_3\text{C}_1\text{im}]\text{Cl}$, >98 wt. %), 1-butyl-3-methylimidazolium chloride ($[\text{C}_4\text{C}_1\text{im}]\text{Cl}$, >99 wt. %), 1-methyl-3-pentylimidazolium chloride ($[\text{C}_5\text{C}_1\text{im}]\text{Cl}$, >98 wt. %), 1-hexyl-3-methylimidazolium chloride ($[\text{C}_6\text{C}_1\text{im}]\text{Cl}$, >98 wt. %), 1-heptyl-3-methylimidazolium chloride ($[\text{C}_7\text{C}_1\text{im}]\text{Cl}$, >98 wt. %), 1-methyl-3-octylimidazolium chloride ($[\text{C}_8\text{C}_1\text{im}]\text{Cl}$, >98 wt. %), 1-methyl-3-nonylimidazolium chloride ($[\text{C}_9\text{C}_1\text{im}]\text{Cl}$, >98 wt. %), 1-decyl-3-methylimidazolium chloride ($[\text{C}_{10}\text{C}_1\text{im}]\text{Cl}$, >98 wt. %), 1-methyl-3-undecylimidazolium chloride ($[\text{C}_{11}\text{C}_1\text{im}]\text{Cl}$, >98 wt. %), 1-dodecyl-3-methylimidazolium chloride ($[\text{C}_{12}\text{C}_1\text{im}]\text{Cl}$, >98 wt. %), 1-methyl-3-tridecylimidazolium chloride ($[\text{C}_{13}\text{C}_1\text{im}]\text{Cl}$, >98 wt. %), and 1-methyl-3-tetradecylimidazolium chloride ($[\text{C}_{14}\text{C}_1\text{im}]\text{Cl}$, >98 wt. %). Before use, all ILs were dried for a minimum of 24 h under constant agitation, at moderate temperature (≈ 353.15 K) and under vacuum, to reduce their volatile impurities to negligible values. After this step, the purity of each IL was confirmed by ^1H and ^{13}C NMR spectra and found to be >98 wt. %. ILs of even alkyl side chains were acquired from Iolitec, whereas ILs of odd alkyl side chains were synthesized by us according to the procedure given in the supplementary material. Ultra-pure water, double distilled and further treated with a Milli-Q plus 185 water purification apparatus, was used.

B Phase diagrams and tie-lines

The binodal curves of the ternary phase diagrams were determined through the cloud point titration method¹⁷ at (298 ± 1) K and atmospheric pressure, with an average uncertainty in the weight fraction compositions of ± 1.5 wt. %. Aqueous solutions of K_3PO_4 or K_2CO_3 at ~ 40 wt. % and aqueous solutions of the different hydrophilic ILs at ~ 60 wt. % were prepared gravimetrically. Starting from a homogeneous mixture, with known composition and under continuous stirring, the aqueous salt solution was added drop-wise until the detection of a cloudy solution (biphasic region). The titration was then followed by the drop-wise addition of ultra-pure water until the detection of a clear and limpid solution (monophasic region). The ternary systems' compositions, at each phase transition, were determined by the weight

quantification of all components added within an uncertainty of $\pm 10^{-4}$ g and at (298 ± 1) K. The experimental binodal curves were fitted using the following equation:²⁸

$$[\text{IL}] = A \exp[(B[\text{Salt}]^{0.5}) - (C[\text{Salt}]^3)], \quad (1)$$

where $[\text{IL}]$ and $[\text{Salt}]$ are, respectively, the IL and salt weight percentages, and A , B , and C are the constants obtained by the regression of the experimental binodal data.

The tie-lines (TLs) were determined by a gravimetric method originally described by Merchuk *et al.*,²⁸ with an average uncertainty of ± 1.5 wt. %. Different initial mixture compositions (IL + K_3PO_4 or K_2CO_3 + water) at the biphasic region were gravimetrically prepared ($\pm 10^{-4}$ g), vigorously stirred, and allowed to reach the equilibrium by the separation of the two phases for at least 12 h at (298 ± 1) K. After the phase separation, both top and bottom phases were separated and weighted.

To improve the accuracy of the determined TLs, the water content in each phase [top (T) and bottom (B) phases, namely, $w_{\text{H}_2\text{O},\text{T}}$ and $w_{\text{H}_2\text{O},\text{B}}$] was determined gravimetrically by evaporation of water at 373 K, performed until constant weight of the non-volatile species (salt and IL). Each individual TL was then determined by applying the lever-arm rule through the phase's mass balances according to the following equations [Eqs. (2)–(9)]:

$$[\text{IL}]_{\text{T}} = A \exp[(B[\text{Salt}]_{\text{T}}^{0.5}) - (C[\text{Salt}]_{\text{T}}^3)], \quad (2)$$

$$[\text{IL}]_{\text{B}} = A \exp[(B[\text{Salt}]_{\text{B}}^{0.5}) - (C[\text{Salt}]_{\text{B}}^3)], \quad (3)$$

$$[\text{IL}]_{\text{T}} = \frac{[\text{IL}]_{\text{M}}}{\alpha} - \frac{1 - \alpha}{\alpha} \times [\text{IL}]_{\text{B}}, \quad (4)$$

$$[\text{Salt}]_{\text{B}} = \frac{[\text{Salt}]_{\text{M}}}{\alpha} - \frac{1 - \alpha}{\alpha} \times [\text{Salt}]_{\text{B}}, \quad (5)$$

$$w_{\text{IL},\text{M}} = w_{\text{T}} \times \frac{[\text{IL}]_{\text{T}}}{100} + w_{\text{B}} \times \frac{[\text{IL}]_{\text{B}}}{100}, \quad (6)$$

$$w_{\text{Salt,M}} = w_T \times \frac{[\text{Salt}]_T}{100} + w_B \times \frac{[\text{Salt}]_B}{100}, \quad (7)$$

$$w_T = w_T \times \frac{[\text{Salt}]_T}{100} + w_T \times \frac{[\text{IL}]_T}{100} + w_{\text{H}_2\text{O,T}}, \quad (8)$$

$$w_B = w_B \times \frac{[\text{Salt}]_B}{100} + w_B \times \frac{[\text{IL}]_B}{100} + w_{\text{H}_2\text{O,B}}. \quad (9)$$

The subscripts T and B represent the IL-rich and salt-rich phases, respectively, and the subscript M represents the initial mixture composition. [Salt] and [IL] represent the weight fraction of the salt (K_3PO_4 or K_2CO_3) and IL, respectively. The parameter α is the ratio between the top and the total weight of the mixture. $w_{\text{IL,M}}$ and $w_{\text{Salt,M}}$ are the amounts of IL and salt weighted for the mixture point preparation, while w_T and w_B represent the weight of the IL- and salt-rich phases, respectively. The simultaneous regression of the equations gives the concentration of the IL and salt in the top and bottom phases. In all systems investigated, the top phase is enriched in IL, whereas the salt-rich phase corresponds to the bottom phase.

For the calculation of the tie-line length (TLL), the following equation was applied:

$$\text{TLL} = \sqrt{([\text{Salt}]_T - [\text{Salt}]_B)^2 + ([\text{IL}]_T - [\text{IL}]_B)^2}. \quad (10)$$

C Critical micellar concentration

The CMC of the studied ILs was determined by electrical conductivity using SevenMulti™ (Mettler Toledo Instruments) at (298 ± 1) K, with an uncertainty of $\pm 0.01 \text{ mS cm}^{-1}$. The equipment was calibrated with standard solutions ($10 \mu\text{S cm}^{-1}$, $84 \mu\text{S cm}^{-1}$, $500 \mu\text{S cm}^{-1}$, $1413 \mu\text{S cm}^{-1}$, and $12.881 \text{ mS cm}^{-1}$) acquired from Sigma-Aldrich. To 10 ml of Milli-Q water under constant stirring, 16 g of each IL stock solution (about 3 times more concentrated than the CMC) were added and the conductivity was determined at each addition. By the graphical representation of the conductivity as a function of the IL concentration, each CMC value was determined by the intersection of the linear functions correlating the conductivities above and below the CMC.

III Results and Discussion

This work aims at evaluating the differences in behavior between even and odd cation alkyl side chains of ILs belonging to the $[\text{C}_n\text{C}_{1\text{im}}]\text{Cl}$ ($n = 2\text{--}14$) series, in aqueous solutions, namely, in the formation of ABSs with two inorganic salts of different salting-out strength (K_2CO_3 and K_3PO_4) and in their nanostructuration behavior addressed by self-aggregation

derived properties. It should be noted that the methyl group is constant in all ILs investigated and odd-even effects will be discussed according to the longest alkyl side chain present at the imidazolium cation. All phase diagrams, determined at 298 K and at atmospheric pressure, are depicted in Fig. 1. The detailed experimental data of all binodal curves are provided in the supplementary material (Tables S1–S22).

In order to appraise the ability of the different ILs to be salted-out and to form ABSs, by eliminating differences which could arise from different molecular weights, the phase diagrams in Fig. 1 are shown in a molality scale. The corresponding representation in weight fraction is presented in the supplementary material (Figs. S1 and S2). Mixture compositions above each binodal/solubility curve correspond to the biphasic region, whereas those below correspond to homogenous solutions. The capability of the studied ILs to promote the formation of ABSs, e.g., using K_3PO_4 at 0.5 mol kg^{-1} , follows the order: $[\text{C}_2\text{C}_1\text{im}]\text{Cl} < [\text{C}_3\text{C}_1\text{im}]\text{Cl} < [\text{C}_4\text{C}_1\text{im}]\text{Cl} < [\text{C}_9\text{C}_1\text{im}]\text{Cl} \approx [\text{C}_5\text{C}_1\text{im}]\text{Cl} \approx [\text{C}_6\text{C}_1\text{im}]\text{Cl} \approx [\text{C}_7\text{C}_1\text{im}]\text{Cl} \approx [\text{C}_{10}\text{C}_1\text{im}]\text{Cl} < [\text{C}_8\text{C}_1\text{im}]\text{Cl} \approx [\text{C}_{11}\text{C}_1\text{im}]\text{Cl} \approx [\text{C}_{12}\text{C}_1\text{im}]\text{Cl}$. A similar trend is obtained using K_2CO_3 at 0.5 mol kg^{-1} : $[\text{C}_2\text{C}_1\text{im}]\text{Cl} < [\text{C}_3\text{C}_1\text{im}]\text{Cl} < [\text{C}_4\text{C}_1\text{im}]\text{Cl} \approx [\text{C}_5\text{C}_1\text{im}]\text{Cl} < [\text{C}_9\text{C}_1\text{im}]\text{Cl} \approx [\text{C}_8\text{C}_1\text{im}]\text{Cl} \approx [\text{C}_6\text{C}_1\text{im}]\text{Cl} \approx [\text{C}_7\text{C}_1\text{im}]\text{Cl} \approx [\text{C}_{10}\text{C}_1\text{im}]\text{Cl} \approx [\text{C}_{11}\text{C}_1\text{im}]\text{Cl} < [\text{C}_{12}\text{C}_1\text{im}]\text{Cl}$.

With both salts, it was obtained a behavior similar to that previously established with ILs composed of cations with even alkyl side chains,¹⁵ and for which a more complex dependency on the cation alkyl chain length was observed above $[\text{C}_7\text{C}_1\text{im}]\text{Cl}$. From $[\text{C}_2\text{C}_1\text{im}]\text{Cl}$ to $[\text{C}_7\text{C}_1\text{im}]\text{Cl}$, the results obtained indicate that the longer the cation alkyl side chain, the higher the IL capacity for phase separation, i.e., the easier it is their salting-out from aqueous media. This behavior is justified by the increase in the hydrophobicity and molar volume of the IL as the aliphatic moiety increases.²⁵ Nevertheless, the ILs' pattern is more intricate for ILs with an alkyl side chain longer than hexyl, above which ILs can self-aggregate in aqueous solution, in good agreement with previous indications that the formation of ABS results from a delicate balance between the hydrophobicity and molar volume of the IL and its ability to self-aggregate as the size of the IL cation alkyl side chain increases.¹⁵

If an even-odd effect of the alkyl side chain associated with the formation of ABSs exists, it is very subtle and it is not possible to observe it from the direct analysis of the binodal curves. As previously suggested by us,¹⁵ a detailed quantitative analysis was here carried out by determining at least 5 TLs for each ABS to allow the determination of the Setschenow coefficient.²⁹ The parameters of Eq. (1) determined by the non-linear regression of the experimental binodal data as well as the detailed data for the TLs, TLLs, and Tie-Line Slope (TLS) of each system are provided in the supplementary material (Tables S23–S26). It should be noted that $[\text{C}_{13}\text{C}_1\text{im}]\text{Cl}$ and $[\text{C}_{14}\text{C}_1\text{im}]\text{Cl}$ present a small liquid-liquid region and most of the selected TLs fall in a solid-liquid region and therefore were not used in the odd-even effect analysis on the ABS formation. They were however used in the study of the odd-even effect in the ILs' self-aggregation phenomenon as discussed below.

Hey *et al.*³⁰ proposed a modification to the original Setschenow equation²⁹ which was successfully used in the description of polymer-based ABSs. Zafarani-Moattar and

Hamzehzadeh^{31,32} later showed that the proposed equation was also useful for the description of IL-based ABSs, being thereafter used by us¹⁵ for the evaluation of the effect of the IL cation alkyl chain length on the ABS formation. Accordingly, this modified equation was used in this work, as described in the following equation:

$$\ln \frac{[IL]_T}{[IL]_B} = k_{IL}([IL]_B - [IL]_T) + k_s([Salt]_B - [Salt]_T), \quad (11)$$

where $[IL]$ and $[Salt]$ represent the molality of IL and salt, T and B designate the top (IL-rich) and bottom (salt-rich) phases, respectively, and k_{IL} and k_s are parameters relating the activity coefficient of the IL to its concentration and the salting-out coefficient, respectively.

The Setschenow constant of each IL-based ABS, k_s , was calculated by the simultaneous regression of five TLs experimentally determined, at initial mixture compositions falling within the biphasic region. The respective values are reported in the supplementary material (Tables S27 and S28 and Figs. S3 and S4). Based on the correlation coefficients obtained, also given in the supplementary material, it can be concluded that the equilibrium compositions of the investigated systems are well described by Eq. (11).

The higher the k_s value, the higher the ability of the salt to salt-out the IL and to create an ABS. When analyzing the Setschenow constant, k_s , as a function of the IL alkyl chain size for the ABS composed of IL + K_3PO_4 + H_2O [Fig. 2(a)], the current results agree with our previous findings.¹⁵ However, in the previous work,¹⁵ only ILs with alkyl chains with an even number of carbons were considered and no odd-even effect was identified. Since K_3PO_4 is a strong salting-out salt, leading thus to high k_s values, the odd-even effect, if it occurs, is to some extent hidden, as shown in Fig. 2(a). Nevertheless, if one evaluates this effect with a weaker salting-out species, namely, K_2CO_3 , the odd-even effect is evident, as depicted in Fig. 2(b).

When analyzing the Setschenow constant as a function of the alkyl chain size, particularly with the weaker salting-out salt (K_2CO_3), the occurrence of an odd-even effect is clear. Although an odd-even effect has been previously identified in several ILs' properties, such as densities, viscosities, and molar volumes^{33,34} and entropy and enthalpy of vaporization,^{35,36} it is here shown that it also occurs in aqueous solutions, meaning that the ILs' organization and their nanostructuration contribute to the observed phenomenon. For the ILs' pure properties, the odd-even effect has been explained based on the orientation of the terminal methyl groups to the imidazolium ring and their influence on the ILs' cohesive energy,^{35,36} which is here shown to have a direct impact on their behavior in aqueous solution.

Considering the ABS formed by K_2CO_3 , the results show that ILs with cations with even alkyl side chains are better salted-out or are more prone to undergo phase separation in aqueous media. In a previous work, we found that for a series of ILs with a common anion and salt, the molar volume of the IL cation plays a dominant role in the formation of IL-ABSs with salts.^{15,25} However, it should be remarked that the scenario is quite different

when evaluating the IL anion effect, where the hydrogen-bonding with water and the IL anion ability to create hydration complexes rules the two-phase formation, thus correlating well with the IL anion hydrogen-bond basicity.¹² It is thus straightforward that even alkyl side chain ILs, with a higher molar volume,³³ more easily phase separate and form ABSs, as reflected by their higher k_s values.

The odd-even effect is also more evident up to $[C_7C_{11}im]Cl$, where the ILs' self-aggregation is yet not playing a role. This intensification on the odd-even effect follows however the opposite pattern to that identified in the ILs' enthalpies and entropies of vaporization, where the phenomenon is more intense with ILs with alkyl side chains longer than hexyl.^{35,36} These differences may be related with the fact of having ILs in aqueous solution versus pure ILs, where the orientation of the terminal methyl groups to the imidazolium ring and their influence on the ILs' cohesive energy is less relevant in aqueous solutions comprising surface-active ILs.

In order to better understand the behaviour of long alkyl chain ILs in the formation of ABS, the critical micellar concentration (CMC) of the surface-active $[C_nC_{11}im]Cl$, with $n = 7-14$, was determined by conductivity measurements. As expected, the $\log(CMC)$ decreases almost linearly with the increase of the IL cation alkyl chain length, as shown in Fig. 3. The ILs' self-aggregation is enhanced by dispersive interactions that become stronger as the cation alkyl chain increases.³⁷ Though, no clear odd-even effect is observed in the CMC values as a function of the length of the alkyl chain of the imidazolium cation.

The degree of ionization³⁸ of the $[C_nC_{11}im]Cl$ micelles, with $n = 7-14$, was further estimated based on the ratio between the slopes of the conductivities above and below the CMC. The results obtained are shown in Fig. 4. Overall, there is a decrease in the degree of ionization with the increase of the IL cation alkyl chain length. The increase of the IL aliphatic moiety causes a compaction of the aggregates, thereby decreasing the micelles degree of ionization. This can be explained by the change in charge density at the micelle surface as the cation alkyl chain increases.³⁹ In addition to this phenomenon, an odd-even effect is clearly seen in the degree of ionization of ILs' micelles, for which ILs with even alkyl side chains display higher degrees of ionization and are thus less compacted. This trend is in close agreement with the above discussion regarding the ILs' molar volume, the Setschenow constant, and the ILs' ability to form ABSs (odd vs. even cation alkyl side chains in ILs) in what concerns the orientation of the terminal methyl groups to the imidazolium ring and their influence on the ILs' cohesive energy.

To appraise the self-aggregation phenomenon of long-chain ILs ($n \geq 7$), the experimental conductivity data were used to estimate the molar conductivities of the micellar species, Λ^M , and the molar conductivity at infinite dilution, Λ^∞ .^{40,41} Λ^M was estimated from the derivative of conductivity as a function of the IL concentration (dk/dc), and the respective results as a function of the IL carbon number at the longest alkyl side chain are depicted in Fig. 5. Λ^M decreases as the length of the aliphatic moiety increases, in agreement with the profile previously reported in the literature.³⁸ Nevertheless, superposed to this expected decrease, it is also observed a clear odd-even effect in the Λ^M values.

From the molar conductivities ($\Lambda = k/C$), it is possible to estimate the molar conductivity at infinite dilution, Λ^∞ , according to the following equation:⁴²

$$\Lambda = \Lambda^\infty - bC^{1/2}, \quad (12)$$

where Λ^∞ is the molar conductivity at infinite dilution and b is an empirical constant.

The molar conductivities at infinite dilution, Λ^∞ , were determined by the extrapolation of the molar conductivity values to the limit of infinite dilution ($C = 0$). The results of Λ^∞ as a function of the size of the cationic aliphatic moiety are depicted in Fig. 6. Also in this property, a clear odd-even effect is observed, suggesting that even before the formation of aggregates an odd-even effect seems to be present in the fluids' conductivity.

In summary, in addition to previously reported odd-even effects in several properties of pure ILs, namely, densities,^{33,43} viscosities,³⁴ and thermodynamic properties of vaporization,^{35,36} a similar phenomenon is here shown to occur in aqueous solutions, i.e., in both ABSs formed by ILs and salts, as well as in the self-aggregation derived properties of surface-active ILs. In general, cations with even alkyl side chains with higher molar volumes are more easily salted-out and thus more prone to undergo phase separation and form ABSs. With the $[C_nC_{11}im]Cl$ ($n = 7-14$) series of ILs, an odd-even effect was also identified in the ILs' ionization degree, molar conductivity, and conductivity at infinite dilution, meaning that the ILs' odd-even effect occurs even in diluted IL aqueous solutions and not just in neat ILs.

IV Final Remarks

In this work, the impact of the cation alkyl side chain length of the series of ILs $[C_nC_{11}im]Cl$ ($n = 2-14$) in the formation of ABSs with salts and in their self-aggregation phenomenon was investigated. Through the analysis of the ternary liquid-liquid phase diagrams, it was not possible to identify a clear odd-even effect according to the IL cation longest alkyl side chain. However, when the Setschenow constants for the various systems were estimated and plotted as a function of the carbon number at the longest cation alkyl chain, n , a clear odd-even effect was observed, particularly for systems formed by a weaker salting-out species, such as K_2CO_3 . In general, ILs with even alkyl side chains display higher k_s values and are more prone to be salted-out and undergo liquid-liquid demixing, a trend driven by their larger volume. When analyzing the self-aggregation ability of ILs with $n \geq 7$, it was observed a decrease in their CMC with the increase of their alkyl chain length, as expected. Although an odd-even effect was not observed in the CMC values, this phenomenon was clearly identified in the ILs' degree of ionization, molar conductivity, and molar conductivity at infinite dilution. In general, ILs with even alkyl side chains display a higher degree of ionization, being thus less compacted, being in agreement with the trend observed in the ABS formation ability. In addition to the previously reported odd-even effects in several properties of pure ILs, here a similar phenomenon is shown to occur in aqueous solutions.

Supplementary Material

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Fig. 1.

Ternary phase diagrams for K_3PO_4 (a) or K_2CO_3 (b) + water + $[\text{C}_n \text{C}_1 \text{im}]\text{Cl}$ systems at 298 K and atmospheric pressure: $[\text{C}_2 \text{C}_1 \text{im}]\text{Cl}$ (■), $[\text{C}_3 \text{C}_1 \text{im}]\text{Cl}$ (□), $[\text{C}_4 \text{C}_1 \text{im}]\text{Cl}$ (◆), $[\text{C}_5 \text{C}_1 \text{im}]\text{Cl}$ (◇), $[\text{C}_6 \text{C}_1 \text{im}]\text{Cl}$ (○), $[\text{C}_7 \text{C}_1 \text{im}]\text{Cl}$ (▲), $[\text{C}_8 \text{C}_1 \text{im}]\text{Cl}$ (●), $[\text{C}_9 \text{C}_1 \text{im}]\text{Cl}$ (○), $[\text{C}_{10} \text{C}_1 \text{im}]\text{Cl}$ (X), $[\text{C}_{11} \text{C}_1 \text{im}]\text{Cl}$ (x), $[\text{C}_{12} \text{C}_1 \text{im}]\text{Cl}$ (+).

Fig. 2. Setschenow constant, k_s , as a function of the carbon number at the longest alkyl chain, n , in $[C_nC_1im]Cl$, for the ABS formed with the salt K_3PO_4 (a) and K_2CO_3 (b). n : even (■) and odd (□).

Fig. 3. Logarithm of the Critical Micellar Concentration (CMC) *versus* the carbon number at the cation alkyl chain, n , in $[C_nC_{1im}]Cl$ ($n = 7-14$).

Fig. 4.
Degree of ionization as a function of the carbon number at the cation alkyl chain, n , in $[C_n C_1 \text{im}] \text{Cl}$ ($n = 7-14$). n : even (■) and odd (□).

Fig. 5.

Molar conductivity of micelles, Λ^M , as a function of the carbon number at the cation alkyl chain, n , in $[C_nC_1\text{im}]\text{Cl}$ ($n = 7-14$). n : even (■) and odd (□).

Fig. 6. Molar conductivity at infinite dilution, Λ^∞ , as a function of the carbon number at the longest alkyl chain, n , in $[\text{C}_n\text{C}_1\text{im}]\text{Cl}$ ($n = 7-14$). n : even (■) and odd (□).