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A New Volume-Based Approach for Predicting Thermophysical Behavior of Ionic Liquids and Ionic Liquid Crystals

Yulia V. Nelyubina,* Alexander S. Shaplov, Elena I. Lozinskaya, Mikhail I. Buzin,† and Yakov S. Vygodskii

A. N. Nesmeyanov Institute of Organoelement Compounds, Vavilova Str., 28, Moscow 119991, Russia

S Supporting Information

ABSTRACT: Volume-based prediction of melting points and other properties of ionic liquids (ILs) relies on empirical relations with volumes of ions in these low-melting organic salts. Here we report an accurate way to ionic volumes by Bader's partitioning of electron densities from X-ray diffraction obtained via a simple database approach. For a series of 1-tetradecyl-3-methylimidazolium salts, the volumes of different anions are found to correlate linearly with melting points; larger anions giving lower-melting ILs. The volume-based concept is transferred to ionic liquid crystals (ILs that adopt liquid crystalline mesophases, ILCs) for predicting the domain of their existence from the knowledge of their constituents. For 1-alkyl-3-methylimidazolium ILCs, linear correlations of ionic volumes with the occurrence of LC mesophase and its stability are revealed, thus paving the way to rational design of ILCs by combining suitably sized ions.

Ionic liquids (ILs) are organic salts that are liquid below 100 °C.[1] A typical IL is a combination of an alkyl derivative of ammonium, imidazolium, pyridinium and a weakly coordinated anion (halide, tetrafluoroborate, etc.);[2] 1,3-disubstituted imidazolium ILs are the most studied.[3] Owing to low melting points and other "unique" properties (negligible vapor pressure, high conductivity, thermal stability, etc.), ILs entered many areas of science and industry,[4] from "designer solvents" to new materials in catalysis, electrochemistry, nano- and biosciences.[5] ILs with a certain chemical composition adopt thermotropic liquid crystalline (LC) mesophases,[6] which are both fluid and anisotropic in a certain temperature range. This type of ILs—ionic liquid crystals (ILCs)—features ionic conductivity and molecular ordering not encountered in conventional LCs formed by neutral compounds. They found use as anisotropic conductors, electrolytes in dye-sensitized solar cells, ordered solvents, or organized reaction media in catalysis and nanotechnology.[7]

By an appropriate choice of ions, ILs can be tailored to specific applications;[8] however, their possible combinations are so many that experimental or computational screening of each is unrealistic. This spurred interest in methods for predicting properties of a new salt from the knowledge of its constituents (various group contribution models, quantitative structure—activity relationships, etc.).[9] Of them, volume-based approaches are gaining increasing attention.[10] They use empirical relations with molecular volumes that allow even nonspecialists to predict melting points[11] and other properties of ILs (density, conductivity, etc.).[10,12−15] Directly accessible by X-ray diffraction for a known IL, the molecular volume for a hypothetical salt is taken as a sum of ionic volumes; those can be found in large databases (see ref 16 and refs therein) or determined from crystal structures containing the ion of interest and a reference ion of known volume in the absence of other species (e.g., solvents such as water).

Another approach to ionic volumes, which may be suitable for volume-based description of ILs,[17] is "atoms in molecules" (AIM) partitioning of electron density[18] from high-resolution X-ray diffraction. Such experimental electron density studies were successfully used in search for "structure—property" relations.[19] They are, however, nearly inaccessible for ILs, as collecting X-ray diffraction data of suitable quality (especially for ILs with long alkyl chains) is a real challenge.[20] As a solution, the invariom concept[21] emerged to be applicable to ILs.[22] Within this approach, experimental electron density is built from aspherical pseudoatoms computed for an atom in a particular covalent environment and stored in a database.[23] By design, they ignore charge transfer between ions, but it has little effect on structural features of ILs[22] as revealed by AIM. This opens a new pathway to ionic volumes from electron density making use of X-ray diffraction data of lower quality and through these, to volume-based description and prediction of ILs properties.

Among these properties, the melting point T_m permits to distinguish an IL and is essential for any application. For popular imidazolium ILs, thermal behavior of 1-alkyl-3-methylimidazolium ($C_n$mim) salts was covered the most. These studies showed that varying length, branching,[24] number or position[25] of the alkyl chain sometimes resulted in ILs with lower/higher T_m. For ILs with different anions, some correlations of their size, shape, and symmetry[13,26,27] with T_m were also observed, e.g., many agree on the success of the NTf_2^- anion in producing low-melting ILs.[24] More consistent data exist on ILs that show liquid crystallinity (ILCs). In the $C_n$mim family, ILCs are salts with at least 12 carbon atoms in the *n*-alkyl chain,[28] although LC properties were just reported for $[C_{10}mim](FH)_2F$.[29] In these materials, LC mesophases are induced by microphase segregation of polar (cationic heads and anions) and nonpolar (alkyl chains) domains. The length of the alkyl chain has little effect on T_m but a huge one on clearing points T_c (in a striking contrast to molecular LCs);[30] the longer the chain, the higher the temperature at which an LC becomes an isotropic liquid and the larger the LC temperature interval

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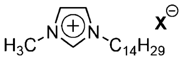
(ΔT) (and so the stability of the LC phase). Yet, the length of the chain at which the LC mesophase appears depends on the anion. With a larger anion (although its shape and symmetry[31,32] are also important), a longer chain is needed for the LC mesophase to occur, and the less stable it is. Thus, 12 carbon atoms are enough for $[C_n\text{mim}]BF_4$ to be ILCs, while at least 14 are needed for $[C_n\text{mim}]PF_6$; the huge NTf_2^- anion is exceptionally unsuccessful at producing ILCs.[6] Mesophase destabilization effects of large anions (size judged by intuition, by poorly defined ionic radius,[33] or, at best, by radius of a central atom in isostructural anions[34]) was observed for imidazolium salts[34,35] and for other, less studied N-heterocycles.[31−33,36,37]

The aim of this study is, therefore, two-fold: to show that ionic volumes from AIM partitioning of electron density do provide meaningful information on thermophysical behavior of ILs and to transfer the concept of volume-based approaches to ILCs where the size of anions clearly matters, for defining the domain of existence of LC mesophase. To do so, we synthesized a series of salts with a $C_{14}\text{mim}^+$ cation and 10 anions (most of them commonly used in ILs and ILCs) of different size, shape, symmetry, etc. (Scheme 1). Half of them featured two reversible phase transitions: solid-to-LC (melting) and LC-to-isotropic liquid (clearing).

Scheme 1. $[C_{14}\text{mim}]X$ Salts with Melting T_m and Clearing T_c Points from DSC and Anionic Volumes V_{an} from Electron Density Partitioning



$X^\ominus$	$Br^\ominus$	$NO_3^\ominus$	$BF_4^\ominus$	$ClO_4^\ominus$	$N(CN)_2^\ominus$ DCA
T_m (°C)	58.9	59.7	50.8	54.8	65.2
T_c (°C)	183.9	135.1	117.9	110.8	-
V_{an} (Å^3)	42.0	58.6	68.9	77.1	79.0

$X^\ominus$	$CF_3COO^\ominus$	$PF_6^\ominus$	$CF_3SO_3^\ominus$ OTf	$CF_3SO_2NCN^\ominus$ TFSAM	$N(SO_2CF_3)_2^\ominus$ NTf_2
T_m (°C)	61.5	67.1	58.0	47.9	41.1
T_c (°C)	-	72.3	-	-	-
V_{an} (Å^3)	93.3	95.5	111.8	146.1	208.3

A combined study by differential scanning calorimetry (DSC) and polarized optical microscopy (POM) showed these salts to be thermotropic ILCs adopting smectic A mesophases (Figures S2−5), as typical of $C_n\text{mim}$-based ILCs.[34] The LC mesophases have different stability with ΔT from 5.2 to 125.0 °C (Scheme 1). For eight of the salts (exceptions being nitrate and tetrafluoroborate), we also collected X-ray diffraction data (Tables S4−5); those for the bromide salt belong to its monohydrate (as suitable crystals have been grown in air). Despite differences in unit-cell composition and alkyl chain conformation, all the X-rayed salts have similar bilayered structures[38] with alternating hydrophilic and hydrophobic regions (Figure S9); the former are formed by imidazolium heads and anions (and by water molecules in $[C_{14}\text{mim}]Br$ monohydrate) and the later by nonpolar alkyl chains that show strong interdigitation and are tilted relative to polar domains, as expected for smectic A phases of ILCs.[6]

From these X-ray diffraction data, we extracted volumes of eight different anions (Table S6) by AIM partitioning of electron densities (into nonoverlapping atomic domains)[18] obtained with the invariom approach,[21] which is applicable to ILs with metal-free ions (an unfortunate limitation, but such are most ILs). These volumes (Scheme 1), for which better accuracy and consistency are achievable by averaging over several crystal structures[11] (beyond the scope of this study), slightly differ from those derived by reference ions[16] (within standard errors 10−20 Å^3).[12] The latter are, however, not available for the $TFSAM^-$ anion, and for others they are found in different databases so that even their relative values may vary ($PF_6^- < CF_3COO^-$ [12] or $BF_4^- > DCA^-$ [14]).

Ionic volumes from AIM partitioning can thus be put into context of thermophysical behavior of ILs. Plotting the melting points T_m against the anionic volumes for $[C_{14}\text{mim}]X$ produces no correlation for the salts with LC mesophases but a linear one (R^2 0.96) for all the non-ILCs (Figures S13−14); the larger the anion, the lower is T_m. The NTf_2^- anion known to give unusually low-melting ILs fits nicely into this trend. Such a linear correlation seems to be inherent to long-chained ILs, for which van der Waals dispersion interactions are the main driving force of ionic aggregation;[27] however, the effect of larger anions (to reduce T_m) seems to compete with that of larger cations (to increase T_m).

Among long-chained ILs, ILCs are often found. They experience little influence of ionic volumes on T_m, as is the case of our X-rayed ILCs. For them, a perfect linear correlation (R^2 1.00) is instead observed for clearing points (T_c): the larger the anion, the lower is T_c (Figure S15). The same is true for the temperature interval ΔT (R^2 0.99), the measure of LC mesophase stability. Of these three ILCs, the bromide salt crystallizes as hydrate, which is common for halide-based ILCs and known to stabilize their LC mesophases.[6] For anhydrous $[C_{14}\text{mim}]Br$, ΔT is lower by 15°,[38] hinting at a higher Br^- volume in it. To prove this, we recalled that electron densities in the invariom approach are reconstructed from fixed fragments.[21] In principle, they may be assigned to any set of 3D coordinates,[39] e.g., from crystal structures in Cambridge structural database (CSD). Although none is available for anhydrous $[C_{14}\text{mim}]Br$, we took advantage of the transferability concept behind the invariom approach[21] and estimated Br^- volumes (Table S7) in another imidazolium-based bromide and its hydrate (by using atomic coordinates available from CSD, refcodes XOQGIV, IJILET; Figure S10) as 47.7 and 42.5 Å^3. Putting these volumes and ΔT for monohydrate and anhydrous $[C_{14}\text{mim}]Br$[38] together with $[C_{14}\text{mim}]ClO_4$ and $[C_{14}\text{mim}]PF_6$ (Figure S16) gives an even better linear correlation (R^2 1.00). Likewise, the volumes of NO_3^- and BF_4^- anions in ILCs that did not form suitable crystals for X-ray diffraction were obtained from crystal structures of $C_2\text{mim}$ salts (KUCPED, LAZRIO; Figure S10). These values (Table S7, Figure S17) nicely fit into the linear correlation for $[C_{14}\text{mim}]X$ (R^2 0.97), providing qualitative evidence for incremental stabilization of LC mesophases by ever-smaller anions (of different shape and H-bonding ability, which do not explain our T_m and T_c).[40]

This trend may result from larger anions keeping imidazolium heads farther apart and thus making the packing of alkyl chains less efficient. It agrees with "local"[40] interaction energies (case specific and not as easily accessible) in

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$[C_{14}mim]Br$, $[C_{14}mim]ClO_4$, and $[C_{14}mim]PF_6$ from AIM analysis of their invariom-based electron densities (Table S9). Total energy of alkyl−alkyl interactions decreases linearly (R^2 0.95) with the anionic volume, but an inverse dependence (R^2 1.00) is observed for cation−anion interactions (Figure S18). The former interactions counteract the latter (which thus help these ILCs to melt, similar to H-bonds in ILs)[25] in decreasing ΔT (R^2 0.90 and 0.98) and mirror a known tendency of longer alkyl chains toward higher-melting ILs that competes with the effect of heads.[27] Yet larger anions (OTf^- in our case) result in the LC mesophase vanishing.

For large anions to form ILCs with wider LC intervals, cations with longer alkyl chains are needed.[6] This behavior is also found in $[C_n mim]ClO_4$ salts: longer (n = 16) and shorter (n = 12) alkyl chains give ILCs with higher and lower ΔT, respectively (Table S3). The major contribution to the trend comes from cationic volumes. For three ILCs, of which only one gave suitable crystals, they were obtained from available structures of bromides (QATNIJ, YORNOJ, SOXGOC01; Figure S11). Plotting these values (Table S7) against ΔT for the chlorate salts produces a straight line (R^2 1.00; Figure S19). From it, we can easily estimate the AIM volume of a $C_n mim^+$ cation (in Å^3) as $114 + 24n$, which nicely matches other linear regressions.[16]

With this incremental scheme for the cationic volume and with volumes of ten anions (and easy access to others via CSD), it is tempting to use them for predicting the domain of existence of ILCs, which depends on both but in an opposite way (as larger cations lead to a more stable LC mesophase but larger anions destabilize it until it vanishes; Figures S17−19). Thus, there may exist some critical ratio of the two volumes at which non-ILC to ILC transition occurs (Figure 1), as supported by the formation of $C_n mim$-based ILCs by BF_4^-, PF_6^-, and OTf^- anions with n of at least 12,[41] 14,[42] and 16,[43] respectively. If the volumes of the corresponding cations (Figure S20) are plotted against those of the anions, they form a straight line (R^2 0.98), which thus separates ILCs from non-ILCs. For example, all $[C_n mim]BF_4$ salts with n < 12 appear below this line (no LC mesophase) and with n = 12, 13, 14, etc. are above it (there is a LC mesophase).[41] For our $[C_{14}mim]X$ series, it separates the salts with three largest anions that are not ILCs (with X = OTf, TFSAM, NTf_2) from those with smaller anions (X = Br, NO_3, BF_4, ClO_4, PF_6), which are. Thus, a given combination of ions that falls above this line can have a LC mesophase (although other factors, such as shape and symmetry,[31,32] start to come into play here, as is the case of our non-ILCs $[C_{14}mim]DCA$ and $[C_{14}mim]CF_3COO$), but another combination that falls noticeably below it cannot (Figure 1).

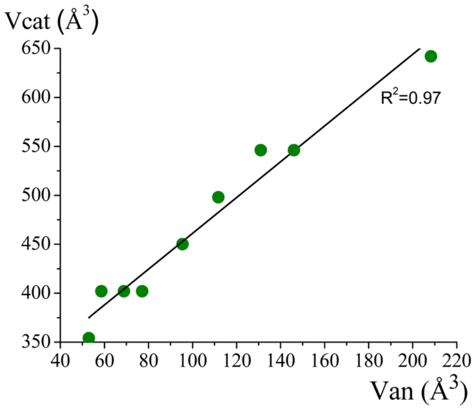

Figure 1. Volumes of cations vs anions' for $[C_n mim]X$ salts with the lowest n for which a LC mesophase appears. Black line is the fit to salts (circles going from the origin) with n = 10, X = $(FH)_2F$;[29] n = 12, X = NO_3 (this study); n = 12, X = BF_4;[41] n = 12, X = ClO_4 (this study); n = 14, X = PF_6;[42] n = 16, X = OTf;[43] n = 18, X = $N(SO_2F)_2$;[44] n = 18, X = TFSAM (this study); n = 22, X = NTf_2.[44] For more details, see Figure S20 and Table S8.

This correlation explains why no ILCs were reported until recently[44] for $C_n mim$ salts with the NTf_2 anion; it requires at least 22 carbon atoms in the cation's alkyl chain to observe a (metastable) LC mesophase.[44] Introducing $[C_{22}mim]NTf_2$ into the correlation (Figure 1) still keeps it highly linear, as does the observation of a LC mesophase[44] for $[C_{18}mim]N(SO_2F)_2$ (V_{an} from C_1mim salt, ZOLVAZ; Figure S12, Table S7). Recall that, whatever the anion, no $C_n mim$-based ILCs with n < 12 were found yet; the only exception being $[C_{10}mim](FH)_2F$.[29] The latter salt (with an estimate of V_{an} from a Me_4N salt, GIPGOB01), as well as the newly synthesized $[C_n mim]ClO_4$ with n of at least 12, also fits nicely into this linear trend (R^2 0.97). Even for planar NO_3^- and asymmetric $TFSAM^-$ anions, it correctly (Figures S4 and S8) predicts that n of at least 12 and 18, respectively, is needed to form ILCs, which have a very narrow mesophase temperature interval that is easy to miss (as, however, common for all the salts along the line at which non-ILC to ILC transition occurs).

The resulting trend line (Figure S20) shows that adding one CH_2 group (24 Å^3) to the cation compensates for an increase in the anionic volume by ∼13 Å^3. The ratio of these volumes, a minimum required for ILC properties to appear, matches a minimum fraction of space[45] occupied by the cation (0.64) that is pretty near the lowest value for a packing coefficient in stable crystals (0.65).

Experimental electron density studies thus emerge as a new volume-based approach for predicting thermophysical behavior of ILs. For 1-alkyl-3-methylimidazolium salts, they reveal a simple linear correlation that allows even a nonspecialist to predict melting point of a given IL, which is important for any application, from the knowledge of ionic volumes. For lower-melting ILs, larger anions are to be used, where NTf_2^- is a typical example. This correlation is valid in the realm of van der Waals interactions populated by cations with large nonpolar domains. The latter are exactly the ones found in $C_n mim$-based ILCs ($n \geq 10$). For them, very good linear correlations with the LC mesophase stability are observed: the longer the alkyl chain in the cation and the smaller the anion, the wider is the LC temperature interval of an ILC. Moreover, by knowing the volumes of individual components (a lot of them can be rather easily obtained from CSD by the invariom approach and gathered in a database for future use), it is possible to predict the domain of ILCs existence. We believe such dependencies govern thermophysical behavior not only of imidazolium-based ILs and ILCs but also of other, less studied classes of similar low-melting and liquid crystalline salts;[31−33,36,37] they are thus useful for making suggestions for the design of new ILs and ILCs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05174.

Experimental details and data (PDF)
Crystallographic data (CIF)
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Crystallographic data (CIF)

AUTHOR INFORMATION

Corresponding Author

*unelya@xrlab.ineos.ac.ru

Present Address

† Moscow Pedagogical State University, Malaya Pirogovskaya str., 1, Moscow 119992, Russia

Notes

The authors declare no competing financial interest.

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