PCCP

Accepted Manuscript

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

PCCP

Physical Chemistry Chemical Physics

www.rsc.org/pccp

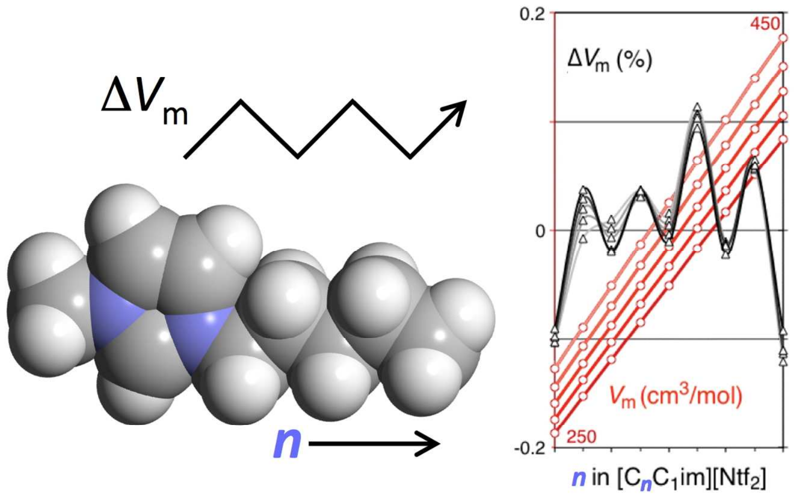
ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

TOC

Understanding density alternation effects in ionic liquid homologous series



Chemical Science Physical Chemistry Chemical Physics

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Edge Article

The alternation effect in ionic liquid homologous series

Gabriela Adamová,[a] José N. Canongia Lopes,[b,c]* Luís Paulo N. Rebelo,[c] Luís M. N. B. Santos,[d] Kenneth R. Seddon,[a,c] and Karina Shimizu[b*]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A recent report on a density odd-even alternation effect in a homologous series of ionic liquids (alkyltrioctylphosphonium chlorides, with the linear alkyl group ranging from ethyl to decyl) led to the detection of a similar trend in another ionic liquid family based on a different cation (1-alkyl-3-methylimidazolium). *Ab initio* calculations and Molecular Dynamics simulations of the corresponding ions confirmed that the charge distribution along the alkyl side chains and the conformations adopted by them are not the direct cause of the odd-even effect. The simulations also showed that all cation side chains tend to adopt *trans*oid conformations that pack head-to-head in the liquid phase. Such types of conformations/packing lead to odd-even alternation effects in properties involving solid phases of different molecular compounds containing linear alkyl chains. The surprising results obtained for the ionic liquid series enabled us to unveil similar trends in the liquid phases of linear alkanes and alkanols *via* the application of a simple corresponding states principle.

Introduction

In recent work, Adamová *et al.*[1] reported an unexpected see-saw pattern in the densities of a series of alkyltrioctylphosphonium chloride ($[P_{8\,8\,8\,n}]Cl$) ionic liquids, as the length of the linear alkyl chain alternated between even and odd numbers of carbon atoms. This fact led us to calculate for another extensively studied homologous series of ionic liquids[2] - 1-alkyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide, $[C_n\mathrm{mim}][NTf_2]$ - the experimental molar volume deviations from the corresponding linear fit. The same density alternation effect between odd- and even-numbered alkyl side chains (albeit reversed) was observed along this second series. These zigzag patterns are persistent at different temperatures and cannot be attributed to a possible lack of precision of the density determinations, all performed with state-of-the-art vibrating-wire densimeters.

In the present work, we address three basic issues concerning the observed trends: (a) Why have they been observed for just two ionic liquid homologous series?; (b) Why is the trend reversed in the two series under investigation?; and (c) What, most importantly, is their origin?

Methods

Ab Initio Calculations

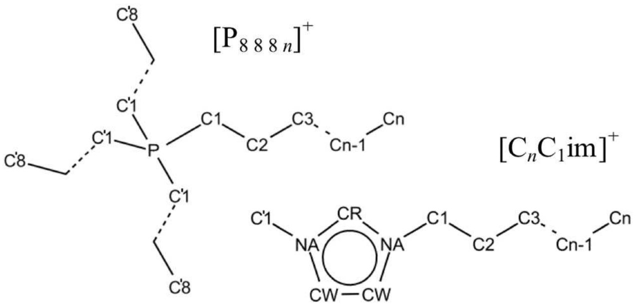
Electrostatic charge distributions along the two homologous series were calculated[3] using Gaussian 03 at the MP2/cc-pVTZ(-f)//HF/6-31G(d) level of theory and ChelpG charge model, thus using the same basis set as in the OPLS-AA model for ionic liquids.[4,5] The cc-pVTZ(-f) basis set[6] was used for single-point energy calculations in geometries optimised at the HF/6-31G(d) level, as is the current practice in the development of force field parameters for molecular simulation, namely in the case of homologous series of ionic liquids.[7,8] For the C and N atoms, the cc-pVTZ-(-f) basis set is created by removing the f functions from the definition of the triple-ccpVTZ basis set of Dunning.[6] The combination of the levels of theory and basis sets used here has been tested on a large collection of molecules (Halgren test) and was demonstrated to yield accurate conformational energetics.[9] It must be stressed that no constraints were placed in any of the molecules during geometry optimisation or point charge calculation in order to reproduce a specific molecular moment.

Molecular Dynamics Simulations

Molecular dynamics simulations were carried out for ionic liquids related to the two homologous series studied in this work ($[P_{6\,6\,6\,14}][O_2CMe]$, $[P_{6\,6\,6\,14}][NTf_2]$ and $[C_n\mathrm{mim}][NTf_2]$, where n = 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10). The $[P_{8\,8\,8\,n}]Cl$ series was not modelled due to the elevated computational costs associated with the corresponding MD runs. The simulations were performed using the DL_POLY code,[10] and an all-atom force field based on the CL&P force-field,[4,5] specially tailored to encompass whole ionic liquid families. For each ionic liquid studied, we started from low-density initial configurations composed of 200 ion pairs. The boxes were equilibrated under isothermal-isobaric ensemble conditions for 0.8 to 1 ns at 300 K using the Nosé-Hoover thermostat and isotropic barostat with time constants of 0.5 and 2 ps, respectively. Further simulation runs of 0.5 to 2 ns were used to produce equilibrated systems at the studied temperature. Electrostatic interactions were treated using the Ewald summation method considering six reciprocal-space vectors, and repulsive-dispersive interactions were explicitly calculated below a cut-off distance of 1.6 nm (long-range corrections were applied assuming the system has an uniform density beyond that cut-off radius). Details concerning this type of simulation can be found elsewhere.[4,5]

Results and Discussion

Scheme 1 provides the nomenclature used throughout this work to define the members of the two ionic liquid homologous series under discussion. Figure 1 shows the corresponding experimental molar volume *versus* alkyl chain length plots.



Scheme 1. Nomenclature for tetraalkylphosphonium and 1-alkyl-3-methylimidazolium cations.

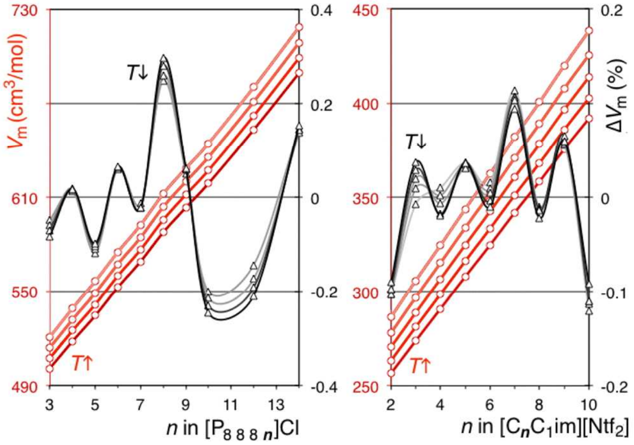


Figure 1. Empirical molar volume (V_m) data (in red) at different temperatures as a function of the alkyl chain length (n) in two ionic liquid homologous series[1,2]: (left) $[P_{888n}]Cl$ at 293, 313, 333 and 353 K; (right) $[C_nC_1im][NTf_2]$ at 293, 333, 373, 413 and 453 K. The graphs also depict on the right y-axes (and in black) the relative deviations of V_m (in %) to $V_m(n)$ linear fits. The arrows in the graphs indicate that whereas the molar volumes increase with temperature, the zigzag trends of the corresponding deviations become less pronounced.

Several observations can be inferred from the Figure1: (i) the zigzag trend is apparent for chains in the C_3 to C_9 range in the case of the phosphonium-based ionic liquids, and in the C_2 to C_{10} range in the case of the imidazolium-based series. In the former case, the effect ceases to exist for alkyl chain lengths larger than C_9 (no data for ionic liquids with odd-numbered chains larger than C_{10} are available); (ii) odd- and even-numbered chains have molar volumes smaller and larger, respectively, than the linear fit in the case of the phosphonium-based series, whereas the reverse is true for the imidazolium-based ionic liquids; and (iii) the alternation effect is more pronounced in the case of the phosphonium series, although the average amplitudes of the oscillations are comparable (0.20% and 0.14% for the phosphonium- and imidazolium-based series, respectively).

The first issue raised in the introduction (why just two ionic liquid families?) can be answered based on this last observation: in the case of the $[P_{888n}]Cl$ series, the amplitudes of the oscillations in terms of molar volume combined with the fact that the mass densities of the ionic liquids do not decrease much as the alkyl chain gets longer (densities at 303 K and atmospheric pressure vary from 0.897 to 0.884 g cm^{-3} in the C_3-C_9 range) has allowed the direct observation of a non-linear (step-like) trend during the density measurements.[1] Such a trend was not apparent in the case of the imidazolium-based volumetric experiments due to the much larger decrease in terms of mass density when going from $[C_2C_1im][NTf_2]$ (1.525 g cm^{-3} at 293 K and 1 bar) to $[C_{10}C_1im][NTf_2]$ (1.285 g cm^{-3} at 293 K and 1 bar).[2] In this latter case, the alternating trend could only be identified when plotting the deviations of the molar volumes from a reference line: a linear fit.

The fact that only two systems have been found so far exhibiting this behaviour is probably related to the size of the effects described in the previous paragraph: they can easily pass unnoticed even when high-precision volumetric determinations are performed in complete ionic liquid homologous series (with odd- and even-numbered side-chains). It must be stressed that the number of systems/experiments fulfilling this last condition is very limited. Indeed, for practical reasons (associated with the cost of the precursors), there are substantially fewer reports of ionic liquids with odd-length chains (*e.g.* n = 3, 5, 7, 9, *etc.*), and one needs to look for the effect in order to find it. Now it has been observed, we anticipate more reports of it with a wide range of different cations.

In order to address the second issue (the reverse odd/even effect in the two systems under discussion), one must first investigate the origin of the effect itself.

The first point to be considered is that all care was taken to discount the possibility of a spurious effect: after all, the intensity of the alternating effect (around 0.2%) is not much greater than the accuracy of many volumetric determinations. In order to discard such possibility, independent experiments were carried out in two different laboratories (QUILL, Belfast and ITQB, Lisbon),[1,2] using densimeters with internal precision better than 0.05% and five reproducible digits (corresponding to a resolution of 0.01%). Moreover, the ionic liquids of the two homologous series were either synthesised and purified in-house using analogous procedures (in the case of $[P_{888n}]Cl$)[1] or purchased from the same supplier, with stated analogous synthetic routes and purity levels (in the case of $[C_nC_1im][NTf_2]$).[2] The main point here was to avoid situations where different families of reactants had been used during the syntheses of the odd- or even-numbered ionic liquids, leading to two sub-families with different levels of impurities.

The second point to be considered is that these alternating trends between even- and odd-chained members have been observed for several other homologous series of compounds (linear alkanes, alcohols, 1-chloroalkanes or carboxylic acids), as far as properties related to their crystalline phases are concerned. One of the most well-known effects in this context is the alternating behaviour of the melting point temperatures of odd-and even-numbered alkanes, between C_1 and C_{11},[11] or linear carboxylic acids between C_5 and C_{14}.[12] It has been demonstrated that this behaviour is linked to the relative stability of the different solid phases, that in turn are a consequence of a more or less efficient packing of the molecules in the "even" or "odd" sub-series. Obviously, those packing issues also affect the densities of the solids, that in turn reflect the same alternation behaviour.[11,12]

The main problem with linking the origin of the effect that has been observed in the liquid phase of ionic liquids to the behaviour of the solid phases of other compounds is that packing issues dominate the latter effect, but not necessarily the former. Other issues must be taken into consideration before attempting such rationalisation. Thus, in order to probe the structure along the two homologous series under discussion, we have used different quantum- and statistical-mechanics methods.

During the modelling of the cations that compose ionic liquids using *ab initio* techniques on isolated ions,[4,5,13] it was found that the positive charge that is formally localised either on the phosphorus central atom of the tetraalkylphosphonium cations or on the imidazolium ring of 1-alkyl-3-methylimidazolium cations is partially delocalised into the alkyl side chain by hyperconjugation effects. Such effects can produce an alternate charge pattern in the even and odd atoms of the chain, at least as far as the three or four carbon atoms nearest the positive centre of the cation are concerned (for modelling purposes carbon and hydrogen atoms more than three bonds away from the positive centre of the cation have been considered to belong to a "normal" alkyl moiety). New *ab initio* calculations with longer alkyl side chains have been implemented to check if the effect could justify the observed zigzag trends. The results are presented for the two types of cation under discussion in Table 1.

Table 1. Charge distributions (in percentage of atomic charge unit, a.c u. %) along the alkyl side chains of isolated $[P_{4\,4\,4\,n}]^+$ and $[C_nC_1im]^+$ ions, calculated *ab initio*. Entries in bold or underlined italics refer to effects discussed in the text.

alkyltributylphosphonium, $[P_{4\,4\,4\,n}]^+$

n	P	C1	C2	C3	C4	C5	C6	C7	C8	C9
4	46	-4	9	**11**	**3**					
5	45	3	5	0	**11**	**-3**				
6	42	*0*	*13*	*-4*	-1	**14**	**-6**			
7	47	*-3*	*10*	*4*	-6	4	**11**	**-6**		
8	45	*1*	*7*	*1*	2	0	-1	**11**	**-6**	

1-alkyl-3-methylimidazolium, $[C_nC_1im]^+$

n	im	C1	C2	C3	C4	C5	C6	C7	C8	C9
1	52	22								
2	50	21	8							
3	51	8	**21**	**-1**						
4	56	0	13	**11**	**-2**					
5	52	10	8	0	**12**	**-3**				
6	53	*5*	*17*	*-5*	0	**14**	**-6**			
7	53	*4*	*13*	*4*	-6	4	**11**	**-6**		
8	53	*7*	*11*	*1*	-3	1	-2	**12**	**-6**	
9	53	*6*	*14*	*-1*	0	7	-3	-2	**12**	**-7**

In order to lower the computational costs associated with the *ab initio* calculations, $[P_{4\,4\,4\,n}]^+$ ions were used instead of $[P_{8\,8\,8\,n}]^+$. Auxiliary *ab initio* calculations using suitable tetraalkylphosphonium ions have shown that the charges on the variable alkyl side chain are not significantly perturbed by the fact that the other three chains are either octyl or butyl groups.

Table 1 shows that there is indeed a hyperconjugation effect - in most cases the charge on the C2 methylene groups of the variable chain are more positive than the charges on either the C1 or C3 groups of the chain (effect highlighted in underlined italics in Table 1). However, it also shows that the effect is rapidly lost for methylene groups further removed from the positive centre of the cation and that the hyperconjugation effect is offset by the fact that for all chains (both odd- and even-numbered) the methyl group at the end of the chain tends to be more negative than the methylene group preceding it (effect depicted in bold in Table 1). In other words the charge distribution along the variable alkyl chain of the two homologous series cannot explain the alternating density effect.

It must be stressed that even if a very refined model in terms of charge distribution was used in Molecular Dynamics simulation studies, these would not be able to yield densities with enough accuracy to show the experimentally observed alternation effect. However, simulation studies (performed with the commonly used force field developed to model complete homologous series of selected ionic liquids) can yield some information pertinent to the present discussion, namely the conformations adopted by the alkyl chains of the cations.[14,15] Such simulation data have been complemented and validated by Raman spectroscopy studies.[16] In the present work, we have focussed on the $[C_nC_1im][NTf_2]$ series and performed new simulations along the entire C_2 to C_{10} range (previous simulations included other ionic liquids with even-numbered chains combined with anions such as $[PF_6]^-$).[14] The conformational analyses obtained from the MD results are summarised in Figure 2.

The graphs show that all cations tend to orient their alkyl side chains in a direction approximately normal to the plane of the aromatic imidazolium ring (the CR-N-C1-C2 dihedral angles are neither 0º nor 180º, but rather 120º, Fig. 2a). In the case of $[C_2C_1im]^+$, the terminal methyl group has enough rotational freedom to adopt in-plane conformations (a peak at 0º and a non-negligible probability density function at 180º distinguish this cation from all others). It must be stressed that although all ions show a peak around 120º, the probability density functions are non-zero elsewhere, which means that there is a large degree of interconversion between conformations around the above-mentioned dihedral angle: in fact, the orientation of the beginning of the alkyl side chain relative to the imidazolium plane is dictated by the presence of the anions that occupy the in-plane space near the CR and CW groups, and "push" the chain to the space above and below the imidazolium ring (and slightly towards the less cluttered "CW" moiety of the ring). There is a dramatic change in the case of the next dihedral angle along the chain (N-C1-C2-C3, Fig. 2b): only three conformations are generally available to the alkyl chain (one "*trans*" at 180º and two symmetrical "*gauche*" at ±60º). The inter-conversion between conformations is now less frequent and the number of *gauche* and *trans* conformers is comparable. In this case, it is the $[C_3C_1im]^+$ cation that shows a larger rotational freedom due to the presence of its terminal methyl group at the end of the dihedral under discussion. The next dihedral angle along the chain (C1-C2-C3-

C4) shows a trend that will be the norm along the remainder of the chain (Figs 2c and 2d): the *trans* conformation is much more probable and the interconversion between conformers is difficult: most of the chains will adopt all-*trans* conformations after the C2 carbon. Figures 2c and 2d also show that it is always the ionic liquid that has the methyl group at the final position of a given dihedral angle that exhibits a larger proportion of *gauche* conformers and that this fact (a larger rotational freedom of the methyl group) is independent of the number of carbon atoms (even or odd) in the remainder of the chain.

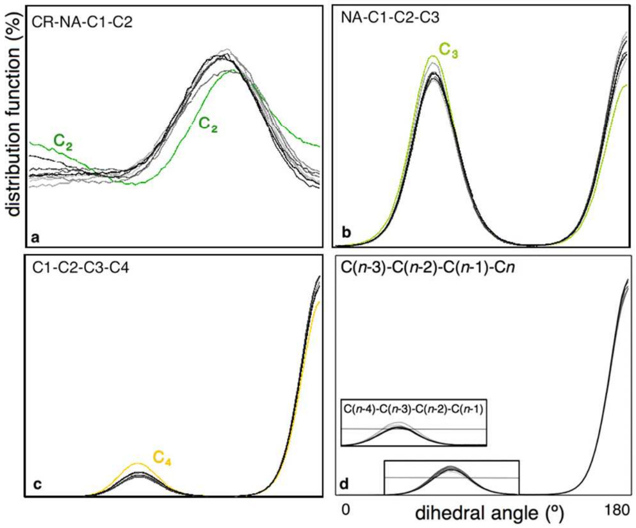


Figure 2. The distribution of the dihedral angles along the alkyl chain of 1-alkyl-3-methylimidazolium bistriflamide, $[C_nC_1im][NTf_2]$, ionic liquids. Panel **a** comprises 11 lines ($2 \leq n \leq 10$), panel **b** comprises 10 lines ($3 \leq n \leq 10$) and panels **c** and **d** comprise 9 lines each ($4 \leq n \leq 10$). Most lines are superimposed but specific C_n labels/colors indicate the distinctive behaviour of some of the members of the homologous series. The inset in panel **d** shows the difference between the conformational freedom – proportion of *gauche* conformers – between the dihedral at the end of the chains (methyl rotation) and the one preceding it (ethyl rotation).

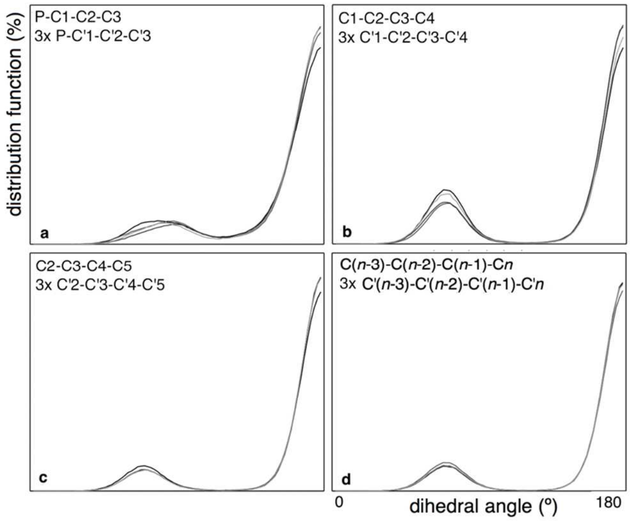


Figure 3. The distribution of the dihedral angles along the alkyl chains of the trihexyl(tetradecyl)phosphonium chloride, $[P_{66614}]Cl$ (each panel depicts 4 lines). Carbon atoms in the three hexyl chains are labelled with a prime.

Finally, if the chain conformations of $[C_nC_1im]^+$ are compared with those of tetraalkylphosphonium cations (Figure 3), a plausible justification for the apparent reversal of the zigzag trend between the two series is discovered: the out-of-the-plane character of the C2 methylene group in imidazolium implies that the C1 methylene group is never part of a “alkane-like” chain where all conformations are either *trans* or *gauche* with a marked preference for the former; such situations never occur in the conformer distribution of a cations like $[P_{4\,4\,4\,n}]^+$, $[P_{6\,6\,6\,n}]^+$ or $[P_{8\,8\,8\,n}]^+$, where the *trans* conformation is the norm along the entire chain. In other words, C1 should not really be counted as part of the alkyl chain in the case of $[C_nC_1im]^+$, which means that if we subtract it from the number of carbon atoms in a given chain, the even chains become odd and vice-versa. In other words, the really important issue is not the fact that densities are higher or lower in a given odd or even sub-series, or that the effect may appear reversed, but that there are indeed alternate effects as one walks along mostly *trans*oid alkyl (side) chains.

Furthermore, the present MD simulation results have also shown (Figure 4) that the terminal methyl groups of these chains tend to be segregated together, confirming previously obtained MD results that analysed the structure of ionic liquids.[17]

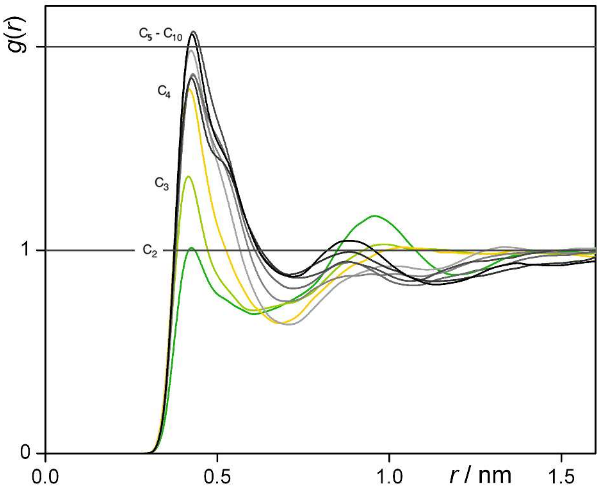


Figure 4. Pair radial distribution functions between the terminal C_n carbon atoms of $[C_nC_1im][NTf_2]$ ionic liquids ranging from C_2 to C_{10}. The labels illustrate the progressively larger C*n*-C*n* correlation as the alkyl chains get longer. The C_2 to C_4 series are colored as in Figure 2.

These structural features (all-*trans* chains packed head-to-head) are the standard in the above-mentioned solid phases of molecular compounds that exhibit alternation effects in their melting point temperatures and densities. After all, such systems must hold the key to explain the origin of the alternation effect in the liquid phase of ionic liquids.

As briefly mentioned at the beginning of the discussion, the alternation effect on the solid phase densities of alkylated compounds has been explained taking into account packing effects. In fact the explanation is more nuanced than that: in alkanes, the head-to-head packing of the terminal methyl groups at the end of the trans alkyl chains are the key to understand the alternation effect;[11] in carboxylic acids, the molecules form dimers *via* double intermolecular bonding and stack into bilayers. The alternation in the overall density may be attributed mainly to the alternating packing density between those bilayers and the different bilayer arrangements can be rationalised on the basis of a balance between the competition between repulsive carbonyl-carbonyl contacts and attractive dispersion interactions between the *trans* linear alkyl chains;[12] in zinc alkanoates (as in the case of ionic liquids, these are also alkylated salts), the packing of bilayer structures emerging from a ionic network formed by tetra-coordinated zinc ions and carboxylate head groups define the alternation effect, but this state of affairs is further complicated by the possibility of interdigitated bilayers for chain lengths above octyl;[18,19] in α,ω-dicarboxylic acids, the effect is attributed to the alternation between twisted and non-twisted conformations of the terminal COOH groups in the odd and even members of the series, respectively;[20] in α,ω-diamines, dinitriles, dialcohols, and dithiols, the alternation effect was rationalised in terms of the interplay between hydrogen bonding and hydrophobic interactions: whereas these forces can generally operate constructively in the even members of the series, they work against each other in the packing arrangements adopted by the odd members.[21-25]

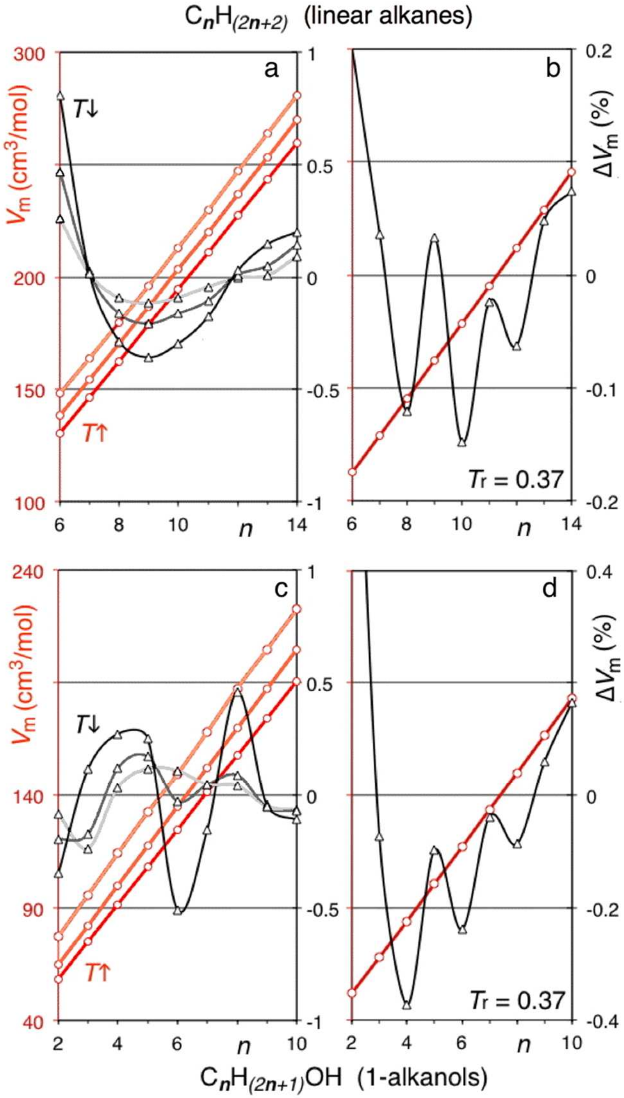


Figure 5. Molar volume (V_m) data[26] (in red) at different temperatures as a function of the alkyl chain length (*n*) in molecular compounds homologous series: (two left panels) linear alkanes at 293, 333 and 373 K and a common reduced temperature of 0.37; (two right panels) 1-alkanols at 293, 373 and 453 K and a common reduced temperature of 0.37. All graphs depict in the right *y*-axes the relative deviations of V_m (in %, in black) to the corresponding $V_m(n)$ linear fits. The arrows in the graphs indicate that when the molar volume increase with temperature, fit deviations become less pronounced.

The final missing link that has to be addressed at this point is why such packing-related issues that are obviously very important in the solid phase are somehow transferred into the liquid phase of ionic liquids; after all no alternation effect has been reported for the liquid densities of alkanes, alcohols or carboxylic acids.

The issue with the three homologous series just mentioned is that the corresponding liquids (delimited by their melting and critical point temperatures) span very different ranges. In other words, if one compares all members of a series at a given temperature, they will not be under similar conditions of the corresponding states principle. This problem was addressed by recalculating, at the same reduced temperature, two sets of volumetric data encompassing two complete homologous series (linear alkanes and alcohols) in the liquid phase[26] (unfortunately, data for compounds with relatively high melting points, like carboxylic acids, diamines, dialcohols or diacids, are not available). Figures 5a and 5b show the liquid molar volumes of these homologous series at three selected temperatures and the corresponding deviations to a $V_m(n_c)$ linear fit. Figures 5c and 5d show the same data represented at a single reduced temperature, in the range of the reduced melting temperatures of the members of the two series. The alternation pattern (at least in a significant part of the range) is obvious when the selected reduced temperature is near the melting points of the selected series and disappears when the reduced temperature is increased. No zigzag pattern is visible if non-reduced temperatures are selected.

In the case of ionic liquids, the hypothetical critical temperature[27] is much higher than that for molecular compounds. This means that, even if a non-reduced temperature is considered, all members of a family for a given ionic liquid will be approximately under conditions of the corresponding states principle. This also explains why the alternation effect is noticeable at a given temperature in the case of ionic liquids and not in the case of liquid molecular compounds.

Conclusions

In conclusion, part of the packing issues that cause the alternation effect in the solid phase of homologous series containing linear alkyl chains can persist in the liquid side near the melting point. Even for molecular compounds, such an effect can be detected if a corresponding states principle is applied. In the case of ionic liquids (where the alkyl side chains are confined and compressed into alkane-like domains by the polar network of the ionic liquid), such an alternation effect can be directly detected or calculated from high-accuracy volumetric measurements performed on complete homologous series. Once more, the unique properties of ionic liquids - their ionic/non-polar nano-segregated nature and the conformity to a corresponding states principle along an ionic liquids homologous series studied at constant temperature - reveal themselves and are applicable in unexpected ways.

Acknowledgements

Financial support provided by Fundação para a Ciência e Tecnologia (FCT) through projects FCT-ANR/CTM-NAN/0135/2012 (including a post-doctoral grant of KS), PTDC/CTM-NAN/121274/2010 and PEst-OE/QUI/UI0100/2013.

Notes and references

[a] *The QUILL Centre, The Queen's University of Belfast, Stranmillis Road, Belfast BT9 5AG, UK.*
[b] *Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal.*
[c] *Instituto de Tecnologia Química e Biológica (www.itqb.unl.pt), Universidade Nova de Lisboa, Av. República, 2780-157 Oeiras, Portugal.*
[d] *Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, R. Campo Alegre 687, 4169-007 Porto, Portugal*
**E-mail: jnlopes@ist.utl.pt, karina.shimizu@ist.utl.pt*

1. G. Adamová, R. L. Gardas, L. P. N. Rebelo, A. J. Robertson, and K. R. Seddon, *Dalton Trans.* 2011, **40**, 12750.
2. M. Tariq, A. P. Serro, J. L. Mata, B. Saramago, J. M. S. S. Esperança, J. N. C. Lopes, and L. P. N. Rebelo, *Fluid Phase Equilib.* 2010, **294**, 131.
3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, revision C.05; Gaussian, Inc.: Wallingford, CT, 2004.
4. J. N. C. Lopes, J. Deschamps, and A. A. H. Pádua, *J. Phys. Chem. B* 2004, **108**, 2038.
5. J. N. C. Lopes and A. A. H. Pádua, *J. Phys. Chem. B* 2004, **108**, 16893.
6. T. H. Dunning Jr., *J. Chem. Phys.* 1989, **90**, 1007.
7. W. D. Cornell, P. Cieplak, C. I. Bayly, I. R. Gould, K. M. Merz, D. M. Ferguson, D. C. Spellmeyer, T. Fox, J. W. Caldwell, and P. A. A. Kollman, *J. Am. Chem. Soc.* 1995, **117**, 5179 (parameters obtained from file parm99.dat corresponding to AMBER versions 1999 and 2002).
8. J. Wang, P. Cieplak, and P. A. Kollman, *J. Comput. Chem.* 2000, **21**, 1049.
9. R. A. Friesner, R. B. Murphy, M. D. Beachy, M. N. Ringnalda, W. T. Pollard, B. D. Drunietz, and Y. Cao, *J. Phys. Chem. A* 1999, **103**, 1913.
10. W. Smith, T. R. Forester, I. T. Todorov, The DL-POLY 2 User Manual, Version 2.20; STFC Daresbury Laboratory: Warrington, U.K., 2009.
11. R. Boese, H.-C. Weiss, and D. Bläser, *Angew. Chem. Int. Ed.* 1999, **38**, 988.
12. A. D. Bond, *New J. Chem.* 2004, **28** , 104.
13. J. N. C. Lopes and A. A. H. Pádua, *J. Phys. Chem. B* 2006, **110**, 19586.
14. J. N. C. Lopes and A. A. H. Pádua, *J. Phys. Chem. B* 2006, **110**, 7485.
15. K. Shimizu, A. A. H. Pádua, and J. N. C. Lopes, *J. Phys. Chem. B* 2010, **114**, 15635.
16. Y. Umebayashi, T. Fujimori, T. Sukizaki, M. Asada, K. Fujii, R. Kanzaki, and S. Ishiguro, *J. Phys. Chem. A* 2005**, 109**, 8976.
17. J. N. C. Lopes and A. A. H. Pádua, *J. Phys. Chem. B* 2006, **110**, 3330.
18. R. A. Taylor and H. A. Ellis, *Spectrochim. Acta A* 2007, **68**, 99.
19. P. N. Nelson, H. A. Ellis, and R. A. Taylor, *J. Mol. Struct.* 2011, **986**, 10.
20. V. R. Thalladi, M. Nüsse, and R. Boese, *J. Am. Chem. Soc.* 2000, **122**, 9227.
21. V. R. Thalladi, R. Boese, and H-.C. Weiss, *Angew. Chem. Int. Ed.* 2000, **39**, 918.
22. V. R. Thalladi, R. Boese, and H-.C. Weiss, *J. Am. Chem. Soc.* 2000, **122**, 1186.
23. E. Badea, G. Della Gatta, D. D'Angelo, B. Brunetti, and Z. Recková, *J. Chem. Thermodyn.* 2006, **38**, 1546.
24. E. Badea, I. Blanco, and G. Della Gatta, *J. Chem. Thermodyn.* 2007, **39**, 1392.
25. E. Badea, B. Nowicka, and G. Della Gatta, *J. Chem. Thermodyn.* 2014, **68**, 90.
26. I. Cibulka, *Fluid Phase Equilib.* 1993, **89**, 1.
27. L. P. N. Rebelo, J. N. C. Lopes, J. M. S. S. Esperança, and E. Filipe, *J. Phys. Chem. B* 2005, **109**, 6040.