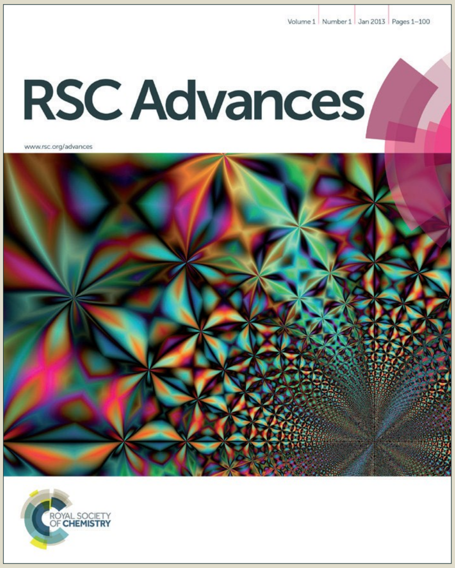
RSC Advances



ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/advances

The Constitutive Behavior of Ammonium Ionic Liquids: A Physiochemical Approach

*Akash Kumar Gupta and Ramesh L. Gardas**

Department of Chemistry, Indian Institute of Technology Madras, Chennai - 600 036, INDIA

*Corresponding author: Phone: +91 44 2257 4248; Fax: +91 44 2257 4202

E-mail: gardas@iitm.ac.in ; Web: http://www.iitm.ac.in/info/fac/gardas

Abstract

A huge mass of possible molecular variants often forms a puzzle on their identity and integrity to the processes which can be resolved by adopting a concrete selection procedure significant for it. This further relies on its relation with some phenomena on microscopic structure and macroscopic behavior. This study recognizes the numerous approaches to answer it on the grounds of Thermodynamics for Ionic Liquids (*ILs*) and conception of middleman in additivity phenomenon through molecular tailoring and validated dataset, wherein Wada's theory for molecular compressibility, *A* is found inconsistent and thus redefined. ILs are found to be divergent into two groups, depending upon the cationic integration rather than anionic, on analysis of close intimacy of the molecular sound velocity, *R* to the molecular weight. Moreover, the study presents ILs in contrast to molecular fluids and physiochemical nature in terms of Jacobson's relation and Mark's study on molecular fluids. The applicability of Newton-Laplace relation has also been deduced The missing links in persisting theories are explored quantitatively and structural descriptors are estimated for structural variability of –CH_2/-CH_3 commonly found in ILs. It seems quite interesting to visualize the appendages like benzyl, methylene and methyl in molecular skeleton being the source of drastic effects on the studied behaviors. By far, these can, more or less, aid in solving molecular puzzle of accessing ionic liquids' potential of structural variability for task-specific applications, say fluid mechanics, organic synthesis, reaction kinetics, antimicrobial activity and CO_2 capture and sequestration.

Keywords: Benzylic quats • Group contribution • Ionic liquids • Physiochemical properties • Structure-activity relationships

Introduction

In contrast to molecular fluids these days, ionic liquids (ILs) have attained widespread dimensions of applicability and versatility[1–6] through the ever-growing interest in their fascinating properties[7,8]. There is enormous possibility for fine-tuning these properties with a little molecular constitution variability[7,9]. In addition, ILs need be explored for unveiled aspects of protic nature.[8,10,11] In the realm of inherent nature and interactive behavior of fluids even for many years before the advent of ILs the common theories whether applicable to these still need be checked over. It is imperative to have insights on the physiochemical-molecular pattern through experimentation and/or theoretical calculations, dynamics[9], predictions[12] to enhance their operational utility.

Benzylic compounds have spanned their usage in day-to-day life in the form of surface active compounds, cosmetics, preservatives, antiseptic, antimicrobial agents, corrosion inhibitors and so on since ages, yet ILs are found to be in lack of such globally relevant moiety at most. Notwithstanding, the Benzylic Quats**,** the benzyl appended quaternary ammonium molten designer salts, herein, can incorporate numerous ecofriendly and industrially relevant peculiarities that can be beautifully adorned through methylene / methyl impregnated in their structural constitution (anionic as well as cationic) in a chemical point of view. Such appendage has predominately been a subject matter of imidazolium skeleton with inorganic anions revealing the fascinating physiochemical response of ILs so far.[13,14] It has also been found in some imidazolium and pyridnium ionic liquids that bearing benzyl appendages has significant potential for use in the separation of carbon dioxide from combustion products on the grounds of the membrane performance tests and CO_2 solubility measurement.[15] Furthermore, the benzylic systems show alluring "benzylic effect", a marked increase in rates of SN_2 reaction in contrast to analogous alkyl derivatives and find constant significance in organic synthesis, specifically as protective groups and pharmaceutical moieties. Benzyl based ammonium compounds have been proven long term effective in large scale microbial eradication and control.[16,17] In addition, these are served as good surface active compounds. Ammonium based ionic liquids have been shown as an effective alternative to the demands for volatile organic compounds (*VOCs*) as solvents, elevated temperature and pressure, and toxic catalysts, in addition to, their ease of preparation at less environmental and economic cost.[18] In the same vein, carboxylate anionic chains of longer size (ca. the range of our study) have shown relatively reduced cytotoxicity.[19] Furthermore, a combined effect of alkyl-aryl substituents on the aliphatic parent structures seems interesting to explore the behavioral pattern of ILs.[20] A systematic unification of such a variation in molecular integrity, aided with some simple chemistry and statistical tools, phrased herein as molecular tools (described in Experimental Section) empowers us to switch to better alternatives even to work out for large scale industrial process design which calls for accurate thermophysical data frequently at large. This report illustrates our efforts in molecular design to visualize the thermophysical behavior of new benzyl appended ionic liquids' structural variants through easy-to-choose molecular shuttle of $–CH_2$ / $–CH_3$ both at anionic and cationic ends.

To name a few key-subjects of this study are synthesis of a new family of 13 ILs' employing benzylic moiety via green normed atom economic protonation-deprotonation, a blend of non-destructive experimental characterizations (FT-NMR, FTIR, TOF MS ES+, Densimetry, Ultrasonics), measurements and evaluation of a number of fundamental cum derived properties (ρ, u, V_m, α, β_S, R, A**,** etc.) with correlations of structural features at the molecular level and subclassification of the family on the grounds of Thermodynamic considerations at temperatures ranging from 293.15 to 343.15 K. In this context, the groups contributing to the thermophysical properties, the structural descriptors, are deduced and validated further with one of the ILs' properties. Employing such an external test data determines the limit of working uncertainty in predictions of the molecular features of other ILs in a green way. The concept of chemical middleman has been deduced in perspectives of additivity principle (referred as the fourth law of Thermodynamics)[21]. Utilizing such tools, methodologies, relevance quantities like ΔpKa (the difference in pKa value for the acid and base determined in dilute aqueous solutions) in molecular tailoring, this study raises questions on proposed feasibility[22,23,8,10] of ILs' macroscopic-microscopic behavior and allied phenomenology substantially. Furthermore, it poses challenges[24] radically to the applicability of numerous theories for molecular fluids[25–28] to ILs, which need be upgraded. In this regard, present work establishes the following aspects: (i) Specific design of ILs showing a commonly seen variation in them, (ii) ILs featured out in an analysis in the framework of Schaaffs' collision factor theory of speed of sound, u, Newton Laplace equation for isentropic compressibility, β_S, Rao's relation for molecular sound velocity, R and Wada's model for molecular compressibility, A over the molecular fluids, and their variation with temperature, (iii) Quest for the middleman in molecular modeling accounting to ILs' inherent behavior to these quantities in terms of structural descriptors and in the light of Jacobson's relation for intermolecular free length, L_f, contributions to molar or molecular volume, V_m, etc.

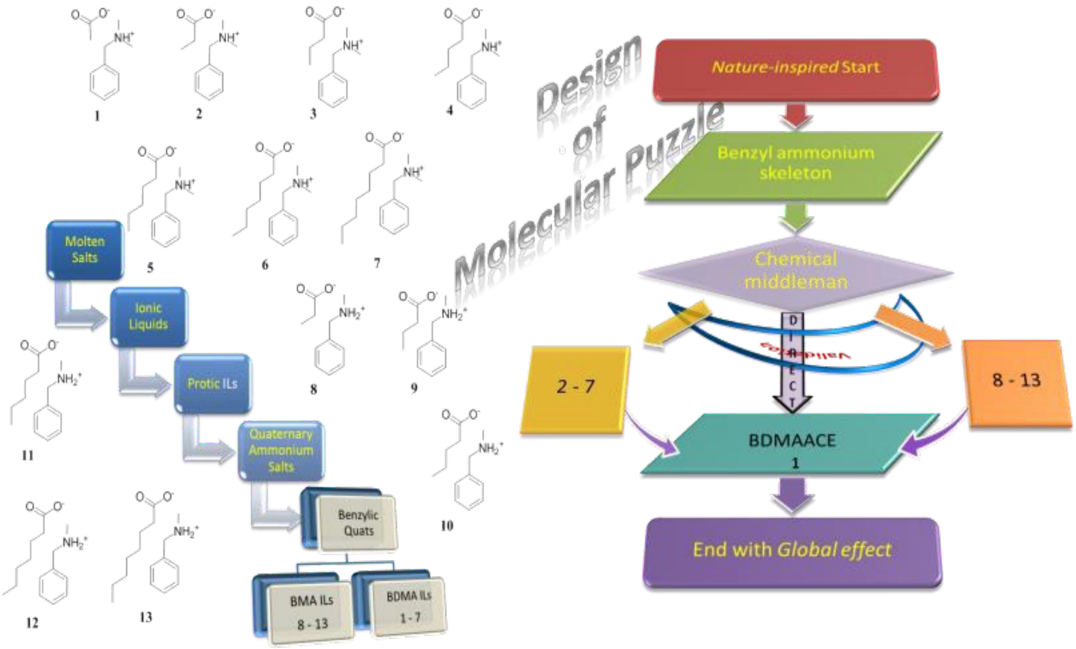


Figure 1. Flowchart showing schematic representation of the basics of our study and Evolutionary tree showing the origin of Benzylic Quats.

Results and Discussion

The Molecular Puzzle

This explorative excursion begins with the inspiration from the nature itself wherein benzylic skeleton is ubiquitous. It is attempted to bring it into designing aspects of molecular puzzle through tailoring[29] in the form of new edition to the outlook to the ILs where it is in scarce. Equipped with molecular tools, it proceeds through feasible synthesis[30,31,29] and other attempts made in Experimentation section, and thorough investigation of the physiochemical behavior[12] of all the variants, followed by logical molecular tailoring (fragmentation while employing group contribution method and reunion while validation approach). The evolutionary history of Benzylic Quats and basics of our study in context to the molecular puzzle have been well depicted through Flowchart in Figure 1 that presents unwinding it through logical breaks and links thenceforth. During the course of progress it gets featured with a multitude of analytical, justifying and/or comparable support from the available literature. Meanwhile, it aids to the analysis of applicability of currently prevailed theories and conceptions on molecular fluids[25–28] to ILs while comprehension, that get depicted in molecular design[32] of the puzzle-

Densimetry

This could be the first tool to be considered in the process of molecular tailoring of the puzzle to grab the probable middleman deciding the design. It can be visualized from Figure 2 and Table S2 that BMAPRO is the densest and BDMAOCT is the lightest one among all the ILs under study. Amidst the ILs of same cation family, there is a prominent effect of anionic alkyl chain-length and our results stand well on the fact that long alkyl chains lower the density, ρ of the corresponding ILs[33]. These follow the order BDMAOCT < BDMAHEPT < BDMAHEX < BDMAPENT < BDMABUT < BDMAPRO and BMAOCT < BMAHEPT < BMAHEX < BMAPENT < BMABUT < BMAPRO as depicted through lower molecular volumes, V_m of Propionate salts in Table 1. Quantitatively, one $-CH_2$ incorporation changes the density by 4.68% amongst ILs in Propionate family rather than 3.52% in Octanoates at ambient condition. As each IL is to be observed individually from the tabulated values, graphically presented as Figure 2, incorporation of $-CH_2$ groups lowers the density, only by 6.55% in BMAOCT relative to BMAPRO whereas this results into 5.41% in BDMAOCT w.r.t. BDMAPRO at 298.15 K. Among the benzylic quats the magnitude of such a contribution for each $-CH_2$ as suggested from group contribution technique through the least square regression procedure[12,34] is to be 0.0289 nm^3 for V_m that agrees quite well with that for alcohols (0.0280 nm^3), n-paraffins (0.0267 nm^3), n-amines (0.0272 nm^3), and for several other ILs reported so far as depicted in the previous work from our group[11].

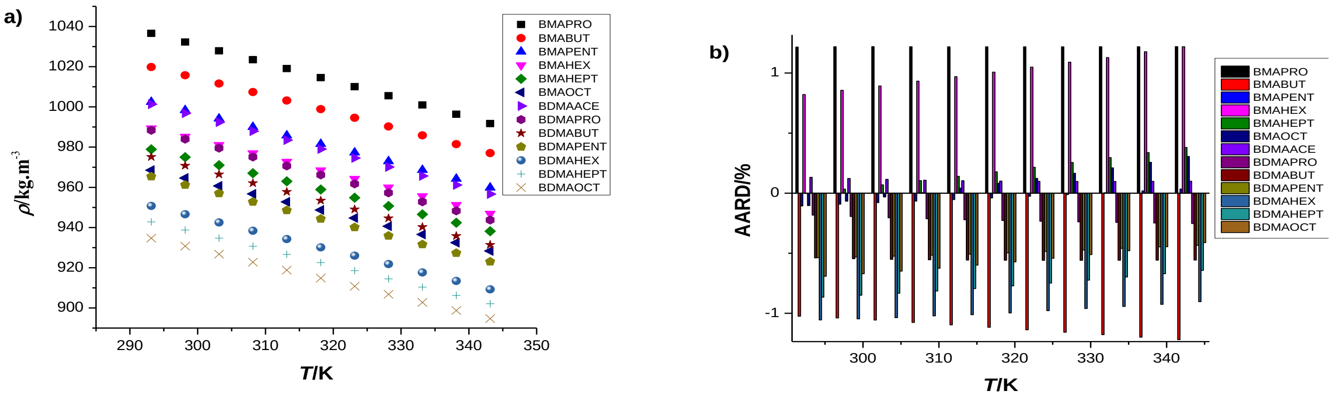


Figure 2. Representation of experimental data showing the thermodynamic profile and agreement between experimental and correlated data (predicted data in case of BDMAACE) at different temperatures and atmospheric pressure.

Comparatively, BMA appending ILs are dense as propounded through their relatively less V_m. Small size of BMA cations makes themselves feasible to be compactly entangled in contrast to the bulkier BDMAs and the availability of free space is being avoided that further causes incompressibility expressible through the speed of sound, u measurements. Literary comparison is not possible so far to account for such molecular variability; however, it is quite reasonable to look through these variants so as to formulate task-specific molecular design. Herein, it can be visualized from the structural constitution of both cations that in each case –CH_3 introduction in place of hydrogen in BMA cation causes decrement in density of BDMA as being reflected from the mean contribution of 0.1080 nm^3 V_m at 298.15 K, similar to –CH_2 impregnation on anionic end. In this way, BDMAOCT portrays the lowest density as predicted from its structural peculiarities. Five more –CH_2 and a –CH_3 in the structural identity of BMAPRO emerge out as BDMAOCT with a tremendous increment in molecular volume that can be ascribed as a possible root of such a huge variation. Table 2 summarizes the mean contribution of the constituting groups of the investigated benzylic quats' variants at ambient temperature and pressure. Overall it seems the dominance of steric factor over the density values for such a class of ILs in relation to both cationic and anionic variability. Extra free volume created by such bulkier groups gets resulted into comparatively lower density found. Moreover, the findings on the density profile are quite consistent to the ΔpK_a approach previously reported[11,8], among the benzylic quats. Greater the ΔpKa, greater is the density found amongst both BMA and BDMA ILs that signifies to the strength of bonding between cationic and anionic counterparts. Such measurements and data compilation on physiochemical behavior can be useful to a restricted mass only, unless it gets aided with analytical features on the obtained trends, that further demands for Thermodynamic and Statistical tools on shortcomings in logical reasoning and interpretation capabilities for a tremendous mass of ILs possible.

Table 1 also presents the values for coefficient of thermal expansion, α at ambient temperature and pressure to have a further understanding of the role of temperature in the volumetric behavior of these fluids. As is customary to say α values are lower for associated liquids like acids and alcohols. It is found that these feature similar to conventional imidazolium based ionic liquids rather than common organic solvents. Such behavior can be ascribed partly to the presence of ionic bond in their constitution at molecular level. Since the densities decrease with temperature it is quite understandable that α values are positive, increasing with temperature. As customary, it attains higher values as the temperature progresses but not at much significant rate, thence the values at only ambient conditions are tabulated. The predominance of the effect can be easily understandable through bond strength among the structural constituents of the ILs, that further raises the significance of u measurements. Atleast at this point of time, the role of temperature increment can be perceived through the rise in average intermolecular separation on high kinetic energy levels. As the temperature of the liquid increases, the mean molecular distance also increases, resulting in a decreased u for at a given temperature it is inversely proportional to ninth power of the mean distance between the molecules at that temperature in the liquid[25].

Ultrasonics

T. S. Khasanehin and T. B. Zykova proclaimed, "*A promising method of drawing up tables of thermodynamic parameters for liquid is provided by using acoustic measurements as input data*".[35] With the same intention, in the similar fashion to the density, the speed of sound data have been taken[34] with reasonable uncertainty and presented over Table S2, following the order: BMA ILs > BDMA ILs. Apparently, alkyl chain elongation lowers the magnitude amidst the ILs of same cation family, in accordance with the expansion of spatial intermolecular void w.r.t. the inherent molecular steric constraints. However, this lies in contrast to the study by M. J. W. Povey *et al*[34] where they claim for end unit, adjacent chain, H-bonding effects, etc. which play a role in magnitude of u in terms of molecular orientation, geometry and assembly and make the effect of carbon chain growth insignificant and can lead to the inversion of observed trends as is featured in the case of BDMAOCT. The study is made further subject to the influence of temperature as correlated through quadratic equation in Table S2 and corresponding parameters can be procured from Table S3 under Electronic Supplementary information (*ESI*). Nevertheless, their high magnitude is accredited to the existing aromatic moiety as featured from the earlier reports[25]. The phenomenon can be easily understood through the conception of inter molecular free length, L_f while the acoustic wave gets transmitted through the fluid, which further calls for the compressibility, β_S or speed of sound data such that $L_f \propto \sqrt{\beta_S} \propto 1/(u\sqrt{\rho})$. The lesser the compressibility, the lesser be the intermolecular free length[36] expressed by Jacobson's relation as such the greater be the efficiency of the wave transmission, resulting into the greater speed of sound. According to W. Schaaffs' collision factor theory[37] of speed of sound in pure liquids, u is proportional to the product of the collision factor that is featured through the elasticity of the mutual molecular collisions, and the space filling factor of the molecules, that adds new insights to visualize the Thermodynamic trends.

Table 1. Various derived properties under consideration at 298.15 K and 0.1 MPa.

Benzylic Quats	$V_{molar}\times10^{6}$ /m^{3}mol^{-1}	$\alpha\times10^{4}$ /K^{-1}	β_s /TPa^{-1}	R	A
BMAPRO	188.37	8.43	413.42	2180.0	80.0
BMABUT	205.21	8.15	429.34	2366.0	86.7
BMAPENT	222.77	8.28	449.38	2556.5	93.5
BMAHEX	239.90	8.38	461.41	2747.3	100.3
BMAHEPT	256.79	8.11	471.04	2935.2	107.0
BMAOCT	274.02	8.24	481.64	3126.2	113.8
BDMAACE	195.00	8.91	501.75	2198.5	80.6
BDMAPRO	211.75	8.97	510.94	2385.3	87.3
BDMABUT	229.01	8.91	530.04	2569.7	93.9
BDMAPENT	245.85	8.70	537.32	2756.6	100.6
BDMAHEX	264.39	8.67	548.19	2962.2	107.9
BDMAHEPT	281.50	8.57	552.47	3153.9	114.7
BDMAOCT	298.95	8.50	555.71	3350.9	121.7

The chemical constitution in molecular scaffold

Let us now look for chemical constitution in molecular scaffold. As mentioned above, the compilation of ***u*** data is quite relevant in plenty of ways that need be elaborated over here. It is worthwhile possibly to get any insight into the chemical constitution of the substance having as ***u*** through the simple laws relating it, for instance, to molecular volume in liquids so as to deduce M. R. Rao's molecular sound velocity $R = u^{1/3}.M/\rho$ where all the terms have their usual meanings. It signifies to the comparison of molecular volumes of two liquids at temperatures at which the acoustic velocity is the same. Notwithstanding, in analogy to V_m, the constant R can be regarded to follow the same additivity being constitutive in nature on the structural aspects. It varies in the same manner as the no. of carbon atoms or the molecular weight unlike the variations on ρ and u profile mentioned above, however, stays almost invariant with temperature alternation as described originally[25]. The observed trend is quite consistent with that in V_m as described above, being as the constitutive property. The values are found higher than those for common liquids as studied so far, leading to inference of these being associative at molecular level due to lower cohesive energy these do possess, as is observed in case of alcohols' constitution study by G. W. Marks[38]. Relying on the R's of C, H, O and double bond contributions reported from the examination of several homologous series of organic liquids in the original findings of Rao[25], years ago before the advent of ILs and deducing the same for N, the missing one, its contribution is assigned to be -91.6. Thenceforth, the contributions for the five candidates have been calculated and listed out over Table 2. The predictions were justified through the external test material BDMAACE revealing only 0.89% deviation relative to the value obtained from the Rao's relation mentioned above. To be frank to say about the predictive behavior of such proposals of contribution, it does rely on nature of molecular constitution[26] that further aids to our approach of validation through external data set of the same family and gives essential clues in the constitutive behavior, designing and modeling aspects of the solutions to the subject of our concern, the molecular puzzles and recognizing the chemical middleman deciding such behaviors. The validated results and the estimated contributions of $–CH_2$, $–CH_3$ along with rest other basic constituents of benzylic quats are addressed in Table 2 along with other constitutive properties under investigation. Such a contraption seems necessity in the lack of u measurements being constitutive and predictive.

At this moment it is noteworthy to point out the constitutive behavior of R's gathered over here that these fluids constitute two homologous series as obvious in various properties under consideration, depending upon the constitutive behavior of cation rather than anion such that it increases in every series with an increase in the molecular chain-length in entirely different manner, as proposed[25,28] from the relation $R = A.M + B$. Here. A and B are empirical constants[25] such that A is a general constant independent of the series (ca. 14 as originally proposed in case of molecular fluids) and B a characteristic constant for anyone homologous series that varies considerably amidst the two. In this context, it is clearly demonstrated now that Rao's work on molecular fluids is still applicable to ILs. In the same vein, it could be added to R of being the constitutive property rather than u.

In common practice, u has so far been chiefly intended in rendering β_S. When the ultrasonic absorption of the acoustic waves is in so far as negligible as the case with the manufacturer's design of the apparatus employed over here, β_S can be deduced from these through the application of well familiar Newton-Laplace equation and tabulated in Table 1. The work signifies the understanding for bond strength and incompressibility terms arisen earlier in this report. As featured above in the discussion part of the density trends, the availability of extra free volume accounted for steric factors of the bulkier groups decreases not only the density but also causes increment in the compressibility values that gives a sense to the wide applicability of Newton-Laplace relation here as well. This is reasonable to add over here that the chain-length dependence of compressibility possesses much more significance over the density, since the latter can be regarded essentially as a geometrical packing phenomenon while the former constitutes two features viz. intramolecular, associated with the flexibility of the covalent bonding in chain, and intermolecular, associated with the flexibilities of a variety of intermolecular interactions[34]. This justifies the inverse profile of the compressibility values w.r.t. those of ρ and u data. Furthermore, higher β_S of benzylic quats compared to the conventional imidazolium ionic liquids can be ascribed to more free volume generated through the constituent bulkier groups. This way, this study also brings into common understanding of molecular features[32] and the variability profiles in our rigorous quest for the chemical middleman in solutions to the molecular puzzle.

Following the goal of understanding the molecular constitution of benzylic quats through Thermodynamic perspectives, a further attempt has been made to deduce Y. Wada's molecular adiabatic compressibility, A employing the bond contributions from his original piece of remarkable work on more than 120 liquids[27] so as to account for numerous factors e.g. constitutive nature of R was assaulted by Wada as mere an approximation to A, temperature independency of the term $\rho.\beta_S^{1/7}$ was appraised by Rao himself, lower *R*'s are often observed for associated liquids. Meanwhile, with the exp. ρ and *u* data *A* has also been calculated out through Wada's own relation $A = M/(\rho.\beta_S^{1/7})$. Huge deviations are observed as illustrated in Table S4 among the values from the two modes applied, revealing that the contributions proposed for normal liquids fail to predict the behavior of ILs, raising the practical need to be redefined and est~~.~~ once again, thus proposed in Table 2. This sort of inconsistency in chemical constitutional behavior deduced on grounds of additivity principle might be arisen on negligence of coulombic forces in such molecular fluids that stay predominant in ILs. The est. derived properties (V_m, *R* and *A*) of BDMAACE and the pred. ones through group contribution approach are in good agreement while validation as presented over Table 2.

Table 2. Constitutive properties of Benzylic Quats.

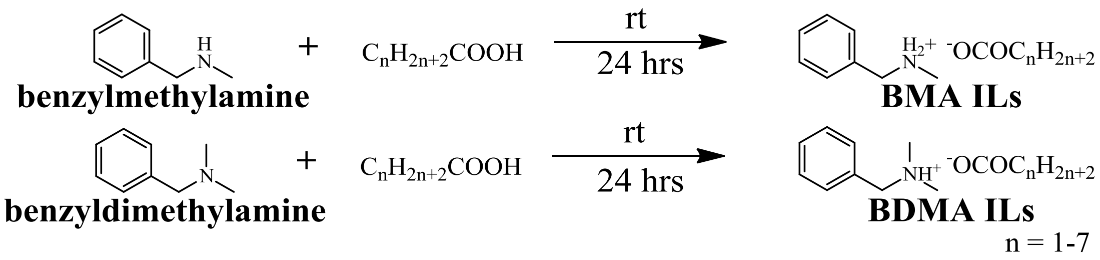
Property	CH_3	$C_6H_5CH_2NH^+$	$C_6H_5CH_2NH_2^+$	CH_3COO^-	CH_2	% AARD	% ARD for BDMAACE
V_m/nm^3	0.1080	0.0133	0.0816	0.0949	0.0289	0.13	0.29
R	287.5	1048.4	1140.9	555.5	195.0	0.34	0.89
A	25.2	5.1	22.8	24.9	6.8	0.13	0.19

This further elucidates that additivity for Wada's quantity might not be the case for ILs, in the broader perspectives, thenceforth in a way demanding for reinvestigations and amendments to be made! In this manner additivity principle thus exercised for bond contributions could not be accountable for non-covalent interactions amongst ionic liquid entities.

To sum up the attempts made so far in unwinding the web interwoven amongst the members of the family of benzylic quats in the form of puzzle, a rigorous investigation through molecular tailoring was executed and connecting links were drawn out through tools of Thermodynamic physiochemical-molecular modeling and constitutive behavior is thoroughly sought out throughout. The five qualified candidates to the title of chemical middleman were thereby analyzed in such terms and the candidates constituting benzyl ammonium skeleton (the two amongst the five) and the one possessing the carboxylate moiety, having been featured as the characteristic to all the variants with impractical physical significance to other sorts of ionic liquids, must have got eliminated out, leaving behind the versatile two which are potentially inter-assimilative. Only their candidatures get qualified in an obvious way to the embellishment for such a title for these stayed as the basics in the molecular integrity and identity of ionic liquids, the benzylic quats' numerous variants.

Experimental Section

Information on chemicals employed, source, purity and prior treatment, if any are provided on Table S1, while synthetic methodology, characterization techniques and mode of experimentation were significantly described in our previous communication[11,39] and schematic representation of synthetic procedure is illustrated in Scheme 1.



Scheme 1. Schematic representation of synthetic methodology adopted.

The structural elucidation of ionic liquids is carried out as follows:

Benzylmethylammonium propionate (*BMAPRO*)

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.89 (broad, 1H) 7.38-7.29 (m, 5H), 3.97 (s, 2H), 2.42 (s, 3H), 2.21 (q, 2H), 1.07 (t, 3H); **^{13}C NMR** (500 MHz, $CDCl_3$): δ ppm 180.4 (C=O), 134.2, 129.0, 128.4 and 127.9 (benzene ring carbons), 52.9 (CH_2-N), 32.4, 29.4, and 9.9 (saturated carbons); **QTOF MS ES+** (m/z): calculated for ($C_8H_{12}N^+$) 122.0970, found 122.0966.

Benzylmethylammonium butanoate (B*MABUT*)

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 9.51 (broad, 2H, NH_2^+), 7.34-7.28 (m, 5H, Ar CH), 3.87 (s, 2H, benzylic CH_2), 2.39 (s, 3H, N-CH_3), 2.15 (t, 2H, $COCH_2$), 1.57 (sextet, 2H, CH_2), 0.90 (t, 3H, CH_3); **^{13}C NMR** (400 MHz, $CDCl_3$): δ ppm 180.1(C=O), 133.5, 129.7, 128.8 and 128.6 (benzene ring carbons), 52.7 (CH_2-N), 39.0, 32.3, 19.5 and 14.1 (saturated carbons) ; **QTOF MS ES+** (m/z): calculated for ($C_8H_{12}N^+$) 122.0970, found 122.0964.

Benzylmethylammonium pentanoate (*BMAPENT*)

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 9.09 (broad, 2H, NH_2^+), 7.38-7.27 (m, 5H, Ar CH), 3.87 (s, 2H, benzylic CH_2), 2.41 (s, 3H, N-CH_3), 2.18 (t, 2H, $COCH_2$), 1.55 (qn, 2H, CH_2), 1.32 (sextet, 2H, CH_2), 0.89 (t, 3H, CH_3); **^{13}C NMR** (400 MHz, $CDCl_3$): δ ppm 180.2 (C=O), 134.0, 129.5, 128.9 and 128.5 (benzene ring carbons), 53.0 (CH_2-N), 36.7, 32.6, 28.3, 22.7, and 14.0 (saturated carbons) ; **QTOF MS ES+** (m/z): calculated for ($C_8H_{12}N^+$) 122.0970, found 122.0974.

Benzylmethylammonium hexanoate (*BMAHEX*)

^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.37-7.26 (m, 5H), 6.27 (broad, 1H), 3.85 (s, 2H), 2.434 (s, 3H), 2.20 (t, 2H), 1.58 (qn, 2H), 1.33-1.28 (m, 4H), 0.89 (t, 3H); **^{13}C NMR** (500 MHz, $CDCl_3$): δ ppm 180.3 (C=O), 135.1, 129.6, 129.0 and 128.6 (benzene ring carbons), 53.7 (CH_2-N), 36.9, 32.2, 32.0, 25.9, 22.8 and 14.3 (saturated carbons); **QTOF MS ES+** (m/z): calculated for ($C_8H_{12}N^+$) 122.0970, found 122.0973.

Benzylmethylammonium heptanoate (*BMAHEPT*)
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 9.15 (broad, 2H, NH_2^+), 7.39-7.28 (m, 5H, Ar CH), 3.89 (s, 2H, benzylic CH_2), 2.42 (s, 3H, N-CH_3), 2.19 (t, 2H, $COCH_2$), 1.57 (qn, 2H, CH_2), 1.36-1.24 (m, 6H, CH_2), 0.89 (t, 3H, CH_3); **^{13}C NMR** (400 MHz, $CDCl_3$): δ ppm 180.1 (C=O), 133.6, 129.7, 128.9 and 128.7 (benzene ring carbons), 52.9 (CH_2-N), 36.7, 32.4, 31.8, 25.8, 22.6, 14.1 (saturated carbons) ; **QTOF MS ES+** (m/z): calculated for ($C_8H_{12}N^+$) 122.0970, found 122.0967.

Benzylmethylammonium octanoate (*BMAOCT*)
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.16 (broad, 2H, NH_2^+), 7.39-7.28 (m, 5H, Ar CH), 3.88 (s, 2H, benzylic CH_2), 2.43 (s, 3H, N-CH_3), 2.20 (t, 2H, $COCH_2$), 1.57 (qn, 2H, CH_2), 1.31-1.27 (m, 8H, CH_2), 0.89 (t, 3H, CH_3); **^{13}C NMR** (400 MHz, $CDCl_3$): δ ppm 180.1 (C=O), 134.3, 129.5~~14~~, 128.9 and 128.5 (benzene ring carbons), 53.2 (CH_2-N), 36.8, 31.9, 29.6, 29.3, 26.1, 22.8 and 14.2 (saturated carbons) ; **QTOF MS ES+** (m/z): calculated for ($C_8H_{12}N^+$) 122.0970, found 122.0973.

Benzyldimethylammonium acetate (*BDMAACE*)
^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.37-7.30 (m, 5H), 6.99 (broad, 1H), 3.72 (s, 2H), 2.39 (s, 6H), 2.03 (s, 3H); **^{13}C NMR** (500 MHz, $CDCl_3$): δ ppm 176.2 (C=O), 134.5, 130.2, 128.7 and 128.3 (benzene ring carbons), 62.4 (CH_2-N), 43.3, and 22.2 (saturated carbons); **QTOF MS ES+** (m/z): calculated for ($C_9H_{14}N^+$) 136.1126, found 136.1128.

Benzyldimethylammonium propionate (*BDMAPRO*)
^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 7.37-7.30 (m, 5H), 6.84 (broad, 1H) 3.71 (s, 2H), 2.38 (s, 6H), 2.32 (q, 2H), 1.14 (t, 3H); **^{13}C NMR** (500 MHz, $CDCl_3$): δ ppm 179.6 (C=O), 135.03, 130.4, 128.8 and 128.4 (benzene ring carbons), 62.7 (CH_2-N), 43.6, 28.8 and 9.9 (saturated carbons); **QTOF MS ES+** (m/z): calculated for ($C_9H_{14}N^+$) 136.1126, found 136.1127.

Benzyldimethylammonium butanoate (*BDMABUT*)
^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.16 (broad, 1H, NH^+), 7.34 (m, 5H, Ar CH), 3.73 (s, 2H, benzylic CH_2), 2.39 (s, 6H, N-CH_3), 2.27 (t, 2H, $COCH_2$), 1.65 (sextet, 2H, CH_2), 0.96 (t, 3H, CH_3); **^{13}C NMR** (500 MHz, $CDCl_3$): δ ppm 178.7 (C=O), 134.6, 130.3, 128.7 and 128.3 (benzene ring carbons), 62.4 (CH_2-N), 43.3, 37.6, 19.0, and 14.0 (saturated carbons); **QTOF MS ES+** (m/z): calculated for ($C_9H_{14}N^+$) 136.1126, found 136.1129.

Benzyldimethylammonium pentanoate (*BDMAPENT*)
^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 8.52 (broad, 1H, NH^+), 7.34 (m, 5H, Ar CH), 3.76 (s, 2H, benzylic CH_2), 2.41 (s, 6H, N-CH_3), 2.28 (t, 2H, $COCH_2$), 1.61 (qn, 2H, CH_2), 1.36 (sextet, 2H, CH_2), 0.91 (t, 3H, CH_3); **^{13}C NMR** (500 MHz, $CDCl_3$): δ ppm 179.0 (C=O), 134.0, 130.4, 128.7 and 128.5 (benzene ring carbons), 62.2 (CH_2-N), 43.1, 35.3, 27.7, 22.6, and 14.0 (saturated carbons); **QTOF MS ES+** (m/z): calculated for ($C_9H_{14}N^+$) 136.1126, found 136.1126.

Benzyldimethylammonium hexanoate (*BDMAHEX*)
^{1}**H NMR** (500 MHz, $CDCl_3$): δ ppm 7.35-7.28 (m, 5H), 6.47 (broad, 1H), 3.66 (s, 2H), 2.35 (s, 6H), 2.28 (t, 2H), 1.63 (qn, 2H), 1.33-1.30 (m, 4H), 0.89 (t, 3H); ^{13}**C NMR** (500 MHz, $CDCl_3$): δ ppm 179.6 (C=O), 135.0, 130.4, 128.8 and 128.4 (benzene ring carbons), 63.2 (CH_2-N), 44.1, 35.9, 32.1, 25.7, 23.0 and 14.4 (saturated carbons); **QTOF MS ES+** (m/z): calculated for ($C_9H_{14}N^+$) 136.1126, found 136.1128.

Benzyldimethylammonium heptanoate (*BDMAHEPT*)
^{1}**H NMR** (400 MHz, $CDCl_3$): δ ppm 10.39 (broad, 1H, NH^+), 7.37-7.30 (m, 5H, Ar CH), 3.73 (s, 2H, benzylic CH_2), 2.39 (s, 6H, N-CH_3), 2.29 (t, 2H, $COCH_2$), 1.62 (qn, 2H, CH_2), 1.37-1.26 (m, 6H, CH_2), 0.88 (t, 3H, CH_3); ^{13}**C NMR** (400 MHz, $CDCl_3$): δ ppm 178.9 (C=O), 130.3, 128.7, 128.3 (benzene ring carbons), 62.4 (CH_2-N), 43.35, 35.6, 31.7, 29.2, 25.6, 22.7, 14.2 (saturated carbons); **QTOF MS ES+** (m/z): calculated for ($C_9H_{14}N^+$) 136.1126, found 136.1131.

Benzyldimethylammonium octanoate (*BDMAOCT*)
^{1}**H NMR** (400 MHz, $CDCl_3$): δ ppm 11.14 (broad, 1H, NH^+), 7.38-7.28 (m, 5H, Ar CH), 3.72 (s, 2H, benzylic CH_2), 2.38 (s, 6H, N-CH_3), 2.21 (t, 2H, $COCH_2$), 1.62 (qn, 2H, CH_2), 1.31-1.27 (m, 8H, CH_2), 0.88 (t, 3H, CH_3); ^{13}**C NMR** (400 MHz, $CDCl_3$): δ ppm 178.9 (C=O), 134.6, 130.2, 128.7 and 128.3 (benzene ring carbons), 62.4 (CH_2-N), 43.3, 31.9, 29.5, 29.2, 25.7, 22.7 and 14.2 (saturated carbons); **QTOF MS ES+** (m/z): calculated for ($C_9H_{14}N^+$) 136.1126, found 136.1127.

All IR graphs show the broad band appeared around 3400 cm^{-1} range exhibiting the characteristic ammonium peak and O-H stretching vibration, N–H plane bending vibrations and aeromatic C-C stretch around 1400 cm^{-1}, C-N stretch for aliphatic amine around 1220 $cm^{-1}$and carbonyl stretching around 1700 cm^{-1}.

Moisture content was analyzed each time before and after use through the application of well-known Karl Fisher Coulometer technique and found to be <0.2% Sampling was done thrice corresponding to each lot synthesized and measured data average is tabulated on Table S2. Though the methodologies adopted are conventional, yet these are having both basic and applied perspectives in ever-expanding and flourishing domains of industrial, academic and R&D infrastructure. To take into account such broad aspects with full sincerity, high precise sophisticated world-class instruments are employed, and accuracy and purity have been given enough significance at each state of experimentation. Thermodynamic profile w.r.t. molecular architecture is defined within reasonable uncertainty and justified adequately through a variety of tools like predictions, correlations, estimations, validations, comparisons and assimilation to the existing trends, models and theories to present the clear-cut description of modeling aspects of application-specific new variants.

Furthermore, a blend of fundamental cum derived properties is assessed through empirical and semi-empirical relations. The external test material from the same family employed over here for validation of the Thermodynamic profile of the system under consideration not only validates the approach of group contribution[12] but also presents the inherent trend explored with reasonable success and gives us the clues for the probable middleman in the additivity principle. Attempts are made, in addition, to execute the assimilation with existing models/theories for general fluid systems.

Thermodynamic insights and group contribution approach

To get insights into the effect of temperature on volumetric properties, ρ and u are measured as a function of temperature and presented in Table S2. $\Delta\rho$ is most pronounced in case of BDMAPRO and ρ decreases 4.52% at 343.15 K as compared to that at 293.15 K and our results stand further well on the fact that there exists inverse relation between temperature and density for liquids, that is herein represented with quadratic empirical correlation. Table S3 lists out their best fit parameters for the investigated benzylic quats that are made subject to further distribution among five structural descriptors without any special weighing. The statistics of these correlations and predictions for error analysis is shown in Figure 2. The study covers 894.683 to 1036.587 $kg.m^{-3}$ density range. The higher density as compared to other conventional liquids can be assigned to $\pi-\pi$ stacking of aromatic rings[33], only characteristic to these benzylic quats. The predictions are justified through the external test material BDMAACE. Such predictive behaviors or contributions are characteristic to constitutive molecular scaffold that raises the necessity of validation. For the same intentions in mind, external data set of the same family was employed to our working data set, segregated out from the designing and modeling aspects and to our delight the deviations are within reasonable limits, that makes us familiar with an array of qualified candidates of the chemical middleman deciding such behaviors. The validated results and the estimated contributions of such candidates are addressed in Table 2 along with other constitutive properties under investigation compiled further to aid on the solutions of Molecular Puzzle woven in the family of benzylic quats. Now an analysis is called for recognizing the odd one out that itself demands for relative weightage of various candidates to the properties for confirming the right authority of being characteristic of middleman. Such an exploration raises the significance of our research enterprise for Thermodynamic profiling at a wide range of state variables, say temperature herein. This is further boosted up with Ultrasonic treatment of the new variants.

The relative relevance of approaches adopted in molecular tailoring for finding the chemical middleman out in molecular puzzle can be summed up in hierarchy as:

Synthesis → Structural elucidation → Property measurements and Thermophysical assessment → Empirical derivations → Correlations-Predictions-Estimations → Analysis and Conceptualization → Statistics and Molecular modeling → Validation and Comparison → Applicability in the process and product design.

Conclusions and prospects

A new family of benzyl appended ammonium ionic liquids has been synthesized. Numerous methodologies were employed for molecular structure confirmation and their physiochemical behavior for a wide temperature range. Molecular volume, V_m, coefficient of thermal expansion, α, adiabatic compression coefficient, β_S, intermolecular free length, L_f have been derived and the inherent nature of the fluids has been deduced as associative. Significant insights have been drawn in the wide applicability of Newton-Laplace relation. Semi-empirical Rao's relation for molecular sound velocity, R is employed to estimate the constitutive peculiarities at the microscopic level through the application of macroscopic properties like density, ρ and speed of sound, u and the missing atomic contribution for Nitrogen is propounded. The class is found to be segregated into two groups, depending upon the cationic integration. Wada's model for liquids has been found inconsistent for ionic liquids, atleast say for these benzylic quats, and thus reformulated. Meanwhile, a number of properties were also parametrized into five forms using twelve of the ILs under investigations whereas the thirteenth one was treated as external test substance on validation and the success is achieved within the limits of experimental error in both the cases of correlations and predictions. On thermodynamic grounds, it gets demonstrated both qualitatively and quantitatively how a small group like $–CH_2$ / $–CH_3$ behaves as the chemical middleman deciding both the micro and macroscopic properties and provides the essential justification to the title of this report. At last, theoretical background in terms of electronic behavior of various intra and intermolecular factors related to ionic charge, dipole moment and polarizability ought be explored in association to such thorough experimental investigations and phenomenology, yet the study seems fruitful to answer the molecular puzzle of structure to property variability and vice versa with reasonable success and lays down the new foundation for voyage on intriguing thoughts with molecular tools. Comparative literary accounts are placed to compensate to the lacunae. Such rigorous attempts in solving molecular puzzle via a middleman can guild a lily in task-specific applications through accessing ILs' potential of structural variability as per wish and/or demand.

The study has formulated several macroscopic properties reflecting the strengths of microscopic intra and intermolecular forces amongst a new family of ILs and its further classification. Moreover, it has employed non-destructive high precise volumetry, defined new variants' Thermodynamic profile, investigated structure-property couple and estimated constitutive behavior without any severity to the environment. In this fashion, key-design in molecular architecture relative to physiochemical behavior can be unlocked and revealed through tailoring, herein molecular shuttle of $–CH_2$ / $–CH_3$ in a green way and a hypothesis for chemical middleman has been propounded in additivity phenomenon.

Acknowledgements

Authors are thankful to Council of Scientific and Industrial Research (CSIR), India, Department of Science and Technology (DST), India and IIT Madras for their financial support through grant numbers 01(2525)/11/EMR-II, SR/FT/CS-45/2011 and CHY/10-11/523/NFSC/RAME, respectively. Authors acknowledge Dasthaiah Keshapolla for the help in synthesis of a few ILs.

References

1. N. V Plechkova and K. R. Seddon, *Chemical Society reviews*, 2008, **37**, 123–150.
2. E. F. Borra, O. Seddiki, R. Angel, D. Eisenstein, P. Hickson, K. R. Seddon, and S. P. Worden, *Nature*, 2007, **447**, 979–981.
3. R. A. Sheldon, *Green Chem.*, 2005, **7**, 267–278.
4. J. Brennecke and E. Maginn, *AIChE Journal*, 2001, **47**, 2384–2389.
5. A. Kumar and P. Venkatesu, *Chem. Rev.*, 2012, **112**, 4283−4307.
6. A. D. Sawant, D. G. Raut, N. B. Darvatkar, U. V. Desai, and M. M. Salunkhe, *Catal. Commun.*, 2010, **12**, 273–276.
7. H. Tokuda, K. Hayamizu, K. Ishii, M. A. B. H. Susan, and M. Watanabe, *J. Phys. Chem. B*, 2005, **109**, 6103–6110.
8. M. Yoshizawa, W. Xu, and C. A. Angell, *J. Am. Chem. Soc.*, 2003, **125**, 15411–15419.
9. C. Chiappe, A. Sanzone, D. Mendola, F. Castiglione, A. Famulari, G. Raos, and A. Mele, *J. Phys. Chem. B*, 2013, **117**, 668−676.
10. H. Ohno and M. Yoshizawa, *Solid State Ionics*, 2002, **154-155**, 303–309.
11. P. Chhotaray and R.L. Gardas, *J. Chem. Thermodyn.*, 2014, **72**, 117–124.
12. J.A.P. Coutinho and R.L. Gardas, in *Ionic Liquids: From Knowledge to Application*, ed. K. R. Plechkova, Natalia V., Rogers, Robin D., Seddon, American Chemical Society, 2009, vol. 1030, pp. 385–401.
13. F. J. Deive, M. A. Rivas, and A. Rodríguez, *J. Chem. Thermodyn.*,2011, **43**, 487–491.
14. R. Tao, G. Tamas, L. Xue, S. L. Simon, and E. L. Quitevis, *J. Chem. Eng. Data*, 2014, **59**, 2717–2724.
15. S. M. Mahurin, T. Dai, J. S. Yeary, H. Luo, and S. Dai, |*Ind. Eng. Chem. Res.*, 2011, **50**, 14061–14069.

16. G. Kaur, A. K. Mandal, M. C. Nihlani, and B. Lal, *Int. Biodeterior. Biodegrad.*, 2009, **63**, 151–155.
17. M. Lavania, P. M. Sarma, A. K. Mandal, S. Cheema, and B. Lai, *J. Environ. Sci.*, 2011, **23**, 1394–1402.
18. C. Wang, L. Guo, H. Li, Y. Wang, J. Weng, and L. Wu, *Green Chem.*, 2006, **8**, 603.
19. N. Muhammad, M. I. Hossain, Z. Man, M. El-Harbawi, M. A. Bustam, Y. A. Noaman, N. B. Mohamed Alitheen, M. K. Ng, G. Hefter, and C.-Y. Yin, *J. Chem. Eng. Data*, 2012, **57**, 2191–2196.
20. S. Ahrens, A. Peritz, and T. Strassner, *Angew. Chem. Int. Ed.*, 2009, **48**, 7908–10.
21. K. Dill, *J. Biol. Chem.*, 1997, **272**, 701–704.
22. C. A. Angell, *Science*, 1995, **267**, 1924–1935.
23. T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2084.
24. M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, and B. Scrosati, *Nature materials*, 2009, **8**, 621–629.
25. M. R. Rao, *J. Chem. Phys.*, 1941, **9**, 682–685.
26. R. T. Lagemann, *J. Chem. Phys.*, 1942, **10**, 759.
27. Y. Wada, *J. Phys. Soc. Jpn.*, 1949, **4**, 280–283.
28. S. Parthasarathy and N. Bakhshi, *J. Phys. Chem.*, 1953, **57**, 453–454.
29. M. Semsarilar and S. Perrier, *Nature chemistry*, 2010, **2**, 811–820.
30. B. Horton, *Nature*, 1999, **400**, 797–799.
31. J. H. Clark, *Nature chemistry*, 2009, **1**, 12–13.
32. H. Weingärtner, *Angew. Chem. Int. Ed.*, 2008, **47**, 654 – 670.
33. J. Kagimoto, S. Taguchi, K. Fukumoto, and H. Ohno, *J. Mol. Liq.*, 2010, **153**, 133–138.
34. M. Povey, Z. Stec, S. Hindle, J. Kennedy, and R. Taylor, *Ultrasonics*, 2005, **43**, 219–226.
35. T. S. Khasanshin and T. B. Zykova, *J.Eng. Physics*, 1984, **46**, 399–405.
36. B. Jacobson, *Acta Chem. Scand.*, 1952, 1485–1498.
37. W. Schaaffs, *Molecular Acoustics*, Springer-Verlag, Berlin/Heidelberg, 1967, vol. 5.
38. G. W. Marks, *J. Acoust. Soc. Am.*, 1967, **41**, 103–117.
39. D. Keshapolla, V. Singh, A. Gupta, and R. L. Gardas, *Fluid Phase Equilib.*, 2015, **385**, 92–104.