Solvent effects on surface activity of aggregate ions in electrospray ionization

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ABSTRACT

A principal feature of electrospray ionization (ESI) is the transfer of ions in solution into the gas-phase for analysis by mass spectrometry. The electrospray process is intricate and therefore each stage of the process must be well-characterized in order to optimize the quality of the data obtained. The surface activity of a given ion is a substantial factor in its likelihood of evaporating from droplets formed by the electrospray, and leads to a differential response of one ion over another. Consequently, investigation of the response of a variety of ions in multiple solvents lends insight toward both desolvation processes and the surface activity of the ions studied in the chosen solvent. In the present work, a cationic ionic liquid, butyl methylimidazolium (BMIM), was paired with a counterion and mixed in various solvents. Subsequently, BMIM paired with a different counterion was added to the solution and analyzed by ESI mass spectrometry to determine the relative response ratio between two observable aggregates. The findings assist in the elucidation of differential surface activity of chemically distinct ions in ESI, with respect to changes in solvent. Furthermore, the results obtained suggest acetonitrile is an optimal solvent for the analysis of ions of this type due to a reduction in differential effects, whereas other common ESI solvents prove to enhance the surface activity of specific aggregate ions.

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1. Introduction

Surface activity is a broad term used in many fields of chemistry including catalysis [1], adsorption [2], host–guest interactions [3,4] and nanoparticles [5,6]. In electrospray ionization mass spectrometry (ESI-MS), surface activity is intricately involved with the mechanism by which charged ions are produced [7–11]. Consider the case where two ions, A^+ and B^+, are present in a solution. If the solvent selected is most different in nature from A, this ion will prefer to be present at an interface which minimizes its overall solvation [7]. If the container in question is a semi-spherical electrospray droplet, the ion A will partition as much as possible to the outer layer becoming surface active, while ion B resides preferentially in the core of the droplet due to its better solvation [7,12]. Essentially, ions that are the least well solvated and/or ion paired are most likely to be found on the surface of a droplet rather than buried in the interior, and so are over-represented in the

spectrum because they are the ions most likely to evaporate from the droplet first [13]. For ions with similar properties, ESI provides a good match between concentration and abundance but, for ions that differ greatly in size or polarity, the results obtained may become distorted from those of the original solution analyzed [12,14]. The nature of the solvent will affect the absolute instrumental response of the ions as well, so we might expect water to have quite different effects compared to dichloromethane, and we would expect methanol and acetonitrile to have effects somewhere between the two extremes [12,14]. The situations in which bias occurs must be understood and accounted for to insure that any ESI-MS data have real quantitative meaning [15].

We wanted to compare the effects of different solvents on the relative propensity of particular ions to appear in the spectrum. Aggregate ions are a common feature of ESI mass spectra, and are even exploited for calibration purposes. The aggregates are of the form $[(\text{cation})_{n+1}(\text{anion})_n]^+$ in the positive ion mode and $[(\text{cation})_n(\text{anion})_{n+1}]^-$ in the negative ion mode. For example, a solution of potassium iodide produces aggregates of the form $[(\text{K})_{n+1}(\text{I})_n]^+$ which are used for mass spectrometer calibration in the positive ion mode. Ionic liquids [16] display this property quite strongly [16], and these "gaseous supramolecules" have been studied in detail [17]. Concentrated solutions ($10^{-4}\,\text{mol L}^{-1}$) are dominated

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by the aggregates, which become less prominent as the concentration diminishes. ESI-MS of dications with mixed counterions of the form [dication][I][NTf$_2$] exhibit positive ions of the type [dication + NTf$_2$]$^+$ preferentially over [dication + I]$^+$, but most markedly in water > methanol > acetone > acetonitrile [18]. However, there are no competitive experiments that we know of that have compared the relative propensity of aggregate ions to appear depending on their nature, nor have such experiments been conducted in different solvents.

We chose five butylimidazolium (BMIM) salts for the investigation (see Table 1 for their physical properties, along with those of water for comparison), with anions ranging from the small and hydrophilic chloride ion to the large and hydrophobic bis (trifluoromethanesulfonyl) imide ion, [N(SO$_2$CF$_3$)$_2$]$^-$ (also known as bistriflimide and abbreviated [NTf$_2$]$^-$). Table 2 details the size, surface area and volume of these anions, along with the standard molar Gibbs transfer energy for anions from water to 60:40 methanol/water (a measure of hydrophilicity).

2. Materials and methods

All salts were purchased from Sigma–Aldrich and used as received, except for [BMIM][NTf$_2$] whose preparation was based on a literature procedure [28]. Lithium bis(trifluoromethanesulfonyl) imide (0.8 g, 0.003 mol, Aldrich) and 1-butyl-3-methylimidazolium chloride (0.5 g, 0.003 mol, TCI America) were each dissolved separately in 50 mL of deionized water. The lithium solution was added to the [BMIM]Cl solution with stirring. The solution became milky immediately and was allowed to sit for 45 min. The solution was heated at 55 °C for 15 min after which point small oily droplets could be observed in the bottom of the flask. This material was extracted with dichloromethane (3 × 15 mL). The organic layer was washed with deionized water (5 × 10 mL) to remove any residual lithium chloride and starting material. The dichloromethane was removed via rotary evaporation resulting in 1.0 mL of liquid. The material was dried under vacuum for 48 h prior to use.

For each test a stable MS signal of a diluted ionic liquid (IL) was obtained (concentrations were 40 μM, 4 × 10^{-5} M). A second solution containing a different IL (in the same solvent) was then added in equal volume. The peaks monitored in this experiment were those representing the [(BMIM)$_2$ + anion]$^+$ cations. For comparison of IL signal intensity a response ratio, defined as the peak area of the IL of interest divided by the second IL peak area, was calculated. In the absence of any signal response discrimination this procedure was expected to result in halving of the signal for the initial IL ions present while a secondary peak should also be observed at equal intensity for the IL added. If one signal is obviously favored, it can be surmised that the ion-solvent interaction for that ion is less favorable resulting in surface enrichment and suppression of the other ion. The clusters were examined in the positive ionization mode using the full scan MS function on a Micromass Q-Tof micro^{TM} mass spectrometer. Cone voltage was set low to minimize fragmentation of the aggregate ions.

Mass spectra were collected on a Micromass Q-ToF micro^{TM} mass spectrometer using pneumatically-assisted electrospray ionization. Capillary voltage: 2900 V. Cone voltage: 10 V. Extraction voltage: 0.5 V. Source temperature: 80 °C. Desolvation temperature: 150 °C. Cone gas flow: 100 L/h. Desolvation gas flow: 200 L/h. Scan time was 3 s and the inter scan time was 0.1 s.

3. Results

Each of the possible combinations of anions were mixed as their BMIM salts in a 1:1 ratio and the relative ratio of the peak areas of the two different aggregate ions [(BMIM)$_2$ + anion]$^+$ measured in four different solvents: equal parts water/acetonitrile, methanol, acetonitrile, and dichloromethane (Table 3). [BMIM]Cl was not soluble in solvents less polar than dichloromethane, and [BMIM] [NTf$_2$] was not soluble in pure water, so these salts set the boundaries of what solvents we could reliably study.

Chloride is the smallest of the anions examined and most likely to be strongly solvated by polar solvents, but is least well solvated by non-polar solvents. The degree to which an analyte's hydrophobicity influences ESI response may be estimated, and because of this, it is expected that more hydrophobic analytes will produce a greater ion count in a mass spectrum [27]. As such, chloride aggregates should be under-represented compared to large, hydrophobic anions in polar solvents, but the reverse should be true in non-polar solvents. This effect is indeed observed; most dramatically in matchups against [PF$_6$]$^-$ and [NTf$_2$]$^-$. Response factors between the BMIM aggregates of chloride and the other anions are similar in acetonitrile, but the [(BMIM)$_2$ + Cl]$^+$ aggregate ion is barely detectable in water/acetonitrile and methanol. Conversely, the [(BMIM)$_2$ + Cl]$^+$ aggregate ion is over-represented against all others in dichloromethane, suggesting that the droplet partitions the chloride ions preferentially at the surface. Fig. 1(a–d) shows the relative intensity comparison between Cl$^-$ and [NTf$_2$]$^-$ aggregate ions in water/acetonitrile, methanol, acetonitrile, and dichloromethane.

It is worth noting that the values observed above were subject to significant variation depending on exact instrumental conditions. The position of the spray head, desolvation, cone gas flow rates, cone voltage, source, desolvation gas temperature, sample concentration etc, all affected the exact ratios obtained. However, the general trends were reproducible.

Iodide is overrepresented with respect to chloride in water/ acetonitrile, but underrepresented in other solvents. When iodide is matched up against the other counterions, the only dramatic difference is seen in the acetonitrile/water and methanol against [PF$_6$]$^-$ and [NTf$_2$]$^-$, where iodide is strongly underrepresented. The iodide aggregate is consistently less abundant than the [BF$_4$]$^-$ aggregate in all solvents, but the difference is least marked in the less polar solvents. The similarity between [BF$_4$]$^-$ and iodide is borne out when it is matched up against the larger anions. The
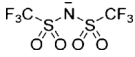
Table 1
Physical properties of water and five butylimidazolium salts [19–22].

Substance	Surface tension (dyn cm^{-1} at 25 °C)	Melting point (°C)	Density(g mL^{-1} at 25 °C)	Dipolarity/polarizability(40 °C)	Molar mass(g/mol)
Water	73	0.0	0.997	n/a	18.0
[BMIM]Cl	n/a (solid)	41	1.08	2.247	174.7
[BMIM]I	54.7	−72	1.44	n/a	266.1
[BMIM][BF$_4$]	46.6	−81[a]	1.12	1.647	226.0
[BMIM][PF$_6$]	48.8	10[a]	1.368	1.914	284.2
[BMIM][Tf$_2$N]	37.5	−25[b]	1.436	1.889	419.4

[a] Dried.
[b] Water equilibrated.

Table 2
Properties of the anions.

Anion	Structure	Molecular weight	Ionic radius (pm) [23–25]	Surface area[a] (Å^2)	Volume[a] (Å^3)	$\Delta_t G^{\circ}$[b] (kJ/mol)
Cl$^-$	Cl$^-$	35.45	184	39.9	23.7	7.0
I$^-$	I$^-$	126.90	220	51.5	34.8	2.6
[BF$_4$]$^-$		86.80	228	76.7	54.6	0.6
[PF$_6$]$^-$		144.96	254	100.7	73.1	−0.7
[NTf$_2$]$^-$		280.15	–	195.5	156.1	–

[a] Values calculated using Hartree–Fock at the 3–21 G level of theory.
[b] Standard molar Gibbs transfer energy for anions from water to 60:40 methanol/water [26].

two large hydrophobic anions, [PF$_6$]$^-$ and [NTf$_2$]$^-$, display similar behavior to one another, and their relative response factors are quite similar to each other, but distinctly different when compared to other, smaller anions.

Overall, the relative surface activity in water/acetonitrile is in the order [NTf$_2$]$^- \sim$ [PF$_6$]$^- >$ [BF$_4$]$^- \sim$ I$^- >$ Cl$^-$, with the difference in magnitude of response greater than 500:1 in favor of [NTf$_2$]$^-$ compared to Cl$^-$. In methanol, it is [NTf$_2$]$^- \sim$ [PF$_6$]$^- >$ [BF$_4$]$^- >$ I$^- \sim$ Cl$^-$, and the range of responses is similar to that observed in water/acetonitrile. In acetonitrile, all five anions provide similar responses, and there is no clear order of preference. In dichloromethane, the most overrepresented ions include chloride, and the overall order is reversed from water/acetonitrile: Cl$^- >$ I$^- \sim$ [BF$_4$]$^- >$ [PF$_6$]$^- >$ [NTf$_2$]$^-$. However, the range of discrepancies is not as great as seen in water/acetonitrile or methanol, with a maximum 6:1 difference in intensity between BMIM aggregates of chloride and [NTf$_2$]$^-$.

The higher order clusters are minimally present, and only in certain solvents. The [(BMIM)$_3$Cl$_2$]$^+$ cluster for example is present with reasonable intensity in CH$_2$Cl$_2$ only. In other solvents [(BMIM)$_3$Cl$_2$]$^+$ is barely registered above background. The same is true for other higher order clusters containing [NTf$_2$]$^-$. If these clusters are present in solution they are not detected by the mass spectrometer even given an extended acquisition time. This is likely an effect of both the instrumental parameters in use, including the capillary position, cone voltage, gas flow rates and cone voltage, as well as the concentrations used. While tuning of

Table 3
Relative ratio of [(BMIM)$_2$+X]$^+$ vs [(BMIM)$_2$+Y]$^+$ aggregates in four different solvents. Response factors that are similar (differing by up to 3:1 in either direction) are represented normally. Those that differ by up to 10:1 are bolded, and those that differ by more than that are bolded and italicised.

Matchups	1:1 H$_2$O: MeCN	MeOH	MeCN	CH$_2$Cl$_2$
Cl$^-$/I$^-$	**0.14**	**3.5**	1.8	**5.4**
Cl$^-$/[BF$_4$]$^-$	1.5	0.17	0.75	1.5
Cl$^-$/[PF$_6$]$^-$	*0.049*	*0.026*	0.74	**3.9**
Cl$^-$/[NTf$_2$]$^-$	*0.0017*	*0.021*	*0.15*	*19*
I$^-$/[BF$_4$]$^-$	0.41	0.69	0.88	0.92
I$^-$/[PF$_6$]$^-$	*0.061*	*0.023*	1.6	1.4
I$^-$/[NTf$_2$]$^-$	*0.025*	*0.018*	1.2	2.6
[BF$_4$]$^-$/[PF$_6$]$^-$	**0.040**	**0.14**	0.34	1.1
[BF$_4$]$^-$/[NTf$_2$]$^-$	*0.051*	**0.040**	0.88	3.0
[PF$_6$]$^-$/[NTf$_2$]$^-$	0.41	0.37	1.3	0.96

these parameters may serve to slightly enhance the detection of these higher-order aggregates, it is likely larger cationic or anionic aggregates are both very fragile and sparingly present in the concentrations used. Conversely, the free anion and cation are present in all solutions with high intensity. The dissociation of the cation from its anionic partner is readily achieved following solvation and it is of no surprise that these uncombined species are a common feature of all spectra acquired.

Given the differences in the mass spectra between identical analyte mixtures in different solvents, we next considered what property or properties are most predictive of the observed behavior. Table 3 assembles some solvent properties. Note that there are literally hundreds of different solvent polarity scales [28], and selecting a representative one for consideration here is no trivial task. Table 4 includes the Hansen solubility parameters [29], which have the advantage that they are designed for solvent mixtures (and can hence cope with water/acetonitrile) and they break down solvent properties into dispersion, polar and hydrogen bonding components. In doing so, they discriminate strongly between methanol and acetonitrile on the basis of their hydrogen bonding behavior, whereas other solvent polarity scales (e.g., the Snyder polarity index [30] and Hildebrand solubility parameter [31]) tend to lump these two solvents closely together.

It is clear that the polarity of the solvent alone is insufficient to account for the ESI-MS observations and is potentially misleading since methanol and acetonitrile would be expected to behave similarly on this basis alone. The solvents that display the strongest selectivity between anions (water/acetonitrile and methanol) are both protic, hydrogen bonding solvents. Acetonitrile, though highly polar, is aprotic and displays behavior that is substantially different from the two protic solvents, suggesting that the solvation of the anion may well involve hydrogen bonding. Dichloromethane is relatively non-polar and aprotic, and the data collected suggests favorable solvation of the most greasy and hydrophobic anions, with the small, now-poorly solvated anions such as chloride forced to the surface of the droplet and thus overrepresented in the resulting mass spectrum. This position is supported by both the positive and negative ion mode data collected. Since the solvent molecules and the charged aggregates are all relatively small in size, it is sensible to suppose the aggregates may freely form in solution (or droplet) and that solvent polarity and hydrogen-bonding capacity have a large role in the point at which these aggregates are released from the electrospray-generated droplets.

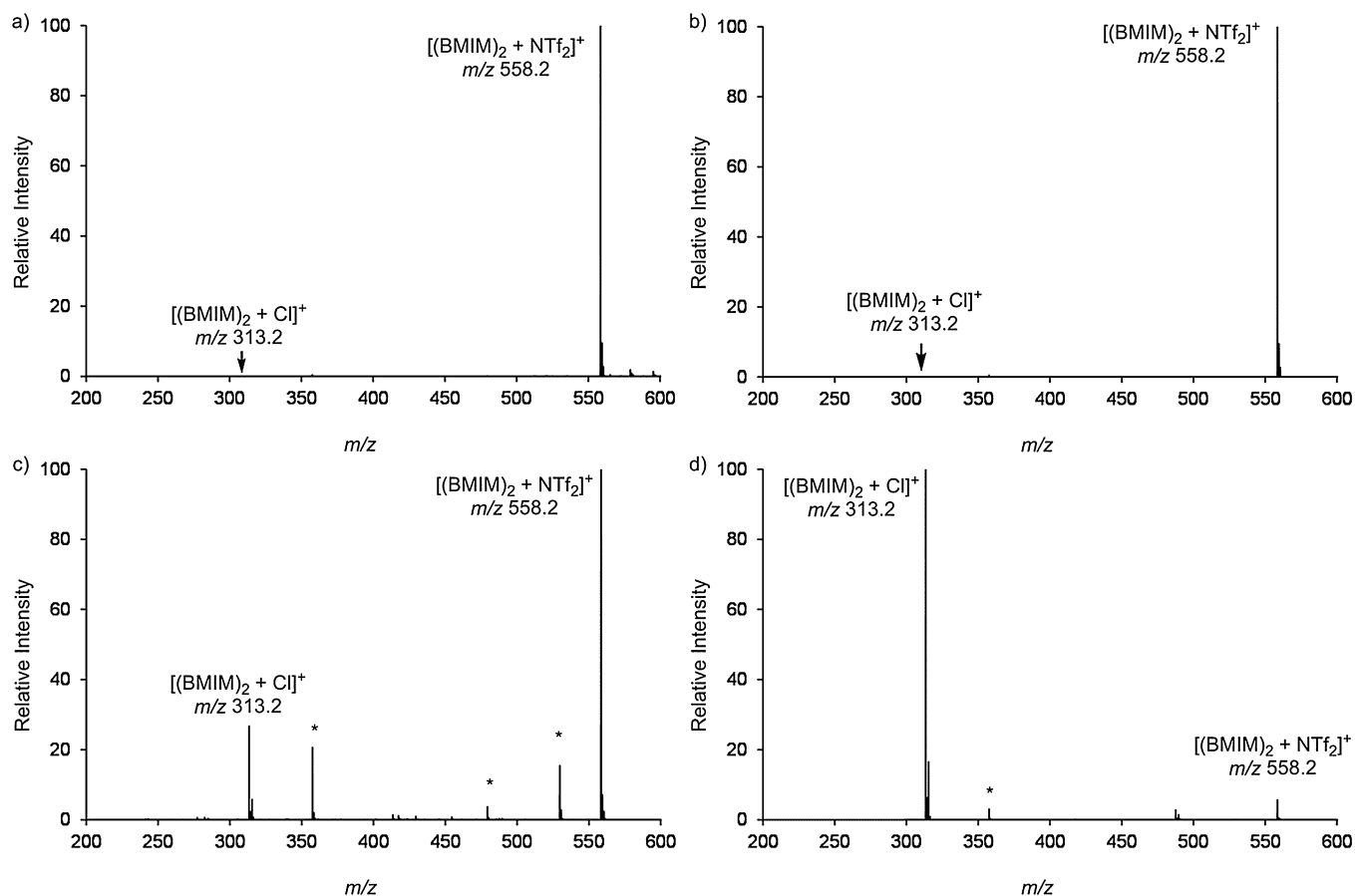**Fig. 1.** Positive ion ESI mass spectrum of a 1:1 mixture of [BMIM]Cl and [BMIM][NTf$_2$], showing the relative intensities of [(BMIM)$_2$ + Cl]$^+$ (m/z 313) vs [(BMIM)$_2$ + [NTf$_2$]]$^+$ (m/z 558) in (a) 1:1 H$_2$O:MeCN, (b) MeOH, (c) MeCN, (d) CH$_2$Cl$_2$. Note: peaks marked with a * are non-aggregate contaminants.

Comparing the least similar anions, Cl$^-$ and [NTf$_2$]$^-$ strong enhancement of the [NTf$_2$]$^-$ anion is seen in the most polar solvent, 1:1 acetonitrile/water (Fig. 1a). This is also true for solutions of methanol (Fig. 1b) and acetonitrile (Fig. 1c) but completely inverts in dichloromethane (Fig. 1d), where the enhancement of [NTf$_2$]$^-$ begins to occur. In practical terms, this means when examining a solution with approximately equal concentrations of anions, a result ranging across two orders of magnitude and demonstrating a change in the primary species produced could be observed by simply adjusting the solvent.

In polar solvents the less polar [NTf$_2$]$^-$ is significantly over-represented. This anion favors the droplet surface as there is decreased solvent interaction at the gas–liquid interface and, as such, it is more easily transferred into the gas phase and detected. This is consistent with the trend in the Gibbs energy of transfer ($\Delta_t G$) which is generally favorable (i.e., a lower value) for the transfer of non-polar anions away from pure water and into a mixed methanol/water phase. In terms of hydration, relatively small anions like those used in this study are expected to have a $\Delta_t G$ value approximately linearly proportional to volume (contrary to larger anions which would be more accurately related to surface area) [32]. The [NTf$_2$]$^-$ anion has a relatively large volume, 6.6 times that of Cl$^-$, and, consequently a small or potentially negative $\Delta_t G$ is expected indicating a propensity to avoid aqueous solvation and therefore preferential migration to the surface of the droplet.

A comparison of the response ratios obtained in acetonitrile shows that 90% of the results fall into the range of 2× enhancement to 1.5× suppression. When this is compared with 1:1 acetonitrile/water as a solvent only 10% of the values are present in this range.

Table 4
Properties of the solvents used in this study.

Solvent	Dielectric constant, ε_r	Dipole moment (D)	Boiling point (°C)	Snyder polarity index, P′	Hildebrand solubility parameter, δ	Hansen solubility parameters		
						δD dispersion	δP polar	δH hydrogen bonding
H$_2$O	80	1.85	100	10.2	21	15.5	16.0	42.3
H$_2$O: MeCN*	59	2.89	76	7.6	16.4	15.4	17.0	24.2
MeCN	37.5	3.92	81	5.8	11.7	15.3	18.0	6.1
MeOH	33	1.70	65	5.1	13.7	14.7	12.3	22.3
CH$_2$Cl$_2$	9.1	4.60	40	3.1	9.6	17.0	7.3	7.1

* All are averaged values, except the boiling point, which is that of the azeotrope.

Further, it may be observed, in the 1:1 acetonitrile/water system, the largest and most non-polar species, $[NTf_2]^-$, was enhanced greatly in each anion pairing as were the majority of the results for $[PF_6]^-$. Anion behavior in methanol appears to parallel that of the 1:1 acetonitrile/water system. Dichloromethane on the other hand, is reasonably similar to acetonitrile; however, a stronger enhancement impact is observed for the smallest anion, Cl^-. That water/acetonitrile does not behave like neat acetonitrile is not surprising; it is protic and it forms an azeotrope that is acetonitrile-rich (84%) and hence the smaller droplets are likely to be mostly water.

Negative ion mode spectra were not thoroughly investigated as the mass range of the instrument used does not extend below m/z 50 (hence excluding chloride as an analyte). Observation of equimolar solutions of [BMIM]Cl and [BMIM][NTf$_2$] demonstrate similar qualitative results. For example, in dichloromethane the $[(BMIM) + Cl_2]^-$ aggregate dominates over the $[(BMIM) + (NTf_2)_2]^-$ species; correspondingly, the reverse is true in methanol. This observation in the negative ion mode is consistent with their behavior in the positive ion mode and further supports the notion that hydrogen-bonding and polarity of the solvents can have a profound effect on preferential ion evaporation. No observable intermediate or higher order clusters for this pair is observed in the negative ion mode. Equimolar mixtures of [BMIM]I and [BMIM] [NTf$_2$] produced negative ion mass spectra dominated by $[NTf_2]^-$ in all instances (see Supporting information).

4. Conclusions

Overall, to minimize the impact of differential surface activity, acetonitrile (a moderate polarity, aprotic solvent), seems to be the optimum choice for ESI analyses of salts. This selection ameliorates surface activity effects by solvating ions of different sizes and masses to a similar degree. This study also provides further evidence against the simultaneous analysis of systems with extremely different physical properties using ESI without careful consideration, as matrix effects are not only likely, but can operate in opposite directions depending on the solvent chosen.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ijms.2014.09.009.

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