MALDI-TOF-MS of Saturated Polyolefins by Coordination of Metal Cations: A Theoretical Study

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Density functional calculations were applied to obtain binding energies for metal cation-oligomer complexes of *n*-alkanes and poly(ethylene glycol)s (PEG). The B3LYP/6-31G* energies for complexing metal cations (Na^+, Li^+, Co^+, Cu^+, Zn^+, and Zn^{2+}) with straight chain aliphatics (C_nH_{2n+2}, $n = 1-12$) are in excellent agreement with the limited available experimental and theoretical data. The strength of the complexes increases with an increasing degree of polymerization and with a decreasing size of the metal ion. The weakest calculated complex is Na^+-CH_4 (7.8 kcal/mol) and the strongest is Co^+−dodecane (52.0 kcal/mol). Smaller sized cations, such as Li^+, induce more polarized hydrocarbons. Transition metals give stronger complexes than the main group metals because their d-electrons shield the nuclear charge less effectively. M^+−methane binding energies, ranging from 12.6 to 23.1 kcal/mol, are also reported for Sc^+, Y^+, La^+, Cu^+, Ag^+, and Au^+. Doubly charged metal ions give much stronger complexes, that is, 67.1 kcal/mol for $Zn^{2+}-CH_4$. Methane binding energies of ca. 20 kcal/mol are obtained when the Be^{2+}, Mg^{2+}, Fe^{2+}, and Zn^{2+} dications are ligated with a cyclopentadienyl anion. The poly(ethylene glycol)s ($HO-[C_2H_4O]_n-H$, $n = 1-5$) bind significantly stronger to the metal cations (Na^+ and Cu^+) than the aliphatics. The Na^+−monomer ($C_2H_6O_2$) already has a complex strength of 48.5 kcal/mol, while that of the pentamer ($C_{10}H_{22}O_6$), which is the smallest observable Na^+−complex by MALDI-TOF-MS, amounts to 88 kcal/mol. The corresponding Cu^+ complexes are even stronger with a value of 79.6 kcal/mol for $Cu^+-C_2H_6O_2$. Binding energies of 53.3 and 64.1 kcal/mol are calculated for the respective K^+−tetramer and K^+−pentamer of which the pentamer is also observed spectroscopically.

Introduction

The molecular weight distribution (MWD) is a key feature of polymers. Obviously, knowledge of the extent to which polymerization takes place is of vital importance. Matrix assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS),[1,2,3] provides a fast and convenient tool for direct analysis of the molecular weight distribution. The technique is generally applicable for the heteroatom containing polyethers, polyamides, methacrylates, polyesteramides and polyesters, aromatic hydrocarbons such as polystyrene, and hydrocarbons with multiple double bonds such as polybutadiene and polyisoprene.[4,5] Generally, ionization of polar polymers occurs by means of sodium or potassium cation adduct formation. The more apolar oligomers such as polystyrene[6] and polybutadiene are ionized by attachment to silver or copper cations upon ionization.

MALDI-TOF-MS has several shortcomings, namely, discrimination of the high molecular end of the MWD of polydisperse ($D > 1.2$) polymers[7], and it does not detect very short oligomers. A serious drawback for petrochemical applications in the field of polyolefins is its inability to detect fully saturated hydrocarbons such as polyethylene and polypropylene. Recently, based on the threshold for detection of Na^+−poly(ethylene glycol) complexes, we calculated that, according to the HF/6-31G* level of ab initio theory, a minimum binding energy of ca. 90 kcal/mol is needed to survive collisional-induced dissociation of the ion/molecule ensemble during ion extraction.[8] The aim of this ab initio theoretical study is to investigate whether adducts can be formed between saturated hydrocarbons and metal cations other than Na^+ that have a sufficiently strong interaction to enable detection by MALDI-TOF-MS.

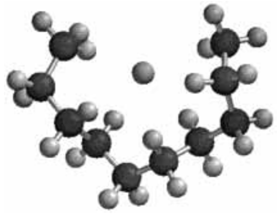

Figure 1. Structure of the $Na^+-C_{10}H_{22}$ complex

Methods

Ab initio geometry optimizations on the free hydrocarbons were performed on their all-trans conformations and in more condensed forms for their metal cation complexes as indicated (see also Figure 1). All calculations were performed using the Gaussian 98 suite of programs.[9] We used a 6-31G* split valence basis set[10] for the first and second row main group elements and a LANL2DZ split valence basis set with (quasi) relativistic effective core potentials[11] for the transition metals. Density functional theory (DFT) was applied in all calculations using Becke's hybrid functional B3LYP[12] including the local correction term developed by Vosko, Wilk, and Nusair [13] as well as the non-local correction term provided by Lee, Yang, and Parr.[14]

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The metal−hydrocarbon and metal−poly(ethylene glycol) complexation energies are defined as $[L-M]^{n+} \rightarrow L + M^{n+} + \Delta H$, where L is the hydrocarbon (C_nH_{2n+2}, $n = 1-12$) or the poly(ethylene glycol) ($HO-[C_2H_4O]_n-H$, $n = 1-5$), respectively, giving positive values for stable complexes.

These complexation energies are approximated from the electronic energies of the components, while contributions from differences in zero point energies (ΔZPE) and thermal corrections are neglected, because these are either small or tend to cancel each other.[8]

Results and Discussion

We start with the structural features of metal complexes with short chain alkanes. Next, their Na^+ complexation energies are compared with those of poly(ethylene glycol)s (PEGs) to establish the minimum complex strength that still enables their detection by MALDI-TOF-MS. Then, the complexation energies of the transition-metal cation Cu^+ are discussed, followed by an evaluation of complexes with a variety of transition metals, such as Co^+ and Zn^+. Finally, we evaluate complexes between hydrocarbons and transition-metal dications in which the metals contain a cyclopentadienyl ligand.

Structural Features. The number of possible structures increases rapidly with the length of the hydrocarbon chain. Therefore, we investigated first the potential-energy surface of complexes with short hydrocarbons. This enabled us to derive the geometries of higher homologues without the need to explore their full conformational space.

For the smallest hydrocarbon, methane, geometry optimizations were performed on the η^3, η^2, and η^1 cation adducts. Both the sodium and copper ions prefer η^3 coordination in which three hydrogens of methane are in contact with the metal center. Coordination of the cation with only two hydrogen atoms (η^2 coordination) results in transition structures (one imaginary frequency) that are higher in energy albeit by only 0.3 kcal/mol for Cu^+ and 1.0 kcal/mol for Na^+. These small energy differences suggest dynamical bonding in which the metal cation is able to move rapidly from one η^3-coordination site to another. Structures with the metal cation coordinated to only one hydrogen atom (η^1 coordination) are higher energy, second-order transition structures (they have two imaginary frequencies and thus represent higher order saddle points). These have no physical relevance for the problem at hand and therefore need no further attention. As expected, the metal−hydrogen bond distances decrease with an increasing number of hydrogen contacts, namely, from 2.181 to 1.962 to 1.698 Å for the η^1, η^2, and η^3 Cu^+ complexes, respectively, and from 2.509 to 2.367 Å to 2.250 Å for the corresponding Na^+-complexes. These data also show that the theoretically predicted M−H distances are much shorter for the methane complexes of copper than those of sodium, which already suggest a difference in binding energies.

Two types of η^3 coordination are possible for ethane. In the end-on adduct, the metal cation complexes with three hydrogens of one methyl group, while in the side-on adduct the cation interacts with both methyl groups that are in a staggered conformation to each other. The end-on Cu^+ (Na^+) adduct is 1.5 (0.8) kcal/mol more stable than the side-on adduct. Cation complexation with two hydrogens of each of the methyl groups is also feasible, but this η^4 coordinated form is less stable because of the unfavorable eclipsed conformation of ethane.

The most stable M^+−propane adducts result on interacting the cation with two hydrogens of each of the terminal methyl groups of staggered propane. This η^4 coordinated form of the Cu^+ (Na^+) adduct is, in fact, lower in energy than the η^3 end-on adduct by 5.2 (2.6) kcal/mol. Bonding of Na^+ and Cu^+ to butane gives complexes similar to those of propane. Again, η^4 complexation is favored with the hydrocarbon frame preferring an anti-conformation, although the gauche form with the alkane wrapped around the metal is only 0.3 kcal/mol higher in energy for the Cu^+ complex. In fact, this type of η^4 complex is the most stable complex for the longer alkanes. All the longer hydrocarbons wrap around the metal ion as much as possible. This is shown in Figure 1 for the Na^+−decane complex.

TABLE 1: Complexation Energies (in kcal/mol) for the M^+−alkane Complexes $M = Na^+$, Cu^+, Co^+, Zn^+, Li^+, and Zn^{2+}, Calculated at B3LYP/6-31G*[a]

M^+	Na^+		Cu^+	Co^+	Zn^+	Li^+	Zn^{2+}
methane	7.8	(2.6)	23.6	19.2	12.4	13.2	67.1
ethane	9.4	(7.0)	26.0	23.5		16.5	75.1
propane	13.0		32.9	30.3	21.9	21.6	101.8
butane	14.0	(8.9)	34.5	32.1		23.3	111.3
pentane	14.6		40.4	34.2		24.3	123.7
hexane	16.9	(10.9)	43.6	41.4		29.5	136.1
octane	17.1	(12.4)	43.2	45.8		26.0	147.8
decane	19.6		46.0	53.0		32.3	161.5
dodecane	20.2	(14.1)	47.0	52.0	30.7	31.1	165.1

[a] Values in parentheses are calculated at HF/6-31G* (ref 8).

TABLE 2: Complexation Energies (in kcal/mol) for the M^+−PEG Complexes, $M = Na^+$, Cu^+, Calculated at B3LYP/6-31G*[a]

M^+	Na^+		Cu^+
$C_2H_6O_2$	48.5	(47.2)	79.6
$C_4H_{10}O_3$	64.6	(66.8)	103.8
$C_6H_{14}O_4$	72.8		112.4
$C_8H_{18}O_5$	77.2	(82.8)	114.0
$C_{10}H_{22}O_6$	88.0	(92.0)	119.9

[a] Values in parentheses are calculated at the HF/6-31G* level (ref 8).

Na^+ Complexation Energies. The B3LYP complexation energies for nine Na^+−hydrocarbon complexes are collected in Table 1 together with six reported earlier at the HF/6-31G* level of theory.[8] Two trends are evident. First, the complexation energy increases steadily as the hydrocarbon chain is lengthened. This is expected because the metal cation is attracted by the electron density of the hydrocarbon which increases with longer chains because of their higher polarizability. The binding energy ranges from 7.8 kcal/mol for methane to 20.2 kcal/mol for dodecane and tailors off with the longer hydrocarbons. Second, the DFT calculated binding energies, which include part of the electron correlation energy, are larger than those obtained with HF theory with a average difference of 4.9 kcal/mol.

Apparently, the influence of electron correlation on the strength of the Na^+−hydrocarbon complexes is pronounced. Therefore, we decided to revisit the strength of the Na^+ complexes of small PEGs. Previously, these were only studied at the HF level of theory. Based on the HF energies, a threshold binding energy of 90 kcal/mol was estimated for Na^+−PEG complexes to be detectable with MALDI-TOF-MS; the smallest observable PEG is a pentamer. In Table 2, we summarize the B3LYP and HF binding energies, including the earlier reported HF results.[8] The effect of electron correlation is evident. Instead of increased binding energies, as found for the hydrocarbons, the B3LYP values for the PEGs are expectantly smaller than those at HF because of overestimation of the electrostatic interaction of the latter method. While the differences are modest, that is, 4 kcal/mol for the pentamer $C_{10}H_{22}O_6$, we confine our previous estimate for the threshold binding energy for observable complexes to the range of 85−90 kcal/mol.

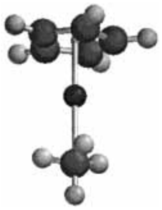

Figure 2. Calculated structure of the (c-C_5H_5)Mg−methane complex.

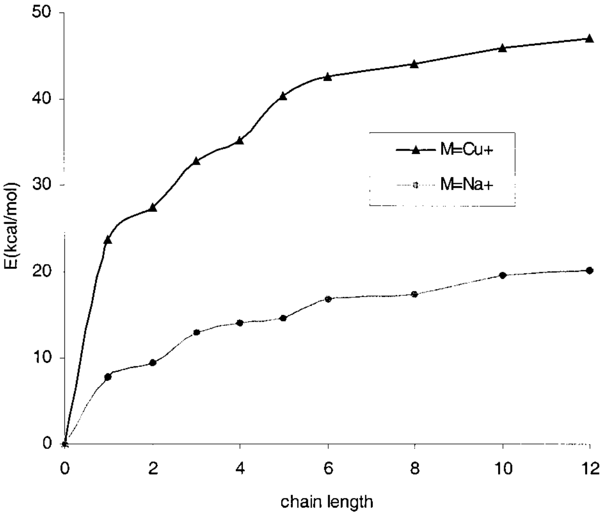

Figure 3. Increase of the complexation energy with chain length for the M^+−alkane complexes, M = Na^+ and Cu^+.

The thermochemistry of the complexation of (alkali) cations by polyethers has been investigated experimentally by Meot-Ner et al.[15] They found that polydentate ethers, having the same number of oxygens, bind weaker to the cations than multiple solvate molecules because of the geometrical constraints of the chain. Our calculated 48.5 kcal/mol Na^+ binding energy for $H-(OC_2H_4)_n-OH$ (n=1) is in excellent agreement with the experimentally observed value of 47.2 kcal/mol for bidentate $Me-(OC_2H_4)-OMe$.[16] It is then not surprising that our computed values of 72.8 ($n = 3$) and 88.0 ($n = 5$) kcal/mol are somewhat smaller than the corresponding binding energies of 82.3 and 105.4 kcal/mol that are obtained by using two and three bidentate ethers, respectively.[16] The difference can be attributed to the destabilizing influence of the additional ethylene bridges.

Cu^+ Complexation Energies. Are there other metal cations that bind more strongly with hydrocarbons than Na^+? Transition metals are obvious candidates for evaluation because their d-orbitals may have a stabilization effect. We choose to explore the copper cation first because the ionic radii of Na^+ (0.95 Å) and Cu^+ (0.96 Å) cations are similiar.[17] The Cu^+ cation was also chosen because it is a d^{10} singlet ground-state species, which can be studied with reasonable computational effort. The Cu^+ complexation energies are given in Table 1.

For each alkane, the interaction is much stronger with the copper cation than with the sodium cation. This is in line with the noted shorter metal−hydrogen bond distances. The higher Cu^+ complexation energy is due to the d-electrons, which shield the nuclear charge more modestly than the s- and p-electrons in the lighter metals. The effect is rather prominent. The Cu^+−methane binding energy of 23.6 kcal/mol is three times stronger than for the Na^+ complex. For the Cu^+−dodecane complex (47.0 kcal/mol), this difference is a significant 26.8 kcal/mol. Figure 3 gives a graphical comparison of the sodium and copper cation complexes. However, even though their binding energies differ substantially, it is clear that if the detection limit for MALDI-TOF-MS is in the order of 85 kcal/mol, no Cu^+−hydrocarbon complex will be detected with this method.

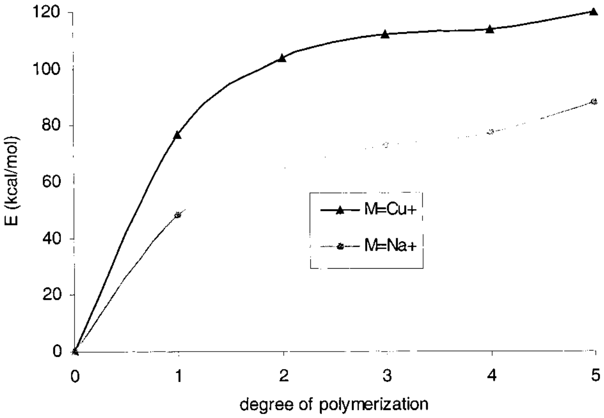

Figure 4. Increase of the complexation energy with chain length for the M^+−PEG complexes, M = Na^+ and Cu^+.

For calibration, we also investigated the copper cation interactions with the PEG oligomers. Does the d-electron effect have a similar influence on their stabilization as found for the hydrocarbons? The calculated complexation energies for both the Na^+ and Cu^+ cations are summarized in Table 2 and visualized in Figure 4. They show the enhanced stabilization (Cu^+ versus Na^+) to be even larger, ranging from ca. 31 kcal/mol for both the monomer and pentamer to ca. 40 kcal/mol for the trimer.

The graphical presentation illustrates that if copper cations are usable in MALDI-TOF spectroscopy, all PEGs are in principle detectable because even the monomer has a calculated complex strength of 79.6 kcal/mol. Of course, the calculations do not take into account the high volatility of the lighter oligomers, which undoubtedly frustrate the experimental setup.

Complexation Energies with Open Shell Transition Metal Cations. Can triplet or doublet cations interact more strongly with hydrocarbons than the singlet? As representative examples, we evaluated the transition-metal cations Co^+ and Zn^+, which reportedly have triplet d^8s^0 and doublet $d^{10}s^1$ ground states.[18] The binding energies of these optimized Co^+ and Zn^+ complexes are summarized in Table 1.

Because the Co^+ complexes of methane, ethane, and propane have been studied before with the modified coupled pair functional (MCPF) method,[18] we evaluate first the performance of the B3LYP method. The MCPF calculations show η^2 Co^+-CH_4 to be 1.3 kcal/mol more stable than the η^3 coordinated complex. In contrast, our B3LYP approach prefers the C_{3v} structure by 3.2 kcal/mol. Still, the complexation energy of 19.2 kcal/mol is in good agreement with the slightly larger MCPF value of 21.4 kcal/mol.[18] Likewise, the complexation energies agree well for $Co^+-C_2H_6$ although in this case the B3LYP value of 23.5 kcal/mol is slightly less (1.5 kcal/mol) than that obtained with MCPF.[18] The B3LYP complexation energy for propane of 30.3 kcal/mol is in excellent agreement with the experimental value of 30.9 ± 1.4 kcal/mol;[19] at MCPF a smaller value of 27.6 kcal/mol was reported.[18] We conclude that the B3LYP method performs well for these complexes.

The Co^+ complexation energies gradually increase with longer hydrocarbons, reaching a value of 52.0 kcal/mol for dodecane. This behavior is much like those already discussed for the singlet Cu^+ complexes for which a value of 47.0 kcal/mol was obtained for dodecane. Apparently, throughout the series the cobalt and copper cation binding energies are alike.

For Co^+, they are slightly smaller for the shorter hydrocarbons and slightly higher for the longer ones. Possibly, this is due to the partly unfilled d-shell of the Co^+−alkane system.

We investigated the interaction between the zinc cation and three hydrocarbons, that is, methane, propane, and dodecane. Much lower complexation energies are expected because the half-filled s-orbital of Zn^+ ($d^{10}s^1$) should shield the nuclear charge considerably better than the d-electrons. This is indeed the case. The Zn^+−methane complexation energy of only 12.4 kcal/mol is in good agreement with the 10 kcal/mol that has been estimated from experimental methods.[20] The Zn^+−dodecane complex is over 20 kcal/mol weaker than the one with Co^+.

Li^+ and Zn^{2+} Complexation Energies. To further evaluate the influence of different metals, we determined the complexation energies with methane for two series (early and late) of 1°, 2°, and 3° row transition metals. For Sc^+, Y^+, and La^+, these are 23.1, 24.9, and 15.0 kcal/mol, respectively, and for Cu^+, Ag^+, and Au^+, these are 23.6, 12.6, and 19.7 kcal/mol, respectively. These data suggest that the strength of the Cu^+−hydrocarbon interaction is not likely to be surpassed significantly by using other transition metals. On this basis, we decided to refocus on the charge of the metal ion.

The interaction between the metal ion and the hydrocarbons becomes stronger, if the charge concentration on the cation is increased, because it increases the polarization of the hydrocarbon and thereby reinforces the interaction. This can be achieved by reducing the ionic size, that is, by going from Na^+ to Li^+. Table 1 summarizes the alkane complexation energies for the lithium cation, which has the smallest ionic radius (0.60 Å) of the monocations. The binding energies for the Li^+ complexes are indeed much larger, by a factor of about 1.5, than those containing the Na^+ cation. They range from 13.2 kcal/mol for methane to 31.1 kcal/mol for dodecane. Nevertheless, they remain well below the complexation energies calculated for the transition-metal cations.

Using a doubly positively charged cation, for example, Zn^{2+} instead of Cu^+, also increases the charge concentration. The binding energies for these complexes, also listed in Table 1, are indeed much higher and range from a substantial 67.1 kcal/mol for the methane complex to an impressive 165.1 kcal/mol for Zn^{2+}−dodecane. The strength of the Zn^{2+} interaction with the alkanes is about three times higher than the corresponding Cu^+ and Co^+ complexes and even five times those of the zinc monocation. Unfortunately, current MALDI-TOF-MS techniques do not enable the routine detection of complexes of doubly charged metals because of rapid electron or hydride transfer mechanisms in the plasma.

Cp−M^+ Complexation Energies. Can the charge of metal dications be tempered with suitable ligands and still give complexes with alkanes of adequate strength? A very recent gas-phase study by Bohme and co-workers[21] does suggest so. They established with multicollisional-induced dissociation (CID) experiments that the monocyclopentadienyl (Cp = c-C_5H_5) ligated Mg^+ cation coordinates much better with saturated straight-chain hydrocarbons (ranging from methane to *n*-heptane) than both the bare cation itself and the magnesocene cation Cp_2Mg^+. The binding energies of Mg^+ with methane and ethane, calculated at only 6.7 and 9.9 kcal/mol by Bauschlicher et al.[22] at the MP2 level, are not enough to enable their detection. Our DFT values of 8.3 and 10.7 kcal/mol compare very well with these data and even better with the experimental one (10.7 kcal/mol [21]) for Mg^+−C_2H_6. In contrast, all alkane complexes with $CpMg^+$ are detected by CID. Their higher stability was explained in terms of formal Cp−Mg^{2+} complexes. No binding energies of these hydrocarbon complexes were provided, but an earlier theoretical study,[23] using the natural bond order (NBO) analysis, indeed reported a rather high positive charge of 1.6e on the ligated Mg.

TABLE 3: Complexation Energies (in kcal/mol) for the $[(c\text{-}C_5H_5)M]^+$−CH_4 Complex, Calculated at B3LYP/6-31G*

cation	energy
Mg^{2+}	18.9
Be^{2+}	24.3
Fe^{2+}	20.3
Zn^{2+}	20.6

We investigated the cyclopentadienyl ligated Mg, Be, Fe, and Zn monocation complexes of methane, the results of which are summarized in Table 3. The complexation energies for the nonligated Mg^+−CH_4 (8.3 kcal/mol) and Mg^{2+}−CH_4 (50.9 kcal/mol) were determined for calibration. As already noted, the doublet Mg^+ complex is rather weak. Its calculated energy for interaction with ethane of 10.7 kcal/mol compares very well with the value of 10.5 kcal/mol that Bohme and co-workers obtained with a much larger basis set, that is, B3LYP/6-31G++G(2d2p). The calculated methane complexation energy for (c-C_5H_5)Mg^+−CH_4 of 18.9 kcal/mol is only modest and lies between those of the nonligated Mg mono and dication complexes. Changing the metal does not modify the binding energy much. Expectantly, the methane complex of (c-C_5H_5)-Be^+ binds stronger (24.3 kcal/mol), but the higher complexation energies of (c-C_5H_5)Zn^+ and (c-C_5H_5)Fe^+ are similar with values of 20.6 and 20.3 kcal/mol, respectively.

Summary

The B3LYP/6-31G* energies for complexing metal cations with straight chain aliphatics are in excellent agreement with the limited available experimental and theoretical data. The strength of the complexes increases with increasing length of the hydrocarbon chain and with decreasing size of the metal ion. The weakest calculated complex is Na^+−CH_4 (7.8 kcal/mol) and the strongest is Co^+−dodecane (52.0 kcal/mol). Smaller sized cations induce more polarized hydrocarbons. Transition metals give stronger complexes than main group metals because their d-electrons shield the nuclear charge less effectively. Singlet and triplet transition-metal cations show little difference in complexation energies but those of doublets (Zn^+−CH_4, 12.4; Mg^+−CH_4, 8.3 kcal/mol) are clearly smaller. Doubly charged metal ions complex much stronger, for example, 67.1 kcal/mol for Zn^{2+}−CH_4, but this is significantly tempered on ligating the metal with an anionic cyclopentadienyl group, for example, 20.6 kcal/mol for $CpZn^+$−CH_4.

The strengths of the poly(ethylene glycol) complexes with metal cations are significantly stronger than the aliphatic complexes. The Na^+−monomer has a strength of 48.5 kcal/mol, while that of the pentamer, which is the smallest observable Na^+ complex by MALDI-TOF-MS, amounts to 88 kcal/mol. The corresponding Cu^+ complexes are even much stronger with already a value of 79.6 kcal/mol for the Cu^+−monomer.

These data suggest that no M^+ aliphatic complex can be observed with the rapid screening MALDI-TOF-MS technique. On the basis of the B3LYP/6-31G* data for the Na^+−PEG complexes, a threshold binding energy of >85 kcal/mol must be assumed. But is this a valid assumption? Closer inspection of the MALDI-TOF-MS spectra also reveals the presence of K^+−PEG complexes as small as the tetramer ($n \geq 4$); K^+ is a common contaminant. The B3LYP/6-31G* complexation energies for K^+−$C_8H_{18}O_5$ (the largest undetected PEG oligomer) and $K^+-C_{10}H_{22}O_6$ (the first observable PEG complex) amount to 53.4 and 64.1 kcal/mol, respectively. These data suggest that the threshold binding energy for observing a M^+ substrate complex may be as small as >64 kcal/mol. This value is substantially lower than the threshold value of >85 kcal/mol that was deduced from the observable Na^+-PEG complexes. We can only speculate as to this discrepancy. Possibly, the difference in binding of the Na^+ and K^+ ions may have its origin in their different kinetic energies. If this is indeed the case, M^+ aliphatic complexes may be observable with MALDI-TOF-MS if the plasma is 'contaminated' with late, first-row transition metals.

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