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Computational probes into the conceptual basis of silver ion chromatography: I. Silver(I) ion complexes of unsaturated fatty acids and esters

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Abstract

Silver ion chromatography of unsaturated fatty acid derivatives can be described satisfactorily by the suggestion of Ag(I) complexation with more than a single bonding site of esters of the 18:1, 18:2, etc. series (that is, one, two, etc. methylene-interrupted double bonds in the C_{18} hydrocarbon chain) and by the formation of chelate-like complexes. Ab initio RHF effective core potential CEP-31G calculations of model C_6 to C_{18} complexes in the gas phase and in solution indicate that the stability of such complexes depends on the position of C=C double bonds in ligand molecules, while a significant part of the complexation energy is contributed by the interaction of Ag(I) and alkoxy- (or aryloxy-)carbonyl groups of fatty acid esters. Factors important to the stability of Ag(I) fatty acid chelates are the ring sizes and strain, particularly manifested in unsaturated acids with the C=C double bond closer to the carboxyl group, i.e. with smaller chelate rings, as well as conformations of larger rings and hydrocarbon chains. Calculated theoretical solvent effects on chelation are more significant for larger Ag(I) containing rings and increase with increasing ring size. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Silver ion chromatography has been and is still the core method of lipid analysis and its achievements and problems have been reviewed recently [1,2]. The method is based on the distinctive property of unsaturated organic compounds to form weak reversible complexes with Ag(I) ions [3]. It is now widely accepted that stabilization of the complex arises due to electron donation from occupied $2p\pi$ orbitals of C–C multiple bonds to the free 5s and 5p orbitals of Ag(I), as well as to 'backbonding' interaction between occupied 4d orbitals of Ag(I) and unoccupied antibonding $2p\pi^*$ orbitals of unsaturated organic molecules [4–6]. It has been found that the larger the number of double bonds, the stronger is the

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complex [1,2,7], though there is no proportionality between the number of double bonds and the respective retention values [1,2]. The practical outcome is that lipid molecules can be separated into groups by overall number, and often by configuration of double bonds in the fatty acid residues. Accordingly, these separations are performed relatively easily, and under special conditions it appears possible even to resolve fatty acids that differ in the position of the double bond in the hydrocarbon chain. However, the basic π-s* bonding plus d-π^* back-bonding interaction model is limited solely to complexation between double bonds and Ag(I), and cannot predict any effect of double bond position. Methyl esters of mono- and methylene interrupted (a lipid specialist term, meaning non-conjugated C=C double bonds, separated by a methylene group) diunsaturated octadecenoic fatty acids have been the first models in studying the effect of double bond position and the technique employed has been thin-layer chromatography in silver ion mode [8–11]. It has been demonstrated that when spotted in sequence according to the position of the double bond next to each other on a single chromatographic plate, fatty acid methyl esters migrate to form a sinusoidal curve of spots. The 'minima' on the curve, that is, strongest retention, correspond to cis-6-18:1 and cis,cis- 6,9-18:2. A 'maximum' is found for cis-13-18:1 while the series of diunsaturated methylene interrupted 18:2 acids has no distinctive maximum [8–11]. In each instance, the first member of the series, i.e. with a double bond in position 2 (when counted from the carboxylic end) migrates well ahead with the front of the eluent and behaves as a non-retained compound. Later, the same retention pattern for the series of cis-18:1 and 18:2 isomeric fatty acids has been found with silver ion high performance liquid chromatography [12], Ag-HPLC. It is thus evident that the effect of the double bond position is not due to the technique employed but to specific interactions between the unsaturated fatty acid molecule and Ag(I) ion. We have shown in a series of papers that the nature of the ester moiety has a distinctive effect both on retention and resolution, although in each instance the retention pattern remained practically the same [8–14]. Therefore, we have suggested that, depending on the position of the double bond in the hydrocarbon chain, possibly a chelate type complex is formed

between the double bond, and a fragment of the ester moiety, as ligands of a silver (I) ion [12–14]. We consider the alkoxy- (or aryloxy-) carbonyl oxygen atoms as possible third ligands coordinating to Ag(I), apart of the gegenanion (nitrate, for example, as in Ag-TLC) and the olefinic C=C bond [8–11]; in addition, the literature offers ample evidence that Ag(I) ions coordinate easily with oxygen [15]. The commonly assumed preference of Ag(I) ions to linear two-ligand coordination [3,16] in water solution should not rule out the above conjecture based on the sufficiently large ionic radius and polarizability of Ag(I) [17]. In fact, the complexes of many nucleophilic solvents with Ag(I) are tetrahedral with the composition AgL$_4$ [18].

A number of papers deal with theoretical studies of silver complexes and olefins. While the interaction of ethylene and Ag(0) is repulsive in the ground state [19], olefin complexes of Ag(I) can be isolated and studied by conventional spectroscopic and mass spectrometric methods. Itoh and coworkers [20] studied butadiene complexes of Ag(I) with 1:1 and 1:2 silver/olefin ratio and satisfactorily predicted their vibrational frequencies by ab initio 4-31G* (with pseudopotential for Ag) calculations. Two groups [15,21] find that ab initio RHF, MP2 and effective core potential (ECP) calculations predict Ag(I)–olefin bond energies in fair agreement with experimental data. The bonding analysis [6,16,22] shows the extent of olefin π-s* donation to Ag(I) is approximately the same as the d-π^* back-donation. The so far highest level theoretical study of Ag(I) complexation with ethylene [22] strongly confirms the classical Dewar–Chatt–Duncanson model [4–6] of metal–olefin complexes as the result of π-ligand donation and d-π^* metal back donation. However, the theoretically revealed nature of Ag(I)–olefin bonding is rather strongly sensitive to the used computational methodology, RHF, DFT, the basis set level, as well as of the used perturbational MP2 or higher level explicit account for electron correlation [6,15,22].

This paper intends to lend theoretical support to the ideas for the formation of chelate complexes between olefinic double bond and carbonyl oxygen of fatty acid derivatives as ligands and Ag(I) by

Table 1
Ag(I) complexation with olefin and carbonyl ligands. Absolute energies are given in a.u., and relative energies in kcal mol^{-1}. Ag(I) associated with carbonyl oxygen, where appropriate

Ligand	E_{ligand}	$E_{complex}$	ΔE_{rel}	ΔE_{exp}
C_2H_4	− 13.2260	− 158.4400	− 22.6	− 33.72
s-cis-C_4H_6	− 25.3075	− 170.5258	− 25.3	
s-trans-C_4H_6	− 25.3139	− 170.5319	− 25.1	
1,4-C_5H_8	− 31.9386	− 177.1685	− 32.6	(− 39.0, − 37.8)[a]
HCOOH	− 37.9478	− 183.1744	− 30.5	
HCHO	− 22.25925	− 167.48716	− 31.4	
HCONH$_2$	− 32.52973	− 177.77546	− 42.5	
CH$_3$CHO	− 28.90627	− 174.14075	− 35.5	− 38.7, − 43.6 [15]

[a] Experimental data for two molecules of 2-pentene [15].

the means of ab initio MO calculations of model complexes of Ag(I) with several kinds of ligands. Among these are olefins, unsaturated carboxylic acids, aldehydes and carboxamides, as well as unsaturated fatty acid esters with one and two isolated C=C double bonds. We also study computationally the effect of two types of solvents, non-polar and polar, on the stability of complexes to additionally clarify their chromatographic behavior.
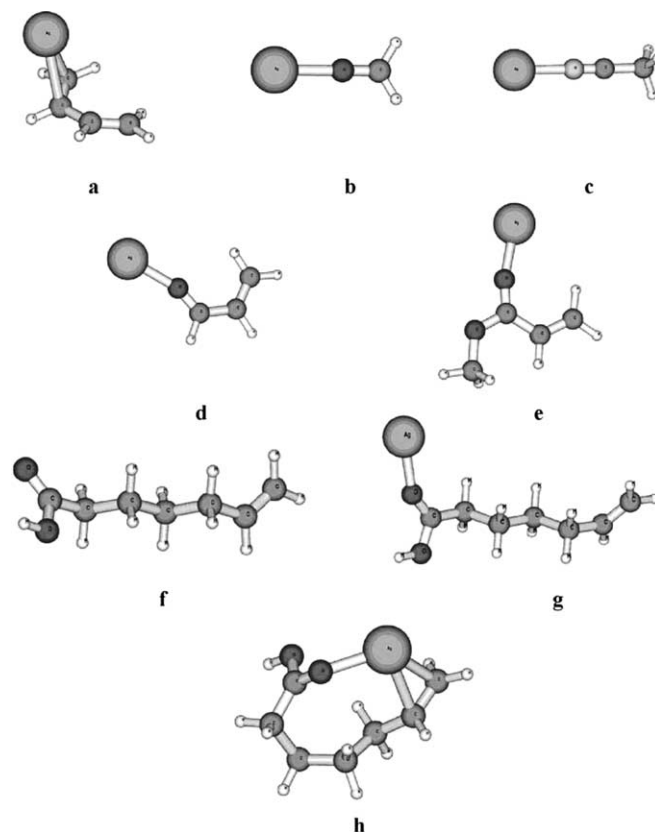

Fig. 1. Ag(I) complexes of small organic ligands.

Table 2

Ag(I) complexation with unsaturated aliphatic aldehydes $H_2C=CH-(CH_2)_nCHO$. Absolute energies are given in a.u., and relative energies in kcal mol^{-1}

N	E_{ligand}	$E_{complex}$	$\Delta E_{complex}$	ΔE_{rel}
0	-34.3506	-179.5872	-36.8	-5.4[a]
1	-40.9769	-186.2158	-38.2	-1.3[b]
2	-47.6114	-192.8585	-43.4	-6.3[b]
3	-54.2445	-199.4793	-35.7	-1.2[b]
4	-60.8747	-206.1102	-36.1	-0.6[b]

[a] Relative to formaldehyde, Table 1.
[b] Relative to $n = 0$, acrolein. $E_{Ag+} = -145.17793$ a.u.

2. Computational details

To reduce the required computational effort for the selected Ag(I) complexes to some reasonable extent, we use ECP ab initio RHF calculations with the CEP-31G basis set [23–25], also known as the SBKJC pseudopotential basis set, reported to provide reliable results on transition metal bonding, structure and reactivity with a number of computational methodologies [26]. Most calculations are carried out with the GAMESS-US program package [27]. Solution calculations are done using GAMESS and Onsager's approximation [28–30] at $\varepsilon = 5$ (hydrocarbon solvent) and $\varepsilon = 36.5$ (acetonitrile, methanol) with a spherical cavity having a radius approximately 1 Å larger than the half of the maximum interatomic distance within the corresponding silver complex,

with full geometry optimization. Correlated calculations of some difficult cases using MP2 or density functional theory (DFT) with the hybrid B3LYP functional [31–34] are done using GAMESS and, as exceptions only, with GAUSSIAN 98 [35].

3. Results

Calculated RHF/CEP-31G energies of Ag(I) complexes and simplest model ligands virtually present as fragments of fatty acids in natural oils are listed in Table 1, with some structures shown in Fig. 1. The complexation energies with Ag(I) are given as relative energies with respect to corresponding free Ag(I) and organic ligands. In the complexes listed in Table 1, Ag(I) is associated with either the carbonyl group, or the double C=C bond. The calculated energy of the Ag(I) cation is -145.17793 a.u., RHF/CEP-31G; -145.27196 a.u., MP2/CEP-31G; -145.27270 a.u., MP2/CEP-31G(d), and -145.92798 a.u., B3LYP/CEP-31G.

Other model ligands in studied Ag(I) complexes comprise the series of unsaturated fatty aldehydes with terminal C=C double bonds of the general formula $H_2C=CH-(CH_2)_nCHO$, where n varies from 0 to 4. In these complexes Ag(I) associates with the carbonyl group, which is therefore assumed to be one of the binding functionalities also with fatty acids and

Table 3

Ag(I) complexes of monounsaturated aliphatic acids with terminal double bond, $H_2C=CH-(CH_2)_nCOOH$. Absolute RHF energies are given in a.u., and relative energies in kcal mol^{-1}

N		E_{ligand}	$E_{complex}$	$\Delta E_{complex}$	ΔE_{rel}	
0		-50.0261	-195.2724	-42.9	-12.3[a]	
1		-56.6586	-201.9034	-42.0	$+0.9$[b]	
2		-63.2883	-208.5339	-42.5	$+0.4$[b]	
3		-69.9220	-215.1660	-41.5	$+1.4$[b]	Open
			-215.1747	-46.9	-4.0[b]	Closed
4	RHF	-76.5520	-221.8041	-46.6	-3.7[b]	Open-ext
			-221.7964	-41.7	$+1.2$[b]	Bent 1:1
		(-76.5702)	-221.8102	-50.4	-7.5[b]	Closed chelate
	MP2	-77.3393	-222.6674	-35.2		Open-ext
			-222.6918	-50.5	-15.3[c]	Closed chelate
Methyl methacrylate		-56.6430	-201.8957	-46.9	-4.0[b]	

[a] Relative to HCOOH.
[b] Relative to acrylic acid.
[c] Relative to the open chain extended form. $E_{Ag+(RHF)} = -145.17793$ a.u. $E_{Ag+(MP2)} = -145.27196$ a.u.

Table 4

Ag(I) complexation with C_5-C_{18} mono-unsaturated fatty acids in the gas phase and in solution. Absolute energies are given in a.u., and relative energies in kcal mol^{-1}; $E_{Ag+} = -145.17793$ a.u. (RHF) and -145.92798 a.u. (B3LYP, bold) with the CEP-31G pseudopotential basis set. Relative energies are given for solvation effects, ΔE_{solv}, for Ag(I) chelates and open (extended) Ag(I) salts, as well as between open and chelated forms, ΔE_{chel}

| Acid	Solvent ε	$\Delta E_{chelated}$	ΔE_{solv}	ΔE_{chel}	$E_{extended}$	ΔE_{solv}
Pent-4-enoic	1	−208.5339	–	−0.1	−208.5337	–
	5.0	−208.5913	−36.0	−0.0	−208.5913	−36.1
	36.5	−208.6049	−44.5	+3.1	−208.6097	−47.7
Hex-5-enoic	1	−215.1660	–	5.5	−215.1747	–
	5.0	−215.2038	−23.7	4.0	−215.2101	−22.2
	36.5	−215.2123	−29.1	3.4	−215.2178	−27.0
Hept-3-enoic, trans	1				−220.6187	–
	5.0				−220.6467	−17.6
	36.5				−220.6528	−21.4
Hept-5-enoic, cis	1	−221.8019	–	0.2	−221.8023	–
	5.0	−221.8392	−23.4	1.3	−221.8412	−24.4
	36.5	−221.8525	−31.7	−1.4	−221.8502	−30.1
Hept-5-enoic, cis, methyl ester	1	−228.4446	–	−8.1	−228.4317	–
	5.0	−228.4836	−24.5	−5.0	−228.4756	−27.5
	36.5	−228.4921	−29.8	−7.5	−228.4802	−30.4
Oct-6-enoic, cis	1	−228.4362	–	−1.8	−228.4333	–
	5.0	−228.4689	−20.5	−0.0	−228.4689	−22.3
	36.5	−228.4740	−23.7	+1.9	−228.4771	−27.5
Non-7-enoic, cis	1	−235.0624	–	3.3	−235.0676	–
	5.0	−235.0960	−21.0	2.7	−235.1002	−20.4
	36.5	−235.1037	−25.9	2.6	−235.1079	−25.3
Dec-8-enoic, cis	1	−241.7014	–	−0.5	−241.7005	–
	5.0	−241.7331	−19.9	+1.8	−241.7359	−22.2
	36.5	−241.7406	−24.6	+2.4	−241.7444	−27.6
Undec-9-enoic, cis methyl ester	1	−254.9737	–	−15.1	−254.9497	–
	5.0	−254.9961	−14.0	−4.6	−254.9887	−24.5
	36.5	−255.0009	−17.1	−1.4	−254.9987	−30.7
Dodec-10-enoic, cis methyl ester	1	−261.6145	–	−18.5	−261.5851	–
	5.0	−261.6476	−20.8	−27.7	−261.6034	−11.5
	36.5	−261.6548	−25.3	−29.7	−261.6076	−14.1
Octadec-6-enoic, cis methyl ester	1	−301.4116	–	−14.5	−301.3885	–
	5.0	−301.4311	−12.2	−10.2	−301.4149	−16.6
	36.5	−301.4355	−15.0	−9.2	−301.4209	−20.3
Octadec-9-enoic, cis methyl ester	1	−301.4127	–	−23.8	−301.3848	–
	5.0	−301.4372	−15.4	−20.1	−301.4088	−19.1
	36.5	−301.4425	−18.7	−18.4	−301.4148	−24.2
Octadec-13-enoic, cis	1	−301.4141	–	−17.3	−301.3866	–
	5.0	−301.4482	−11.8	−26.8	−301.4054	−21.4
	36.5	−301.4558	−14.7	−28.7	−301.4100	−26.1
Octadec-14-enoic, cis	1	−301.4122	–	−15.8	−301.3870	–
	5.0	−301.4416	−18.4	−17.8	−301.4133	−18.4
	36.5	−301.4481	−22.5	−17.6	−301.4201	−22.5
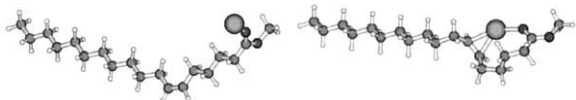
Fig. 2. Ag(I) complexes of 6-18:1 carboxylic acid methyl ester.

their derivatives. Total and relative energies, i.e. of complexation with Ag(I), are listed in Table 2.

As close models of unsaturated aliphatic acids in natural oils we use several acids with a terminal double bond, $H_2C=CH-(CH_2)_nCOOH$. Calculated energies of these models and their Ag(I) complexes are listed in Table 3. In these complexes, similar to the case with aldehydes, Ag(I) is associated with the carbonyl oxygen only, see Fig. 1. Using the complexes of the 6-7:1 unsaturated fatty acid, i.e. hept-6-enoic acid, and Ag(I) we study also the relative energies of open (extended) and closed (chelate) forms, as well as the conformational effects on these relative energies. In the latter case we use MP2/CEP-31G calculations to evaluate the contributions of dynamic electron correlation effects to Ag(I) complexation energies with unsaturated fatty acids. A point of difference between RHF and MP2/CEP-31G calculations is that, while the former locate an open bent conformer of the 6-7:1 enoic acid complex with Ag(I), the electron-correlated calculation does not find an energy minimum for the same conformer, see also Fig. 1. On the other hand, the MP2/CEP-31G calculation gives approximately the same relative energy of the chelate complex with respect to its open form as the RHF/CEP-31G calculation, which substantiates the further use of RHF/CEP-31G in our studies of larger unsaturated fatty acid–Ag(I) complexes.

One more table, Table 4, summarizes the results calculated for unsaturated fatty acids, C_5 to C_{18}, and methyl esters of most of these, with one isolated double bond, with or without terminal $-CH=CH_2$ groups, in two types of solvents—a 'hydrocarbon' solvent with dielectric permittivity $\varepsilon = 5$ and a polar solvent with $\varepsilon = 36.5$ (acetonitrile or methanol). These models are the closest to the fatty acids of natural oils considered here, having the silver(I) ion associated to both carbonyl oxygen and the C=C double bond in their chelated forms, Figs. 2–4, and to the carbonyl oxygen in their extended open forms. Relative energies are given for chelated vs. open
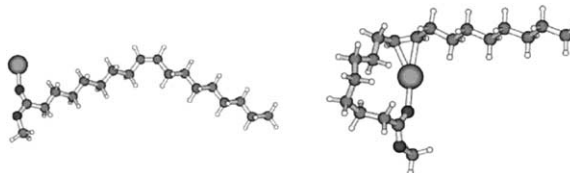

Fig. 3. Ag(I) complexes of 9-18:1 carboxylic acid methyl ester.

forms, and solvent effects at the two values of ε vs. the gas phase energy of the corresponding Ag(I) chelate or extended open form.

Table 5 summarizes calculated energies of Ag(I) complexes with methyl esters of dienoic fatty acids with non-conjugated methylene interrupted double bonds, Figs. 5–7. Again, relative energies of these complexes are calculated with respect to their gas phase energies to give the solvent effects, and chelation energies are given as the differences in energy between bidentate (or in cases of dienoic acids also tridentate) forms and the open extended complexes.

Theoretical geometries of studied Ag(I) complexes, see Figs. 2–7, can be characterized briefly as follows. The strongest bound ligand to Ag(I), carbonyl oxygen, is usually located within the small range of distances between 2.15–2.21 Å (B3LYP) and 2.22–2.28 Å (RHF). Bonding distances of Ag(I) to olefin carbons of fatty acid complexes vary in a considerably wider range, between 2.36 and 2.92 Å (B3LYP/CEP-31G), respectively, 2.56–2.70 Å (RHF/CEP-31G), depending on size, conformation, and possibly also of ring strain, although we did not study the latter specifically. Evidently enough, silver–carbon distances should be most closely related to experimental chromatographic retention, and the relationship between these quantities is confirmed theoretically by the predicted stabilization energies of Ag(I) fatty acid chelate complexes.
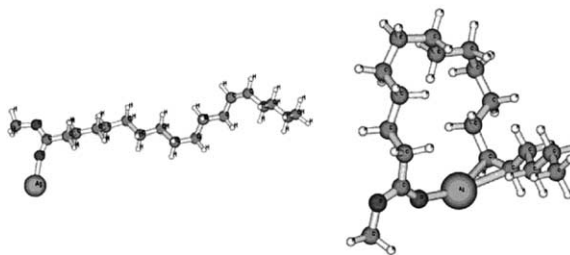

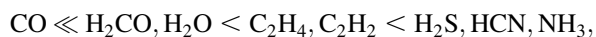Fig. 4. Ag(I) complexes of 13-18:1 carboxylic acid methyl ester.

Table 5

Calculated energies of Ag(I) complexes of C_{10}–C_{18} dienoic fatty acid methyl esters. Absolute energies are given in a.u., and relative energies in kcal mol^{-1}. $E_{Ag+} = -145.17793$ a.u. (RHF) and -145.92798 a.u. (B3LYP) with the CEP-31G pseudopotential basis set. Relative energies are given for the solvation effect, ΔE_{solv}, for Ag(I) chelates and open (extended) Ag(I) salts, as well as between open and chelated forms, ΔE_{chel}

Acid	Solvent ε	$E_{chelated}$	ΔE_{solv}	ΔE_{chel}	$E_{extended}$	ΔE_{solv}
Deca-5,8-dienoic, 8-complex	1	− 247.1575	–	− 14.1	− 247.1350	–
	5.0	− 247.1960	− 24.2	− 17.7	− 247.1677	− 20.5
	36.5	− 247.2044	− 29.5	− 18.1	− 247.1755	− 25.4
Undeca-6,9-dienoic; *cis,cis*-9-complex	1	− 253.7782	–	− 9.6	− 253.7629	–
	5.0	− 253.8005	− 14.0	− 7.7	− 253.7882	− 15.9
	36.5	− 253.8074	− 18.3	− 8.4	− 253.7939	− 19.4
Undeca-6,9-dienoic; *cis,cis*-6-complex	1	− 253.7645	–	− 1.0	− 253.7629	–
	5.0	− 253.8025	− 14.1	− 8.9	− 253.7882	− 15.9
	36.5	− 253.8204	− 25.4	− 16.7	− 253.7939	− 19.4
Undeca-6,9-dienoic; *cis,cis*-6,9-complex	1	− 253.7782	–	− 10.7	− 253.7629	–
	5.0	− 253.8109	− 14.1	− 8.9	− 253.7882	− 15.9
	36.5	− 253.8179	− 25.4	− 16.7	− 253.7939	− 19.4
Undeca-6,9-dienoic; *cis,trans*-9-complex	1	− 253.7933	–	− 9.5	− 253.7782	–
	5.0	− 253.8025	− 5.7	− 1.2	− 253.8005	− 14.0
	36.5	− 253.8074	− 8.8	− 1.2	− 253.8054	− 17.0
Dodeca-7,10-dienoic; *cis,cis*-7,10-complex	1	− 260.4193	–	− 12.6	− 260.3992	–
	5.0	− 260.4525	− 20.8	− 11.0	− 260.4351	− 22.5
	36.5	− 260.4344	− 9.4	+6.1	− 260.4440	− 28.1
Octadeca-9,12-dienoic; *cis,cis*-9-complex	1	− 300.2232	–	− 14.3	− 300.2004	–
	5.0	− 300.2522	− 18.2	− 15.0	− 300.2347	− 21.5
	36.5	− 300.2586	− 22.2	+8.1	− 300.2458	− 28.5

4. Discussion

The relative stabilities of silver Ag(I) complexes with various ligands have been studied both experimentally [15] and theoretically [15,17,36,37]. According to earlier theoretical calculations, the affinity of small molecular ligands to Ag(I) follows the ordering [36]:

$$CO \ll H_2CO, H_2O < C_2H_4, C_2H_2 < H_2S, HCN, NH_3,$$

and the typical binding energies of organic ligands to Ag(I) cation are within the range of 30–50 kcal mol^{-1} [36]. Present calculations, although employing the RHF methodology, an inferior basis set
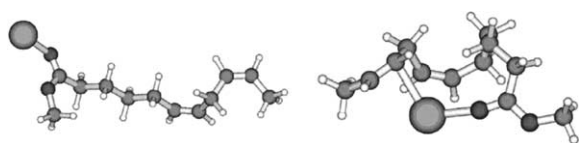

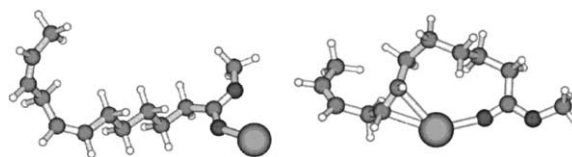Fig. 5. Ag(I) complexes of 6,9-11:2 carboxylic acid methyl ester.

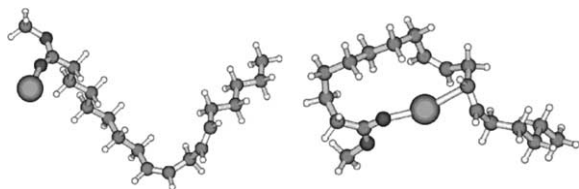Fig. 6. Ag(I) complexes of 7,10-12:2 carboxylic acid methyl ester.

Fig. 7. Ag(I) complexes of 9,12-18:2 carboxylic acid methyl ester.

with respect to the recommended 6-31 + G(d,p) for the ligands [36], and without any account for electron correlation and relativistic effects, reproduce qualitatively the above ordering of affinities of small ligands, and bring about details on the affinity of carboxylic acid derivatives to Ag(I), see Table 1. Calculated RHF/CEP-31G stabilization energies of simple olefin–Ag(I) complexes are somewhat lower than corresponding MP2/CEP-31G(d) values, which in turn reproduce well the experimental data [38]. On the other hand, density functional (B3LYP [31–34]) calculations tend to overestimate Ag(I)–olefin complexation energies [22,38], a trend reproduced with unsaturated fatty acid complexes of Ag(I) as well, see below.

The described findings justify the choice of the very moderate size CEP-31G basis set as well as of the RHF methodology for the calculations of Ag(I) complexes of large unsaturated carboxylic acids and esters, for which MP2 calculations are evidently unfeasible, and even DFT (B3LYP) is laborious enough. Our theoretical interpretation of chromatographic behavior of fatty acids and esters is in fact facilitated by the necessity of knowledge of no more than the relative energies of their Ag(I) complexes. In addition, even present pseudopotential RHF calculations reproduce relatively correct experimental trends in Ag(I) affinities of organic carbonyl and unsaturated ligands [36,38], showing larger dissociation energies for the former, Table 1. Our calculations clearly indicate the capacity of Ag(I) to accommodate more than one C=C double bond from the fatty acid in its coordination sphere, thus supporting the assumption of a coordination number of Ag(I) for alkenes higher than 2, confirmed by correlated MP2/CEP-31G* calculations [38], as well as by gas phase studies of Ag(I)–alkene complexes, [15] matrix isolation experiments on Ag(I) carbonyl

[39] and CO_2 complexes [40], and solution studies [18].

The relative energies of the 'open' extended and chelated forms of monoenoic (Figs. 2–4) and dienoic (Figs. 5–7) fatty acids given in Tables 3–5 are compared within each series to provide information relevant to their resolution by silver ion chromatography. The chelated form represents the simultaneous interaction of Ag(I) with a double bond and the carbonyl oxygen of a fatty acid methyl ester molecule while the open form represents interaction of Ag(I) with the carbonyl oxygen only. First and most important, it is evident that the simultaneous binding of two ligands by Ag(I), the C=C double bond and carbonyl oxygen of fatty acid ester to give a chelate complex is energetically preferable not only in gas phase but should be the case in solution as well. Our calculations show that the absolute values of complexation energies and, more importantly, of Ag(I) chelation energies by unsaturated fatty acids definitely depend on the conformation of the hydrocarbon chain for the open chain 'extended' complex, the differences between the global minimum and less preferable conformers varying in the range of 3–5 kcal mol^{-1}. The same holds also for the ring conformations of the Ag(I) chelate complexes. Therefore, the finding that the gas phase chelation energy of Ag(I) with 13-18:1 acid methyl ester is −35.8 kcal mol^{-1}, B3LYP/CEP-31G, and with 14-18:1 acid methyl ester, −35.1 kcal mol^{-1}, B3LYP/CEP-31G, is significant in as much as the two chelation energies are essentially equal, and the experimental retention times of these compounds are equal as well [8–14]. Practically the same result is given by the RHF/CEP-31G calculations of the two open vs. the two chelated Ag(I) complexes of 13-18:1 and 14-18:1 acids: −17.3 vs. −15.8 kcal mol^{-1} respectively, Table 4.

Second, data in Tables 4 and 5 provide unambiguous indication about the impact of the double bond position on the chelate complex formation although the determination of the preferable position is not unambiguous. Indeed, there is a clear difference between the ΔE_{chel} values (Table 4) between the 6-18:1, 9-18:1, 13-18:1, and 14-18:1 methyl esters, with a minimum for 9-18:1. This result is in some contradiction to the experimental data [8–14]. Both Ag-TLC and Ag-HPLC demonstrate that 6-18:1 alkyl or aromatic esters are held stronger, i.e. the 6-18:1

Table 6
B3LYP/CEP-31 absolute and relative energies of mono- and dienoic fatty acid complexes of Ag(I)

Acid	Solvent ε	$E_{chelated}$	ΔE_{solv}	ΔE_{chel}	$E_{extended}$	ΔE_{solv}
Undeca-6,9-dienoic; *cis,cis*-6,9-complex	1	−257.2666	–	−21.6	−257.2320	–
	5.0	−257.2997	−20.8	−22.2	−257.2644	−20.2
	36.5	−257.3067	−25.2	−22.1	−257.2722	−24.7
Dodeca-7,10-dienoic; *cis,cis*-7,10-complex	1	−264.0943	–		−264.0502	–
	5.0	−264.1225		−264.0804		
	36.5	−264.1286		−264.0876		
Octadeca-6-enoic acid, Me-ester	1	−306.23226	–	−30.2	−306.18414	–
	5	−306.25177	−12.2	−27.2	−306.20848	−15.3
	36.5	−306.25617	−15.0	−26.0	−306.21476	−19.2
Octadeca-9-enoic acid, Me-ester	1	−306.23656	–	−36.7	−306.17812	–
	5	−306.26059	−15.1	−38.2	−306.19964	−13.5
	36.5	−306.26620	−18.6	−38.5	−306.20483	−16.8

fatty acid ester complexes are supposedly more stable [8–14]. This discrepancy comes to remind that Ag(I) chelate stabilization energies cannot be the only factor determining chromatographic retention. The reasons for the discrepancy, as comparison of present calculations and experiment show, can be searched in the hydrocarbon chain/ring conformational dependencies as mentioned above, on the conformation of the alkoxy (or aryloxy) group in the chelate complex, with minimum for RO− at the largest possible distance from the chelate ring, which may differ from the case in real solution and would additionally bring a few kcal mol^{-1} into consideration. Also, present calculations do not account for specific solvation of alkoxy (aryloxy) ester groups by e.g. protic solvents like CH_3OH, widely used in fatty acid chromatography. Another most important reason is apparently the occurrence of additional interactions in the chromatographic system which effect the formation of chelate complexes with silver ions favoring these with rings of moderate size (the 6-complex) over the complexes with larger rings (the medium 9, and large 13- or 14-complexes. Modeling of the latter kind of interactions is completely out of our reach with the present type of calculations.

Some verification of the discussed RHF predictions of relative strengths of Ag(I) chelates is provided by parallel correlated calculations of the same species, using MP2 or B3LYP/CEP-31G, Tables 3 and 6. However, even the quantitatively different description of Ag(I) binding to C=C (double bonds) and C=O (carbonyl groups) ligands by the two approaches used, simple RHF and correlated MP2 or DFT/B3LYP, as demonstrated also with shorter chain dienoic fatty acid derivatives, Table 6, does confirm the deduction, that calculations consistently predict the chelate complexes of 9-enoic fatty acids relatively more stabilized than those of 6-enoic fatty acids. Their chromatographic behavior showing the opposite, namely, the smaller ring complex (as in 6-18:1) is held stronger than the larger ring complexes (as in 9-18:1, 13-18:1, 14-18:1), [42] should therefore be understood as an indication that additional interactions we cannot account for, e.g. solute-stationary phase or/and solute-mobile phase, take place, and tune the observed retention. Note of course that the Ag(I) fatty acid chelates bear no direct analogy to 8- and 11-membered homocyclic or heterocyclic ring compounds of first row elements, like hydrocarbons, lactones, lactams, etc.

On the other hand, two possible interactions were calculated for undeca-6,9-dienoic acid methyl ester, via the double bond in position 6 and via the double bond in position 9 (Table 5). Here, the double bond in position 6 is found to form the more stable chelate complex, exactly as expected. The ΔE_{chel} values for undec-9-enoic and for undeca-6,9-dienoic methyl esters, both interacting predominantly through the double bond in position 9, are practically equal.

A different and important case is presented by the

comparison of 9,12-18:1 and 9-18:1 Here, the calculated values of complexation energy favor complexes of 9,12-18:2 (cf. Fig. 7 vs. Fig. 4; note that the two double bonds in Fig. 7 are associated with a single Ag(I) ion) over 9-18:1, which result is in full agreement with the experiment: in Ag-HPLC, for example, the 9,12-18:2 methyl ester is held about three times stronger than is the 9-18:1 methyl ester [12]. The result shows that the complex of a single Ag(I) with two double bonds is much stronger, than the complex between Ag(I), double bond and carbonyl oxygen as has been supposed for silver ion chromatography [1,2].

Third, there is some indication in the computational data that the hydrocarbon chain length may have certain impact on the formation of chelate complexes. Calculated relative stabilization energies of chelates vs. open chain forms of fatty acids as either free acids or methyl esters are practically equal, as shown in Table 3. It is not possible, therefore, to conclude unambiguously whether the longer chain or acid derivatization cause the preferable formation of a chelate complex. Experiments with both Ag-TLC and Ag-HPLC have shown so far, that longer chain fatty acids are usually retained less strongly than shorter chain fatty acids [41,42] but the experiments are limited to C_{16}, C_{18}, C_{20} and C_{22} and do not include C_5-C_{10} fatty acids. Also, it appears easier to resolve C_{20} than C_{18} positionally isomeric fatty acids as aromatic derivatives (depending on the double bond position [42]), which additionally puts the emphasis on the occurrence of additional interactions of unsaturated fatty acid esters in the chromatographic system.

5. Conclusion

MO RHF/CEP-31G and DFT computations of Ag(I) chelates of unsaturated fatty acids are consistent with the conjecture that the chromatographic resolution of positionally isomeric unsaturated fatty acid esters is due to a significant extent of the formation of Ag(I) chelate complexes in which these derivatives interact with the metal ion both through the double bond and the carbonyl oxygen in alkoxy- or aryloxy-groups. The theoretical results clearly indicate that the position of double bond as well as the chain length

have a significant impact on the interaction energies of fatty acid derivatives and the stationary chromatographic phase via Ag(I), while leaving recognizable role also to the additional tuning interactions of these compounds with the mobile and/or stationary phase. Calculations thus supports the assumed chromatographic effect of chelate complexes of unsaturated fatty acid esters and Ag(I) and agree reasonably well with experimental chromatographic results. MO and DFT computational data thus expose features, which are of importance to the better understanding of interactions in silver ion chromatography and offer the possibility to underlay an independent theoretical base under important chromatographic experiments of significant practical value.

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