Experimental and DFT Study on Methylbenzenes-Silver(I) Ion Complexes Thermodynamics

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Abstract

Motivation. For the purpose of understanding structure-reactivity relationship in organic chemistry, followed by the computer prediction of the constants of chemical equilibrium, comparisons of corresponding experimental data with the results of quantum-chemical calculation were done.

Method. Experimental data of high performance liquid chromatography for polymethylbenzens on Silver-loaded stationary phase combined with results of calculations with Gaussian98 program.

Results. The thermodynamic model of sorption - desolvation in connection with two-component mobile phases was developed. Different approximation equations were obtained. The best correspondence between the experiment and the calculation is observed for neutral silver with the use of results of the quantum-chemical calculation (ΔH_{qc}, ΔS_{vib}), and also two parameters of solvent - the experimentally obtained relative degree of desolvation *N* and *ortho*-effect *R12*.

Conclusions. Combined high performance liquid chromatography and quantum-chemical study allow to obtain thermodynamic parameters of complexing and the evaluations of enthalpy and entropy of complexing. Besides the quantum-chemical calculations data of complexing, the indicator variable was used. As a result, approximating equations are obtained with a prediction error, corresponding to accuracy of experimental data.

Keywords. High performance liquid chromatography, *ab initio*, relative degree of desolvation, aromatic compounds, *ortho*-effect.

Abbreviations and notations. DFT-B3LYP, density functional method using functional of Becke, Lee, Young and Par; HPLC - high performance liquid chromatography;

1 INTRODUCTION

The task of the quantitative calculation of various characteristics of the reacting system, which substantially influence mechanism and results of chemical transformation, was formulated for the first time at the end of the 19th century as the method of studying energetics of chemical reactions. However, at that time there were no examples of the methods of calculating the energies of molecules. The idea of replacing of real experiment by the computational appeared considerably later, with the development of quantum-chemical calculation programs during the 1960s.

For many year, the development of the quantitative methods of chemistry was by using the theory of similitude/resemblance of chemical systems and beginning from the work of Hammett (1933) [1], the search for the relationship between the rate constants and equilibria, which were not connected with the specific types of reactions, was under way. As a result of the subsequent works during the 1960s, an entire series of the reactivity scales had been developed on the basis of scaling the chemical objects whereby these, or other, chemical reactions were used. By the sum of these, the classification of the effects of substituents was developed. These studies are widely used today for the analysis of reactivity of organic compounds and for diagnostics of reaction mechanism. However, even this comprehensive classification of effects does not allow to reliably predict the results of chemical experiment.

In actual fact, the problem of the additivity of effects and specificity of reaction center had not been solved. The problem of the additivity of effects is directly influenced by the nature of three-dimensional effects. This problem was especially complex when trying to apply it to the reactions in the solvents. Different attempts of the calculation of environment on their formalism are similar to Hammett's equation in that the specific scale for the evaluation of effect of the environment a certain chemical reaction or another characteristic of environment is used. In fact at that time, the principle of the distribution of the effects of the compound structure and environment was eventually formulated.

However, an attempt at the multirange ranking of the effects of environment was very ambiguous, according to its results. The complexity of the selection of test reactions was due to the fact that the correlation coefficient between the scales must be close to zero. In respect of the entire set of solvents, this task does not have a solution and therefore the selection of the set of solvents with such data processing cannot be random. These works led to the clearer classification of solvents in type (associated - not associated, proton - aproton). However, the model was inadequate for the quantitative description of reactions in the mixtures of solvents.

All these studies indicate the absence in the correlations of a certain fundamental energy parameter of chemical systems. Today’s expectations for the discovery of such general parameter are based on the results of the quantum-chemical calculations, which allow to obtain the evaluations of free energy, enthalpies and entropies for the reactions, which occur in a vacuum. The interest of chemists in such calculations mainly caused by the impossibility of the formulation of the simple and universal rules, which allow to make the specific conclusions about reactivity of compounds.

Due to the inability of quantum-chemical study of the integrated system solvent - the dissolved molecule at high level at present time, the state-of-the-art today is calculations of the dissolved molecule with only few layers of the solvent. In view of this, various other simplified models have been developed in which it is possible to calculate different contributions to the solvation energy: electrostatic (usually dipole and quadrupole), dispersion (Van der Waals polarization) and cavitation (the work of the formation of the cavity, in which was placed the molecule).

Such calculations require the introduction of a number of model presentations regarding the nature of the interaction between the dissolved molecule and the solvent. Differences in the selection of the initial conditions lead to the appearance of a number of the specific methods of calculation (method of dielectric continuum, the model of solvation, the method of point charges, the method of pair empirical potential). All these quantum-chemical models for the calculation of the influence of solvent have their limitations, it is in particular random in the description of specific solvation. Furthermore, there is no evidence that the dielectric constant of solvent ε undergoes substantial change near the dissolved molecule. Moreover, consideration of this change by quantum-chemical calculations is practically impossible because this requires not only the calculation of a large quantity of solvation shells, but also the transition from the microscopic characteristics of solvent to the macroscopic.

Furthermore, checking the validity of the calculation of specific solvation requires an appropriate set of experimental data. However, the traditional way of kinetic experiments does not anticipate the extraction of this type of information from the experiment. Additionally, the results of kinetic experiments (rate constant of the separate steps of reaction and their dependence on the temperature) are interpreted through the view of various representations about the mechanism of the investigated reaction, which are considered today as conventional.

The final limitation is removed, if the reversed equilibrium reaction was examined. In this case there is essential advantage by the velocity, the accuracy and the permitted capacity of experiment have reactions under the conditions of liquid chromatography, namely:

- chromatographic experiments are allowed to obtain relative empirical equilibrium constants in a number of analytes with the accuracy, as the minimum, by an order of the exceeding possibility of the classical kinetic experiment, which requires calibrations for the determining compounds, and also the procedures of the differentiation
- High performance liquid chromatography (HPLC) is allowed to determine the equilibrium constants for a number of substrates under the stable conditions of experiment. It is obvious that the result of seeking the relationship between the experiment and the quantum-chemical calculation must be not single agreement for the single reaction, but parallelism for a number of the substrates
- HPLC in principle is allowed to obtain the quantitative experimental estimation of the effects of specific solvation, which substantially decrease requirements for the size of solvation shells up to the complete it neglecting in the quantum-chemical calculation.

The purpose of this paper is give an insight into understanding structure-reactivity relationship based on combination of state-of-the-art DFT method and experimental

HPLC data. Section 2 presents the computational and experimental methods. Section 3 discusses the results of HPLC and computational study of methylbenzenes-silver (I) ion complex thermodynamics. Section 4 summarizes the conclusions.

2 MATERIALS AND METHODS

All structures were fully optimized at B3LYP level of theory where density functional (DFT) theory [2] with Becke's three parameter functional (B3) [3] and Lee, Yang, and Parr (LYP) [4] correlation functional and Hartree-Fock have been utilized as implemented in the Gaussian98 [5] program package. For all atoms LANL2DZ pseudopotential basis set have been used. Harmonic vibrational frequencies were computed to ascertain the nature of all stationary points (the number of the imaginary modes, NIMAG, is 0 for minima and 1 for transition structures). The geometry optimization and frequency calculations were performed on an AMD Athlon 1.4 Ghz. The following set of key words were used in all quantum computations: OPT FREQ=NORAMAN.
All experimental results were obtained with the procedure as described in reference 6.

3 RESULTS AND DISCUSSION

For the purpose of the interpretation of chromatographic experiments we developed the thermodynamic model of sorption - desolvation in connection with two-component mobile phase. In accordance with this model the dependence of the capacity factor on the experimental condition takes the form:

$$\ln k' = \ln\frac{V_{SP}\rho_S A_L^{\infty}}{V_{MP}} - \frac{\Delta G_I^0}{RT} - N_I\left[\frac{1}{A_L^{\infty}}\cdot\frac{\Delta G_{SI}^0}{RT} + \ln K_L x_L\right], \qquad (1)$$

where $k' = \dfrac{t_R - t_0}{t_0}$ - the capacity factor of investigated analyte;

t_R - the retention time of the analyte in the column;

t_0 - the time of the output of unretained analyte (t_0=2.05 min);

x_L - the mole fraction of modifier (well sorbing component) in the mobile phase (MP);

V_{SP}, V_{MP} - volumes of stationary (SP) and mobile (MP) phases in the column;

$\rho_S = \dfrac{V_{SP} + V_{MP}}{V_{MP}} \rho_{add.}$ - density of the adsorbent (~ 1,87 g/cm 3);

ΔG_I^0 - a change in the free energy of analyte with the transfer of 1 moles of analyte I from the liquid phase (pure analyte I) to an equivalent quantity of adsorbent S, kJ/mole;

ΔG_{SI}^0 - a change of the free energy of an equivalent quantity of adsorbent in this process, kJ/kg;

A_L^∞ - the maximum sorption capacity of the adsorbent of the relatively well sorbing component MP (modifier) - the quantity of moles of the sorbing component MP L, which is adsorbed on one kilogram of adsorbent, mmole/kg;

$N_I = \dfrac{A_L^\infty}{A_I^\infty}$ - the degree of desolvation - correlation between the sorption capacities of adsorbent for the modifier and analyte. It is determined a quantity of moles of modifier, displaced from the surface of adsorbent by one mole of analyte, and is served as the empirical evaluation of the degree of the desolvation of adsorbent in the process of equilibrium sorption of analyte.

K_L - the constant of the equilibrium adsorption of modifier in accordance with Langmuir's isotherm.

Equation (1) allows varying the composition of mobile phase (*?L*), experimentally estimate the degree of desolvation *N* in the process of adsorption. Specifically, this parameter is allowed quantitatively considered changes in the specific solvation.

In connection with the quantum-chemical calculations of the adsorption process equation (1) is possible to rewrite in the approximation form:

$$\Delta G_{\exp} = a_0 + a_1 \Delta G + a_2 N + a_3 z, \qquad (2)$$

where $\Delta G_{\exp} = -RT \ln k^{/}$

ΔG - the result of the quantum-chemical calculation of the equilibrium adsorption;

N - experimental degree of desolvation;

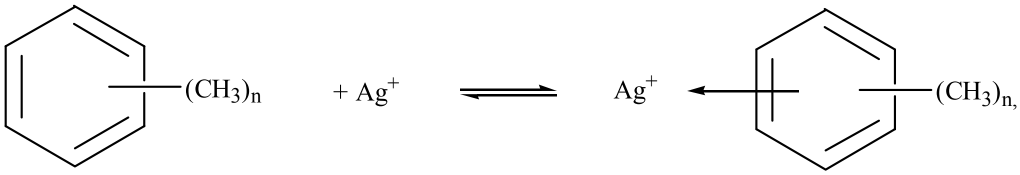
z - the possible parameter of the influence of the nonspecific solvation of analyte in MP.

The advantage of equation (2) is, first of all, the fact that the additional parameters *N* and *z* are allowed experimentally considers the part of the solvation energies, and, thus, it weakened requirements for the complexity of quantum-chemical models. Nevertheless calculated value ΔG is always dependent on the selection of the theoretical adsorptive equilibrium (i.e. resemblance/the similarity). Therefore the parameter $a1$ can be significantly differed from one.

For seeking the correspondences of quantum-chemical calculations to experiment, we have used HPLC silver-ion chromatography data in the row of the substituted benzene

[6]. Data in energetic of the adsorption of polymethylbenzene and also relative degrees of desolvation at 338,15 K are collected in Table 1[6].

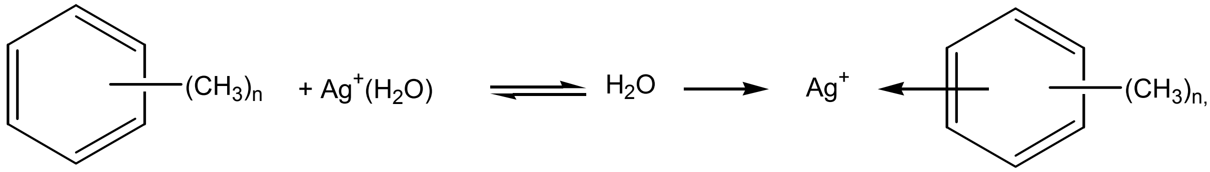
In this liquid-chromatographic system the process of adsorbing aromatic analytes is localized in the centers containing silver ion, and, therefore, it is possible to describe it by the equilibrium formation of appropriate π-complexes:



(1)

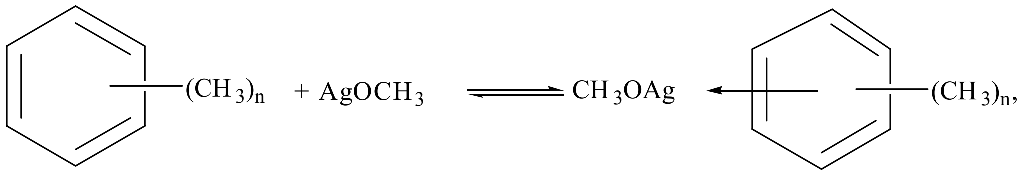
Thus, value ΔG is possible to calculate on the basis of the results of quantum-chemical calculation for the components of equilibrium in accordance with the thermodynamic balance.

It is known that silver ion can be coordinate up to four molecules of water [7], moreover the first two (binding energy of approximately 85 kJ/mole) are retained considerably stronger than last two. Taking into account this fact it can then be assumed that under the experimental conditions silver can retain at least one molecule of water, that could be possible considered by the following thermodynamic equilibrium:



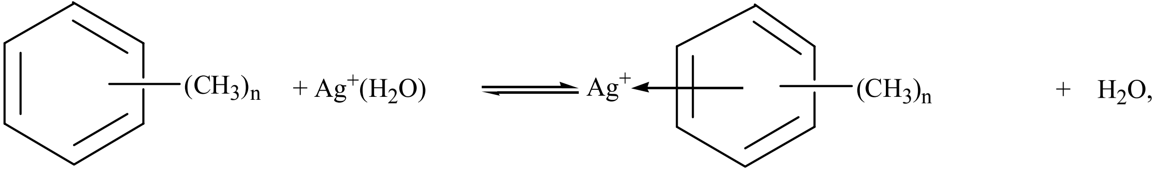
(2)

Since in the experimental chromatographic system silver most likely does not carry the localized positive charge, we have considered this fact by carrying out the quantum-chemical calculation of the complexes of polymethylbenzene with the hypothetical neutral molecule - silver methylate (thermodynamic equilibrium (3)):



(3)

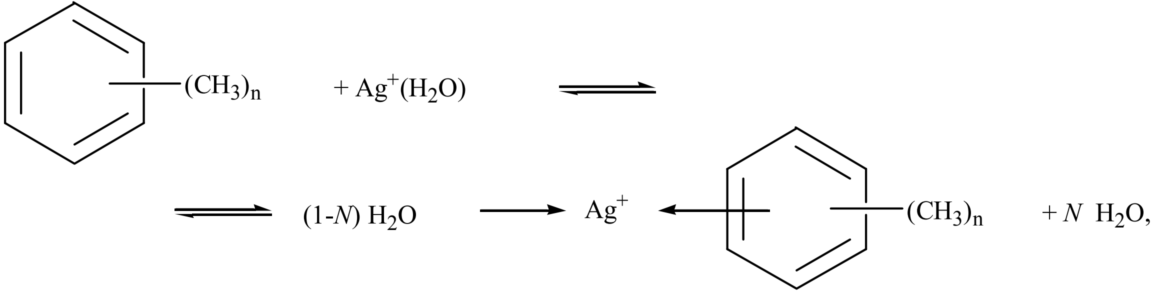
The equilibrium process of adsorbing any analyte in HPLC is always accompanied by the desolvation of certain quantity of modifier, which, in our opinion, requires the examination of thermodynamic equilibrium (4):



(4)

Free energies, enthalpies and entropies for equilibrium reactions (1-3) in the vacuum are collected in Tables 2-5, correlation coefficients between the calculated parameters of equilibrium are presented in Table 6. As can be seen from Table 6, complete similarity between the equilibrium is observed only for the translational and rotational components of entropy. There is also a similarity of enthalpies between equilibrium (1) and (2), and also between (2) and (4). However, the absolute similarity of the results of calculation is for only equilibrium (1) and (4). The reason for this is obvious: in both cases the variable components of calculation are the same values - data for the methylbenzenes and their complexes with silver ion. Remaining components - are constants. Thus, this similarity is allowed to exclude from the study equilibrium (1) or equilibrium (4).

Additional possibilities for obtaining the adequate description of absorption give a combination of equilibrium (2) and (4), which includes degree of desolvation *N*:



(5)

which is equivalent to additive energetics of the equilibrium: (1- *x*)(equilibrium 2) + *x*(equilibrium 4).

In the work [6] as the internal standard was arbitrarily selected well-retained 1,2,3,4-tetramethylbenzene, for which the relative degree of the desolvation was accepted as one. Then for all remaining analytes the equation 3 is correct:

$$\ln k_I^{/} = \ln k_{I0}^{/} + N_{Irel}\left(\ln k_{st}^{/} - \ln k_{st0}^{/}\right), \qquad (3)$$

where $\ln k_{I0}^{/}, \ln k_{st0}^{/}$ - the capacity factors of analytes with a certain arbitrarily selected composition of MP;

$\ln k_I^{/}, \ln k_{st}^{/}$ - the capacity factors with any other ratio of the MP components (*n*-heptane - water);

$N_{Irel} = \dfrac{N_I}{N_{st}}$ - the relative degree of desolvation, which does not depend on the composition of MP at given temperature.

As shown in the work [6], the energy contribution of desolvation to the equilibrium process of adsorption on the Ag-loaded column with $k_{st}^{/} \approx 5$ (338.15 K) is absent and, thus, it is possible not to consider the degree of desolvation for the analysis of adsorption energetic. However, data for integral adsorption energetic are obtained for the composition of MP, for which at 338,15K $k_{st}^{/} = 5.829$. Therefore, for the comparison of quantum-chemical calculations with the experiment it is expedient to include the relative degree of desolvation in the list of the parameters of calculation.

On Figure 1 the dependence of the experimental values Δ*G*exp from calculated Δ*G*calc, obtained from the equation 4 is shown:

$$\Delta G_{\exp} = a_0 + a_1 \times \Delta G, \qquad (4)$$

where $\Delta G = \Delta H - \dfrac{T \times \Delta S}{1000}$;

$$\Delta S = \Delta S_{tr} + \Delta S_{rot} + \Delta S_{vib};$$
$$\Delta G_{\exp} = -RT \ln k';$$
$$T = 338.15 \text{ K}.$$

Despite the fact that the experimental and calculated data does correspond, the quality of the prediction is not high ($r = 0.953$ Sy=0.36 kJ/mole). In this case the major disagreement was observed for the benzene (therefore this point was excluded from the calculation).

It is completely logically to assume that one of the reasons is the nonequivalent contribution of the components of entropy upon transfer from the gas phase to the condensed phase. In Figure 2 this consideration in accordance with the following correlation equation is demonstrated:

$$\Delta G_{\exp} = a_0 + a_1 \times \Delta H + a_2\left(-\frac{T\Delta S_{vib}}{1000}\right) + a_3\left(-\frac{T\Delta S_{tr}}{1000}\right) + a_4\left(-\frac{T\Delta S_{rot}}{1000}\right). \qquad (5)$$

In this case the benzene does not fall out from the overall dependence, and the quality of prediction is noticeably better ($r = 0.984$, S$y = 0.29$ kJ/mole).

In the work [6] it is claimed that essential influence on the entropy of the adsorption of methylbenzenes on the Ag-loaded column is due to a quantity of 1,2-substituents in the aromatic ring of analytes. The 3D-volume of substituents plays an insignificant role. The demonstration of this dependence is given in Figure 3. The corresponding correlation equation has the form:

$$\Delta S_{\exp} = a_0 + a_1\left(0.707 \times \frac{N_{rel}}{S_N} + 0.707 \times \frac{R_{12}}{S_{R12}}\right), \qquad (6)$$

where R_{12} - quantity of 1,2-substitutions in the molecule;

$S_N = 0.1513997;$

$S_{R12} = 2.828427.$

The points, which significantly fall out from this dependence, correspond to hexamethylbenzene, which was noted in work [6], and to benzene itself. These points are not included in correlation ($r = 0.989$, $Sy = 0.452$ kJ/mole).

For checking the role of *ortho*-effects in the prediction of the behavior of the substituted benzene we carry out the search for the suitable equation for the thermal prediction of boiling temperatures (values d_4^{20} are n_D^{20} the less suitable, since 1,2,4,5-tetramethyllbenzene, pentamethylbenzene and hexamethylbenzene under these conditions are solids). The results of such search by means of the method of step-by-step regression analysis are shown on Figure 4.

As we found out, for prediction *tb* with the accuracy of 1-2°C it is sufficient to have two parameters - *ortho*-effect *R*12 and data of quantum-chemical calculation of translational component of entropy *Str* (Table 2). This result is completely logical, since the translational component of entropy must give the greatest contribution to overcoming of the energy barrier at the border it dressed phases. The corresponding correlation equation is (r = 0.999, Sy=1.138° C):

$$t = a_0 + a_1 \times S_{tr} + a_2 \times C_n, \tag{7}$$

where C_n - quantity of methyl-substituents.

As was shown already by Hammett, the *ortho*-effect is an artefact of environment and, therefore, it must not to arise in the quantum-chemical calculations for the gas phase. Taking this consideration into account, the *ortho*-effect also has been included in the list of the independent parameters.

The results of the calculation of parameters *Nrel* and *ortho*-effect *R12* for the prediction of the behavior of methylbenzenes under the HPLC conditions by the method of principal components are shown on Figure 5. For the six-component equation

$$\Delta G_{\exp} = a_0 + a_1 \times \Delta H + a_2\left(-\frac{T\Delta S_{tr}}{1000}\right) + a_3\left(-\frac{T\Delta S_{rot}}{1000}\right) + a_4\left(-\frac{T\Delta S_{vib}}{1000}\right) + a_5 N_{rel} + a_6 R_{12}, \tag{8}$$

a prediction error Sy = 0.17 kJ/mole (r=0.997).

During the partial reset of the cross-correlations of regressors by the method of the principal components (equation is reduced from the six- to the four-component) a prediction error is 0.24 kJ/mole (r = 0.991).

The results of analogous calculations for the remaining equilibrium taking into account only three components are presented in the Table 7.

Table 7. Evaluations of similarity between the different versions of complexing (B3LYP/LANL2DZ)

Kind of equilibrium	The standard deviation *S*y, kJ/mole	Correlation coefficient, *r*
(1)	0.2964	0.9844
(2)	0.3498	0.9781
(3)	0.1662	0.9951

Such limitation in a quantity of components of system is connected with the need for an increase in the degrees of freedom of system (a "quantity of experimental points" minus a "quantity of components" minus 1) and will make prediction not only more reliable (it decreases a relative error in the coefficients of equations), but also it will compensate for the low quality of the plan of the experiment (in this case the plan can be improved only by introduction of the new compounds into experiment). The evaluations given above testify that the best result of the predictions is obtained with the use of data of quantum-chemical calculation for the neutral silver (silver methylate) (Figure 6, correlation equation 8, Sy=0.17 kJ/mole, r = 0.995).

Step-by-step regression analysis with the subsequent application of analysis of principal components is carried out for the purpose of the elimination of the weak influencing parameters. The two-component model (Figure 7) of neutral silver was the best, moreover only the vibrational component of the entropy was important:

$$\Delta G_{\exp} = a_0 + a_1 R_{12} + a_2 \Delta H + a_3 N + a_4\left(-\frac{T\Delta S_{vib}}{1000}\right). \tag{9}$$

The quality of this result is higher (*Sy*=0.175 kJ/mole, r=0.994) in comparison with the three-component models.

However, any attempt to use energetic of two quantum-chemical calculations (equilibrium (5)) was unsuccessful due to the impossibility of dividing the entropies on the components - the complexity of the processed equations is always limited by quality and capacity of chemical experiment.

Thus, the best correspondence between the experiment and the calculation is observed for neutral silver with the use of results of the quantum-chemical calculation (ΔHqc, $\Delta Svib$), and also two parameters of solvent - the experimentally obtained relative degree of desolvation *N* and *ortho*-effect *R12*.

The fact that from the calculations only the vibrational component of entropy was used - another evidence of the fact that, both in the solvent cage and on the surface of adsorbent, molecule of analyte predominantly fluctuating at some steady positions, jumping over to the adjacent steady position sufficiently rarely (1 passage to ~100 of fluctuations in the cell) and only in the case of appearance of the cavity of solvent (vacancy, lacuna). The rotation of molecules in the cage is also braked because of the presence of intermolecular interactions. As a result the translational and rotational components of entropy do not provide any the contribution to the interpretation of experimental data.

4 CONCLUSIONS

A successful application of HPLC and quantum-chemical calculations was presented in this study for the thermodynamics of Methylbenzenes - Silver(I) complexes. The quantum-chemical calculations were done for methylbenzenes and their complexes with Ag+, Ag(H2O)+ and AgOCH3. On the basis of the results, geometry of aromatic compounds and their complexes, thermodynamic parameters of complexing and the evaluations of enthalpy and entropy of complexing were obtained.

For the purpose of the computer prediction of the constants of chemical equilibrium, comparisons of corresponding experimental data with the results of quantum-chemical calculation were done. In this case as the independent variables, besides the quantum-chemical calculations data of complexing, the indicator variable, which includes chemical representations about the influence of the arrangement of substituents on the properties of aromatic ring (*ortho*-effect), was used.

As a result of analysis, approximating equations are obtained with a prediction error, corresponding to accuracy experimental data. In this case it is shown that the indicator variable remains significant, which indicates the insufficiency of the results of the quantum-chemical calculation on the energetics of substrates and effectors for the prediction of experimental data without the classical representations about reactivity of aromatic compounds. From other side, quantum-chemical calculations are allowed to substantially improve the quality of prediction.

Supplementary Material

Cartesian coordinates of all optimized structures are available.

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Table 2. Calculated values of thermodynamic parameters of complexation of polymethylbenzenes with Ag^+ (B3LYP/LANL2DZ)

Compound	$-\Delta E$, kJ·mol^{-1}	$-\Delta E_0$, kJ·mol^{-1}	$-\Delta H$, kJ·mol^{-1}	$-\Delta G$, kJ·mol^{-1}	ΔS, J·mol^{-1}·K^{-1}	ΔS_{tr}, J·mol^{-1}·K^{-1}	ΔS_{rot}, J·mol^{-1}·K^{-1}
Benzene	156,247	2,253	148,212	177,277	97,479	10,761	33,497
Toluene	169,432	2,302	161,447	180,968	65,471	9,611	11,648
o-Xylene	178,104	1,783	170,340	193,862	78,902	8,694	10,439
m-Xylene	178,138	2,804	170,188	181,979	39,551	8,694	9,832
p-Xylene	175,420	3,036	167,281	182,478	50,974	8,694	15,933
1,2,3-Trimethylbenzene	186,303	2,007	178,398	199,536	70,898	7,941	9,238
1,2,4-Trimethylbenzene	185,626	2,156	177,823	196,569	62,869	7,941	8,979
1,3,5-Trimethylbenzene	184,757	2,712	177,090	186,371	31,121	7,941	7,694
1,2,3,4-Tetramethylbenzene	194,568	2,221	186,618	207,688	70,672	7,309	8,314
1,2,3,5-Tetramethylbenzene	191,688	2,986	183,549	198,099	48,802	7,309	7,376
1,2,4,5-Tetramethylbenzene	186,266	1,942	178,400	200,205	73,141	7,309	13,154
Pentamethylbenzene	197,734	1,413	190,063	213,065	77,149	6,778	6,954
Hexamethylbenzene	194,602	2,246	186,442	204,941	62,036	6,314	5,494

Table 3. Calculated values of thermodynamic parameters of complexation of polymethylbenzenes with Ag^+, solvated with H_2O (B3LYP/LANL2DZ)

Compound	$-\Delta E$, $kJ \cdot mol^{-1}$	$-\Delta E_0$, $kJ \cdot mol^{-1}$	$-\Delta H$, $kJ \cdot mol^{-1}$	$-\Delta G$, $kJ \cdot mol^{-1}$	ΔS, $J \cdot mol^{-1} \cdot K^{-1}$	ΔS_{tr}, $J \cdot mol^{-1} \cdot K^{-1}$	ΔS_{rot}, $J \cdot mol^{-1} \cdot K^{-1}$
Benzene	135,996	3,245	130,380	100,578	-99,956	-157,034	-49,463
Toluene	146,689	3,091	143,694	97,272	-155,699	-158,264	-71,806
o-Xylene	153,479	2,788	148,107	112,219	-120,357	-159,247	-73,350
m-Xylene	151,311	3,179	145,820	106,924	-130,457	-159,247	-73,839
p-Xylene	151,056	4,088	145,259	102,061	-144,879	-159,247	-67,785
1,2,3-Trimethylbenzene	160,093	3,454	154,316	116,879	-125,570	-160,063	-74,525
1,2,4-Trimethylbenzene	159,129	2,666	153,952	115,976	-127,365	-160,063	-75,082
1,3,5-Trimethylbenzene	158,344	3,637	152,962	106,120	-157,109	-160,063	-76,366
1,2,3,4-Tetramethylbenzene	166,042	3,117	160,481	123,357	-124,507	-160,745	-75,873
1,2,3,5-Tetramethylbenzene	163,107	3,625	157,378	116,268	-137,888	-160,745	-76,848
1,2,4,5-Tetramethylbenzene	158,934	1,878	156,359	115,120	-138,302	-160,745	-71,044
Pentamethylbenzene		2,346	165,118	122,149	-144,122	-161,327	-77,366
Hexamethylbenzene	163,033	3,453	157,357	115,512	-140,356	-161,829	-78,948

Table 4. Calculated values of thermodynamic parameters of complexation of polymethylbenzenes with $AgOCH_3$ (B3LYP/LANL2DZ)

Compound	$-\Delta E$, kJ·mol^{-1}	$-\Delta E_0$, kJ·mol^{-1}	$-\Delta H$, kJ·mol^{-1}	$-\Delta G$, kJ·mol^{-1}	ΔS, J·mol^{-1}·K^{-1}	ΔS_{tr}, J·mol^{-1}·K^{-1}	ΔS_{rot}, J·mol^{-1}·K^{-1}	J
Benzene	60,124	2,388	57,456	18,620	-130,231	-157,498	-62,007	
Toluene	63,989	2,922	58,761	17,089	-139,746	-158,774	-84,680	
o-Xylene	66,992	2,794	61,783	22,117	-133,005	-159,804	-86,354	
m-Xylene	67,591	3,158	62,327	15,753	-156,189	-159,804	-86,851	
p-Xylene	67,851	3,408	62,327	19,355	-144,101	-159,804	-80,651	
1,2,3-Trimethylbenzene	69,781	2,643	64,456	25,375	-131,055	-160,653	-87,914	
1,2,4-Trimethylbenzene	69,715	2,306	64,551	27,203	-125,244	-160,653	-88,136	
1,3,5-Trimethylbenzene	67,706	3,503	62,390	12,335	-167,862	-160,653	-89,408	
1,2,3,4-Tetramethylbenzene	73,391	2,558	68,153	28,657	-132,432	-161,373	-89,182	
1,2,3,5-Tetramethylbenzene	69,074	2,693	63,729	24,921	-130,139	-161,373	-90,069	
1,2,4,5-Tetramethylbenzene	68,087	2,400	62,870	25,402	-125,637	-161,373	-84,107	
Pentamethylbenzene	70,857	1,438	65,995	33,473	-109,052	-161,984	-90,772	
Hexamethylbenzene	66,071	3,181	60,565	18,439	-141,269	-162,515	-92,174	

Table 5. Calculated values of thermodynamical parameters for equilibrium Ar + AgH_2O = ArAg + H_2O (B3LYP/LANL2DZ)

Compounds	$-\Delta E$, kJ·mol^{-1}	$-\Delta E_0$, kJ·mol^{-1}	$-\Delta H$, kJ·mol^{-1}	$-\Delta G$, kJ·mol^{-1}	ΔS, J·mol^{-1}·K^{-1}	ΔS_{tr}, J·mol^{-1}·K^{-1}	ΔS_{rot} J·mol^{-1}·
Benzene	-9,742	-6,769	-6,734	-0,415	21,196	-13,389	-8,76
Toluene	3,443	-6,721	6,501	3,277	-10,811	-14,539	-30,61
o-Xylene	12,115	-7,239	15,393	16,170	2,619	-15,456	-31,81
m-Xylene	12,150	-6,219	15,241	4,287	-36,731	-15,456	-32,42
p-Xylene	9,432	-5,987	12,335	4,786	-25,309	-15,456	-26,32
1,2,3-Trimethylbenzene	20,314	-7,015	23,451	21,844	-5,385	-16,209	-33,02
1,2,4-Trimethylbenzene	19,637	-6,866	22,876	18,877	-13,414	-16,209	-33,28

1,3,5-Trimethylbenzene	18,768	-6,311	22,143	8,680	-45,162	-16,209	-34,56
1,2,3,4-Tetramethylbenzene	28,579	-6,801	31,671	29,996	-5,611	-16,841	-33,94
1,2,3,5-Tetramethylbenzene	25,699	-6,037	28,602	20,408	-27,481	-16,841	-34,88
1,2,4,5-Tetramethylbenzene	20,278	-7,081	23,454	22,514	-3,142	-16,841	-29,10
Pentamethylbenzene	31,746	-7,609	35,116	35,373	0,866	-17,372	-35,30
Hexamethylbenzene	28,614	-6,776	31,496	27,250	-14,247	-17,836	-36,76

Table 6. Evaluation of similarity between energetics of different complexations (B3LYP/LANL2DZ)

Correlations.	$-\Delta H$, kJ·mol^{-1}	$-\Delta G$, kJ·mol^{-1}	ΔS, J·mol^{-1}·K^{-1}	ΔS_{tr}, J·mol^{-1}·K^{-1}
Correlation Ag^+-$Ag(H_2O)^+$ (1-2)	0,9846	0,9477	0,6504	1,0000
Correlation Ag^+-$AgOCH_3$ (1-3)	0,7885	0,7868	0,7335	1,0000
Correlation Ag^+-$Ag(H_2O)^+$ (1-4)	1,0000	1,0000	1,0000	1,0000
Correlation $Ag(H_2O)^+$-$AgOCH_3$ (2-3)	0,8054	0,7957	0,3350	1,0000
Correlation $Ag(H_2O)^+$ –$Ag(H_2O)^+$ (2-4)	0,9846	0,9477	0,6504	1,0000
Correlation $AgOCH_3$-$Ag(H_2O)^+$ (3-4)	0,7885	0,7868	0,7335	1,0000

Table 1.

Retention times (t_R, min), capacity factors (k') and calculated thermodynamic parameters of methylbenzenes retention on silver(I)-loaded stationary phase at 338 K.

Compound	t_R, min	k'	$-\Delta G_{\exp}$, kJ·mol^{-1}	$-\Delta H^{=}$, kJ·mol^{-1}
Benzene	6.23	2.041	2.00	9.37
Toluene	8.28	3.039	3.12	9.73
o-Xylene	12.17	4.936	4.49	9.83
m-Xylene	9.82	3.792	3.75	9.94
p-Xylene	9.28	3.530	3.54	9.69
1,2,3-Trimethylbenzene	18.24	7.898	5.81	10.09
1,2,4-Trimethylbenzene	12.92	5.304	4.69	10.06
1,3,5-Trimethylbenzene	9.75	3.756	3.72	10.03
1,2,3,4-Tetramethylbenzene	22.71	10.078	6.49	10.20
1,2,3,5-Tetramethylbenzene	14.90	6.268	5.16	9.60
1,2,4,5-Tetramethylbenzene	14.00	5.829	4.95	9.77
Pentamethylbenzene	-	-	-	-
Hexamethylbenzene	20.38	8.942	6.16	8.59