Short communication

Application of the solvation parameter model to the characterisation of gas chromatographic stationary phases containing tris[3-(trifluoromethylhydroxymethylene)camphorato] derivatives of lanthanides

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Abstract

The solvation parameter model proposed by Abraham has been applied to retention factors, k, of over fifty different solutes on stationary phases containing tris[3-(trifluoromethylhydroxymethylene)camphorato] derivatives of Pr, Eu, Dy, Er and Yb dissolved in poly(dimethylsiloxane). Application of the solvation equation, $\log k = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + l \log L^{16}$ at 393 K showed that the stationary phases studied had significant values of the descriptors 'a' and 'b' which describe the reversible complexation between lanthanide chelates and nucleophilic solutes. Increasing the atomic number of the lanthanide led to an increase of the 'a' descriptor and a simultaneous decrease of the 'b' descriptor. This behaviour was correlated with changes of the Lewis acidity of the lanthanide ions studied.   © 1998 Elsevier Science B.V.

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1. Introduction

Linear solvation energy relationships (LSERs) have been proposed by many authors to relate such properties of organic liquids as polarity, ability to form hydrogen bonds, and structural arrangement of molecules to diverse processes in solution such as solubility, absorption of light, NMR chemical shift, rates of reactions, free energy and enthalpy of equilibria of distribution between two liquids and retention in chromatography. The solvation parameter model proposed and developed by Abraham and co-workers [1] and developed and extended by the groups of Poole et al. [2] and Carr et al. [3] has been applied to the logarithmic gas chromatographic (GC)

retention factor, $\log k$, for over fifty different solutes in order to characterise GC stationary phases containing lanthanide chelates. The following general solvation equation derived by Abraham and co-workers for application in GC, in which k is the GC retention factor, was used in this study:

$$\log k = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + l \log L^{16}$$

(1)

(The use of logarithms of the gas–liquid partition coefficient $\log K$, or the specific retention volume, $\log V_g$, was also proposed.) R_2 is defined as the molar refraction of the solute minus the molar refraction of an alkane of the same characteristic volume [4], π_2^H

is the effective solute dipolarity/polarizability, $\Sigma\alpha_2^{\mathrm{H}}$ the effective solute hydrogen-bond acidity, $\Sigma\beta_2^{\mathrm{H}}$ the effective solute hydrogen-bond basicity, and $\log L^{16}$ is the solute gas–liquid partition coefficient on hexadecane at 298 K [5]. The stationary phase descriptors *r, s, a, b* and *l* in Eq. (1) have a distinct chemical interpretation: the *r* descriptor refers to the ability of the stationary phase to interact with the solute n- or p-electron pairs, the *s* descriptor to the ability of the stationary phase to take part in dipole–dipole and dipole–induced dipole interactions; the *a* descriptor is a measure of the hydrogen-bond basicity of the stationary phase; the *b* descriptor is a measure of the hydrogen-bond acidity of the stationary phase; and the *l* constant incorporates contributions from solvent cavity formation and solute–solvent dispersion interactions. In gas–liquid chromatography *l* indicates how well the phase will separate members of a homologous series [6].

This equation has been used to describe processes in which a series of solutes are distributed between the gas phase and a condensed phase. These processes include gas–liquid chromatography [7] and gas–solid chromatography [8].

The solvation parameter model is derived from a cavity model of solvation [9], in which the process of solvation of a gaseous solute is broken down into three stages:

1. A cavity of suitable size to accommodate the solute must be created in the solvent; work is required in order to disrupt solvent–solvent interactions and hence this process is endoenergetic.
2. Solvent molecules around the cavity are reorganised; the Gibbs energy change for this process is generally assumed to be negligible.
3. The solute is introduced into the cavity, and various solute–solvent interactions are set up, all of which is exoenergetic.

In this work the retention of over fifty solutes on five stationary phases containing tris[3-(trifluoromethyl-hydroxymethylene)camphorato] derivatives of lanthanides was measured. The initial motivation for this work was to explore the utility of the solvation parameter model given in Eq. (1) for complexing stationary phases containing metal coordination centres, and at the same time to check if their chemical properties, as defined by the coefficients *l, s, a* and *b*, could be rationalised.

2. Experimental

The solutes studied were commercial analytical-grade reagents obtained from Aldrich-Chemie (Steinheim, Germany), E. Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland).

GC measurements were performed on wall-coated open tubular capillary columns installed in a Chrom-5 gas chromatograph from Laboratorni Pristroje NP (Czech Republic), equipped with a flame ionisation detector. High-purity helium, free from water and oxygen, was used as the carrier gas. The split ratio was 1:50. The injector temperature was ca. 70°C above the column temperature. The samples were injected either as head-space vapours (for liquid solutes) or as very dilute solutions of the solids. Sample sizes were varied to ensure that the retention times were independent of the amount injected. All data were collected by the integrator. Corrected retention times and retention factors were calculated relative to the retention of methane.

GC measurements were obtained isothermally at 393 K (120°C). Complexing stationary phases included tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato] derivatives of praseodymium(III) [Pr(tfc)$_3$], europium(III) [Eu(tfc)$_3$], dysprosium [Dy(tfc)$_3$], erbium [Er(tfc)$_3$] and ytterbium(III) [Yb(tfc)$_3$]. The lanthanide tris-β-diketonates (obtained from Aldrich-Chemie GmbH and Co. KG, Steinheim and E. Merck, Darmstadt, Germany) were purified by vacuum sublimation and dissolved in poly(dimethylsiloxane) (OV-1) (obtained from Chrompack, Middelburg, The Netherlands), to achieve a molal concentration of 0.1 mol kg^{-1}. The film thickness of capillary columns was 0.25 μm. The fused-silica capillary column length was 25 m, and the internal diameter was 0.25 mm for all the columns used. The reference stationary phase was OV-1, film thickness 0.25 μm.

Coating of the open-tubular columns was performed by the static method [10].

In order to check the presence (or the formation possibility during prolonged use of the GC columns) of acidic sites capable of interacting with solute hydrogen-bond bases, the IR spectra of the GC stationary phases were recorded on a Fourier transform (FT) IR-Magna 560 spectrometer (Nicolet, USA), using the attenuated total reflection sampling

technique. The instrumental working conditions were as follows: number of sample scans: 1000, number of background scans: 500, resolution: 4.000, detector: DTGS KBr, beam splitter: KBr, source: IR.

Samples of the lanthanide chelates dissolved in poly(dimethylsiloxane), (0.1 mol kg^{-1}), were thermostated during 72 h at 120°C under helium before recording the IR spectra.

Multiple linear regression analysis was performed using the Statistica program (StatSoft, Tulsa, OK, USA) on a Pentium$^®$ P-100 personal computer. The numerical values of the solute descriptors used as the independent variables for multiple linear regression analysis were taken from the collection of Abraham and co-workers [1,11,12].

3. Results and discussion

In this study linear solvation energy relationships (LSERs) are used to explore and rationalise retention relationships on a set of capillary columns coated with complexing stationary phases containing lanthanide chelates. Fused-silica capillary columns were chosen for the studies, as they have a low ratio surface area/phase volume and so the amount of underlying adsorptive surface is less than those of porous supports used in packed columns. This helps minimise interfacial absorption effects [13].

The dependent variable in Eq. (1) was log k, where k is the retention factor. (The numerical values of log K, where K is the gas–liquid partition coefficient, will give rise to the same coefficients in Eq. (1) except for the constant term, c [14,15]). The logarithmic values of the retention factors, log k, determined at 393 K for the listed solutes on the complexing stationary phases studied are presented in Table 1.

Numerical values obtained by multiple regression analysis for the dependent variable log k are given in Table 2. The calculated coefficients (i.e. the system constants) are characterised by their standard error and the probability-level, p-level, (in the case of p-level>0.0001, the numerical values are presented in the table, for most of the data, however, these values are lower than 0.0001). The correlation coefficients, R^2, and the standard errors of the

estimates were calculated for the stationary phases studied. In the product (rR_2), where R_2 is the excess molar refraction, and r is claimed to characterise the ability to interact with the solute n or p electronic pairs [2], the obtained numerical values of r are close to zero and the corresponding values of the probability level exceed 0.01, suggesting that the r coefficients are statistically non-significant for the systems studied in this work.

The regression analysis was repeated without considering the r coefficient in Eq. (1). The results are presented in Table 3.

Plots of the stationary phase descriptors s, a, b and l vs. lanthanide ionic radii are given in Fig. 1.

The lanthanide ions, being the hard acids, do not manifest notable changes of their electronic structure in interactions with organic nucleophiles.

The product ($s\pi_2^H$), where π_2^H is a measure of dipolarity and polarizability of a solute, and s the ability of a stationary phase to participate in dipole–dipole and dipole–induced dipole interactions, does not influence the ability of stationary phases in the system studied to change interactions when the ionic radii of lanthanide chelates are changed.

The s coefficient indicates that the dipole–dipole and dipole–induced dipole interactions are comparable with those of the 'low-polarity' GC stationary phases i.e. squalane and poly(dimethylsiloxane) (SE-30) [1].

The product ($l \log L^{16}$) together with the c coefficient defines energetic conditions of cavity formation for the series of stationary phase studied and does not change significantly for the chelates of the different lanthanides.

The significant values of the system constants a (the hydrogen bond basicity) and b (the hydrogen bond acidity) obtained for the complexing stationary phases studied show that the nucleophilic solutes with free electron pairs interact strongly with the lanthanide central ion, forming reversible complexes.

The complexation between the lanthanide chelate and nucleophilic solutes contributes predominantly to the origin of the significant values of the b coefficient in the GC stationary phases [16–18] (Fig. 2). The stationary phases studied could also contain hydrogen-bond acidic sites capable of interacting with solute hydrogen-bond bases [7]. This problem was resolved by inspecting the FTIR spectra of the

Table 1
Numerical values of logarithm of the retention factor, log k

Solute	Pr(tfc)$_3$	Eu(tfc)$_3$	Dy(tfc)$_3$	Er(tfc)$_3$	Yb(tfc)$_3$
Methanol	0.739	0.843	0.949	1.090	1.177
Ethanol	1.319	1.412	1.498	1.595	1.654
Propan-1-ol	1.625	1.690	1.773	1.849	1.899
Butan-1-ol	1.832	1.930	1.983	2.051	2.096
2-Methylpropan-1-ol	1.743	1.828	1.899	1.970	2.016
Butan-2-ol	1.721	1.803	1.873	1.941	1.983
tert.Butanol	1.601	1.686	1.759	1.827	1.866
Pentan-1-ol	2.059	2.133	2.194	2.279	2.294
2-Methylbutan-1-ol	2.017	1.987	2.154	2.216	2.257
3-Methylbutan-1-ol	2.022	1.988	2.156	2.234	2.255
Hexan-1-ol	2.287	2.352	2.404	2.457	2.491
Hexan-2-ol	2.163	2.239	2.292	2.344	2.374
Hexan-3-ol	2.208	2.252	2.333	2.384	2.427
2-Methylpentan-2-ol	2.079	2.189	2.243	2.294	2.331
3-Methylpentan-3-ol	2.140	2.226	2.281	2.332	2.3623
Heptan-1-ol	2.545	2.597	2.654	2.689	2.689
Octan-1-ol	2.776	2.819	2.824	2.899	2.894
Propan-2-one	1.388	1.386	1.374	1.408	1.387
Butan-2-one	1.609	1.589	1.593	1.597	1.569
Pentan-2-one	1.667	1.634	1.628	1.621	1.592
Hexan-2-one	1.988	1.974	1.903	1.887	1.831
Cyclohexanone	2.152	2.140	2.116	2.104	2.0857
Heptan-2-one	2.186	2.175	2.110	2.081	2.031
Octan-2-one	2.398	2.389	2.318	2.281	2.225
Acetophenone	2.610	2.602	2.745	2.576	2.547
Diethyl ether	1.047	1.035	1.043	1.026	0.994
Di-*n*-butyl ether	1.981	1.892	1.884	1.829	1.754
1,4-Dioxane	1.957	1.917	1.931	1.902	1.828
1-Nitropropane	1.641	1.637	1.639	1.711	1.644
1-Cyanobutane	1.829	1.815	1.804	1.789	1.756
Benzonitrile	2.350	2.327	2.295	2.294	2.302
Pyridine	2.000	2.003	2.012	2.011	2.008
n-Propyl acetate	1.705	1.696	1.620	1.610	1.698
n-Butyl acetate	1.872	1.856	1.840	1.824	1.808
Pentyl acetate	2.099	1.974	1.960	1.946	1.962
1-Iodobutane	1.644	1.661	1.802	1.704	1.755
Benzene	1.308	1.339	1.371	1.443	1.450
n-Hexane	0.790	0.801	0.783	0.834	0.866
n-Heptane	1.029	1.029	0.995	1.036	1.060
n-Octane	1.131	1.235	1.260	1.244	1.262
n-Nonane	1.459	1.459	1.470	1.458	1.464
n-Decane	1.689	1.685	1.679	1.674	1.666
n-Undecane	2.021	1.9032	1.889	1.871	1.867
n-Dodecane	2.169	2.121	2.099	2.079	2.071
n-Tridecane	2.382	2.322	2.302	2.288	2.262
n-Tetradecane	2.611	2.564	2.519	2.486	2.460
Hex-1-ene	0.842	0.854	0.856	0.887	0.914
Hept-1-ene	1.030	1.029	1.072	1.089	1.111
Oct-1-ene	1.295	1.306	1.282	1.298	1.313
Non-1-ene	1.521	1.511	1.509	1.459	1.515
Dec-1-ene	1.727	1.723	1.702	1.715	1.699
Undec-1-ene	1.947	1.935	1.915	1.899	1.8958
Dodec-1-ene	2.169	2.169	2.129	2.110	2.094
Phenol	3.020	3.186	3.339	3.479	3.609
o-Cresol	3.068	3.211	3.356	3.463	3.573
m-Cresol	3.232	3.382	3.531	3.646	3.757
p-Cresol	3.210	3.356	3.505	3.625	3.739

Values determined at 120°C on the complexing stationary phases containing tris[3-(trifluoromethylhydroxymethylene)camphorato] derivatives of praseodymium-Pr(tfc)$_3$, europium-Eu(tfc)$_3$, dysprosium-Dy(tfc)$_3$, erbium-Er(tfc)$_3$ and ytterbium-Yb(tfc)$_3$.

Table 2
Summary of results from regression analysis for dependent variables, log k, using Abraham's equation 1

Stationary phase		r	s	a	b	l	Correlation coefficent (R^2)	Std. Error of estimate
Pr(tfc)$_3$		−0.20	0.93	1.43	0.69	0.46	0.997	0.05
	Std. Error	0.05	0.04	0.03	0.04	0.004		
	p-level	0.006						
Eu(tfc)$_3$		−0.15	0.92	1.69	0.59	0.44	0.997	0.05
	Std. Error	0.04	0.04	0.03	0.04	0.005		
	p-level	0.002						
Dy(tfc)$_3$		0.025	0.83	1.89	0.62	0.43	0.996	0.03
	Std. Error	0.04	0.04	0.03	0.05	0.005		
	p-level	0.05						
Er(tfc)$_3$		−0.065	0.92	2.17	0.43	0.41	0.9992	0.03
	Std. Error	0.02	0.02	0.02	0.02	0.002		
	p-level	0.003						
Yb(tfc)$_3$		0.024	0.88	2.35	0.31	0.40	0.9992	0.1
	Std. Error	0.02	0.02	0.02	0.02	0.003		
	p-level	0.3						

Values obtained for $n = 57$ solutes (only the numerical values of the probability level $p > 0.0001$ are presented).

stationary phases. The samples of the stationary phases used {i.e. the tris[3-(trifluoromethylhydroxymethylene)camphorato] derivatives of lanthanides dissolved in poly(dimethylsiloxane)} were thermostated for 72 h at 120°C under helium in order to simulate the ageing process. The FTIR spectra, presented in Fig. 3, contain no substantial absorption bands representing the stretch vibrations of the –O–H groups in the region between 3000 and 4000 cm^{-1}.

The value of the system constant a increased when the lanthanide ion radius was reduced. Simultaneously the value of the b coefficient decreased when the lanthanide ion radius was reduced. These trends observed in the system constants a and b could be related to changes in the complexation ability of lanthanide ions in the chelates studied, and in particular to their Lewis acidity. The lanthanide contraction (i.e. the decrease in ionic radii with increasing atomic number) gives rise to higher

Table 3
Summary of results from regression analysis for dependent variables, log k, using the simplified Abraham's equation 1

Stationary phase		s	a	b	l	Correlation coefficent (R^2)	Std. Error of estimate
Pr(tfc)$_3$		0.74	1.34	0.82	0.46	0.995	0.04
	Std. Error	0.03	0.03	0.04	0.005		
Eu(tfc)$_3$		0.796	1.62	0.69	0.44	0.996	0.04
	Std. Error	0.03	0.03	0.04	0.005		
Dy(tfc)$_3$		0.85	1.89	0.60	0.43	0.996	0.04
	Std. Error	0.02	0.03	0.04	0.005		
Er(tfc)$_3$		0.86	2.14	0.47	0.41	0.999	0.02
	Std. Error	0.02	0.02	0.02	0.003		
Yb(tfc)$_3$		0.90	2.36	0.29	0.40	0.9995	0.02
	Std. Error	0.01	0.02	0.02	0.003		

Values obtained without considering the independent variable R_2 for $n = 57$ solutes. (All calculated values of the probability level are lower than 0.0001)
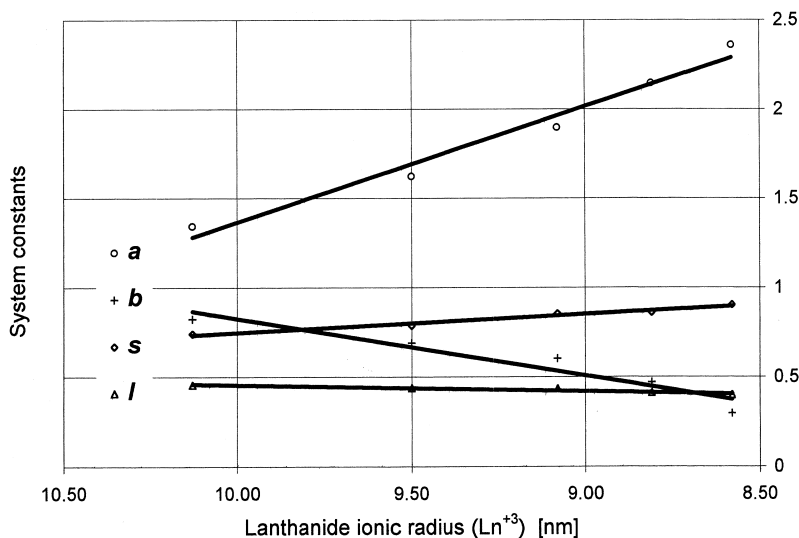
Fig. 1. The values of the system constants *s*, *a*, *b* and *l* determined for the complexing stationary phases at 120°C vs. the lanthanide ionic radii.

electron density and consequently to 'more hard' acids, in agreement with Pearsons's principle of hard and soft acids and bases (HSAB) [19]. With decreasing ionic radii, the lanthanide chelates change from 'more soft' to 'more hard' acids according to Pearson's principle of HSAB.

The stationary phases studied and the 'H-10' acidic phase proposed recently by Poole and Ab-

raham [20] present outstanding examples of the system constants *a* and *b* which characterise GC stationary phases having hydrogen-bond donor and acceptor capacities.

4. Conclusions

The study of complexing stationary phases indicates the possibility of extending the applicability of the solvation parameter model from hydrogen-bonding interactions to more general coordination interactions between Lewis acid and bases in condensed phases.

The lanthanide chelates used in complexing the GC stationary phases studied are 'hard acids' and interact primarily with 'hard bases' e.g. aliphatic alcohols, and to a lesser extent with the 'more soft bases', e.g. carbonyl compounds, aliphatic ethers, and very weakly with nitro and cyano compounds, aromatic and olefinic solutes.

In the system studied the alcohol solutes contribute significantly to the numerical values of the system constants *a* and *b*; in both cases interacting as Lewis bases with the lanthanide chelates. The numerical value of the constant *a* is mainly determined by the $\alpha \, \Sigma \alpha_2^H$ values of alcohols, and the value of

$$Ln(tfc)_3 + \quad :N \quad \rightleftharpoons \quad Ln(tfc)_3 \cdots :N$$
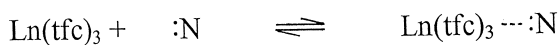
Ln - Pr, Eu, Dy, Er, Yb
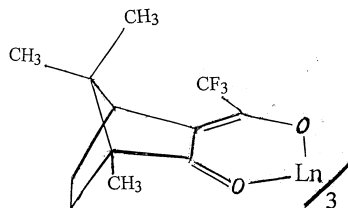
(tfc) - 3-(trifluoromethylhydroxymethylene)camphorate

:N - nucleophilic solutes: alcohols, phenols, ketones, carboxylic acid esters, ethers, etc.

Fig. 2. Reversible complexation of tris[3-(trifluoromethylhydroxymethylene)camphorato] derivatives of lanthanides with nucleophilic solutes.
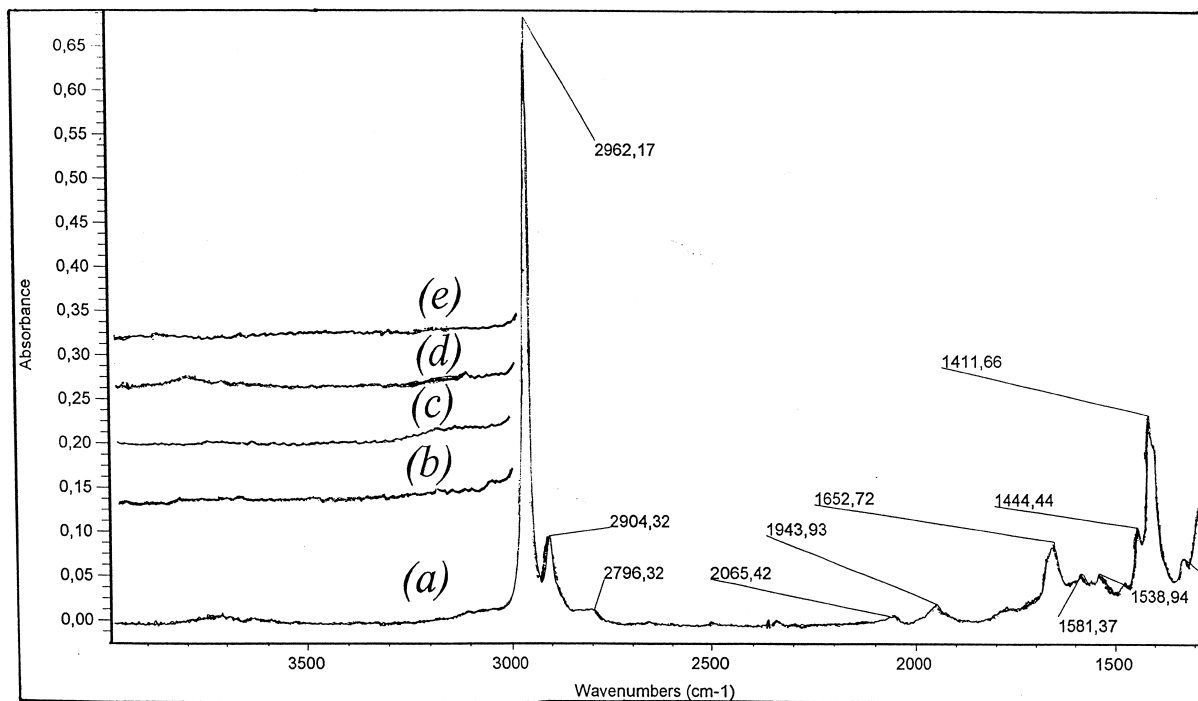
Fig. 3. FTIR spectra of the gas chromatographic stationary phases containing: (a) Pr(tfc)$_3$, (b) Eu(tfc)$_3$, (c) Dy(tfc)$_3$, (d) Er(tfc)$_3$ and (d) Yb(tfc)$_3$.

the descriptor b is determined by the $\Sigma\beta_2^{\mathrm{H}}$ values accessible for alcohols, ketones, alkyl acetates, alkyl ethers and other nucleophilic solutes studied.

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