

TOWARDS THE THERMODYNAMIC TREATMENT OF HUMIC SUBSTANCES IN SOILS

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RESUMO

Este trabalho tem como objetivo apresentar um modelo para abordar a estabilidade termodinâmica de substâncias húmicas no ambiente de interação entre solo, planta e água. Nas últimas décadas, muitas pesquisas foram dedicadas ao estudo das propriedades estruturais e físico-químicas das substâncias húmicas, tendo sido acumulado um grande número de resultados. Para contribuir às interpretações sobre a evolução da matéria orgânica nos solos, este trabalho apresenta uma abordagem baseada numa “diferenciação imaginária de grupo atômico” (CH_2O , CO , CH_2 e C), derivada da composição elementar (C, H, O e N), e da estequiometria das reações, que auxilia nos raciocínios termodinâmicos e procedimentos para balanços de massa ou cálculos de transferências no âmbito dos sistemas solo-planta-água.

Palavras-chave: termodinâmica, substâncias húmicas, evolução da matéria orgânica nos solos.

ABSTRACT

This paper presents a model for understanding the thermodynamic stability of humic substances in soil-plant-water environments. During the past few decades, a great amount of research has been devoted to the structural and physico-chemical properties of humic substances, and very many results have accumulated. As a contribution to interpretations of the evolution of organic matter in soils, this paper presents an approach based on an imaginary atomic-group differentiation (CH_2O - CO - CH_2 - C) derived from the elemental species composition (CHON) and on the stoichiometry of the reactions, without which it would seem impossible to outline any thermodynamic reasoning, and to delineate any mass balance or account for transfers in soil - plant - water systems.

Keywords: thermodynamics, humic substances, organic matter in soils.

1 ELEMENTAL COMPOSITION OF HUMIC SUBSTANCES

KONONOVA (1966) presented a synthesis concerning the soil organic matter which seems essential as a starting point. This important publication is a highly documented historical review which provides precise and abundant information. Mulder (1862, *apud* KONONOVA 1966), distinguished several humic substances of different elemental compositions, variously referred to, respectively, as ulmin and humin, ulmic and humic, or crenic and apocrenic acids. Much earlier,

in 1826, Sprengel coined the terms “humic-coal” and “ulmic-coal”, later called humin and ulmin: an interesting concept which may justify considering kerogens as humic substances, in the broadest sense of the term. Some general tendencies in chemical compositions can be clearly identified in van Krevelen’s diagrams (see TISSOT & WELTE 1978, DURAND 1980): O/C decreases as H/C increases; ulmin and humin are characterized by low O/C and high H/C, while apocrenic and crenic acids are characterized, on the contrary, by low H/C and high O/C ratios. Despite their age, these pioneering works remain absolutely pertinent.

1.1 The so-called CHO fraction and the localization of nitrogen

What is called here the CHO fraction of humic substances is the part which excludes nitrogen. There are various ways (reflecting our ignorance) to approach this concept. The first is to suppose that nitrogen comes entirely from a separate protein phase (microorganisms). The second way is to consider that individual aminoacid residues are chemically slurled into the CHO substrate and have to be considered as a part of the humic molecules. In this case, it is speculatively proposed that the peptide bond: [-CO-HN-] would be a common bridge between cells of macromolecules. Thus, either NH₂ (amines) or COHN (peptides) has to be subtracted from the global humic substance formula to get the CHO fraction, elemental formulae have to be recalculated for 1 N, so that the ratio C/N is simply given by the amount of C remaining in the CHO fraction.

1.2 An imaginary atomic-group differentiation (IAD)

This method was proposed by TARDY *et al.* (2000). The so-called imaginary atomic-group differentiation is an easy way to evaluate the degree of hydration or oxidation of carbon within a given elemental formula (C_mH_nO_p). Then, oxygen is first used to create CH₂O (C^x=0); if some oxygen remains, CO (C^x=+2) is created; on the other hand, if all the oxygen is used and excess hydrogen remains, CH₂ (C^x=-2) is generated. The remaining carbon is written C (C^x=0), so that the structural formula could reflect either the degree of hydration of carbon (Cdry = C/Ct, Cwet = CH₂O/Ct, and Cdry/Cwet = C/CH₂O, where C_i is the total number of carbon atoms counted in the elemental CHO formula). If not enough carbon is present, free H₂O, considered as a sign of hyperhydration, is counted as (CH₂O - C). The advantage of such a procedure will be seen later.

1.3 Oxidation state of carbon within the CHO fraction

After subtracting NH₂, the oxidation state of carbon (C^x) is distributed between - 4, as in CH₄, and + 4, as in CO₂. In all cases, the average degree of oxidation of carbon is given by either C^x+ = 2CO/Ct or C^x- = -2CH₂/Ct.

1.4 Humic substances from Vaughan and Ord (1985)

The elemental analyses given in Table 1, taken from VAUGHAN & ORD (1985), are in good agreement with those of MULDER (1862, apud KONONOVA 1966), including humin and ulmin. They are also roughly concordant with those proposed by KONONOVA (1966), particularly for fulvic acids (FA) and humic acids (HA), but not for humin (HU), which has been regarded as similar to HA.

If fulvic acids are regarded as eventual precursors of humic acids or humins, one may note that the poorly polymerized fraction (FA) is highly hydrated (CH₂O/Ct = 0.636) while HU, which is highly polymerized, is less hydrated (CH₂O/Ct = 0.501). Thus, the ratios CH₂O/Ct and CO/Ct are indexes of de-polymerization. Similarly, C/CH₂O may be considered as an index of polymerization. On the other hand, (1) if the imaginary atomic-group CO (C=O) stands for the hydrophilic functional group COOH, it is also an index of oxidation, and (2) if CH₂ stands for hydrogenated carbon (hydrophobic radical), it is also an index of reduction. Surprisingly, but finally logical, the hydrophilic index (CO/Ct = 0.221 in FA) follows hydration, and the hydrophobic index (CH₂/Ct = 0.114 in HU) tends to accompany carbon dehydration (H-C-OH to C + H₂O) as, for instance, during the transformation of alcoholic groups (de-polymerized) into aromatic groups (more condensed carbon compounds).

TABLE 1 - Humic, fulvic and humin substances from VAUGHAN & ORD (1985).

Name	Formula for IN	C/N	CHO fraction		H/C	O/C	H/O	C ^x
Humic acid	C _{20.790} H _{24.438} O _{12.166} N	20.790	C ₂₀₁₉₀ H ₂₂₄₃₈ O _{12.166}		1.079	0.585	1.844	+0.091
Fulvic acid	C _{29.908} H _{40.053} O _{25.646} N	29.910	C _{29.908} H _{38.050} O _{25.646}		1.272	0.857	1.484	+0.442
Humin	C _{72.431} H _{91.098} O _{36.283} N	72.430	C _{72.431} H _{89.098} O _{36.283}		1.230	0.501	2.456	-0.228
	Imaginary atomic group differentiation		CH ₂ O/Ct	CO/Ct"	CH ₂ /Ct	C/Ct	C/CH ₂ O	
Humic acid	11.219 CH ₂ O + 0.946 CO + 8.624 C		0.540	0.046	0.000	0.415	0.769	
Fulvic acid	19.027 CH ₂ O + 6.618 CO + 4.263 C		0.636	0.221	0.000	0.143	0.224	
Humin	36.283 CH ₂ O + 8.267 CH ₂ + 27.882 C		0.501	0.000	0.114	0.385	0.768	

Furthermore, we introduce new considerations, concerning the two paths of condensation by dehydration, i.e. a loss of H₂O: path n° 1 FA to HA, in oxidized environments with decreasing C/N ratio, and path n°. 2: FA to HU, in reduced environments with increasing C/N ratio.

Consequently, condensation or polymerization, if properly tracked by the ratio C/N, in the series FA to HA it is not necessarily true for the series FA to HU or HA to KE (kerogens). The chemical nature or the tendencies separating FA, HA and HU of VAUGHAN & ORD (1985) are similar to those of SCHNITZER & KHAN (1972), SCHNITZER (1977, 1978), CHEN *et al.* (1978), KERNDORF & SCHNITZER (1979), PRESTON *et al.* (1989), RICE & MACCARTHY (1989a and 1989b, 1991), CHEN & WANG (1992), STEVENSON (1994), and many other works of high quality.

2 SOIL CONDITIONS AND SEDIMENTARY ENVIRONMENTS

Are the chemical compositions of humic substance dependent on soil, sedimentary or diagenetic environmental conditions? The answer is definitely yes.

2.1 Humic substances in soils

In tropical soils, for instance, the ratio FA/HA is inversely related to the length of the dry season. Wet conditions act in favor of FA; dry conditions are favorable to HA (FERRY 1994). The amounts of organic carbon and particularly HU and to a lesser extent HA are directly related to the amounts of kaolinite in humid countries and particularly to smectites in subarid zones (PERRAUD 1971). It is clear that the clay mineral interlayer acts in favor of polymerization and local dehydration in capillary waters. Furthermore, it is well known that brown eutrophic subarid soils (dry and hot) develop large amounts of HA, while Podzols and Histosols, always humid and often cold, exhibit large quantities of FA.

In temperate regions, in Podzols (wet and cold) compared to Chernozems (dry and hot) as well as in common soils (drier) compared to peats (wetter), the imaginary atomic-group differentiation (IAD) denotes the degree of polymerization and clearly, while sometimes surprisingly, reflects environmental conditions. It also seems obvious that populations of so-called HA and FA slightly overlap (Table 2). It is thought that the IAD approach may help define a new classification of humic substances.

TABLE 2 - Humic, fulvic and humin substances in soils and peats, from KONONOVA (1966) and RICE & MACCARTHY (1989a and 1989b, 1991).

<i>Elemental Formula</i>	<i>Ratio C/N</i>	<i>CH₂O/Ct</i>	<i>CO/Ct</i>	<i>CH₂/Ct</i>	<i>C/Ct</i>	<i>C/CH₂O</i>	<i>C^ε</i>
Podzols (KONONOVA, 1966)							
FA: C _{50.472} H _{40.541} O _{31.032} N	50.472	0.382	0.233	0.000	0.386	1.010	+0.466
HA: C _{14.992} H _{13.510} O _{6.198} N	14.992	0.413	0.000	0.070	0.516	1.248	-0.141
Chernozems (KONONOVA, 1966)							
FA: C _{22.251} H _{20.401} O _{18.388} N	22.251	0.413	0.412	0.000	0.174	0.421	+0.825
HA: C _{20.238} H _{11.296} O _{7.674} N	20.238	0.230	0.150	0.000	0.621	2.700	+0.299
Soils (Average of RICE & MACCARTHY, 1989a and 1989b, 1992)							
FA: C _{20.318} H _{26.724} O _{15.775} N	20.318	0.608	0.168	0.000	0.224	0.368	+0.335
HA: C _{17.946} H _{18.528} O _{8.852} N	17.946	0.461	0.033	0.000	0.507	1.100	+0.066
HU: C _{24.774} H _{13.588} O _{10.473} N	24.774	0.234	0.189	0.000	0.577	2.468	+0.378
Peats (Average of RICE & MACCARTHY, 1989a and 1989b, 1992)							
FA: C _{31.603} H _{36.825} O _{16.721} N	31.603	0.529	0.000	0.022	0.520	0.849	-0.043
HA: C _{23.781} H _{24.815} O _{11.068} N	23.781	0.465	0.000	0.014	0.520	1.118	-0.029
HU: C _{41.311} H _{54.827} O _{17.628} N	41.317	0.427	0.000	0.212	0.361	0.845	-0.425

2.2 Water-soluble humic substances

Water-soluble humic substances (HS) have been analyzed in soil solutions (GUIRESSE *et al.* 2000). Three analysis have been selected, concerning the hydrophilic (XAD4) and the hydrophobic fraction (XAD8), accounting respectively for 10% and 90% of the total water-soluble humic substances. It appears that HS, and particularly their hydrophilic part, are also oxidized and hydrated, as confirmed by an excess of water or a deficit of free carbon is shown in the imaginary atomic-group differentiation, while the hydrophobic part is less hydrated and show a small amount of residual free carbon. Furthermore, C^x in the hydrophobic fraction (0.301) is four times smaller than the corresponding value for the hydrophilic counterpart (1.220). The hydrophilic part is much more oxidized, hydrated and de-polymerized, while the hydrophobic one is less so. Considering the total fraction of water-soluble (HS) humic substances, we conclude that they could be considered as *hyper-fulvic* acids.

As a matter of fact, in each sample, the fulvic character of HS (hydration, oxidation, de-polymerization) increases together with the humidity and the coldness of the season. Again their chemical composition clearly reflects soil environment conditions.

2.3 Kerogens of Vandenbroucke *et al.* (1976)

VANDENBROUCKE *et al.* (1976), ALBRECHT *et al.* (1976), TISSOT & WELTE (1978), and DURAND (1980) have published the elemental compositions (accompanied by a calculated temperature of the diagenetic reservoir) of about 210 kerogens. Kerogens fall between soil humin and graphite; their chemical composition clearly reflects diagenetic environmental conditions: the higher the temperature, the greater the dehydration and the higher the aromatic (free C)/aliphatic (CH₂O + CH₂) ratio. Kerogens may be considered as *hyper-humins* (C^x = - 0.638) or *coal-humins* evolving with temperature, even in liquid water, towards complete graphitization.

TABLE 3 – Water-soluble humic substances according to GUIRESSE *et al.* (2000). The elemental composition of the CHO fraction has been calculated by subtracting NH₂ from the global formula written for 1 N.

<i>Imaginary radical differentiation (with deficit of free carbon)</i>	<i>CH₂O/Ct</i>	<i>CO/Ct</i>	<i>C/CH₂O</i>	<i>ClCt</i>	<i>C^x</i>
Hydrophilic: 19.532 CH ₂ O + 8.248 CO -14.260 C	1.446	0.610	- 0.730	- 1.054	+ 1.220
Hydrophobic: 19.997 CH ₂ O + 2.878 CO - 0.970 C	0.758	0.242	0.025	+ 0.023	+ 0.301
Hydrosoluble: 19.951 CH ₂ O+ 3.924CO -1.909 C	0.908	0.178	- 0.095	- 0.087	+ 0.357

TABLE 4 - Kerogens from VANDENBROUCKE *et al.* (1976)

<i>Imaginary radical differentiation</i>	<i>C/N</i>	<i>CH₂O/Ct</i>	<i>CH₂/Ct</i>	<i>C/Ct</i>	<i>C/CH₂O</i>	<i>C^x</i>
Kerogen (average): 3.752 CH ₂ O + 16.929 CH ₂ + 32.417 C	53.097	0.071	0.319	0.610	8.640	-0.638

TABLE 5 - Linear relationships: Log Y function of X, as a de-polymerization index (inverse of polymerization). Functional groups Y (meq g⁻¹ C) or molecular weight (MW) in HS, HU and KE are estimated as a function of X, based on results (in bold characters), obtained for FA and HA by SCHNITZER (1977) and KERNDORF & SCHNITZER (1979).

Log Y = aX + b	<i>HS</i>	<i>FA</i>	<i>HA</i>	<i>HU</i>	<i>KE</i>
X = (CH ₂ O + CO) / Ct = (CH ₂ O - CH ₂) / Ct =	0.999	0.857	0.586	0.387	- 0.248
Total acidity Log Y = 0.689 X - + 0.422	12.9	10.3	6.7	4.9	1.8
Carboxylic COOH LogY = 1.319 X -0.217	12.6	8.2	3.6	2.0	0.3
Alcoholic OH Log Y = 1.366 X - 0.385	9.5	6.1	2.6	1.4	0.2
Alcoholic/Phenolic Log Y = 1.682 X - 1.141	2.7	2.0	0.7	0.3	0.03
E ₄ /E ₆ Log Y = 1.111 X - 0.030	13.8	9.6	4.8	2.9	0.6
Log MW Log Y = - 4.902 X + 7.897	3.0	3.7	5.0	6.0	9.1

3 AN APPROACH TO A THERMODYNAMIC TREATMENT

Any thermodynamic approach, i.e., a search for the rational conditions of the stability field of involved substances, necessarily requires (1) precise knowledge of the stoichiometry of the reactions based on the elemental composition (with C-H-O-N as the strict minimum composition required) of all individual phases, be they insoluble, poorly soluble or highly soluble; (2) a set of thermodynamic data on relatively simple molecules that can be used to estimate thermodynamic parameters for complex compounds whose elemental composition may vary; (3) a precise inventory of variables affecting the equilibria, such as gas fugacity of O_2 , CO_2 , and H_2O , or simply the activity of the corresponding aqueous species $[O_2]$, $[CO_2]$, and $[H_2O]$; and (4) field measurements to test the consistency of the models and their adequacy with respect to reality. As an encouraging example, we present a rough estimation of molecular weights and relative amounts of some major functional groups delineated in HS, FA, HA, HU, and KE (Table 5).

In this approach, Y designates a physico-chemical property such as: total acidity (meq $g^{-1}C$), carboxylic acidity (COOH, meq $g^{-1}C$), alcoholic acidity (OH, meq $g^{-1}C$) phenolic acidity (OH, meq $g^{-1}C$) and molecular weight (MW, $g^{mol-1}C$). Additional parameters are taken into account: (1) ratio: Alcoholic (OH) / Phenolic (OH) and (2) ratio E_4 / E_6 , detected in ultraviolet spectra, supposed to be dependent on the ratio (1).

X is proposed as an index of depolymerization: $X = (CH_2O + CO) / C_t = (CH_2O - CH_2) / C_t$, calculated from the imaginary radical differentiation (Tables 1 to 4).

The data set with averages and ranges (minima-maxima) of composition for each element, among other things, presented by SCHNITZER & KHAN (1972), SCHNITZER (1977, 1978), CHEN *et al.* (1978), KERNDORF & SCHNITZER (1979), though interesting for rough differentiation of the families of compounds, is useless for the identification of the degree of depolymerization of individual samples. However, averages for Fulvic Acids (FA) and Humic Acids (HA) are conserved to calculate the parameters a and b of each of the linear functions: $\log Y = ax + b$, so that any physico-chemical property ($\log Y$) is proportional to the degree of depolymerisation (X) for all the humic substance molecules: HS, FA (measured), HA (measured), HU and KE (estimated).

This degree of polymerization (X), based on average properties (y) of humic substances such as HS, HU and KE, may be expressed as a linear relationship: $\log Y = aX + b$, in which the coefficients a and b are determined for each property (total acidity, carboxylic COOH, alcoholic OH, alcoholic/phenolic OH, and MW).

4 CONCLUSIONS

The data in table 5 confirm the validity of the proposed model. When the degree of polymerization increases (i.e. the degree of depolymerization decreases) regularly from HS to KE, the relative contributions of (1) carboxylic radicals (COOH) decreases, (2) both phenolic and alcoholic radicals decrease but also (3) the ratio Alcoholic (OH) / Phenolic (OH) decreases, all in full concordance with what is observed. Consequently, the more hydrated and oxidized, the more depolymerized the molecule. Conversely, the less hydrated and the more reduced, the more polymerized the molecule.

This offers encouragement that the thermodynamic properties and stability of humic substances may be delineated as a function of polymerization indexes. It is suggested that functional groups, as well as the large variety of chemical radicals or sites, are balanced in a kind of intra-molecular equilibrium reflecting environmental conditions. These considerations, though abstract, may be helpful, however, to solve the arduous problem of estimating thermodynamic properties of humic substances, approached by SCHAUL *et al.* (1997) and TARDY *et al.* (1997), among others.

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