

Dielectric Spectroscopy of Aqueous Solutions of Fulvic Acids

Francisco J. Gonzalez-Vila¹, Udo Kaatze², Harro Lentz³,
Francisco Martin¹ and Reinhard Pottel²

¹ Instituto de Recursos Naturales y Agrobiologica, C.S.I.C., Apartado 1052,
E-41080 Sevilla, Spain

² Drittes Physikalisches Institut, Universität Göttingen, Bürgerstrasse 42-44, D-3400
Göttingen, F.R. Germany

³ Fachbereich 8, Universität-Gesamthochschule Siegen, Postfach 101240, D-5900
Siegen, F.R. Germany

Abstract

The complex dielectric spectrum of aqueous solutions (10% w/w) of fulvic and polymaleic acids has been measured at various frequencies between 1 MHz and 40 GHz. Similar to pure water a dispersion/dielectric loss region emerges in the range above 1 GHz. The measured spectra have been analytically represented by the empirical Cole-Cole relaxation spectral function to yield values for the extrapolated high- and low-frequency permittivity, the principal dielectric relaxation time, the relaxation time distribution parameter and the specific electric d.c. conductivity. In correspondence with aqueous solutions of synthetic organic molecules, the low-frequency permittivity of the fulvic acid/water mixtures is reduced, and the principal dielectric relaxation time is enhanced with respect to the pure water value. As with solutions of polyacrylic acid no solute contributions to the real part of the dielectric spectrum are found.

Introduction

As an important component of natural waters, humic substances play a significant role in geochemical and ecological processes. These acids act as complexing agents and, by this means, mobilize metal ions and organic pollutants in an aquatic environment [1,2]. Though some information exists on the physico-chemical and structural characteristics of humic substances in solution [3], many physical properties of these systems are still unclear. An open problem is the tertiary structure of humic substances in water. Other than with aqueous solutions of synthetic polymers, micellar or membrane-like aggregates have been recently proposed for the humic acid/water mixtures [4].

Aiming at information on specific solute-solvent interactions which might be associated with the tertiary structure of humic substances in water, we performed a dielectric relaxation study on aqueous solutions of fulvic acids (FA) and polymaleic acid (PA). The latter, a recently characterized [5-7] polycarboxylic acid formed by hydrolysis of base-catalyzed homopolymerized maleic anhydride, is assumed to be an interesting model of FA [8,9]. The microwave dielectric spectrum of aqueous solutions clearly reflects hydration properties of the solutes [10-18]. The evaluation of the measured spectra in terms of molecular models, however, is not unambiguously possible. We therefore restrict ourselves to a comparative discussion of the present data and of results for aqueous solutions of synthetic polymers, as well as of low-molecular solutes.

Materials and Methods

Samples

Two fulvic acids were isolated from the Bh horizons of Humic Haplorthod (podzol) located in Vollbüttel, West Germany (FA-PV) and Armadale, Canada (FA-PC), respectively. A third fulvic acid was isolated from water of a lake in Huelva, Spain (FA-T). This lake is surrounded by peatland. Details of the extraction and purification procedures have been published elsewhere [19-21].

The polymaleic acid (PMA-I) was prepared according to Braun and Pomakis [22] and subsequently acidified with a strong cation exchange resin in the protonated form. A purified PMA sample (free of pyridine and other aromatics) was obtained by redissolution of freeze-dried PMA-I in acetone and coagulation by addition of chloroform in excess. The coagulate was removed by filtration and dried at room temperature afterwards (PMA-II). The results of an elementary composition and a functional group analysis of the samples is presented in Table 1. C and H were determined by dry combustion, N by the automated Dumas method, and O was estimated from the difference. The total acidity was determined by the barium hydroxide method and the carboxyl groups by calcium acetate exchange, as previously described by Schnitzer and Khan [23]. Phenolic hydroxyls were considered to be equal to the difference between the total acidity and the carboxyl groups.

Table 1 Elementary composition (% w/w) and concentration of oxygen-containing functional groups (meq/g) of the humic acid samples. All values are calculated on a dry, ash-free humic acid.

Sample	C	H	N	O + S	Total Acidity	COOH	Phen. OH
FA- PV	46.2	3.4	0.8	49.6	11.2	8.8	2.4
FA- PC	50.9	3.3	0.7	45.1	11.5	9.1	2.4
FA- T	43.4	4.2	1.3	48.9	12.7	7.6	5.1
PMA	45.9	4.4	0.6	49.1	12.0	8.8	3.2

Table 2 Concentration data (c_s , weight of solute per volume of solution; s , weight per cent), density ρ , molarity c_w , of solvent, volume fraction v of solute, and pH value of the humic acid solutions at 25°C.

Solute	c_s g/cm ³ ± 0.0002	s % w/w. ± 0.02	ρ g/cm ³ ± 0.004	c_w mol/l ± 2	v ± 0.004	pH ± 0.05
FA-PV	0.0990	9.59	1.033	51.8	0.065	1.80
FA-PC	<0.015	<1.5	≈1.002	>54.8	≈0.008	-
FA-T	0.0954	9.16	1.041	52.5	0.052	2.25
PMA-I	0.1000	9.70	1.031	51.7	0.066	2.75
PMA-II	0.1000	9.77	1.023	51.2	0.074	-

Aqueous solutions with a concentration of about 10 % w/w have been prepared of FA-PV, FA-T, PMA-I, and PMA-II by adding bidistilled water to a preweighed amount of the respective fulvic acid. FA-PC was less soluble (< 1.5 % w/w). Concentration data, density, and pH value of the solutions, as well as the volume fraction of solute, are given in Table 2.

Complex Permittivity Measurements

The complex (relative) electric permittivity (ϵ , imaginary unit)

$$\epsilon(v) = \epsilon'(v) - i\epsilon''(v) \quad (1)$$

of the sample liquids has been determined as a function of frequency ν (Fig. 1) by frequency domain measurements [24]. The liquids have been exposed to harmonically alternating, weak electric fields to observe the responding dielectric polarization. Three different methods, which had been successfully applied in various previous studies on aqueous solutions, have been used to cover the frequency range between 1 MHz and 40 GHz.

From 1 to 100 MHz we utilized a sensitive rf-admittance bridge (Boonton 33D/1) to perform at seven fixed frequencies input impedance measurements on a small specimen cell. This cell contains the sample in a short piece of a circular waveguide, which is excited far below its cut-off frequency [25]. Modal analysis of the transition between the coaxial line feeder and the waveguide-below-cut-off section has been performed [26]. It was found that the cell can be represented by a simple equivalent network [26]. For the liquids under consideration ($\epsilon' > 60$) this network simply consists of two capacitors, the capacitances of which have been determined by calibration measurements with the empty cell and with water as reference liquid.

Between 1 MHz and 1 GHz a vector voltmeter (Rohde & Schwarz ZPU) has been additionally used to measure the transmission coefficient of a cell in which the sample is also placed in a waveguide-below-cut-off section [26]. This cell essentially consists of a coaxial line, the inner conductor of which is interrupted for a certain

distance to form a small piece of circular cylindrical waveguide. This waveguide contains the liquid sample between two dielectric windows. This "transmission" cell, in analogy to the "reflection" cell, has been likewise treated by modal analysis [26]. A π -network representation follows thereby. The values of the capacitors of this lumped-element circuit have also been found by calibration measurements.

At frequencies above 1 GHz a travelling-wave method has been applied. The wave transmitted through a liquid-filled circular cylindrical waveguide was balanced against a reference wave by a doublebeam interferometer technique [27-29]. Five small-band microwave bridges, consisting of standard coaxial line components or waveguide devices, were used to cover the frequency range.

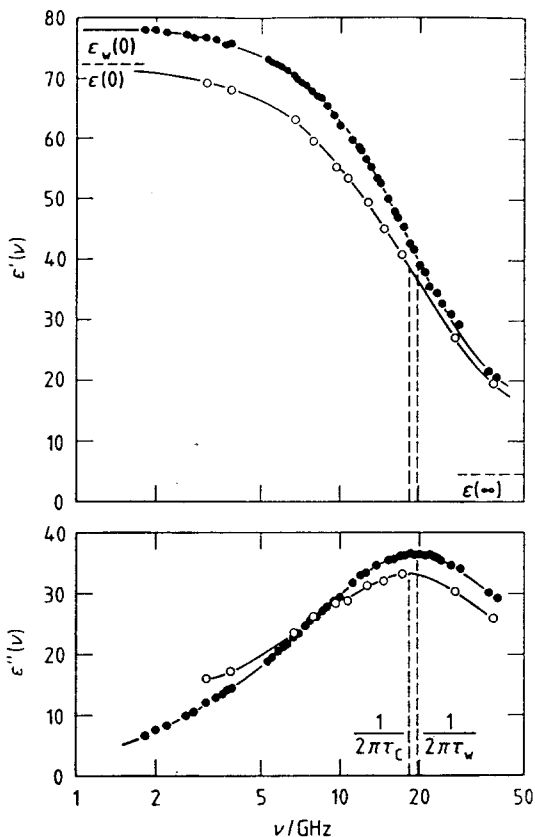


Figure 1 Real part $\epsilon'(\nu)$ and negative imaginary part $\epsilon''(\nu)$ of the complex (electric) permittivity plotted versus frequency ν for pure water (\bullet [30]) and for the aqueous PMA-I solution (\circ) at 25°C. The curves represent the relaxation spectral functions eq. (3) and eq. (4), respectively, with the parameter values given in Table 3.

Experimental Errors

The experimental error in the complex permittivity data depends on the frequency of measurement and also on the applied method. Above 200 MHz it may be globally characterized by an uncertainty of $\pm 2\%$ for both ϵ' and ϵ'' . Due to the high d.c. conductivity of the samples, measurements below 200 MHz were substantially affected by electrode polarization effects. We therefore restrict the following discussion to the microwave part ($\nu > 200$ MHz) of the dielectric spectra. Errors in the determination of the frequency ν were negligibly small. The temperature was controlled to within ± 0.1 K during the measurements.

Results and Treatment of Data

In Fig. 1 the real part ϵ' and the negative imaginary part ϵ'' of the complex permittivity are displayed as a function of frequency ν for the PMA-I solution at 25°C. Also shown for comparison is the complex dielectric spectrum of pure water at the same temperature. The curves for the mixture resemble the corresponding curves for the solvent. Some differences, however, emerge, which are characteristic for all measured spectra of humic acid solutions. The extrapolated static permittivity $\epsilon(0)$ of each solution is smaller than that of water, $\epsilon_w(0)$. We shall comment on this effect below. The frequency $\nu_c = (2\pi\tau_c)^{-1}$ at which $\epsilon''(\nu)$ adopts its relative maximum ($d\epsilon''(\nu_c)/d\nu = 0$, $d^2\epsilon''(\nu_c)/d\nu^2 < 0$) is different from that of water, $(2\pi\tau_w)^{-1}$. The dispersion region ($d\epsilon'(\nu)/d\nu < 0$) of the mixture extends over a slightly broader frequency band. Finally, at low frequencies ($\nu < 7$ GHz) the $\epsilon''(\nu)$ values of the solution exceed those of the pure solvent. This finding is an indication that the total loss is a sum

$$\epsilon''(\nu) = \epsilon_d''(\nu) + \sigma/(\epsilon_0\omega) \quad (2)$$

of a contribution $\epsilon_d''(\nu)$ originating in dielectric relaxation processes and of another one resulting from the specific electric conductivity σ . In eq. (2), ϵ_0 denotes the electrical field constant and $\omega = 2\pi\nu$ the angular frequency.

Within the limits of experimental error, the microwave dielectric spectrum of pure water is characterized by a relaxation with one discrete relaxation time τ_w [30,31]. It can thus be represented by the Debye-type relaxation function [32] given by

$$\epsilon(\nu) = \epsilon_w(\infty) + [\epsilon_w(0) - \epsilon_w(\infty)] / (1 + i\omega\tau_w) \quad (3)$$

The values of the parameters of eq. (3) at 25°C are given in Table 3.

Empirically, the dielectric spectra of the solutions can be described by the Cole-Cole relaxation spectral function [33]. The function

$$\epsilon(\nu) = \epsilon(\infty) + [\epsilon(0) - \epsilon(\infty)] / [1 + (i\omega\tau_c)^{(1-h)}] - i\sigma/\epsilon_0\omega \quad (4)$$

is therefore appropriate to analytically represent the frequency-dependent complex permittivity data. In this relation parameter h is a measure of the width of the underlying relaxation time distribution. The values of the parameters $\epsilon(\infty)$, $\epsilon(0)$, τ_c , h , and σ have been found by fitting eq. (4) to the measured spectra using a nonlinear least-squares regression analysis. The results obtained by this fitting procedure are also presented in Table 3. Also included in this table for comparison are data for a nearly 1-molar aqueous solution of polyacrylic acid, PAA.

The PMA-II solution has been measured below 1 GHz only. In correspondence with the other samples no dispersion/dielectric loss region has been found in this frequency range. This finding is in accordance with previous results for aqueous solutions of PAA [34]. In contrast, solutions of salts of polyacrylic acid, like NaPA, at frequencies below about 1 GHz, clearly exhibit solute contributions in their dielectric spectra [34].

The solution of FA-PC has been measured at one frequency only ($\nu = 6.0$ GHz). For this reason parameters $\epsilon(\infty)$ and h have been fixed at reasonable values in the above fitting procedure. By that means estimates for the extrapolated static permittivity $\epsilon(0)$ and the principal dielectric relaxation time τ_c have been obtained.

Table 3 Parameters of the relaxation spectral functions for water (eq. 3) and for aqueous solutions (eq. 4) of fulvic acids, polymaleic acid, and polyacrylic acid at 25°C. Values marked by an asterisk (*) have been fixed during the fitting procedure.

Sample	s % w/w	$\epsilon(\infty)$	$\epsilon(0)$	τ ps	h	σ S/m
Water [29]	-	5.16±0.08	78.36±0.05	8.27±0.02	-	-
FA-PV	9.59	5.0±0.5	72.3±0.5	8.50±0.05	0.03±0.03	1.25±0
FA-PC	<1.5	4.7*	76.9±0.5	8.34±0.1	0*	0.5±0
FA-T	9.16	4.5±0.5	72.1±0.5	8.41±0.15	0.05±0.05	2.52±0
PMA-I	9.70	4.5±0.5	72.5±0.5	8.64±0.15	0.05±0.05	0.80±0
PMA-II	9.77	-	70.0±1	-	-	0.78±0
PAA [33]	6.95	5.5±0.5	73.0±0.5	8.69±0.15	0.02±0.02	0.17±0

Discussion

To look for potential special properties of the fulvic acid/water mixtures it is useful to compare the parameter values (Table 3) of the relaxation spectral function (eq. 4) with data for aqueous solutions of other organic solutes. For this purpose, the extrapolated static permittivity values of the fulvic acid solutions are plotted in Fig. 2 as a function of volume fraction ν of the solute. Also presented in that diagram are data for aqueous solutions of non-dipolar small organic molecules, of PAA, and of other synthetic polymers. The latter solutes are dipolar themselves. The contributions of the solvents to the static permittivity are therefore used here as $\epsilon(0)$ value. This

value should compare with the static permittivity of aqueous solutions of non-dipolar solutes.

As a result of the increasing dilution of the dipolar solvent by solute molecules there is a general tendency in the $\epsilon(0)$ values to decrease with v . The static permittivity data of the fulvic acid and PAA solutions nicely fit into this trend (Fig. 2). There are no indications of special effects in the fulvic acid solutions. Such effects could be due to a particular shape of the solute particles or to uncommon hydration properties.

The principal dielectric relaxation time τ_c of the fulvic acid solutions is enhanced with respect to the pure water value τ_w . Such an enhancement, however, is a common feature of aqueous solutions of organic solutes [10-15, 17, 18, 35-38]. The shift $\tau_c - \tau_w$ in the dielectric relaxation time of the present solutions has reasonable values. With the fulvic acid/water mixtures (10% w/w) it is even somewhat smaller than with the less concentrated PAA solution (7% w/w). We therefore conclude that the fulvic acids do not seem to induce unusual hydration water properties.

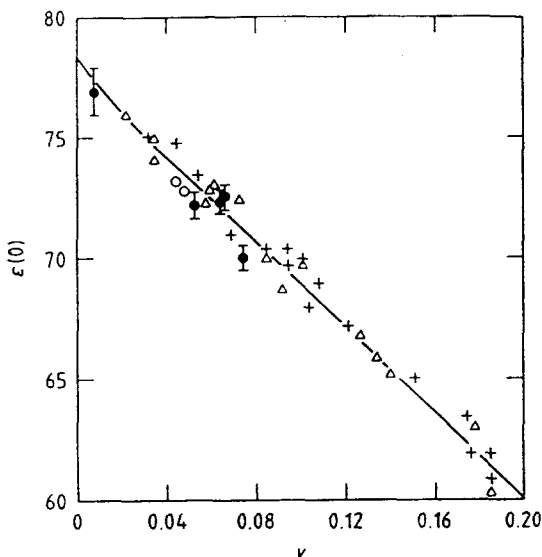


Figure 2 Plot of the extrapolated static permittivity $\epsilon(0)$ as a function of the volume fraction v of solute for aqueous solutions of fulvic acids (+), polyacrylic acid (o) [34], nonionic synthetic polymers (Δ) [10,12,18] and small non-dipolar organic molecules (+) [35,39] at 25°C. With the solutions of dipolar synthetic polymers (Δ) only the solvent contribution to $\epsilon(0)$ is considered here. The curve is hand drawn to indicate the trend in the data.

The specific electric d.c. conductivity σ of the fulvic acid solutions is higher than expected from the pH values. This enhanced conductivity is most probably due to the presence of small amounts of inorganic salts which, possibly, were not removed by the sample purification and preparation procedure.

References

1. Oliver, B.G., E.M. Thurman and R.L. Malcolm. *Geochim. Cosmochim. Acta* **47**:2031 (1983).
2. Aiken, G.R., D.M. McKnight, R.L. Wershaw and P. McCarthy. *Humic Substances in Soil, Sediment and Water. Geochemistry, Isolation and Characterization* (New York: John Wiley, 1985).
3. Ziechmann, W. *Huminstoffe* (Weinheim: Verlag Chemie, 1980).
4. Wershaw, R.L. *J. Contaminant Hydrol.* **1**:29 (1986).
5. Bracewell, J.M., G.W. Robertson and D.J. Welch. *J. Anal. Appl. Pyrolysis* **2**:239 (1980).
6. Spitteller, M. and M. Schnitzer. *J. Soil Sci.* **34**:525 (1983).
7. Martin, F., F.J. Gonzalez-Vila, and H.-D. Lüdemann. *Z. Naturforsch.* **39c**:244 (1984).
8. Anderson, H.A. and J.D. Russell. *Nature* **260**:597 (1976).
9. Young, S.D., B.W. Bache, D. Welch, and H.A. Anderson. *J. Soil Sci.* **11**:597 (1981).
10. Kaatze, U. *Advan. Mol. Relaxation Processes* **7**:71(1975).
11. Kaatze, U. and R. Pottel. *Colloques internationaux du C.N.R.S.* **246**:111(1976).
12. Kaatze, U., O. Göttmann, R. Podbielski, R. Pottel, and U. Terveer. *J. Phys. Chem.* **82**:112 (1978).
13. Pottel, R., U. Kaatze, and St. Müller. *Ber. Bunsenges. Phys. Chem.* **82**:1086 (1978).
14. Kaatze, U. *Progr. Colloid Polymer Sci.* **65**:214 (1978).
15. Pottel, R., K.-D. Göpel, R. Henze, U. Kaatze, and V. Uhlendorf. *Biophys. Chem.* **19**:233 (1984).
16. Kaatze, U., A. Dittrich, K.-D. Göpel, and R. Pottel. *Chem. Phys. Lipids* **35**:279 (1984).
17. Kaatze, U. and R. Pottel. *J. Mol. Liquids* **30**:115 (1985).
18. Kaatze, U., O. Göttmann, R. Podbielski, and R. Pottel. *J. Mol. Liquids* **37**:127 (1988).
19. Schnitzer, M. and S.I.M. Skinner. *Soil Sci.* **105**:392 (1968).
20. Martin, F. and F.J. Gonzalez-Vila. *Z. Pflanzenernähr. Bodenk.* **146**:409 (1983).
21. Martin, F. and F.J. Gonzalez-Vila. *Chem. Geol.* **67**:353 (1988).
22. Braun, D. and J. Pomakis. *Makromol. Chem.* **175**:1411 (1974).
23. Schnitzer, M. and S.V. Khan. *Humic Substances in the Environment* (New York: Marcel Dekker, 1972).
24. Kaatze, U. and K. Giese. *J. Phys. E: Sci. Instrum.* **13**:133 (1980).

25. Kaatze, U. and D. Woermann. *Ber. Bunsenges. Phys. Chem.* **86**:81 (1982).
26. Görmann, O. and A. Dittrich. *J. Phys. E: Sci. Instrum.* **17**:279 (1984).
27. Pottel, R. *Ber. Bunsenges. Phys. Chem.* **69**:363 (1965).
28. Kaatze, U. *Mikrowellen Magazin* **6**:46 (1980).
29. Kaatze, U. and K. Giese. *J. Mol. Liquids* **36**:15 (1987).
30. Kaatze, U. and V. Uhlendorf. *Z. Phys. Chem. N. F.* **126**:151 (1981).
31. Kaatze, U. *Chem. Phys. Lett.* **132**:291 (1986).
32. Debye, P. *Polare Molekeln* (Leipzig: Hirzel, 1929).
33. Cole, K.S. and R.H. Cole. *J. Chem. Phys.* **9**: 341 (1941).
34. Uhlendorf, V. *Messungen der dielektrischen Relaxation wässriger Polyelektrolyt-Lösungen zwischen 5 MHz und 40 GHz*, Diplom-Thesis (Göttingen: University, 1978).
35. Pottel, R. and U. Kaatze. *Ber. Bunsenges. Phys. Chem.* **73**:437 (1969).
36. Kaatze, U. and W.-Y. Wen. *J. Phys. Chem.* **82**:109 (1978).
37. Kaatze, U., H. Gerke and R. Pottel. *J. Phys. Chem.* **90**: 5464 (1986).
38. Kaatze, U., R. Pottel and P. Schmidt. *J. Phys. Chem.* **92**:3669 (1988).
39. Akerlöf, G. and A.O. Short. *J. Am. Chem. Soc.* **58**:1241 (1936).