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PHYSICAL CHEMISTRY OF SOLUTIONS

Intermolecular Interactions in Aqueous Solutions of Gallic Acid at 296–306 K According to Spectrofluorimetry and Densimetry Data

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Abstract—Features of intermolecular interactions in aqueous solutions of gallic acid (GA) are studied by means of densimetry and fluorescence spectroscopy (intrinsic fluorescence, 2D spectra, and excitation/emission matrix fluorescence spectra, 3D) at 296.15, 301.15, and 306.15 K in the concentration range of 5.88×10^{-4}–5.88×10^{-2} mol L^{-1}. It is shown by analyzing the concentration and temperature dependences of the apparent molar volumes and fluorescence parameters of GA that the equilibrium between nonassociated and associated species in the solution and the hydration of these species undergo changes.

Keywords: gallic acid, densimetry, apparent molar volume, fluorescence spectroscopy, three-dimensional excitation/emission matrix fluorescence spectroscopy, 3D spectra.

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INTRODUCTION

Gallic acid (3,4,5-trihydroxybenzoic acid, GA) and its derivatives are biologically active [1–3]. They belong to the family of easily hydrolyzable natural polyphenolic compounds. The field of application of natural polyphenols is quite wide: they are mainly used as antimicrobial, antibacterial, and antioxidant agents [4, 5]. The preferential intermolecular interactions in aqueous solutions of polyphenolic compounds affect their reactivity, which plays a crucial role in regulating the interactions between GA and biological compounds. Data on preferential intermolecular interactions can be obtained by means of spectroscopy (electronic absorption and fluorescence) and conventional study methods (e.g., viscometry, densimetry) [6–8].

To thoroughly study the interactions between GA and biomolecules (in particular, proteins), we need a comprehensive understanding how GA behaves in aqueous solutions, depending on different physicochemical parameters of the solution (e.g., solvent type, presence of a co-solvent, pH, temperature, concentration of a compound). Below, we present the results from the studies on the effect of temperature and concentration on intermolecular interactions in aqueous GA solutions by means of fluorescence spectroscopy and densimetry.

EXPERIMENTAL

Materials and experimental conditions. GA was purchased from Sigma Aldrich (Germany). All GA solutions were prepared using bidistilled water. GA concentration was varied from 5.88×10^{-4} to 5.88×10^{-2} mol L^{-1}. The experiments were performed at 296.15, 301.15, and 306.15 K. Cell temperature was held constant with circulating water in a LAUDA Alpha thermostat connected to a spectrophotometer (Germany).

Densimetric measurements were performed on an Anton Parr DMA 4500 instrument (Austria). The measurement error was $\pm 5 \times 10^{-5}$ g cm^3 for density and ± 0.03 K for temperature. Temperature stability was maintained using a built-in thermostat. Partial molar volumes of GA were calculated using data on solution density according to equation [9]:

$$_{\phi}V = \frac{(\rho_0 - \rho)}{mp\rho_0} + \frac{M}{\rho}, \quad (1)$$

where $_{\phi}V$ is the apparent molar volume of GA, ρ_0 is solvent density, ρ is solution density, m is molality of the solution, and M is the molecular weight of GA.

Fluorescence measurements were performed on a Varian Cary Eclipse spectrophotometer (Australia). 2D spectra of GA solutions were recorded in the range of λ= 280–400 nm at excitation wavelength λ_{ex}= 270 nm, determined from the electronic absorption spectra of GA recorded on a Specord 50 spectrophotometer (Germany). Excitation-emission matrix fluorescence spectra (3D spectra) were recorded in the following mode: excitation range λ_{ex} = 200–500 nm; emission range λ_{em} = 200–500 nm; $\Delta\lambda_{incr}$= 5 nm. A total of sixty scans were obtained. The inlet and outlet

Spectral parameters of our 2D fluorescence spectra of GA at 296.15 and 306.15 K (F, rel. units)

c_{GA}, mol L^{-1}	$T = 296.15$ K				$T = 306.15$ K			
	F	ΔF	λ, nm	Δλ, nm	F	ΔF	λ, nm	Δλ, nm
5.88×10^{-4}	264.6	0	355.0	–	322.1	0	352.0	–
7.35×10^{-4}	208.7	55.9	355.0	0	294.9	27.2	355.0	3.0
1.47×10^{-3}	113.6	151.0	355.0	0	231.5	90.6	357.0	5.0
2.94×10^{-3}	74.2	190.4	358.0	3.0	186.6	135.5	359.0	7.0
5.88×10^{-3}	49.4	215.2	371.0	16.00	157.1	165.0	365.0	13.0
4.50×10^{-2}	34.1	230.5	385.0	30.00	103.0	219.1	375.0	23.0
5.88×10^{-2}	31.8	232.8	391.0	36.00	54.2	267.9	382.0	30.0

slits were 10 nm wide. Quartz cells with $l = 1$ cm were used for measurements.

The reduced diagrams were plotted and analyzed using the ORIGIN 8.0 software.

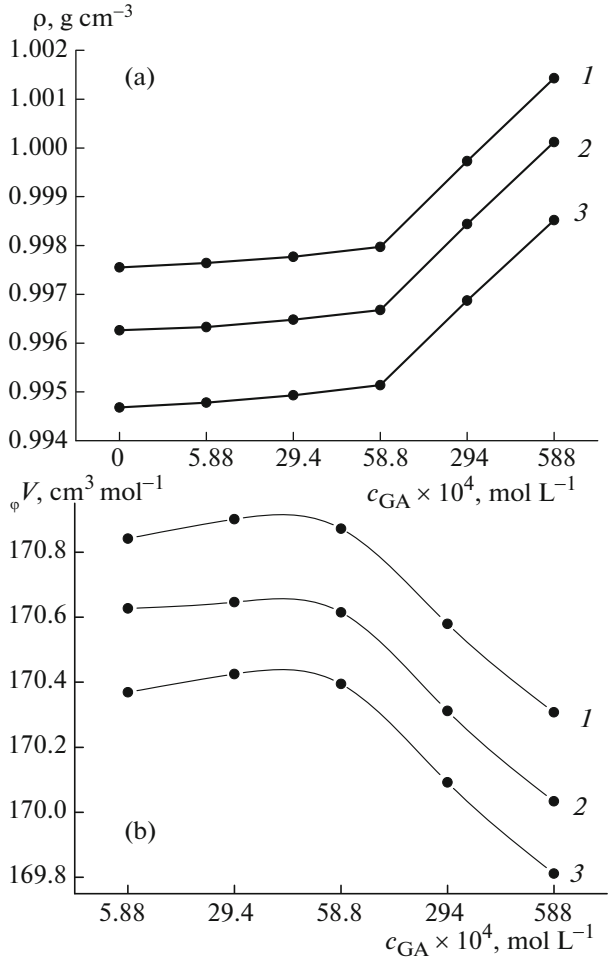

Fig. 1. Concentration dependences of (a) the densities of GA solutions and (b) partial molar volumes of GA; $c_{GA} = 5.88 \times 10^{-4}$–$5.88 \times 10^{-2}$ mol L^{-1}; T = (*1*) 296.15, (*2*) 301.15, and (*3*) 306.15 K.

RESULTS AND DISCUSSION

Figure 1a shows the densities of GA solutions in the concentration range of 5.88×10^{-4}–5.88×10^{-2} mol L^{-1} at 296.15, 301.15, and 306.15 K; Fig. 1b, the dependences of the apparent molar volumes of GA ($_{\phi}V$) calculated using Eq. (1). These dependences show that the density of solutions remains virtually unchanged at low GA concentrations, while it changes very abruptly at high concentrations due to the formation of GA associates. The density of solutions falls as the temperature rises, but the shape of the curves remains the same. An abrupt decrease in $_{\phi}V$ is observed at high GA concentrations (~5.88×10^{-2} mol L^{-1}). This shape of the curves can be attributed to the solution containing both associated and nonassociated GA species. The shape of the curves remains the same as the temperature rises, but the $_{\varphi}V$ values generally tend to decrease. These changes in $_{\varphi}V$ can be explained by the associated GA species being hydrated to a lesser extent than the nonassociated species and the increased temperature causing greater changes in the hydration shells of the associated species than in those of nonassociated species.

Fluorescence studies were performed to investigate the associated and nonassociated GA species in aqueous solutions more thoroughly. Intrinsic fluorescence spectroscopy (2D spectra) and three-dimensional excitation/emission fluorescence spectroscopy (3D spectra) were used. Figure 2 shows the 2D fluorescence spectra of GA as functions of concentration; the table lists the spectral parameters of 2D fluorescence spectra of GA at 296.15 and 306.15 K. Figure 2 shows that fluorescence intensity falls and the maximum of GA emission are simultaneously shifted toward longer wavelengths as GA concentration rises. Spectroscopic parameters are very sensitive to structural changes in a compound caused by such diverse factors as temperature, pH and solvent type. Results from spectroscopic studies (electronic absorption spectra and fluorescence spectra) of GA solutions were reported in [10] showing that either the neutral ($pK = 3.4$) or anionic GA species that formed due dissociation of molecules

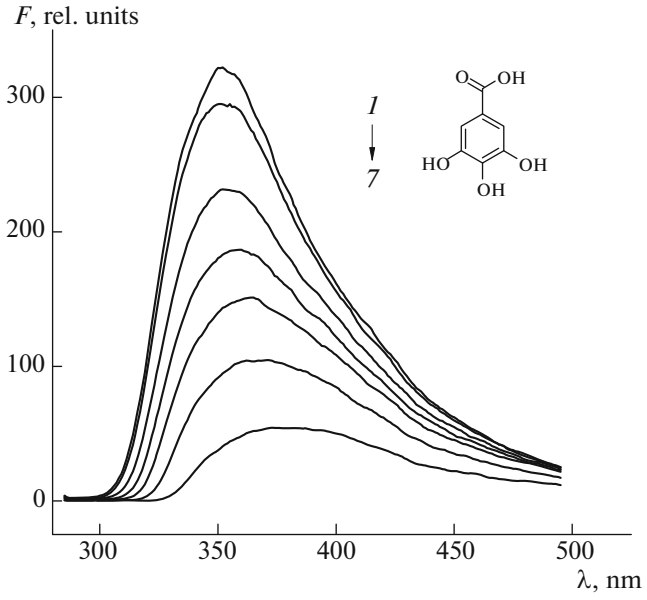

Fig. 2. 2D fluorescence spectra of GA at 306.15 K and different GA concentrations: (*1*) 5.88×10^{-4}, (*2*) 7.32×10^{-4}, (*3*) 1.47×10^{-3}, (*4*) 2.94×10^{-3}, (*5*) 5.88×10^{-3}, (*6*) 4.5×10^{-2}, and (*7*) 5.88×10^{-2} mol L^{-1}.

predominated in the solution, depending on pH variation and solvent type. In the fluorescence spectra of GA in aprotic and nonpolar solvents, the emission maximum is shifted toward shorter wavelengths, indicating the presence of associated GA species: the formation of excimers (excited dimers). Quantum-mechanical calculations for water–GA interactions showed that water molecules form a sphere around the hydrophobic portion of GA without directly contacting the molecule, while forming strongly oriented bonds with the hydrophilic part of dissolved compound [11]. Our studies conducted in an aqueous medium showed that the intensity of GA fluorescence falls abruptly as concentration rises, while remaining virtually unchanged at high concentrations. The maximum of GA fluorescence is also shifted toward longer wavelengths (see table). These phenomena can be attributed to the formation of GA–GA (molecule association) and GA–H_2O (molecule hydration) hydrogen bonds. The intensity of fluorescence increases with temperature, while the shift in the emission maximum becomes less pronounced.

This change in the fluorescence parameters of GA can be explained both by the change in the hydration state of GA and the weakening of associated structures in the solution. We also used three-dimensional excitation/emission matrix fluorescence spectroscopy (3D spectra) to study this system. Figures 3a and 3b show the 3D spectra of GA characterized by a single nonresolved peak ($\lambda_{ex}/\lambda_{em}$ = 250/353, F = 585.4 rel. units) that undergoes notable changes as either the concentration or temperature rises (F = 84.1 and 555.5 rel. units, respectively). Increased GA concentration ($\approx 10^{-3}$ mol L^{-1}) results in the signal splitting into two parts: one of these is eliminated as the concentration is further increased ($=10^{-2}$ mol L^{-1}), while the other is shifted toward longer wavelengths (the maximum of the shifted fluorescence signal is not detected in the abovementioned range). The increased temperature mostly affects quantitative spectral parameters rather than qualitative ones.

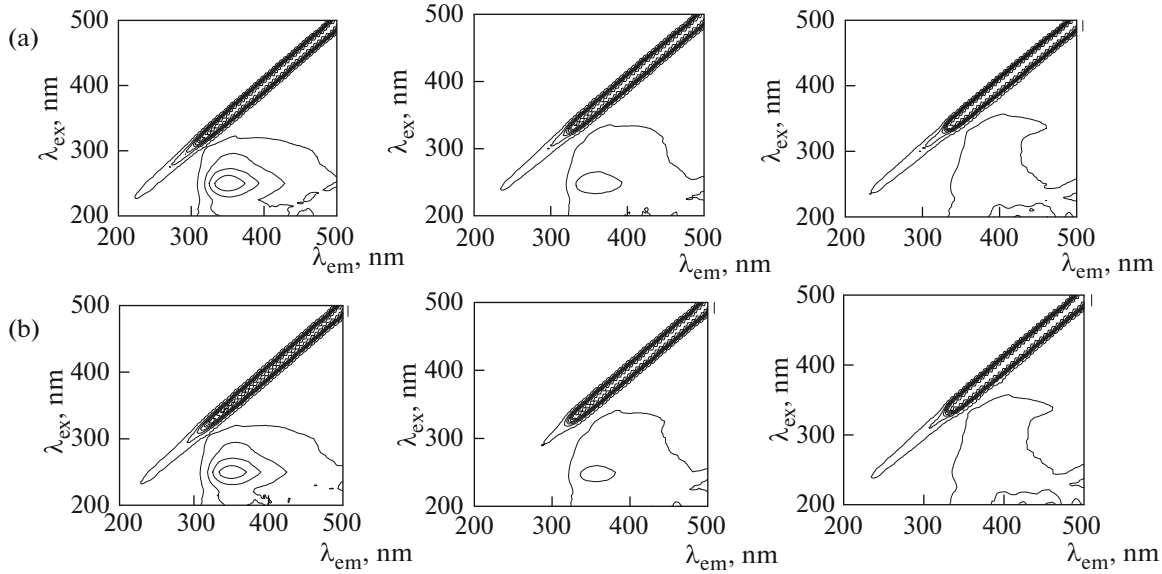

Fig. 3. 3D fluorescence spectra of GA at (a) 296.15 and (b) 306.15 K; GA concentrations are (from left to right): 5.88×10^{-4}, 5.88×10^{-3}, and 5.88×10^{-2} mol L^{-1}.

Our 3D spectra of GA (Fig. 3) also display a Rayleigh scattering peak ($\lambda_{ex}/\lambda_{em}$ = 235/240 nm). The intensity of Rayleigh scattering rises (F = 35.7 to 42.4 rel. units) along with GA concentration, and the signal shifts toward longer wavelengths. At increased temperatures, the intensity of Rayleigh scattering rises (F = 35.7 to 43.2 rel. units) for low GA concentrations (10^{-4} mol L^{-1}) and remains virtually unchanged (F = 42.4 to 41.4 rel. units) at higher GA concentrations (10^{-2} mol L^{-1}). These spectral changes show that the association of GA occurs.

CONCLUSIONS

Our results from physicochemical studies of the features of intermolecular interactions in aqueous solutions of GA have shown that the preferability of competitive interactions of self-association (GA–GA) and the hydration of monomolecular (GA–H_2O) and associated (GA–GA–H_2O) species depend both on concentration and temperature.

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