Solubilities of Gallic Acid and Its Esters in Water

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The solubilities of gallic acid and its esters (methyl gallate, propyl gallate, and octyl gallate) in water were determined in the temperature range (273.15 to 363.15) K by a static analytical method. The concentrations of gallic acid and the esters in saturated solution were analyzed by reverse-phase high-performance liquid chromatography. An "S" type curve was found for the solubilities of gallic acid and octyl gallate in water over the investigated temperature range. An empirical equation was proposed to fit the data for gallic acid and octyl gallate. On the other hand, the data of methyl gallate and propyl gallate were in good agreement with the simplified $\lambda - h$ equation.

Introduction

Gallic acid (3,4,5-trihydroxybenzoic acid) and its esters are industrially important chemicals widely used in the pharmaceutical, food, and pigment industries. Another application extensively implemented for ultra-high-purity gallic acid and its esters is to act as processing chemicals to rinse integrated circuits.[1] Furthermore, they have been proved to have many significant biological activities, such as antioxidant and antivirus abilities.[2]

The importance of these products has pushed forward the development of many processes for the manufacture of gallic acid. Two methods have been reported for the preparation of gallic acid from hydrolyzable tannin-containing materials, such as tara pods, Chinese gall nuts, Chinese gall flowers, sumach leaves, and maple leaves. One is alkaline or acid hydrolysis;[3,4] the other is enzyme hydrolysis.[4,5] For both methods, steps like decolorization with activated carbon and crystallization are employed in the subsequent purification of gallic acid. In fact, only alkaline or acid hydrolysis has been industrially put into application. Gallic acid esters are prepared by the esterification of gallic acid with alcohols.

A process combining crystallization with resin column chromatography has been under development in our laboratory for preparing ultra-high-purity gallic acid and its esters for use in the semiconductor industry. While the solubility information of gallic acid and its esters in water is crucial in the development, insufficient data were available in the literature.

Experimental Section

Chemicals. Gallic acid, methyl gallate, propyl gallate, and octyl gallate (> 99 % purity) were obtained from the Shanghai Chemical Reagent Co., China. HPLC grade methanol was from Merck. All chemicals were used as received.

Apparatus and Procedure. The solubilities of gallic acid, methyl gallate, propyl gallate, and octyl gallate in water were measured by a static analytical method. First, excess solute and 100 mL of double-distilled water were put into a three-necked round-bottom flask, which was placed in a constant-temperature water bath (type CH1015, Cany Precision Instrument Co. Ltd.). The flask was then heated, and the temperature was maintained within ± 0.05 K of the desired value. Next, the solution was constantly agitated at 200 rpm using an electric stirrer. After 2 h of stirring, the solution was kept still for at least 6 h allowing undissolved solid to settle. Finally, samples were taken with a burette and analyzed by HPLC.

The time required to establish solid−liquid equilibrium was experimentally determined by repetitively measuring the solubilities at certain time intervals until reproducible data were obtained. The reproducibility was found to be within 0.5 % after 6 h of settling time.

Analysis. About 0.5 g of saturated solutions was quickly taken out, weighed, and diluted with 1:1 (volume ratio) methanol−water solution to a certain volume. Then the composition of the pretreated samples was directly determined by reverse-phase HPLC (Agilent 1100). The HPLC column was a DIAMONSIL C18 (Dikma Technologies, 250 × 4.6 mm, 5 μm). Methanol−water−phosphoric acid was used as the mobile phase at a flow rate of 0.5 mL·min^{-1}. Other conditions are shown in Table 1. The analysis method was found to be simple, fast, accurate, and reliable.

Results and Discussion

At each temperature, six samples were taken and analyzed. The experimental data for the solubilities of gallic acid, methyl gallate, propyl gallate, and octyl gallate in water are listed in Table 2, with error limits using the 95 % confidence level. Also listed in the table are some data from the literature[6,7] for comparison. The unit for solubility is gram per 100 g water. To better understand the temperature dependence of the dissolution in water for these solutes investigated, the solubility data are depicted as a function of temperature in Figures 1 and 2. As seen from Table 2 and Figures 1 and 2, our experimental results are in good agreement with available literature data. It is also interesting to note that the plots for gallic acid (Figure 1) and octyl gallate (Figure 2) exhibit an "S"-shaped curve.

The experimental solubilities of methyl gallate and propyl gallate can be well-correlated with temperature using a simplified $\lambda - h$ equation:

$$\ln S = A + B/T \qquad (1)$$

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Table 1. HPLC Conditions for Gallic Acid, Methyl Gallate, Propyl Gallate, and Octyl Gallate

solute	mobile phase[a]	wave length/nm	column temp/K	linear range/mg·mL^{-1}	correlation coeff, R^2	rsd ($n = 6$)
gallic acid	20:80	267	313.15	0.02~0.31	0.9999	0.21 %
methyl gallate	50:50	275	313.15	0.04~0.75	0.9994	0.23 %
propyl gallate	50:50	275	313.15	0.06~1.55	0.9999	0.12 %
octyl gallate	80:20	280	313.15	0.006~0.18	0.9996	0.10 %

[a] Methanol:0.7% phosphoric acid aqueous solution in volume ratio.

Table 2. Solubilities of Gallic Acid, Methyl Gallate, Propyl Gallate, and Octyl Gallate in Water

T/K	gallic acid	methyl gallate	propyl gallate	octyl gallate
		This Work, g·100 g water^{-1}		
273.15	0.72 ± 0.01	0.30 ± 0.01	0.12 ± 0.01	
293.15	0.96 ± 0.01	0.99 ± 0.01	0.28 ± 0.01	
298.15	1.00 ± 0.02	1.06 ± 0.03	0.35 ± 0.01	
303.15	1.38 ± 0.01	1.26 ± 0.02	0.38 ± 0.01	0.0020 ± 0.00003
308.15	1.79 ± 0.01	1.79 ± 0.02	0.70 ± 0.01	0.0024 ± 0.00004
313.15	2.36 ± 0.02	2.53 ± 0.02	1.04 ± 0.01	0.0032 ± 0.00007
318.15	3.07 ± 0.05	3.24 ± 0.05	1.51 ± 0.02	0.0051 ± 0.0001
323.15	4.02 ± 0.06	4.91 ± 0.06	2.52 ± 0.02	0.0089 ± 0.0002
328.15	5.15 ± 0.06	8.66 ± 0.10	5.18 ± 0.05	0.0119 ± 0.0002
333.15	6.86 ± 0.06	12.14 ± 0.10	16.72 ± 0.19	0.0133 ± 0.0002
338.15	8.23 ± 0.12	16.71 ± 0.19	30.84 ± 0.30	0.0143 ± 0.0003
343.15	11.46 ± 0.06	24.08 ± 0.22		
348.15	13.66 ± 0.10			
353.15	19.27 ± 0.21			
358.15	25.60 ± 0.20			
363.15	29.09 ± 0.29			
		Literature		
288.15	0.95[a,6]			
298.15		1.1[b,7]	0.34[b,7]	0.0014[b,7]
373.15	33.33[a,6]			

[a] Unit converted from percentage concentration to g·100 g water^{-1}. [b] Unit converted from mol·L^{-1} to g·100 g water^{-1}.

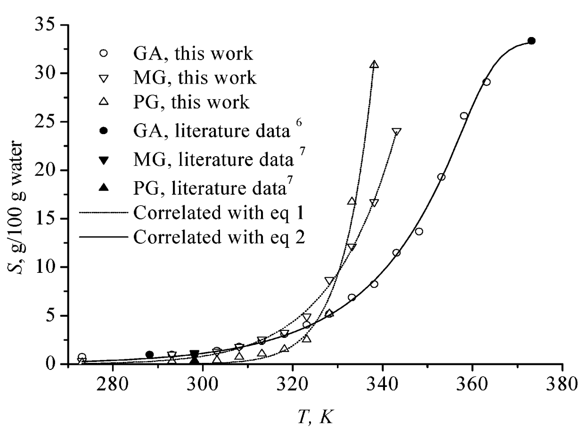

Figure 1. Solubilities of gallic acid (GA), methyl gallate (MG), and propyl gallate (PG) in water.

where S refers to solubility, T is temperature, and A and B are parameters.

An empirical equation, called the Richards equation[8] for simulating growth processes of living organisms as shown below, is adopted to correlate the "S" type solubility of gallic acid and octyl gallate:

$$S = [a^{1-d} + e^{-k(T-T_c)}]^{1/(1-d)} \tag{2}$$

where a, k, d, and T_c are parameters.

The parameters A and B in eq 1 for methyl gallate and propyl gallate and values of a, k, d, and T_c in eq 2 for gallic acid and octyl gallate are presented in Tables 3 and 4, respectively, with

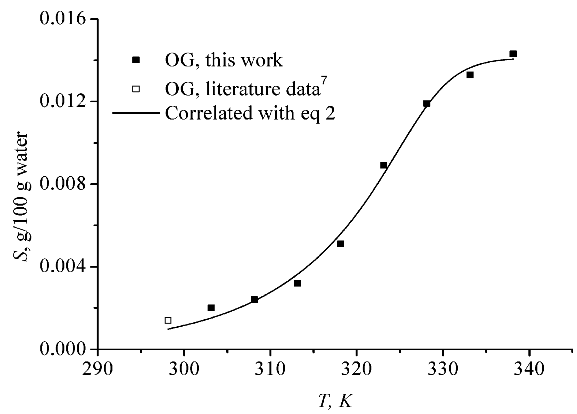

Figure 2. Solubility of octyl gallate (OG) in water.

Table 3. Parameters in Equation 1 for Methyl Gallate and Propyl Gallate

solute	A	B	σ
methyl gallate	26.804	−8106.5	0.11
propyl gallate	52.946	−16739.4	0.27

Table 4. Parameters in Equation 2 for Gallic Acid and Octyl Gallate

solute	a	T_c	k	d	σ
gallic acid	33.45	298.17	0.3181	6.901	0.11
octyl gallate	0.01414	377.55	0.3939	5.516	0.00016

the root-mean-square deviations (rmsd) defined by

$$\sigma = [\sum_{i=1}^{n} (S_{ci} - S_i)^2/n]^{1/2} \tag{3}$$

where S_i is experimental solubility, S_{ci} is the calculated solubility, and n is the number of experimental points. The calculated curves from eqs 1 and 2 are also shown in Figures 1 and 2, suggesting that the equations fit the data well.

Conclusion

The solubilities of gallic acid, methyl gallate, propyl gallate, and octyl gallate in water were determined in the temperature range (273.15 to 363.15) K by a static analytical method. The information yielded from this work is essential for the industrial development of purification processes of gallic acid and its esters. Additionally, a simplified $\lambda-h$ equation was employed to correlate the solubilities of methyl gallate and propyl gallate at various temperature. An empirical equation was proposed to correlate the "S" type data of gallic acid and octyl gallate. Both equations explain the data satisfactorily.

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