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Temperature Effect on the Distribution of Some Phenolic Compounds: An Experimental Measurement of 1-Octanol/Water Partition Coefficients

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The partition coefficient, K_{OW}, of some phenolic compounds, PhC, between water and 1-octanol, was determined at six temperatures from (293.15 to 318.15) K using a slow-stirring method. The log K_{OW} values of protocatechuic acid, vanillic acid, and vanillin range from (0.78 to 0.61), (1.46 to 1.18), and (1.25 to 0.99), respectively, over the temperature range studied. Obtained values at 298.15 K agree well with literature data. The van't Hoff plots of log K_{OW} versus T^{-1} exhibit linearity with values of K_{OW} increasing by 13 % to 21 % over this temperatures range. On the basis of the fluid phase equilibrium theory, a temperature-dependent thermodynamic relationship of the 1-octanol/water partition coefficient is proposed, and the changes of enthalpy, entropy, and the Gibbs energy function for phenolic compounds partitioning in 1-octanol/water were determined. In all cases, the thermodynamic functions of transfer of PhC from the water to the organic phase were negative. The Gibbs energy of transfer ranges from (3.69 to 8.29) $\text{kJ}\cdot\text{mol}^{-1}$. The temperature effect coefficient of the 1-octanol/water partition coefficient is also discussed, showing slight and negative values.

Introduction

The partition coefficient between water and 1-octanol for organic compounds, K_{OW}, is an important property to model the fate and transport of organic chemicals in the environment. The determination of this coefficient requires the establishment of an equilibrium between a polar phase and a nonpolar one. The polar phase is commonly water, while the nonpolar phase is a chemical solvent presenting a low partial miscibility for water, such as 1-octanol. This coefficient, K_{OW}, is defined as the ratio of the molar concentration of an organic compound in the octanol phase saturated with water to the molar concentration in the water phase saturated with octanol at equilibrium and at a specified temperature. Most frequently, it is given as the logarithm to the base 10 (log K_{OW}).

This coefficient can be considered as an important physicochemical parameter for characterizing the lipophilicity and hydrophobicity of a compound. It was found to be related to water solubility, soil-sediment adsorption coefficients, and bioconcentration factors for aquatic life.[1−6] Although many studies have been conducted on the solubility in the water and K_{OW}, data on temperature dependence of both properties are scarce and often unavailable. Bahadur et al.[7] investigated the partition coefficient of chlorobenzenes in a water and 1-octanol system over the temperature range (278.15 to 318.15) K in an attempt to elucidate the thermodynamics of the partitioning process, and found the van't Hoff plots of log K_{OW} versus T^{-1} exhibited linearity with values of K_{OW} increasing by 10 % to 14 % over the temperature range studied. In fact, temperature dependence of K_{OW} can be an important factor but is not often taken into account in environmental models. The present paper would contribute to the existing results based on the temperature dependence data and could be important for modeling the fate and behavior of chemicals or for use in situations where data are unviable or suspect.

This work is a continuous effort concerning the temperature dependence for physical-chemical properties.[8−10] We report here on the temperature dependence of partition coefficients for some phenolic compounds, PhC, contained in Olive-mill wastewater: protocatechuic acid (3,4-dihydroxybenzoic acid), vanillic acid (4-hydroxy-3-methoxybenzoic acid), and vanillin (4-hydroxy-3-methoxybenzaldehyde). These PhCs are antioxidants, are phytotoxic and toxic to bacteria, and are used in common biological wastewater treatment.[11,12] The partition coefficients of selected PhC in the 1-octanol/water system were measured by a slow-stirring method from (298.15 to 318.15) K and HPLC analysis. On the basis of the fluid phase equilibrium theory, the thermodynamic relationship of the 1-octanol/water partition coefficient depending on the temperature is proposed. The data obtained for each PhC were used to calculate appropriate thermodynamic properties, such as Gibbs free energy of transfer, enthalpy of transfer, and entropy of transfer from aqueous solutions to the organic phase, which have practical importance for industrial optimization processes. The influence regularity of temperature on the 1-octanol/water partition coefficient is discussed.

Materials and Methods

The source and mole fraction purity x of the chemicals were as follows: protocatechuic acid ($C_7H_6O_4$, $x > 0.97$), vanillic acid ($C_8H_8O_4$, $x > 0.985$), vanillin ($C_8H_8O_3$, $x > 0.98$), and 1-octanol ($C_8H_{18}O$, $x > 0.99$) were obtained from Sigma-Aldrich (Germany). The phenolic compounds were used without prior treatment but stored in a desiccator with P_2O_5 once the bottle was opened. Distilled water (conductivity around 1.5 $\mu\text{S}\cdot\text{Cm}^{-1}$) was used.

There are many methods to determine the 1-octanol/water partition coefficient K_{OW} values, such as the shake-flask

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Table 1. Logarithm of 1-Octanol/Water Partition Coefficient of Some Phenolic Compounds at 298.15 K

phenolic compounds	log K_{OW}, this work	log K_{OW}, literature values
vanillic acid	1.42	1.43,[18] 1.40[19]
protocatechuic acid	0.76	0.80[20]
vanillin	1.19	1.22,[21] 1.17[22]

method,[13] the slow-stirring method,[14] and the generator-column method.[15] A slow-stirring method was used to determine the 1-octanol/water partition coefficients of vanillic acid, protocatechuic acid, and vanillin from (298.15 to 333.15) K. PhC was added to an aqueous solution saturated with 1-octanol to obtain 25 mL solutions at 0.005 M. Each obtained solution was introduced in a double-jacketed reactor thermostatted at $T \pm 0.1$ K (Polystat Huber CC2), and a 25 mL saturated water/octanol solution was added. Finally, the reactor was closed with a cork and agitated with a magnetic stirrer. Preparation of the aqueous solutions of PhC and the procedure for PhC concentration measurements were largely described in our previous publications.[8−10,16,17] A preliminary study showed that liquid−liquid equilibrium was reached after three days. In fact, the time required to establish this equilibrium of the phenolic compounds between water and 1-octanol was experimentally determined by repetitively measuring the concentration of PhC in each phase by HPLC at various time intervals until reproducible data were obtained. The HPLC device manufactured by Varian is composed of a pump (VARIAN Prostar HPLC pump), a UV detector (Knauer K2501 detector), and a software of results treatment (Varian Star workstation). Samples were analyzed on an Intertsil ODS-3, 150 × 4.6 mm, 4 μm column (Mark, Germany). The injection loop was 50 μL. The elution solution for the aqueous phase was methanol, water, and acetic acid (25 %) (30:68:2, v/v) at 0.5 $\text{mL}\cdot\text{min}^{-1}$. On the other hand, methanol was the organic phase elution solution. It is noticed that the ratio of the concentrations between the two phases becomes constant after three days of contact. Two independent experiments were realized to determine the PhC concentration. The maximum deviation from the average value was found to be ± 5 %. Information about the reproducibility of the method was mentioned previously.[8−10]

Results and Discussion

The 1-octanol/water partition coefficients of phenolic compounds were determined at different temperature using the method described above. The K_{OW} was determined from the concentrations of PhC in the 1-octanol and aqueous phases expressed by molarity. The partition coefficient K_{OW} was calculated using the following definition

$$K_{OW} = \frac{c^{O}}{c^{W}} \qquad (1)$$

where c_T^O and c^W are the molar concentration of PhC in the 1-octanol layer and water layer, respectively. The logarithm of the 1-octanol/water partition coefficients for selected phenolic compounds at 298.15 K are given in Table 1 with reported literature values for comparison. As can be seen from this table, a good agreement between experimental results and those cited in the literature can be observed. From the point of view of chemical structure, it seems to indicate that the methoxy group (OCH_3) has a notable effect.[16] In fact, the protocatechuic acid not bearing a methoxy group presents the lowest K_{OW} value. The variation of the K_{OW} as a function of temperatures is given in Table 2 and represented in Figure 1. From Figure 1, it can be found that the logarithm of the 1-octanol/water partition coefficient is inversely proportional to T.

Table 2. 1-Octanol/Water Partition Coefficients (log K_{OW}) for PhC at Different Temperatures

T/K	protocatechuic acid	vanillic acid	vanillin
	log K_{OW}		
293.15	0.78 ± 0.01	1.46 ± 0.02	1.25 ± 0.02
298.15	0.76 ± 0.02	1.42 ± 0.02	1.19 ± 0.02
303.15	0.71 ± 0.03	1.36 ± 0.01	1.15 ± 0.01
308.15	0.67 ± 0.02	1.30 ± 0.02	1.11 ± 0.01
313.15	0.63 ± 0.01	1.26 ± 0.03	1.06 ± 0.01
318.15	0.61 ± 0.01	1.18 ± 0.02	0.99 ± 0.01

In all cases, the van't Hoff plots of log K_{OW} versus T^{-1} exhibit linearity with log K_{OW} increasing by 13 % to 21 % over the temperature range of (293.15 to 318.14) K. Increasing the temperature increases the preference of these compounds for the aqueous phase. The linear increase in log K_{OW} with $1/T$ clearly indicates that the partition is enhanced in the lipid phase at low temperature.

From an energetic aspect, the partition of PhC between water and 1-octanol is related to some thermodynamic changes, specifically the Gibbs energy, the molar enthalpy, and molar entropy of the association equilibrium between the compositions of a component in two liquids, and hence, from the van't Hoff isotherm, the Gibbs energy of transfer from aqueous phase to organic phase can be expressed by[23,24]

$$\Delta_{tr}G^{o} = -2.303RT \log K_{OW} \qquad (2)$$

where R is the gas constant ($R = 8.134\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and T is the temperature (K). K_{OW} is the partition equilibrium constant for phenolic compounds in the 1-octanol/water system.

However, it should be remembered that the Gibbs energy is the difference between the enthalpy changes ($\Delta_{tr}H°$) and the entropy changes ($\Delta_{tr}S°$) of transfer in the partitioning process[23]

$$\Delta_{tr}G^{o} = \Delta_{tr}H^{o} - T\Delta_{tr}S^{o} \qquad (3)$$

The Gibbs energy of transfer, $\Delta_{tr}G°$, of one phenolic compound mole, at constant temperature and pressure, from aqueous solutions to the organic phase was calculated using eq 2. $\Delta_{tr}H°$ was assumed constant and estimated from the regressed K_{OW} values,[23] using the van't Hoff approach, which involves plotting the log K_{OW} of a PhC versus reciprocal temperatures. $\Delta_{tr}S°$ was then calculated from eq 3. The values of $\Delta_{tr}G°$, $\Delta_{tr}H°$, and $\Delta_{tr}S°$ obtained at 298.15 K and at different temperatures

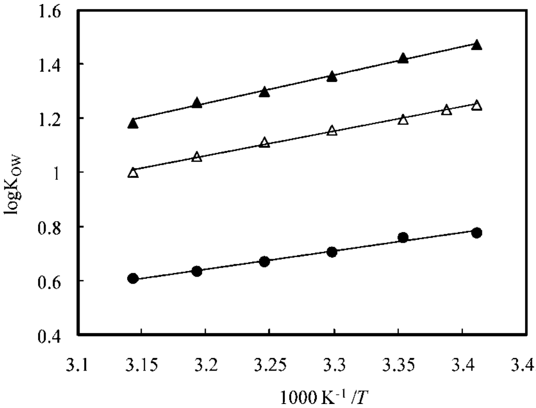

Figure 1. van't Hoff plot of log K_{OW} versus reciprocal absolute temperature for selected phenolic compounds: ●, protocatechuic acid; Δ, vanillin; ▲, vanillic acid.

Table 3. Values of the Standard Thermodynamics Functions of Transfer of the PhC From Water to 1-Octanol at 298.15 K

phenolic compounds	$\Delta_{tr}H°$ $kJ\cdot mol^{-1}$	$\Delta_{tr}S°$ $J\cdot mol^{-1}\cdot K^{-1}$	$\Delta_{tr}G°$ $kJ\cdot mol^{-1}$	r^2
vanillic acid	-20.20 ± 0.15	$-40.64 \pm 0. 74$	-8.09 ± 0.14	0.994
vanillin	-17.35 ± 0.11	$-35.20 \pm 0. 61$	-6.85 ± 0.11	0.995
protocatechuic acid	-12.42 ± 0.05	-27.41 ± 0.37	-4.24 ± 0.06	0.996

Table 4. Standard Molar Gibbs Energy of Transfer $\Delta_{tr}G°$ of PhC from the Aqueous Phase to the Organic Phase, at Various Temperatures

T/K	protocatechuic acid	vanillic acid	vanillin
		$\Delta_{tr}G°/kJ\cdot mol^{-1}$	
293.15	-4.38 ± 0.05	-8.29 ± 0.11	-7.03 ± 0.11
298.15	-4.24 ± 0.06	-8.09 ± 0.14	-6.85 ± 0.11
303.15	-4.10 ± 0.06	-7.88 ± 0.06	-6.68 ± 0.11
308.15	-3.97 ± 0.05	-7.68 ± 0.11	-6.50 ± 0.06
313.15	-3.83 ± 0.07	-7.48 ± 0.17	-6.33 ± 0.06
318.15	-3.69 ± 0.06	-7.27 ± 0.12	-6.15 ± 0.06

for the all systems studied are summarized in Tables 3 and 4, respectively.

From Table 3, it can be found that $\Delta_{tr}H°$ values from the aqueous phase to the organic phase for the phenolic compound partitioning in the 1-octanol/water system are all negative, which shows that the process is exothermic. In addition, entropy changes of transfer $\Delta_{tr}S°$ for PhC from the aqueous phase to the organic phase are also all negative indicating that the turbidity of the partitioning system did not increase (the system gets ordered). Furthermore, this result shows that conformations of phenolic compound molecules have an affinity to 1-octanol molecular layers. Similarly, Van Wezel et al.[25] reported that the negative values of entropy of chlorobenzenes change from the aqueous phase to the organic phase at different temperatures.

The temperature effect coefficient of the 1-octanol/water partition coefficient is defined as the ratio of the change logarithm of the 1-octanol/water partition coefficient to the transfer of the temperature and expressed as $d(\log K_{OW})/dT$. The temperature effect coefficient of the 1-octanol/water partition coefficient shown in Figure 2 can be calculated to

$$\frac{d(\log K_{OW})}{dT} = \frac{\Delta_{tr}H^{o}}{2.303RT^{2}} \qquad (4)$$

From Figure 2, it can be found that the temperature effect coefficients of the 1-octanol/water partition coefficient for phenolic compounds are all slight and negative. The variation was between (-0.007 and -0.012) K^{-1} with a mean value around -0.01 K^{-1}. Bahadur et al.[7] indicated a similar mean value of approximately -0.01 K^{-1} for variation of log K_{OW} of selected chlorobenzenes with T. From the viewpoint of the fluid phase equilibrium theory, the effect on the 1-octanol/water partition coefficient cannot be ignored when temperature varies considerably. It is necessary that the temperature should be controlled exactly on determining the 1-octanol/water partition coefficient.

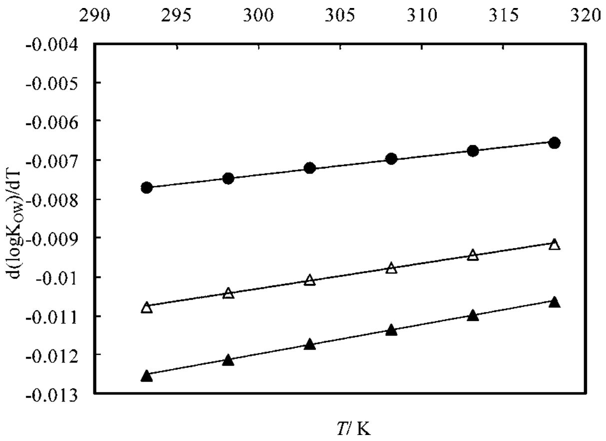

Figure 2. Temperature effect coefficients of 1-octanol/water partition coefficients (log K_{OW}) for phenolic compounds: ●, protocatechuic acid; Δ, vanillin; ▲, vanillic acid.

Conclusions

The partition coefficients of some phenolic compounds in two immiscible solvents, water and 1-octanol solutions, were determined experimentally. New values for K_{OW} as a function of temperature for some phenolic compounds are presented. The results showed that the K_{OW} of each phenolic compound decreases with the increase of temperature. The thermodynamic relationship of the 1-octanol/water partition coefficient depending on the temperature is proposed based on the chemical theory, and from temperature relationships, the transfer thermodynamics properties from water to 1-octanol were derived. The temperature effect coefficient of the 1-octanol/water partition coefficient is discussed.

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