Solubility of Canthaxanthin in Pure Solvents from (293.15 to 343.15) K

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The solubilities of β,β-carotene-4,4′-dione (canthaxanthin) in methanol, ethanol, acetone, ethyl acetate, toluene, cyclohexane, 1,2-dichloroethane, and trichloromethane were measured by a synthetic method over the temperature range from (293.15 to 343.15) K at atmospheric pressure. A laser monitoring observation technique was employed to determine the dissolution of the solid phase in a solid−liquid system. The experimental solubilities were fitted by the modified Apelblat equation with the deviation less than 2.7 %.

Introduction

The carotenoid pigment canthaxanthin (β,β-carotene-4,4′-dione; CAS RN 514-78-3), whose molecular structure is shown in Figure 1, has gained increasing attention in recent years because of its strong antioxidant properties and biological activities.[1,2] Canthaxanthin is usually obtained from the extraction of some organism fermentation liquid.[3] To separate and purify canthaxanthin, its solubility in different solvents is needed. However, the solubility of canthaxanthin in organic solvents does not seem to have been studied previously.

In this paper, the solubility of canthaxanthin in pure methanol, ethanol, acetone, ethyl acetate, toluene, cyclohexane, 1,2-dichloroethane, and trichloromethane over the temperature range from (293.15 to 343.15) K under atmospheric pressure was determined using a synthetic method and a laser monitoring observation technique.

Experimental Methods

Chemicals. Canthaxanthin with a mass fraction purity of 0.983 was supplied by Xinchang Pharmaceuticals Factory, Zhejiang Medicine Co., Ltd. of China, and was purified by recrystallization from cyclohexane (1) + trichloromethane (2) with volume ratio $V_1/V_2 = 5$. The crystalline canthaxanthin thus obtained had a mass fraction purity of 0.996. Deionized water was used throughout all the experiments. Organic solvents of analytical grade were supplied by Hangzhou Chemical Reagent Co., Ltd. of China and had a mass fraction purity greater than 0.995. These pure organic solvents were dried over 4 Å molecular sieves and degassed in an ultrasonic bath prior to use. The purity of these materials was ascertained by HPLC or GC.

Apparatus and Procedure. The solubility of a solid in a solvent was measured by a synthetic method that has been described in the literature.[4,5] The solubility apparatus was composed of a 200 mL jacketed glass vessel kept at the desired temperature by continuous forced water circulation from a thermostat (type CH1015, Shanghai Hengping Instruments Works Co. Ltd., China). A magnetic stirrer (type 85-1, Shanghai Zhiwei Co. Ltd., China) achieved continuous stirring of the solution. A mercury-in-glass thermometer with an uncertainty of ± 0.05 K was used to measure the temperature in the vessel. A laser beam was used to observe the dissolution of the solid + liquid mixture. The light signal transmitted through the vessel was collected by a detector (type FGF-III), which determined the disappearance of the last crystal in the solid + liquid mixture and estimated the equilibrium point of the given system on the basis of the signal change.

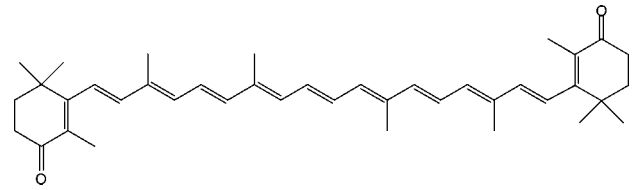

Figure 1. Structure of canthaxanthin.

The method for the solubility measurement was based on the fact that the laser intensity penetrating through the vessel would increase with the dissolution of the solid canthaxanthin when the amount of the solvent was gradually increased. At the beginning of each experiment, a known mass of solute determined by an electronic analytical balance (type BS210S, Sartorius Scientific Instrument Co. Ltd.) with an uncertainty of ± 0.0001 g was added to a known mass of solvent at a known temperature. The undissolved solid particles were completely suspended in the jacketed vessel by continuous stirring for 30 min, and then a quantitative additional solvent was added into the vessel through a burette. The intensity of the penetrated light increased with the increase of the amount of solvent in the vessel, and the penetrated light intensity reached its maximum value when the last portion of the solid solute just disappeared. Then the mass of the solute and the total solvent was recorded. Together with the mass of the solute, the solubility would be obtained by the following equation

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \quad (1)$$

where m_1 and m_2 represent the mass of the solute and the solvent and M_1 and M_2 are the molecular weight of the solute and the solvent, respectively. All the experiments were repeated three times. The uncertainty of the experimental solubility values is about 0.5 %. The uncertainty in the solubility values is due to

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Table 1. Solubility (x_1) of Canthaxanthin (1) in Pure Solvents (2) from T = (293.15 to 343.15) K

T/K	$10^5 x_1$	$100(x_1 - x_1^{calcd})/x_1$	T/K	$10^5 x_1$	$100(x_1 - x_1^{calcd})/x_1$
Methanol			Ethanol		
293.15	0.2610	−0.55	293.15	0.4500	−1.0
303.15	0.2930	1.2	303.15	0.5600	2.6
313.15	0.3270	−0.30	313.15	0.6350	−1.6
323.15	0.3770	−0.93	323.15	0.7480	−0.61
333.15	0.4530	0.53	333.15	0.8720	0.50
			343.15	0.9900	0.050
Acetone			Ethyl Acetate		
293.15	1.950	0.27	293.15	2.710	0.040
298.15	2.451	−1.2	303.15	3.674	−0.020
303.15	3.100	1.1	313.15	5.430	1.4
308.15	3.720	1.0	323.15	8.581	0.060
313.15	4.220	−2.0	333.15	14.40	−0.020
318.15	4.942	0.74	343.15	25.60	0.050
Toluene			Cyclohexane		
293.15	11.80	0.060	293.15	1.268	−1.5
303.15	14.60	−0.12	303.15	1.331	2.6
313.15	17.11	0.020	313.15	1.377	0.46
323.15	19.05	0.10	323.15	1.482	−1.9
333.15	20.23	−0.050	333.15	1.711	−0.79
343.15	20.75	0.30	343.15	2.055	1.0
1,2-Dichloroethane			Trichloromethane		
293.15	1820	0.050	293.15	1810	−0.77
303.15	2240	−0.090	303.15	2640	0.68
313.15	2580	−0.12	313.15	3420	1.4
323.15	2810	0.29	323.15	3920	−0.28
333.15	2880	−0.10	333.15	4090	−2.7
343.15	2900	2.4			

Table 2. Parameters of the Modified Apelblat Equation for Canthaxanthin in Different Solvents

solvent	A	B	C	100rmsrd
methanol	−214.893	8561.624	31.641	0.777
ethanol	19.689	−2489.821	−2.920	1.345
acetone	560.077	−28533.700	−82.152	1.086
ethyl acetate	−635.748	25825.986	95.770	0.112
toluene	281.911	−14260.270	−41.439	0.142
cyclohexane	−307.574	13434.878	45.310	1.533
1,2-dichloroethane	355.924	−17290.260	−51.762	0.981
trichloromethane	575.053	−28201.900	−83.783	1.313

uncertainties in the temperature measurements, weighing procedure, and instabilities of the water bath.

Results and Discussion

The solubilities of canthaxanthin in the selected solvents at different temperatures were measured over the temperature range from (293.15 to 343.15) K and presented in Table 1, where T is the absolute temperature and x_1 and x_1^{calcd} denote the experimental and calculated values of the solubility, respectively. From Table 1, it can be seen that the solubility of canthaxanthin in all selected solvents increases with an increase in temperature. It is also shown that the solubility of canthaxanthin is especially high in 1,2-dichloroethane and trichloromethane but low in methanol, ethanol, acetone, ethyl acetate, toluene, and cyclohexane. Furthermore, the solubility in ethyl acetate varies much more obviously with temperature than in the other seven solvents.

The solubility of canthaxanthin as a function of temperature was fitted by the modified Apelblat equation[6−8]

$$\ln(1000x_1) = A + B/(T/\mathrm{K}) + C\ln(T/\mathrm{K}) \quad (2)$$

where A, B, and C are empirical constants and were obtained using the least-squares method and were presented in Table 2 together with the root-mean-square relative deviation (rmsrd) which is defined as

$$\mathrm{rmsrd} = \sqrt{\frac{\sum_{i=1}^{N}\left(\frac{x_i^{calcd} - x_i}{x_i}\right)^2}{N}} \quad (3)$$

where N is the number of experimental points.

It is seen that the calculated solubilities by the modified Apelblat equation are in good agreement with the experimental values.

Conclusions

The solubility of canthaxanthin in all selected solvents is a function of temperature and increases with the rise in temperature.

The solubility of canthaxanthin is especially high in 1,2-dichloroethane and trichloromethane.

The solubility in ethyl acetate varies much more obviously with temperature than in the other seven solvents.

The calculated solubility data by the modified Apelblat equation are in good agreement with the experimental values.

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