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Solubility of β-Sitosteryl Maleate and Stigmasteryl Maleate in Acetone and Ethyl Acetate

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The solubility of β-sitosteryl maleate and stigmasteryl maleate in acetone and ethyl acetate was determined by a dynamic method. The results show that the solubility of β-sitosteryl maleate or stigmasteryl maleate in ethyl acetate or acetone increases when temperatures increase, and the solubility of β-sitosteryl maleate is higher than that of stigmasteryl maleate in two solvents in the range of experimental temperatures. The relation between the experimental solubility as mole fractions and temperatures could be correlated by means of expressions of the form $\log(1/x) = A/T + B$ for the researched systems.

Introduction

Phytosterols belong to the relatively few naturally occurring organic compounds which usually contain stigmasterol, β-sitosterol, campesterol, and brassicasterol and can be obtained from some sorts of vegetable oils. Sterols and their derivatives are widely used in the pharmaceutical,[1,2] food,[3,4] and cosmetic industries[5,6] due to their special biological activity as well as physical and chemical properties. A common feature of phytosterols is the presence of oxygen at C-3, as a hydroxyl group. The presence of a hydroxyl group confers asymmetry upon this position and makes possible two modifications that are both naturally occurring. The differences between naturally occurring sterols are due to variations of the number and locations of double bonds and to the number of carbon atoms composing the side chain.[7,8] These differences are rather small, so it is not surprising that many sterols show such similarities in their solubility as to make their separation difficult by conventional methods such as recrystallization.

Separation and purification of phytosterol mixtures by chemical methods (e.g., esterification) will not only broaden the gap among physical properties of phytosterol mixtures so as to separate but also prepare useful derivatives of phytosterols.

β-Sitosteryl and stigmasteryl are the two most abundant and important sterols, and the aim of this work is to obtain solubility data of β-sitosteryl maleate and stigmasteryl maleate in several organic solvents and possibly correlate them by a best-fit equation. So far, the available information on the solubility of sterols and their derivatives in different solvents is quite scarce,[9] while there are no reports about the solubility of β-sitosteryl maleate and stigmasteryl maleate. Taking into account the chemical stability and toxicity, two solvents such as ketones and esters were selected. The aim of this work is to obtain the solubility data of β-sitosteryl maleate and stigmasteryl maleate in acetone and ethyl acetate at different temperatures and the correlation between the solubility and temperatures.

Experimental Section

Materials. β-Sitosterol and stigmasterol were obtained from Merck (95 %). β-Sitosteryl maleate and stigmasteryl maleate with a purity of 95 % were synthesized.[10] Acetone and ethyl acetate of analytical grade were supplied by Shanghai Chemistry and Medicine Corporation and were used without further purification.

Apparatus and Procedure. The solubility of β-sitosteryl maleate and stigmasteryl maleate was determined by a dynamic method[11,12] described briefly here. The experiment was performed in a cylindrical double-jacketed glass vessel, and the volume of this vessel was 50 mL. The vessel was put in a

Table 1. Mole Fraction Solubility of β-Sitosteryl Maleate in Acetone and Ethyl Acetate

acetone		ethyl acetate	
T/K	$x/10^{-4}$	T/K	$x/10^{-3}$
289.75	4.899	288.15	3.501
304.15	8.994	293.15	4.773
310.65	12.75	298.15	5.864
313.35	16.02	303.15	7.755
317.15	19.78	308.15	9.282
320.95	23.43	313.15	12.18
325.15	31.14	317.85	18.00
		322.15	25.19

Table 2. Mole Fraction Solubility of Stigmasteryl Maleate in Acetone and Ethyl Acetate

acetone		ethyl acetate	
T/K	$x/10^{-4}$	T/K	$x/10^{-3}$
293.15	3.826	288.15	1.460
296.65	4.312	298.15	2.025
303.65	5.346	308.65	3.951
317.15	7.852	317.35	5.301
325.65	10.21	293.25	1.789
		302.65	2.801
		312.65	4.382

Table 3. Best-Fit Correlation Parameters for Solubility of β-Sitosteryl Maleate in Acetone and Ethyl Acetate

solvent	A	B	r	rmsd
acetone	2141.62	−4.0409	0.9920	$1.4208 \cdot 10^{-4}$
ethyl acetate	2225.87	−5.2450	0.9901	$1.6724 \cdot 10^{-3}$

Table 4. Best-Fit Correlation Parameters for Solubility of Stigmasteryl Maleate in Acetone and Ethyl Acetate

solvent	A	B	r	rmsd
acetone	1237.26	−0.80332	0.9997	$1.6887 \cdot 10^{-4}$
ethyl acetate	1838.53	−3.5222	0.9928	$1.5415 \cdot 10^{-4}$

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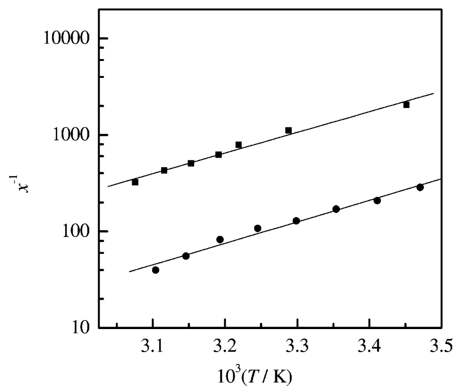

Figure 1. Solubility of β-sitosteryl maleate at different temperatures in two solvents: —■—, acetone; —●—, ethyl acetate.

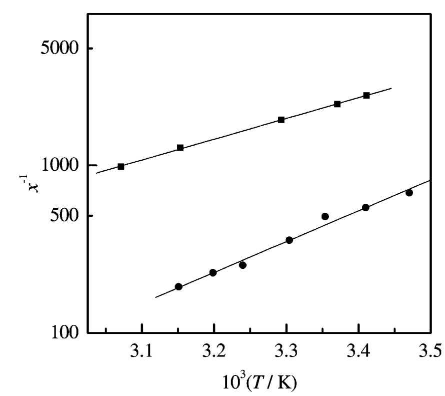

Figure 2. Solubility of stigmasteryl maleate at different temperatures in two solvents: —■—, acetone; —●—, ethyl acetate.

thermoelectric controller to maintain desired temperatures. A condenser was connected to the vessel to prevent the solvents from evaporating. A mercury-in-glass thermometer was set in the inner chamber of the vessel with an uncertainty of 0.01 K.

β-Sitosteryl maleate or stigmasteryl maleate was weighed using an electronic balance (type GT33A, Shanghai Instruments Co.), which has an accuracy of $\pm$ 0.0001 g, and was transferred into the vessel. Then the quantitative solvent (acetone or ethyl acetate) was also poured into the vessel. The solid + liquid system was heated at a very slow rate which was less than 1 $K \cdot h^{-1}$, and the temperature when the solid (solute) was dissolved completely was recorded. The solubility at the recorded temperature was calculated with the amount of the solid and liquid added into the vessel. After that, the solid of known mass was added again, and the system was continuously heated at the very slow rate until the added solid was dissolved completely. This procedure might be repeated according to the experimental demand.

Results and Discussions

The solubilities of β-sitosteryl maleate and stigmasteryl maleate in acetone and ethyl acetate are listed in Table 1 and Table 2, respectively.

The data are fitted by a least-squares method to an equation of the form

$$\log(1/x) = A/T + B \quad (T/\mathrm{K}) \tag{1}$$

where x is the mole fraction solubility of β-sitosteryl maleate or stigmasteryl maleate; T is the absolute temperature; and A and B are the parameters.

Root-mean-square deviation (rmsd) is defined as follows

$$\mathrm{rmsd} = [\sum_{i=1}^{N} (x_i^{\mathrm{calcd}} - x_i^{\mathrm{exptl}})^2/(N-1)]^{1/2} \tag{2}$$

where N is the number of experimental points; x_i^{calcd} represents the solubility calculated from eq 1; and x_i^{exptl} represents the experimental values of solubility, that is, x in eq 1.

The regressed values of parameters A and B, the correlation coefficients r, and the root-mean-square deviations (rmsd) for β-sitosteryl maleate and stigmasteryl maleate are listed in Table 3 and Table 4, respectively.

The experimental values and the regression lines are shown in Figure 1 and Figure 2 for β-sitosteryl maleate and stigmasteryl maleate, respectively.

As the correlation coefficients indicate, the linear expression describes satisfactorily the solubility dependence on temperatures in the given temperature range.

Conclusions

From the tables and figures above, the following conclusions can be drawn: (i) with increasing temperatures, the solubility of β-sitosteryl maleate and stigmasteryl maleate increases in ethyl acetate and acetone; (ii) at constant temperature, the solubility of the β-sitosteryl maleate and stigmasteryl maleate in ethyl acetate is higher than that in acetone; (iii) the solubility of β-sitosteryl maleate is higher than that of stigmasteryl maleate in two solvents at constant temperature; (iv) the solubility dependence on temperatures could be regressed by the equation log(1/x) = $A/T + B$ for the systems in the given temperature range.

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