Solubility of β-Carotene in Binary Solvents Formed by Some Hydrocarbons with 2,5,8-Trioxanonane, 2-Propanone, and Cyclohexanone

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Experimental results are reported for the solubility of β-carotene in six binary mixed solvents formed by 2,5,8-trioxanonane with 1-hexene, cyclohexane, hexane, and toluene and by 1-hexene with 2-propanone and cyclohexanone at 293.15 K. A spectral colorimeter was used for analysis of β-carotene concentration. The β-carotene solubility in the pure solvents increases in the order: 2-propanone < hexane < 2,5,8-trioxanonane < 1-hexene < cyclohexane < cyclohexanone < toluene. The solubility data as a function of the binary solvent mass fractions were smoothed by the Myers and Scott equation for asymmetric functions. The Flory and Huggins theory of non-athermal mixtures and the Acree and Rytting model were used for prediction of experimental data for the solubility of β-carotene in the six binary above listed mixed solvents.

Introduction

This study deals with the solubility of β-carotene at 293.15 K in mixed binary solvents formed by 2,5,8-trioxanonane with hydrocarbons such as 1-hexene, hexane, cyclohexane, and toluene as well as 1-hexene with 2-propanone and cyclohexanone. Currently, only limited solubility data on solid nonelectrolytes in binary mixed solvents are known,[1−4] and no other data on biologically active substances such as carotenoids are available. This work continues our earlier studies on the solubility of β-carotene in mixed solvents formed by hydrocarbons such as hexane, cyclohexane, and toluene with 2-propanone, 2-butanone,[1] cyclohexanone, 1-octanol,[2] 1,2-dimethoxyethane, dibutyl ether,[3] *tert*-butyl methyl ether, and *tert*-amyl methyl ether.[4] Two simple models are tested: the Flory and Huggins theory (FH) of non-athermal mixtures and the Acree and Rytting model (AR) are used for the prediction of experimental data for the solubility of β-carotene in the six binary above listed mixed solvents.

Experimental Section

Materials. β-Carotene (Sigma, declared purity $x = 0.95$) was used as received. The analysis of β-carotene samples by liquid chromatography showed that the mole fraction purity was > 0.95 of the trans-isomer (main impurities are α-carotene and lycopene). Organic solvents 1-hexene (Sigma, analytical grade declared purity $x > 0.99$) and 2,5,8-trioxanonane (Aldrich Chemical Co, labeled $x = 0.99$) were purified by fractional distillation over sodium and stored in the dark over type 3 Å molecular sieves. Hexane (Chemipan, Poland) analytical grade standard labeled $x = 0.999$; cyclohexanone (Chemipan, Poland) pure grade declared purity $x = 0.99$; toluene (supplied by the Płock Refinery Industry R & D Center) analytical reagent grade declared purity $x = 0.99$; and cyclohexane (Ubichem Ltd.) standard labeled $x = 0.99$ were distilled and stored over type 4 Å molecular sieves. The refractive indices are listed in Table 1 and agree well with the literature values.[5]

Table 1. Physicochemical Properties of the Solvents Studied[a]

solvent	M^b g·mol^{-1}	d^b g·cm^{-3}	n_D exp	n_D lit.^{b}
2,5,8-trioxanonane	134.175	0.9434	1.4057	1.40576
2-propanone	58.080	0.78998	1.3562	1.35596
cyclohexanone	98.144	0.9452	1.4498	1.4500
1-hexene	84.161	0.67317	1.3853	1.38502
cyclohexane	84.161	0.77855	1.4236	1.42354
hexane	86.177	0.65933	1.3724	1.37226
toluene	92.140	0.86683	1.4942	1.49411
β-carotene^c	536.85	1.00^c		

[a] M, molecular mass; d, density at 293.15 K; n_D, refractive index at 298.15 K. [b] Ref 5. [c] Ref 6.

The binary solvent mixtures were prepared by mass; therefore, the solvent compositions could be uncertain to within 0.0001 mole fraction. The temperature was kept during saturation period within ± 0.1 K. The methods of sample equilibration and analysis were presented in an earlier paper.[1]

Results and Discussion

Table 2 presents the experimental solubilities of β-carotene in binary mixed solvents expressed as molar concentrations (c_β) and in mole fractions (x_β) together with mean standard deviations (σ_n) and with the mixing function (x_β^M). The experimental results of the β-carotene solubilities obtained primarily as mass fractions were recalculated to mole fractions by using data listed in Table 1. The detailed procedure was presented in a previous paper.[1] The molar concentrations c_β given in Table 2 were calculated by using the data of Table 1 and the following relationship:

$$c_\beta = \frac{10^3 x_\beta}{V_\beta^0 x_\beta + (1 - x_\beta)V_{12}^0} \tag{1}$$

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Table 2. Solubility of *β*-Carotene in Mixed Solvent Hydrocarbon (1) + 2,5,8-Trioxanonane (2), + 2-Propanone (2), + Cyclohexanone (2) at 293.15 K[a]

x_1^0	$10^3 c_\beta$ / mol·L^{-1}	$10^4 x_\beta$	$10^4 x_\beta^M$	x_1^0	$10^3 c_\beta$ / mol·L^{-1}	$10^4 x_\beta$	$10^4 x_\beta^M$	x_1^0	$10^3 c_\beta$ / mol·L^{-1}	$10^4 x_\beta$	$10^4 x_\beta^M$
Cyclohexane (1) + 2,5,8-Trioxanonane (2)											
0	0.67	0.96 (0.06)	0	0.4036	4.14	5.33 (0.37)	3.54(0.46)	0.7025	4.77	5.65 (0.31)	3.24(0.39)
0.1013	1.53	2.13 (0.07)	0.96(0.18)	0.4984	4.64	5.82 (0.24)	3.83(0.33)	0.8133	4.39	5.04 (0.28)	2.41(0.35)
0.2037	2.53	3.43 (0.19)	2.05(0.29)	0.6007	4.93	6.01 (0.35)	3.81(0.43)	1	2.79	3.02 (0.11)	0
Hexane (1) + 2,5,8-Trioxanonane (2)											
0	0.67	0.96(0.06)	0	0.3935	1.82	2.51(0.07)	1.58(0.12)	0.8546	1.79	2.37(0.07)	1.47(0.13)
0.0956	0.96	1.35(0.09)	0.40(0.14)	0.4997	2.04	2.79(0.12)	1.86(0.17)	1	0.68	0.89(0.05)	0
0.2015	1.56	2.18(0.18)	1.23(0.23)	0.5958	2.30	3.12(0.19)	2.20(0.25)				
0.3014	1.94	2.70(0.09)	1.76(0.14)	0.7003	2.03	2.72 (0.11)	1.81(0.17)				
Toluene (1) + 2,5,8-Trioxanonane (2)											
0	0.67	0.96 (0.06)	0	0.3969	1.74	2.23 (0.09)	−2.69(0.22)	0.9018	9.32	10.28 (0.28)	0.31(0.35)
0.1055	0.98	1.36 (0.16)	−0.65(0.33)	0.5053	2.65	3.29 (0.25)	−2.72(0.37)	1	10.26	10.95 (0.18)	0
0.2015	0.95	1.28(0.12)	−1.69(0.286)	0.6032	3.75	4.53 (0.37)	−2.46(0.48)				
0.3035	1.10	1.45 (0.08)	−2.54(0.22)	0.6988	5.18	6.08 (0.16)	−1.86(0.26)				
1-Hexene (1) + 2,5,8-Trioxanonane (2)											
0	0.67	0.96(0.06)	0	0.3988	1.74	2.35(0.11)	1.03(0.16)	0.8046	2.25	2.89(0.05)	1.20(0.11)
0.1032	0.78	1.10(0.07)	0.05(0.11)	0.5029	2.23	2.98(0.14)	1.56(0.19)	0.8966	1.81	2.30(0.05)	0.52(0.11)
0.2045	1.15	1.59(0.11)	0.44(0.15)	0.6048	2.39	3.15(0.06)	1.64(0.11)	1	1.49	1.87(0.04)	0
0.3013	1.44	1.98(0.13)	0.75(0.18)	0.7024	2.31	3.01(0.08)	1.41(0.13)				
1-Hexene (1) + 2-Propanone (2)											
0	0.19	0.14(0.01)	0	0.3988	1.77	1.67(0.06)	0.84(0.09)	0.7933	1.77	2.03(0.03)	0.52(0.05)
0.1004	0.43	0.34(0.02)	0.03(0.06)	0.4997	2.17	2.16(0.05)	1.16(0.07)	1	1.49	1.87(0.04)	0
0.2029	1.18	0.99(0.03)	0.50(0.05)	0.4997[b]	2.12	2.11(0.05)	1.11(0.07)				
0.3008	1.28	1.14(0.03)	0.48(0.06)	0.6066	1.95	2.04(0.06)	0.85(0.08)				
1-Hexene (1) + Cyclohexanone (2)											
0	3.08	3.20(0.21)	0	0.4137	5.25	5.93(0.33)	3.28(0.44)	0.7023	3.69	4.39(0.26)	2.12(0.42)
0.0991	4.81	5.11 (0.37)	2.04(0.43)	0.4137[b]	5.10	5.75(0.34)	3.10(0.45)	0.7960	2.73	3.30(0.20)	1.16(0.38)
0.2151	5.16	5.60(0.36)	2.69(0.44)	0.4983	4.66	5.34(0.30)	2.80(0.42)	0.9057	2.04	2.51(0.06)	0.51(0.25)
0.3001	5.59	6.18(0.39)	3.38(0.48)	0.5972	4.80	5.23(0.38)	2.82(0.52)	1	1.49	1.87(0.04)	0

[a] x_1^0, hydrocarbon mole fraction in binary solvent; c_β, molar concentrations of β-carotene; x_β, solubility of β-carotene in mole fractions, x_β^M, of eq 2 and mean standard deviation σ_n (in parentheses). [b] Separate run.

where $V_{12}^0 = V_1^0 x_1^0 + V_2^0 x_2^0$ and x_1^0, $x_2^0 = 1 - x_1^0$ are mole fractions of components of the binary solvent mixture (without the solute, β-carotene), and V_β^0, V_1^0, and V_2^0 are the molar volumes of the pure components.

The mixing function x_β^M proposed by Heric and Posey[7] (called the "deviation function", cf. previous papers[1−4]) was applied to better represent the behavior of the solute in the mixed solvent. The function describes the difference between the solubility of β-carotene in the mixed solvent and the linear dependence of β-carotene solubility on a mole fraction basis:

$$x_\beta^M = x_\beta - \sum_{i=1}^{n=2} x_i^0 x_\beta^{(i)} \tag{2}$$

where x_β, $x_\beta^{(1)}$, and $x_\beta^{(2)}$are the solubilities in the mixed and pure solvents 1 and 2, respectively. The x_β solubilities were smoothed by means of the rational type equation (adequate for mixing functions[8]):

$$x_\beta = \sum_{i=1}^{n=2} x_i^0 x_\beta^{(i)} + x_1^0(1 - x_1^0)\frac{\sum_{i=0}^{m} a_i(2x_1^0 - 1)^i}{1 + b(2x_1^0 - 1)} \tag{3}$$

Parameters a_i and b were calculated by using the Levenberg−Marquardt nonlinear least-squares method[9] and are listed in Table 3 together with the standard deviations:

$$\sigma_s = \sqrt{\frac{\sum_{i=1}^{n}(x_{\beta,i}^{M,expt} - x_{\beta,i}^{M,calc})^2}{n - k}} \tag{4}$$

where n is the number of experimental points and k is the number of parameters of eq 3.

The experimental solubilities of the β-carotene expressed in mole fractions x_β are presented for the binary solvents in Figure 1 for 2,5,8-trioxanonane with hexane, cyclohexane, and toluene and in Figure 2 for 1-hexene with 2-propanone, 2,5,8-trioxanonane, and cyclohexanone. For the mixed solvents formed by the polar solvents (2,5,8-trioxanonane, cyclohexanone, and 2-propanone) with hexane, cyclohexane, and 1-hexene, the mixing function x_β^M (see Table 2) is positive in the whole concentration range, and the solubility curves are characterized by a maximum (cf. solubility in binary solvents formed by 2-propanone,[1] cyclohexanone,[2] and 1,2-dimethoxyethane[3] with saturated hydrocarbons). For the binary systems formed by 2,5,8-trioxanonane with toluene, the β-carotene solubility curves x_β are concave downward, and the mixing function x_β^M is negative over the whole concentration range (cf. binary solvents formed by toluene with polar component[1−4]).

Such a behavior is explained by the model calculations using the FH theory of non-athermal mixtures[10,11] and the AR model,[12] which describes the solubility of a solute in the binary solvent as a function of the residual contribution to excess Gibbs energy

Table 3. Coefficients a_i and b and Standard σ_s and Maximum Δ Deviation for the Mole Fraction Solubility of β-Carotene in Binary Solvents by Equation 3 and Maximum of the Excess Gibbs Energy of the Binary Solvent Studied, $G_{12}^{E,max}$, at 293.15 K

	2,5,8-trioxanonane (2)		
	cyclohexane	hexane	toluene
$10^4 a_0$	15.361	7.8457	−11.564
$10^4 a_1$	2.6539	−5.4223	4.8808
$10^4 a_2$	−3.6895		12.869
b		−0.93058	
$10^4 \sigma_s$	0.05	0.20	0.21
$10^4\Delta$	0.07	0.22	0.26
$G_{12}^{E,max}$/J·mol^{-1}	712	748	194

	1-hexene (1)		
	2,5,8-trioxanonane	2-propanone	cyclohexanone
$10^4 a_0$	5.7866	4.0885	12. 040
$10^4 a_1$		0.78845	
$10^4 a_2$	−6.3180	−4.2900	
$10^4 a_3$			−7.6454
b	−0.86123		0.38357
$10^4 \sigma_s$	0.090	0.14	0.16
$10^4\Delta$	0.11	0.17	0.27
$G_{12}^{E,max}$/J·mol^{-1}	587	762	354

of a mixed solvent ($G_{12}^{E,res}$). In the FH theory, the solubility x_β of a solute is described by[10,11]

$$\ln x_\beta = \ln a_\beta^{st} - 1 + \frac{\varphi_\beta}{x_\beta} - \ln\frac{\varphi_\beta}{x_\beta} - \frac{(1-\varphi_\beta)^2}{RT}\left[\sum_{i=1}^{2}\frac{(\mu_\beta^E)_i^{res}}{(1-\varphi_\beta^{(i)})^2}\varphi_i^0 - \frac{V_\beta^0}{V_{12}^0}G_{12}^{E,res}\right] \quad (5)$$

where the logarithm of the activity of the solid solute in the reduced form is given by $\ln a_\beta^{st} = -\Delta_{fus}H_\beta(1 - T/T_f)/RT$, wherein $\Delta_{fus}H_\beta$ is the molar enthalpy of fusion at the normal melting point and T_f is 56 kJ·mol^{-1} at 456 K for the β-carotene. These values were taken from Lenfant and Thyrion.[6] The$x_\beta^{(i)}$, $\varphi_\beta^{(i)}$, x_β, and φ_β are the mole and the volume fractions of the solute in the ith pure solvent and in the mixed solvent, $x_i^0$and φ_i^0 are the mole and the volume fractions of the ith solvent in the mixed solvent (without solute). The residual contribution to excess Gibbs energy, $G_{12}^{E,res} = G_{12}^E - G_{12}^{E,comb}$was calculated from combinatorial contribution $G_{ij}^{E,comb} = RT(x_i^0 \ln(\varphi_i^0/x_i^0) + x_j^0 \ln(\varphi_j^0/x_j^0))$ and the values of excess Gibbs energy G_{12}^E of the mixture of solvents 1 and 2 estimated by means of the UNIFAC group interactions method[13] $(\mu_\beta^E)_i^{res}$ is the residual contribution to the excess of chemical potential of the solute at the saturated concentration in pure component i. This contribution can be calculated as

$$(\mu_\beta^E)_i^{res}/RT = \ln(a_\beta^{st}/x_\beta^{(i)}) - \left(1 - \frac{\varphi_\beta^{(i)}}{x_\beta^{(i)}} + \ln\frac{\varphi_\beta^{(i)}}{x_\beta^{(i)}}\right) \quad (6)$$

In the AR model,[12] the solubility φ_β of a solute is described by

$$\ln\varphi_\beta = \ln a_\beta^{st} - (1-\varphi_\beta)\left(1 - \frac{V_\beta^0}{V_{12}^0}\right) - \frac{(1-\varphi_\beta)^2}{RT}\left[\sum_{i=1}^{2}\varphi_i^0 (\Delta\bar{G}_\beta^{fh})_{x_i=1} - \frac{V_\beta^0}{V_{12}^0}\Delta G_{12}^{fh}\right] \quad (7)$$

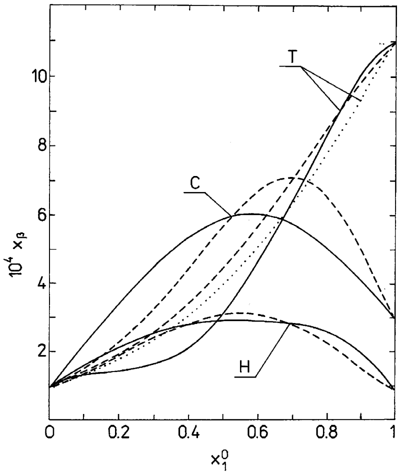

Figure 1. Solubility of β-carotene x_β in the binary solvents hydrocarbon (1) + 2,5,8-trioxanonane (2) at 293.15 K vs mole fraction of hydrocarbon x_1^0. Curves are labeled with C, cyclohexane; H, hexane; and T, toluene. Curves: —, smoothed experimental data, calculated with coefficients from Table 3; - - -, based on the Flory and Huggins model, eq 5; • • •, based on the Acree and Rytting model, eq 7. For systems formed by a saturated hydrocarbon, the predicted curves coincide for both models.

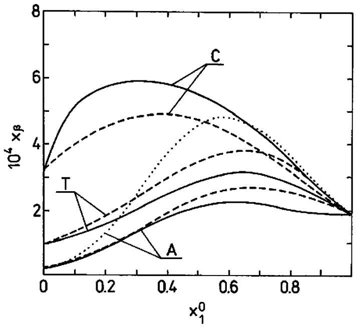

Figure 2. Solubility of β-carotene x_β in the binary solvents 1-hexene (1) + polar solvent (2) at 293.15 K vs mole fraction of 1-hexene x_1^0. Curves are labeled with A, 2-propanone; C, cyclohexanone; and T, 2,5,8-trioxanonane. Remaining notations as above (Figure 1). The predicted curves coincide for both models except for the 2-propanone system.

where $(\Delta\bar{G}_\beta^{fh})_{x_i=1} = RT \ln(a_\beta^{st}/x_\beta^{(i)}) - 1 + V_\beta^0/V_{12}^0$ is the limiting value of the chemical potential of the solute at infinite dilution and $\Delta G_{12}^{fh} = G_{12}^{E,res}$.

Both discussed models predict qualitatively well the solubility in the systems formed by 2,5,8-trioxanonane with cyclohexane, hexane, 1-hexene, and toluene and by 1-hexene with 2-propanone and cyclohexanone, including the shift of the maximum toward the component dissolving more β-carotene, as shown in Figures 1 and 2. To estimate G_{12}^E for the investigated binary solvents the UNIFAC method[13] was used. UNIFAC molecular parameters R and Q for the CH_2O group were used to describe so-called screening effect in 2,5,8-trioxanonane, which was discussed by Treszczanowicz and Lu.[14] These results and previous calculations[3,4] indicate an important role of the excess Gibbs energy of the binary mixed solvent as well as the difference of the solubility of the solute in component solvents $|x_\beta^{(1)} - x_\beta^{(2)}|$ on the shape of the solubility curve.

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