Solubility of β-Carotene in Binary Solvents Formed by Some Hydrocarbons with Cyclohexanone and 1-Octanol

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Experimental results are reported for the solubility of β-carotene in six binary mixed solvents formed by cyclohexanone with cyclohexane, hexane, and toluene and by 1-octanol with cyclohexane, hexane, and toluene at 293.15 K. A colorimeter was used for analysis of the β-carotene concentration. The β-carotene solubility in pure solvents increases in the order 1-octanol < hexane < cyclohexanone < cyclohexane < toluene. The solubility data as a function of binary solvent mass fractions were smoothed by a rational type equation.

Introduction

This study deals with the solubility of β-carotene in mixed binary solvents formed by 1-octanol with hydrocarbons at 293.15 K and is a continuation of our earlier studies on the solubility of β-carotene in mixed solvents formed by 2-propanone and 2-butanone with hexane, cyclohexane, and toluene.[1] Currently, only limited solubility data on solids of non-electrolytes in binary mixed solvents are known, but no data are known of any biologically active substances such as β-carotene.

Experimental Section

Materials. β-Carotene (Sigma, 95 mol % purity) was used as received. The analysis of the β-carotene samples by liquid chromatography showed that the purity was >95% of the trans isomer. Organic solvents [hexane (99.95 mol %), standard, from Chemipan, Poland; toluene (99 mol %), analytical reagent grade, from the Płock Refinery Industry R&D Centre, and cyclohexane (99 mol %), standard, from Ubichem Ltd.] were distilled; cyclohexanone and 1-octanol, of analytical reagent grade (99 mol %) supplied by Fluka, were twice distilled. All reagents were stored over molecular sieves type 4A. Refractive indices are listed in Table 1 and agree well with the literature values.[2] Binary solvent mixtures were prepared by mass; therefore, solvent compositions could be uncertain to 0.0001 mole fraction. The methods of sample equilibration and analysis were presented in an earlier paper.[1]

Results and Discussion

Table 2 presents the results of the β-carotene solubility in the binary mixed solvents expressed in molar concentrations c_β/mol·L^{-1}, mole fractions x_β together with the mean standard deviation[4] σ_n, and mixing function x_β^{M}. Experimental results of the β-carotene solubilities obtained primarily in mass fractions were recalculated to mole fractions using data in Table 1. The detailed procedure was given in a preceding paper.[1] The molar concentrations c_β given in Table 2 are calculated using data in Table 1 and the relationship

Table 1. Physicochemical Properties of the Solvents Studied: *M* = Molecular Mass, *d* = Density at 293.15 K, n_{D} = Refractive Index at 298.15 K

solvent	M^a/g·mol^{-1}	d^a/g·cm^{-3}	n_{D} exptl	n_{D} lit.^{a}
cyclohexanone	98.145	0.9452	1.4498	1.4500
1-octanol	130.231	0.82499	1.4273	1.4276
cyclohexane	84.162	0.77855	1.4236	1.42354
hexane	86.178	0.65937	1.3722	1.37226
toluene	92.141	0.86693	1.4941	1.49413
β-carotene^b	536.85	1.00		

[a] Riddick et al.[2] [b] Lenfant and Thyrion.[3]

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

where $V_{12}^{id} = V_1^0 x_1^0 + V_2^0 x_2^0$ 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 molar volumes of the pure components.

The β-carotene solubility in pure solvents (including ketones measured in a previous paper[1]) increases in the order 1-octanol < 2-propanone < hexane < 2-butanone < cyclohexanone <cyclohexane < toluene.

The mixing function x_β^{M} proposed by Heric and Posey[5] (called the “deviation function”, cf. previous paper[1]) was applied for better representation of the behavior of the solute in mixed solvents. The function describes the difference between β-carotene solubility in mixed solvent and the linear dependence of β-carotene solubility on a mole fraction basis:

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

In eq 2 x_β, $x_\beta^{(1)}$, and $x_\beta^{(2)}$ are the solubilities in the mixed and pure solvents 1 and 2, respectively. Results of x_β were

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10.1021/je010147l CCC: $20.00

Table 2. Solubility of the β-Carotene in Mixed Solvent Hydrocarbon (1) + Cyclohexanone (2) and Hydrocarbon (1) + 1-Octanol (2) at 293.15 K: x_1^0 = Hydrocarbon Mole Fraction in Binary Solvent, c_β = Molar Concentrations of the β-Carotene, x_β = Solubility of the β-Carotene in Mole Fractions, x_β^M of Equation 2, and Mean Standard Deviation σ_n (in Parentheses)

x_1^0	$10^3 c_\beta$/mol·L^{-1}	$10^4 x_\beta$	$10^4 x_\beta^M$
	Cyclohexane (1) + Cyclohexanone (2)		
0	3.08	3.20 (0.15)	0
0.0991	2.87	3.00 (0.07)	−0.23 (0.13)
0.3000	6.84	7.22 (0.29)	3.92 (0.37)
0.4030	8.42	8.92 (0.24)	5.59 (0.33)
0.4996	8.55	9.09 (0.13)	5.73 (0.23)
0.5955	8.03	8.57 (0.14)	5.18 (0.25)
0.7079	8.13	8.72 (0.09)	5.28 (0.21)
0.7870	7.15	7.69 (0.09)	4.23 (0.21)
0.8011	6.23	6.70 (0.07)	3.23 (0.20)
0.9036	4.53	4.89 (0.12)	1.39 (0.26)
1	3.26	3.53 (0.05)	0
	Hexane (1) + Cyclohexanone (2)		
0	3.08	3.20 (0.15)	0
0.0954	4.85	5.17 (0.55)	2.20 (0.62)
0.2019	4.56	4.99 (0.14)	2.27 (0.21)
0.2019	5.02	5.50 (0.12)	2.78 (0.19)
0.4100	4.65	5.34 (0.15)	3.11 (0.24)
0.5003	3.36	3.95 (0.09)	1.94 (0.19)
0.5017	3.77	4.43 (0.23)	2.42 (0.33)
0.6034	2.75	3.31 (0.09)	1.54 (0.20)
0.6940	2.40	2.94 (0.12)	1.39 (0.24)
0.8011	1.99	2.49 (0.08)	1.19 (0.21)
0.8947	0.89	1.13 (0.12)	0.06 (0.26)
1	0.63	0.845 (0.050)	0
	Toluene (1) + Cyclohexanone (2)		
0	3.08	3.20 (0.15)	0
0.0973	3.52	3.67 (0.13)	−0.32 (0.56)
0.1899	3.52	3.68 (0.61)	−1.06 (1.00)
0.2992	4.40	4.61 (0.10)	−1.02 (0.47)
0.3947	5.71	6.00 (0.19)	−0.40 (0.53)
0.5014	6.74	7.10 (0.17)	−0.17 (0.48)
0.5992	7.43	7.85 (0.05)	−0.21 (0.33)
0.6940	7.23	7.65 (0.08)	−1.18 (0.33)
0.7910	8.68	9.21 (0.07)	−0.41 (0.29)
0.8972	9.17	9.76 (0.06)	−0.72 (0.25)
1	10.59	11.31 (0.46)	0
	Cyclohexane (1) + 1-Octanol (2)		
0	0.177	0.279 (0.015)	0
0.1992	0.166	0.246 (0.023)	−0.681 (0.062)
0.3010	0.171	0.245 (0.009)	−1.013 (0.045)
0.3948	0.566	0.783 (0.061)	−0.780 (0.094)
0.4011[a]	0.516	0.712 (0.025)	−0.871 (0.058)
0.5016	0.493	0.655 (0.016)	−1.255 (0.046)
0.6088	0.809	1.032 (0.015)	−1.227 (0.042)
0.6965	1.015	1.251 (0.044)	−1.293 (0.068)
0.7972[a]	1.228	1.453 (0.028)	−1.420 (0.049)
0.8000	1.438	1.699 (0.063)	−1.182 (0.083)
0.8994	2.298	2.602 (0.055)	−0.602 (0.072)
1	3.262	3.531 (0.046)	0
	Hexane (1) + 1-Octanol (2)		
0	0.177	0.279 (0.015)	0
0.1997	0.090	0.137 (0.017)	−0.255 (0.060)
0.2926	0.273	0.409 (0.011)	−0.036 (0.050)
0.3979	0.169	0.248 (0.021)	−0.256 (0.057)
0.4954	0.359	0.519 (0.040)	−0.040 (0.073)
0.5978	0.258	0.366 (0.021)	−0.251 (0.050)
0.6046	0.318	0.450 (0.010)	−0.171 (0.038)
0.6970	0.486	0.675 (0.022)	0.002 (0.047)
0.7982	0.600	0.817 (0.027)	0.086 (0.048)
0.8997	0.768	1.025 (0.062)	0.237 (0.081)
1	0.646	0.845 (0.050)	0
	Toluene (1) + 1-Octanol (2)		
0	0.177	0.279 (0.015)	0
0.2028	0.309	0.411 (0.034)	−2.06 (0.44)
0.3101	0.593	0.841 (0.082)	−2.86 (0.40)
0.4012	0.615	0.844 (0.116)	−3.86 (0.40)
0.4922	1.185	1.57 (0.18)	−4.14 (0.43)
0.5940	1.877	2.39 (0.20)	−4.44 (0.40)
0.7026	2.706	3.29 (0.14)	−4.74 (0.29)
0.7545[a]	4.927	5.87 (0.14)	−2.73 (0.27)
0.8995	8.230	9.21 (0.27)	−1.00 (0.33)
1	10.596	11.31 (0.46)	0

[a] Separate run.

Table 3. Coefficients a_i and b for Representation Solubility of the β-Carotene Expressed in Mole Fractions in Binary Solvents at 293.15 K by Equation 3 and Standard Deviation σ_s

	solvent (1)		
	cyclohexane	hexane	toluene
	Cyclohexanone (2)		
$10^4 a_0$	23.798	9.2206	−1.5743
$10^4 a_1$	0	−4.9690	0.62672
$10^4 a_2$	−20.190	0	−9.5093
$10^4 a_3$	23.570	0	0
b	0	0.92731	0
$10^4 \sigma_s$	0.52	0.37	0.38
	1-Octanol (2)		
$10^4 a_0$	−4.4752	−0.6338	−19.939
$10^4 a_1$	−2.7393	0	0
$10^4 a_2$	−3.8966	1.2192	18.949
$10^4 a_3$	0	4.8901	0
b	0	0	−0.36443
$10^4 \sigma_s$	0.23	0.10	0.50

smoothed by means of a rational type equation (adequate for mixing functions[6]):

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

Parameters a_i and b in the above formulas were calculated using the Levenberg−Marquardt nonlinear least-squares method[7] and are listed in Table 3 together with the standard deviation

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

where n is the number of experimental points and k is the number of parameters of eq 3. Experimental solubilities of the β-carotene expressed in mole fractions x_β are illustrated in Figure 1 for binary mixed solvents formed by

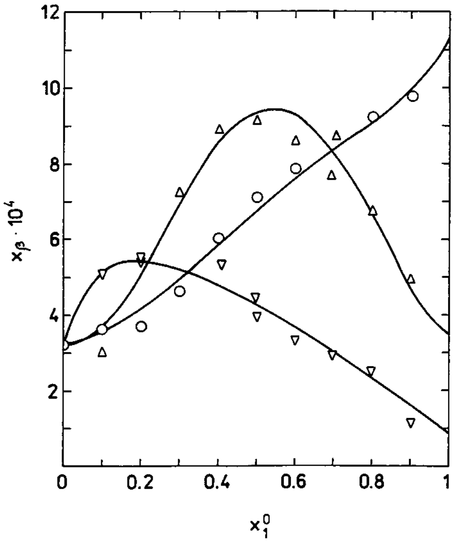

Figure 1. Solubility of β-carotene in mixed solvents hydrocarbon (1) + cyclohexanone (2) at 293.15 K expressed in mole fractions x_β versus mole fraction of hydrocarbon x_1^0: △, cyclohexane (1); ▽, hexane (1); ○, toluene (1). Solid lines are calculated from eq 3 with coefficients from Table 3.

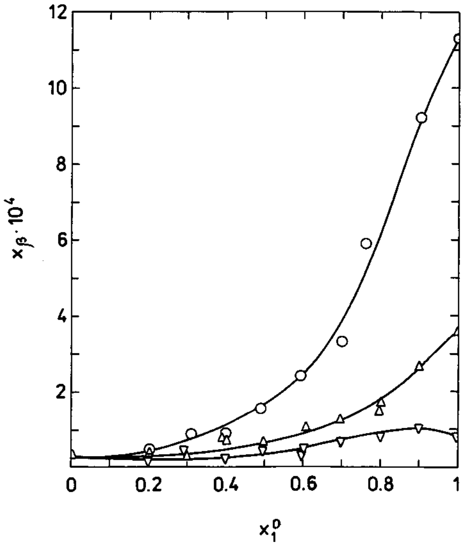

Figure 2. Solubility of β-carotene in mixed solvents hydrocarbon (1) + 1-octanol (2) at 293.15 K expressed in mole fractions x_β versus mole fraction of hydrocarbon x_1^0: △, cyclohexane (1); ▽, hexane (1); ○, toluene (1). Solid lines are calculated from eq 3 with coefficients from Table 3.

cyclohexanone with hydrocarbons and for 1-octanol with hydrocarbons in Figure 2. For mixed solvents cyclohexanone + saturated hydrocarbons the solubility curves are characterized by a significant maximum, whereas for the cyclohexanone + toluene system the solubility curve is concave and the mixing function x_β^M is negative over the whole concentration range. Similar behavior was observed for other mixed solvent ketone + saturated hydrocarbon systems.[1] For mixed solvents formed by 1-octanol with hexane an insignificant maximum solubility of β-carotene is observed in the hexane-rich region, but the solubility curve is concave and x_β^M is negative in the 1-octanol-rich region (see Table 2). For the 1-octanol + cyclohexane system, in contrast to the cyclohexanone + cyclohexane system, a maximum is not observed. For this system, as well as for the 1-octanol + toluene system, the mixing function x_β^M is negative over the whole concentration range. For both of the above-mentioned systems concave solubility curves x_β (see Figure 2) and negative values of the x_β^M mixing function (see Table 2) are observed.

The different behavior of mixed solvents formed by 1-octanol and hydrocarbons in comparison with the systems containing cyclohexanone, as well as of other systems formed by ketones with saturated hydrocarbons,[1] is due to alkanol self-association.[8] The appearance of an insignificant maximum on the solubility curve for 1-octanol + hexane system is due to close solubilities of the solute in both pure solvents. In the case of the cyclohexanone + cyclohexane system presented in Figure 1, solute solubilities in pure component solvents are close and the maximum is significant and nearly at equimolar mixture. For the cyclohexanone + hexane solvent, for which the differences in solubilities of the solute in pure solvents are higher, the maximum is shifted toward mixtures rich in cyclohexanone, that is, the solvent with higher solute solubility. This is confirmed by preliminary calculations performed by Treszczanowicz et al.[9] and Kasprzycka-Guttman et al.[10] The Acree[11] solubility model as well as the models based directly on the Flory and Huggins theory shows that for the same value of excess Gibbs energy for mixed solvent, the position of the maximum shifts toward solvent with greater solute solubility and that for sufficiently large differences the maximum disappears. This phenomenon can be compared with the shift of the maximum on the vapor−liquid equilibrium curve.

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Received for review May 2, 2001. Accepted July 23, 2001.

JE010147L