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Solubility of β-Carotene in Binary Solvents Formed by Some Hydrocarbons with Dibutyl Ether and 1,2-Dimethoxyethane

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Experimental results are reported for the solubility of β-carotene in six binary mixed solvents formed by dibutyl ether with cyclohexane, hexane, and toluene and by 1,2-dimethoxyethane with cyclohexane, hexane, and toluene 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 1,2-dimethoxyethane < hexane < dibutyl ether < cyclohexane < toluene. The solubility data as a function of the binary solvent mass fractions were smoothed by the Myers Scott equation for asymmetric functions.

1. Introduction

This study deals with the solubility of β-carotene at 293.15 K in mixed binary solvents formed by 1,2-dimethoxyethane and dibutyl ether with hydrocarbons. The 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, cyclohexanone, and 1-octanol.[1,2] Currently, only limited solubility data on solid nonelectrolytes in binary mixed solvents are known, and no data on any biologically active substances such as β-carotene and lycopene are available.

2. Experimental Section

Materials. β-Carotene (Sigma, 95 mol % purity) was used as received. The analysis of β-carotene samples by liquid chromatography showed that the purity was better than 95% of the trans isomer. Organic solvents—hexane (Chemipan, Poland, 99.95 mol %, standard), toluene (99 mol %, analytical reagent grade, supplied by the Płock Refinery Industry R & D Center), and cyclohexane (Ubichem Ltd., 99 mol %, standard)—were distilled; dibutyl ether and 1,2-dimethoxyethane (analytical reagent grade, Fluka, 99 mol %) were twice distilled. All reagents were stored over type 4A molecular sieves. The refractive indices are listed in Table 1 and agree well with the literature values.[3] The binary solvent mixtures were prepared by mass; therefore, solvent compositions could be uncertain to within 0.0001 mole fraction. The methods of sample equilibration and analysis were presented in an earlier paper.[1]

3. Results and Discussion

Table 2 presents the experimental solubilities of β-carotene in binary mixed solvents expressed as molar concentrations, c_β/mol·L^{-1}, and in mole fractions, x_β, together with the 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 the data listed in Table 1. The detailed procedure was presented in the preceding paper.[1] The molar concentrations c_β given in Table 2 were calculated by using the data of Table 1 and the relation

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 exp	n_D lit.^{a}
1,2-dimethoxyethane	98.145	0.8691	1.3783	1.3781
dibutyl ether	130.231	0.7684	1.3970	1.3968
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^b		

[a] Riddick et al.[3] [b] Lenfant and Thyrion.[4]

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

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

The solubility of β-carotene in the pure solvents (including ketones measured in previous papers[1,2]) increases in the order 2-propanone < 1,2-dimethoxyethane < hexane < 2-butanone < dibutyl ether < cyclohexanone < cyclohexane < toluene.

The mixing function x_β^M proposed by Heric and Posey[5] (termed the “deviation function”, cf. previous paper[1]) 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 solubility of β-carotene on a mole fraction basis:

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

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Table 2. Solubility of β-Carotene in the Mixed Solvents Hydrocarbon (1) + 1,2-Dimethoxyethane (2) and Hydrocarbon (1) + Dibutyl Ether (2) at 293.15 K: x_1° = Hydrocarbon Mole Fraction in Binary Solvent, c_β = Molar Concentrations of β-Carotene, x_β = Solubility of β-Carotene in Mole Fraction, x_β^M from Eq 2 with the Mean Standard Deviation σ_n in Parentheses

x_1°	10^3c_β/mol·L^{-1}	10^4x_β	$10^4x_\beta^M$	x_1°	10^3c_β/mol·L^{-1}	10^4x_β	$10^4x_\beta^M$
Cyclohexane (1) + 1,2-Dimethoxyethane (2)							
0	0.61	0.63 (0.04)	0	0.4996	5.70	6.05 (0.08)	3.97 (0.13)
0.0954	1.24	1.29 (0.07)	0.38 (0.12)	0.6150	6.12	6.53 (0.18)	4.12 (0.22)
0.1974	2.63	2.75 (0.13)	1.55 (0.18)	0.7008	6.03	6.46 (0.09)	3.80 (0.13)
0.3017	3.79	3.99 (0.19)	2.49 (0.24)	0.8019	5.19	5.58 (0.07)	2.62 (0.11)
0.3043[a]	3.87	4.07 (0.20)	2.56 (0.25)	0.9365	3.58	3.87 (0.10)	0.52 (0.14)
0.3962	5.37	5.68 (0.16)	3.90 (0.21)	1	3.26	3.53 (0.05)	0
Hexane (1) + 1,2-Dimethoxyethane (2)							
0	0.61	0.63 (0.04)	0	0.6028	1.73	2.08 (0.08)	1.32 (0.12)
0.1013	0.82	0.87 (0.02)	0.21 (0.07)	0.6951	1.71	2.10 (0.10)	1.32 (0.14)
0.1986	1.26	1.37 (0.07)	0.70 (0.12)	0.7977	1.52	1.91 (0.09)	1.11 (0.13)
0.2990	1.69	1.89 (0.03)	1.20 (0.08)	0.7982[a]	1.43	1.79 (0.08)	0.99 (0.12)
0.4004	1.70	1.95 (0.03)	1.23 (0.08)	0.8997	1.00	1.28 (0.09)	0.46 (0.13)
0.5040	1.93	2.27 (0.10)	1.53 (0.14)	1	0.65	0.845 (0.05)	0
Toluene (1) + 1,2-Dimethoxyethane (2)							
0	0.61	0.63 (0.04)	0	0.4968	3.05	3.21 (0.06)	−2.49 (0.17)
0.1115	1.07	1.11 (0.02)	−0.66 (0.18)	0.6079	2.90	3.06 (0.23)	−3.77 (0.32)
0.2004	1.50	1.56 (0.61)	−1.12 (0.76)	0.7035	4.34	4.59 (0.27)	−3.22 (0.35)
0.3089	1.92	2.01 (0.05)	−1.77 (0.19)	0.8043	6.99	7.42 (0.41)	−1.42 (0.48)
0.4057	2.52	2.64 (0.18)	−2.13 (0.30)	0.9079	7.73	8.22 (0.36)	−1.68 (0.41)
				1	0.00	10.84 (0.18)	0
Cyclohexane (1) + Dibutyl Ether (2)							
0	0.93	1.58 (0.08)	0	0.6000	2.52	3.35 (0.15)	0.78 (0.22)
0.1031	1.34	2.18 (0.11)	0.40 (0.16)	0.7001	2.87	3.64 (0.12)	0.69 (0.19)
0.2018	1.65	2.60 (0.19)	0.63 (0.25)	0.7990	3.16	3.81 (0.14)	0.67 (0.21)
0.3021	1.79	2.70 (0.21)	0.53 (0.27)	0.8252[a]	3.03	3.60 (0.10)	0.41 (0.17)
0.4040	2.29	3.31 (0.13)	0.94 (0.19)	0.9013	3.24	3.70 (0.09)	0.36 (0.17)
0.4981	2.35	3.27 (0.10)	0.72 (0.16)	1	3.26	3.53 (0.05)	0
Hexane (1) + Dibutyl Ether (2)							
0	0.93	1.58 (0.08)	0	0.5199[a]	0.71	1.06 (0.03)	−0.14 (0.10)
0.1067	0.89	1.47 (0.13)	−0.03 (0.28)	0.6033	0.69	1.01 (0.06)	−0.13 (0.13)
0.1481[a]	0.83	1.36 (0.18)	−0.11 (0.23)	0.7136	0.66	0.93 (0.04)	−0.13 (0.10)
0.2022	0.79	1.28 (0.12)	−0.15 (0.18)	0.7974	0.69	0.95 (0.03)	−0.04 (0.10)
0.3049	0.81	1.27 (0.08)	−0.09 (0.11)	0.8004	0.64	0.89 (0.04)	−0.10 (0.11)
0.3049[a]	0.78	1.23 (0.06)	−0.13 (0.16)	0.8330[a]	0.62	0.85 (0.06)	−0.12 (0.13)
0.4153	0.73	1.12 (0.09)	−0.15 (0.15)	0.8997	0.65	0.87 (0.05)	−0.05 (0.13)
0.4910	0.75	1.13 (0.05)	−0.09 (0.11)	1	0.65	0.845 (0.050)	0
Toluene (1) + Dibutyl Ether (2)							
0	0.93	1.58 (0.08)	0	0.6034	2.87	3.78 (0.15)	−3.39 (0.38)
0.1047	0.99	1.61 (0.04)	−0.94 (0.46)	0.6795[a]	3.48	4.41 (0.19)	−3.46 (0.39)
0.2020	1.14	1.78 (0.10)	−1.67 (0.48)	0.7038	3.91	4.89 (0.24)	−3.21 (0.43)
0.2991	1.47	2.22 (0.13)	−2.13 (0.48)	0.7982	4.70	5.61 (0.33)	−3.36 (0.49)
0.4074	1.45	2.09 (0.10)	−3.26 (0.41)	0.9024	6.58	7.42 (0.28)	−2.52 (0.40)
0.5098	2.29	3.14 (0.22)	−3.16 (0.49)	1	10.15	10.84 (0.46)	0

[a] Separate run.

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

	solvent (1)		
	cyclohexane	hexane	toluene
1,2-Dimethoxyethane (2)			
10^4a_0	16.721	5.8640	−11.447
10^4a_1	0	1.4595	0
10^4a_2	−13.537	−1.7474	−6.8048
b	−0.46308	0	−0.64324
$10^4\sigma_s$	0.16	0.09	0.45
Dibutyl Ether (2)			
10^4a_0	3.2246	−0.55858	−12.819
10^4a_1	0	0.06721	0.59151
b	0.031592	0	−0.89574
$10^4\sigma_s$	0.13	0.03	0.16

where x_β, $x_\beta^{(1)}$, and $x_\beta^{(2)}$ are the solubilities in the mixed solvent and in pure solvents 1 and 2, respectively. The x_β solubilities were smoothed by means of the rational type equation (adequate for mixing functions[6]):

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

The parameters a_i and b were calculated by using the Levenberg–Marquardt nonlinear least-squares method;[7] they are listed in Table 3 together with the standard deviations:

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

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

The experimental solubilities of β-carotene expressed in mole fractions, x_β, are presented graphically in Figure 1

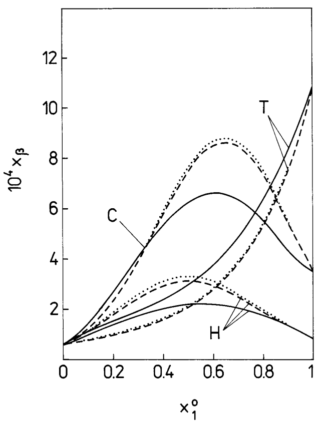

Figure 1. Solubility of β-carotene x_β in the binary solvents hydrocarbon (1) + 1,2-dimethoxyethane (2) at 293.15 K vs mole fraction of hydrocarbon x_1°: curves are labeled with *C* for cyclohexane, *H* for hexane, and *T* for toluene. Curves: —, smoothed experimental data, calculated with coefficients from Table 3; - - -, on the basis of the Flory and Huggins model, eq 5; · · ·, on the basis of the Acree and Rytting model, eq 7.

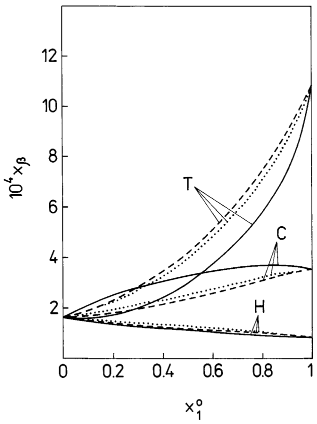

Figure 2. Solubility of β-carotene x_β in the binary solvents hydrocarbon (1) + dibutyl ether (2) at 293.15 K vs mole fraction of hydrocarbon x_1°: curves are labeled with *C* for cyclohexane, *H* for hexane, and *T* for toluene. Curves: —, smoothed experimental data, calculated with coefficients from Table 3; - - -, on the basis of the Flory and Huggins model, eq 5; · · ·, on the basis of the Acree and Rytting model, eq 7.

for the binary solvents formed by 1,2-dimethoxyethane with hydrocarbons and by dibutyl ether with hydrocarbons in Figure 2. For the mixed solvents formed by 1,2-dimethoxyethane with saturated hydrocarbons, the solubility curves are characterized by a significant maximum. A similar behavior was presented earlier for the mixed solvent formed by ketone with saturated hydrocarbons.[1,2] For the mixed solvent formed by dibutyl ether with cyclohexane, an insignificant maximum occurs in the solubility curve of β-carotene in the cyclohexane-rich region (see Table 2). In contrast to the case of the 1,2-dimethoxyethane + hexane system, in the dibutyl ether + hexane system no maximum is observed (see Figure 2). For the binary systems formed by toluene with either of the ethers, the β-carotene solubility curves x_β are concave and the mixing function x_β^{M} is negative over the whole concentration range.

Such a behavior is explained by the model calculations using the Flory and Huggins theory (FH) of nonathermal mixtures[8−10] and the Acree and Rytting model (AR),[11] which describes the solubility of a solute in the binary solvent as a function of the excess Gibbs energy of a solvents mixture (without solute). In the FH theory, the solubility x_β of solute β is described by the mole fraction of the solute:[8−10]

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

where the logarithm of the activity of the solid solute in the reduced form is given by $\ln a_\beta^{\mathrm{st}} = -\Delta h_{\mathrm{f},\beta}(1 - T/T_{\mathrm{f},\beta})/RT$, where, for the β-carotene, $\Delta h_{\mathrm{f},\beta} = 56\ \mathrm{kJ{\cdot}mol^{-1}}$ is the molar enthalpy of fusion at the normal melting point $T_{\mathrm{f},\beta} = 456$ K. These values were taken from Lenfant and Thyrion.[4] The $x_\beta^{(i)}$ and $\varphi_\beta^{(i)}$ are the mole and the volume fractions of the solute in the *i*-th pure solvent, and x_i° and φ_i° are the mole and the volume fractions of the i-th solvent in the mixed solvent (without solute). The residual contribution to excess Gibbs energy, $G_{12}^{\mathrm{E,res}} = G_{12}^{\mathrm{E}} - G_{12}^{\mathrm{E,comb}}$, was calculated from the combinatorial contribution $G_{ij}^{\mathrm{E,comb}} = RT(x_i^\circ \ln(\varphi_i^\circ/x_i^\circ) + x_j^\circ \ln(\varphi_j^\circ/x_j^\circ))$ and values of the excess Gibbs energy G_{12}^{E} of the 1 and 2 solvent mixture estimated by means of the UNIFAC group interaction method;[12] $(\mu_\beta^{\mathrm{E}})_i^{\mathrm{res}}$ is the residual contribution to the excess chemical potential of the solute at the saturated concentration in pure component *i*. This contribution can be calculated as

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

In the AR model[11] (see ref 10) the solubility φ_β of solute β is described by the volume fraction of the solute:

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

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

The two models predict very well the maximum solubility in the systems formed by 1,2-dimethoxyethane with cyclohexane and hexane, including the shift of the maximum toward the component dissolving more β-carotene, as shown in Figure 1. The appearance of the maximum is due to a relatively high excess Gibbs energy (at the maximum, it attains 450 J·mol^{-1} at $t = 20$ °C as estimated by using the UNIFAC vapor−liquid set of parameters[12]). On the contrary, as shown in Figure 2, the dibutyl ether + hexane system does not exhibit a maximum solubility and the dibutyl ether + cyclohexane system exhibits only a slight maximum (at the maximum, the excess Gibbs energy attains 100 J·mol^{-1} at $t = 20$ °C as estimated by using UNIFAC[12]). For systems formed by toluene with 1,2-dimethoxyethane and dibutyl ether, the solubility curves are concave, as shown in Figures 1 and 2. This is because the excess Gibbs energy is much lower due to n−π interactions between the free pair of electrons on the ether oxygen and the π electrons of the aromatic ring as well as the bigger difference of the solubilities of β-carotene in pure solvents.[9,10]

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