J. Chem. Eng. Data **2005,** *50,* 973−976

Solubility of β-Carotene in Binary Solvents Formed by Some Hydrocarbons with *tert*-Butyl Methyl Ether and with *tert*-Amyl Methyl Ether

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Experimental results are reported for the solubility of β-carotene in six binary mixed solvents formed by *tert*-butyl methyl ether or *tert*-amyl methyl ether with cyclohexane, hexane, and toluene at 293.15 K. A spectral colorimeter was used for the analysis of β-carotene concentration. The β-carotene solubility in the pure solvents increases in the order hexane < *tert*-butyl methyl ether < *tert*-amyl methyl ether < cyclohexane < toluene. The solubility data as a function of the binary solvent mole fractions were correlated by the Myers and Scott equation. Results of these measurements were used to test the predictive ability of β-carotene solubility in the binary mixed solvents using the Treszczanowicz and the Acree and Rytting models. Both models qualitatively predict the solubility of β-carotene in the above-mentioned mixed solvents.

Introduction

This study deals with the solubility of β-carotene at 293.15 K in mixed binary solvents formed by *tert*-butyl methyl ether and *tert*-amyl methyl ether with hydrocarbons. This work continues our earlier studies on the solubility of β-carotene in binary mixed solvents formed by hydrocarbons such as hexane, cyclohexane, and toluene with 2-propanone, 2-butanone, cyclohexanone, 1-octanol, 1,2-dimethoxyethane, and dibutyl ether.[1−3] 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 are available.

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 (main impurities are α-carotene and lycopene). We used the following organic solvents: hexane (Chemipan, Poland 99.95 mol % standard) was used as received; toluene (99 mol % analytical reagent grade, supplied by the Płock Refinery Industry R & D Center) and cyclohexane (Ubichem Ltd., 99 mol % standard) were distilled; *tert*-butyl methyl ether (Fluka, 99.8 mol % analytical grade) was used as supplied; and *tert*-amyl methyl ether (Fluka, 97 mol % pure grade) was twice distilled. All reagents were stored over type 4A molecular sieves. The densities and refractive indices are listed in Table 1 and agree well with the literature values.[4] The binary solvent mixtures were prepared by mass so that compositions could be calculated to 0.0001 mole fraction. The methods of sample equilibration and spectral colorimeter analysis determination of β-carotene solubility are 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 mole fractions, x_β, together with the mean standard deviations σ_n and with the mixing function x_β^{M}. The standard deviation σ_n was calculated from 9 to 12 repeated experimental measurements.[1] 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 following relation

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

where $V_{12}^{\mathrm{id}} = V_1^0 x_1^0 + V_2^0 x_2^0$, x_1^0 and $x_2^0 = 1 - x_1^0$ are the mole fractions of the 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 solubility of β-carotene in the pure solvents (including ketones and ethers measured in previous papers[1−3]) increases in the order 1-octane < 2-propanone < 1,2-dimethoxyethane < hexane < 2-butanone < *tert*-butyl methyl ether < *tert*-amyl methyl ether < *tert*-amyl methyl ether < dibutyl ether < cyclohexanone < cyclohexane < toluene.

The mixing function x_β^{M} proposed by Heric and Posey[7] (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 of the solubility of β-carotene on a mole fraction basis:

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

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10.1021/je0495583 CCC: $30.25

Table 1. Physicochemical Property Data of the Solvents Studied[a]

solvent	M^b g·mol^{-1}	d/g·cm^{-3} exp	d/g·cm^{-3} lit^b	n_D exp	n_D lit^b
tert-butyl methyl ether	88.150	0.7405	0.7406^c	1.3660	1.3663^c
tert-amyl methyl ether	102.177	0.7706	0.7703^c	1.3867	1.3861^c
cyclohexane	84.162	0.7784	0.77855	1.4236	1.42354
hexane	86.178	0.6594	0.65937	1.3722	1.37226
toluene	92.141	0.8662	0.86693	1.4941	1.49413
β-carotene^c	536.85		1.00^d		

[a] M − molecular mass, d − density at 293.15 K, n_D − refractive index at 298.15 K. [b] Riddick et al.[4] [c] API Res. Rep.[5] [d] Lenfant and Thyrion.[6]

Table 2. Solubility of *β*-Carotene in Mixed Solvent Hydrocarbon (1) + *tert*-Butyl Methyl Ether (2) and Hydrocarbon (1) + *tert*-Amyl Methyl Ether (2) at 293.15 K[a]

x_1^0	10^3c_β mol·L^{-1}	10^4x_β	$10^4x_\beta^M$	x_1^0	10^3c_β mol·L^{-1}	10^4x_β	$10^4x_\beta^M$
Cyclohexane (1) + *tert*-Butyl Methyl Ether (2)							
0	0.99 (0.02)	1.19 (0.03)	0	0.5010	2.45 (0.14)	2.78 (0.05)	0.71 (0.15)
0.1003	1.42 (0.05)	1.68 (0.08)	0.31 (0.24)	0.6047	2.45 (0.10)	2.75 (0.18)	0.50 (0.27)
0.2028	1.72 (0.04)	2.01 (0.06)	0.46 (0.20)	0.6961	2.65 (0.04)	2.95 (0.06)	0.53 (0.13)
0.3054	2.18 (0.08)	2.52 (0.14)	0.79 (0.27)	0.7995	2.84 (0.12)	3.14 (0.25)	0.54 (0.31)
0.3976^b	2.32 (0.14)	2.66 (0.37)	0.77 (0.48)	0.8979	2.79 (0.10)	3.05 (0.19)	0.28 (0.23)
				1	2.73 (0.09)	2.95 (0.17)	0
Hexane (1) + *tert*-Butyl Methyl Ether (2)							
0	0.99 (0.03)	1.19 (0.03)	0	0.6014	0.93 (0.08)	1.17 (0.10)	0.15 (0.14)
0.2042	1.14 (0.04)	1.38 (0.05)	0.25 (0.10)	0.7981	0.86 (0.06)	1.11 (0.08)	0.15 (0.11)
0.4043	1.12 (0.16)	1.39 (0.20)	0.32 (0.24)	0.8068	0.78 (0.03)	1.00 (0.04)	0.04 (0.07)
0.5020	1.14 (0.06)	1.42 (0.08)	0.38 (0.12)	1.0000	0.69 (0.04)	0.90 (0.05)	0
Toluene (1) + *tert*-Butyl Methyl Ether (2)							
0	0.99 (0.03)	1.19 (0.03)	0	0.4946	3.73 (0.10)	4.21 (0.11)	−1.72 (0.36)
0.1003	1.55 (0.06)	1.82 (0.07)	−0.33 (0.49)	0.6009	4.30 (0.16)	4.80 (0.18)	−2.15 (0.38)
0.2047	1.81 (0.12)	2.11 (0.14)	−1.04 (0.51)	0.6982	5.03 (0.20)	5.55 (0.22)	−2.33 (0.38)
0.3005	2.04 (0.02)	2.35 (0.02)	−1.72 (0.35)	0.8104	5.93 (0.19)	6.46 (0.21)	−2.49 (0.32)
0.3998	2.67 (0.04)	3.04 (0.04)	−1.98 (0.33)	0.8992	7.07 (0.19)	7.63 (0.20)	−2.17 (0.27)
				1	10.09 (0.43)	10.77 (0.46)	0
Cyclohexane (1) + *tert*-Amyl Methyl Ether (2)							
0	1.36 (0.05)	1.80 (0.06)	0	0.4901	2.29 (0.03)	2.76 (0.04)	0.40 (0.16)
0.1012	1.53 (0.02)	1.99 (0.03)	0.07 (0.19)	0.6066	2.40 (0.01)	2.83 (0.01)	0.33 (0.11)
0.1960	1.74 (0.03)	2.23 (0.04)	0.20 (0.19)	0.6872	2.93 (0.04)	3.40 (0.05)	0.81 (0.14)
0.2923	1.98 (0.06)	2.49 (0.08)	0.35 (0.22)	0.7957^b	2.63 (0.10)	2.98 (0.01)	0.26 (0.09)
0.4011	2.51 (0.07)	3.08 (0.08)	0.82 (0.21)	0.8994	2.78 (0.12)	3.08 (0.13)	0.25 (0.20)
				1	2.73 (0.16)	2.95 (0.17)	0
Hexane (1) + *tert*-Amyl Methyl Ether (2)							
0	1.36 (0.05)	1.80 (0.06)	0	0.6005	1.06 (0.11)	1.39 (0.15)	0.13 (0.21)
0.1052	1.49 (0.33)	1.97 (0.44)	0.26 (0.49)	0.6980	0.78 (0.04)	1.02 (0.05)	−0.15 (0.11)
0.2006	1.41 (0.22)	1.87 (0.30)	0.25 (0.35)	0.7994	0.80 (0.05)	1.05 (0.06)	−0.03 (0.12)
0.3064	1.46 (0.18)	1.93 (0.24)	0.41 (0.29)	0.8002	0.80 (0.04)	1.05 (0.05)	−0.03 (0.11)
0.3987	1.20 (0.06)	1.58 (0.08)	0.14 (0.13)	0.8981	0.75 (0.02)	0.98 (0.03)	−0.01 (0.09)
0.5024	1.14 (0.19)	1.50 (0.25)	0.15 (0.31)	1	0.69 (0.04)	0.90 (0.05)	0
Toluene (1) + *tert*-Amyl Methyl Ether (2)							
0	1.36 (0.05)	1.80 (0.06)	0	0.4973	3.55 (0.10)	4.25 (0.12)	−2.01 (0.38)
0.1089	1.73 (0.04)	2.24 (0.05)	−0.54 (0.47)	0.5890	4.33 (0.34)	5.08 (0.40)	−2.00 (0.62)
0.2013	2.20 (0.04)	2.80 (0.05)	−0.81 (0.43)	0.6910	4.57 (0.22)	5.24 (0.26)	−2.76 (0.44)
0.2948	2.49 (0.08)	3.11 (0.10)	−1.33 (0.44)	0.8170	5.63 (0.75)	6.27 (0.83)	−2.86 (0.96)
0.4164	2.82 (0.11)	3.43 (0.13)	−2.11 (0.42)	0.9001	7.07 (0.29)	7.72 (0.32)	−2.15 (0.42)
0.4973	3.52 (0.13)	4.21 (0.15)	−2.05 (0.41)	1	10.09 (0.43)	10.77 (0.46)	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 fraction, x_β^M of eq 2 with mean standard deviation σ_n in parentheses. [b] Separate run.

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

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

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

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

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

Table 3. Coefficients a_i and b and Standard Deviation σ_s 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[a], $G_{12}^{E,max}$/J·mol^{-1}, at 293.15 K

	solvent (1)		
	cyclohexane	hexane	toluene
	tert-Butyl Methyl Ether (2)		
10^4a_0	2.8655	1.0940	−8.1119
10^4a_1	0	0	0
10^4a_2	0	0	0
10^4a_3	2.7114	0	0
b	0.53813	0.61177	−0.80182
$10^4\sigma_s$	0.07	0.06	0.23
$G_{12}^{E,max}$	300	267	126
	tert-Amyl Methyl Ether (2)		
10^4a_0	2.3301	0.52495	−8.3887
10^4a_1	0.62060	−1.9280	0
10^4a_2	−1.0699	0.89804	0
10^4a_3	0	0	0
b	0	0	−0.83429
$10^4\sigma_s$	0.18	0.07	0.20
$G_{12}^{E,max}$	239	219	102

[a] Estimated by using UNIFAC, Fredenslund et al.[13]

The experimental solubilities of β-carotene expressed in mole fraction, x_β, are presented graphically in Figure 1 for the binary solvents formed by *tert*-butyl methyl ether with hydrocarbons and by *tert*-amyl methyl ether with hydrocarbons in Figure 2. For the mixed solvents formed by the two ethers with hydrocarbons, the solubility curves are characterized by an insignificant maximum shifted toward solvent showing better solubility of β-carotene and slightly positive values of the mixing function x_β^M (Table 2). Our earlier solubility results of β-carotene for the mixed solvent formed by dibutyl ether with cyclohexane are similar,[3] but they differ markedly from those observed for binary solvents formed by ketones[1,2] or 1,2-dimethoxyethane[3] with saturated hydrocarbons. These systems exhibit a significantly high maximum of β-carotene solubility. For the binary systems formed by toluene with the *tert*-butyl methyl ether and the *tert*-amyl methyl ether, the β-carotene solubility curves x_β are concave downward, and the Heric and Posey mixing function x_β^M is negative over the whole concentration range.

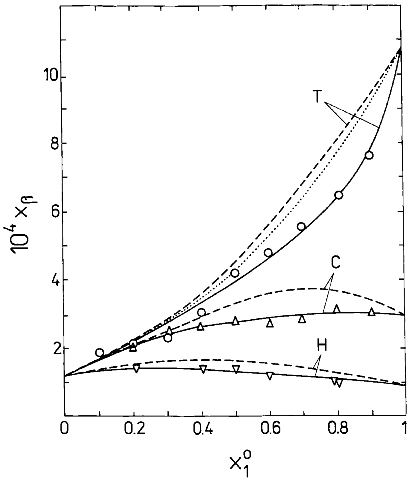

Figure 1. Solubility of β-carotene x_β in the binary solvent hydrocarbon (1) + *tert*-butyl methyl ether (2) at 293.15 K vs mole fraction of hydrocarbon x_1^0. Curves are labeled with C − cyclohexane, H − hexane, and *T* − toluene. Curves: —, smoothed experimental data calculated with coefficients from Table 3; - - -, Flory−Huggins model, eq 5; ···, Acree−Rytting model, eq 7. Points denote experimental results: ○, toluene; ▽, hexane; and △, cyclohexane. For systems formed by a saturated component, the predicted curves coincide for both models.

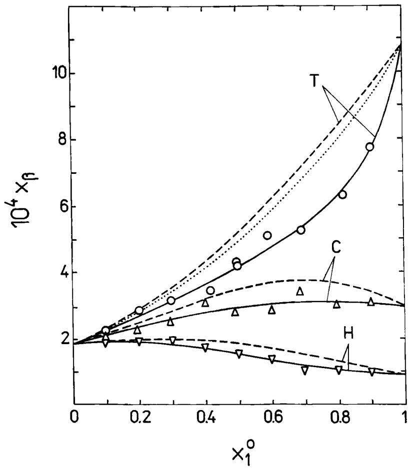

Figure 2. Solubility of β-carotene x_β in the binary solvent hydrocarbon (1) + *tert*-amyl methyl ether (2) at 293.15 K vs mole fraction of hydrocarbon x_1^0. Curves are labeled C − cyclohexane, H − hexane, and T − toluene. Curves: —, smoothed experimental data calculated with coefficients from Table 3; - - -, Flory−Huggins model, eq 5; ···, Acree−Rytting model, eq 7. Points denote experimental results: ○, toluene; ▽, hexane; and △, cyclohexane. For systems formed by a saturated component, the predicted curves coincide for both models.

Such a behavior can be explained by using the Flory and Huggins theory (FH) of non-athermal mixtures[10,11] and the Acree and Rytting model (AR),[12] which describes the solubility of a solute in a binary solvent, x_β, as a function of the excess Gibbs energy of the solvent mixture (without solute). In the FH theory, the solubility x_β of solute β is described by the mole fraction of the solute[10,11]

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

where the logarithm of the activity of the solid solute in reduced form is given by $\ln a_\beta^{st} = -\Delta h_{f,\beta}(1 - T/T_{f,\beta})/RT$, where for the β-carotene $\Delta h_{f,\beta} = 56$ kJ mol^{-1} is the molar enthalpy of fusion at the normal melting point, $T_{f,\beta} = 456$ K. These values were taken from Lenfant and Thyrion.[6] $x_\beta^{(i)}$ and $\varphi_\beta^{(i)}$ are the mole fraction and the volume fraction of the solute in the *i*th pure solvent, and x_i^0 and φ_i^0 are the mole fraction and the volume fraction of the *i*th solvent in the mixed solvent (without solute). The residual contribution to the excess Gibbs energy, $G_{12}^{E,res} = G_{12}^E - G_{12}^{E,comb}$, was calculated from the 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 1 and 2 solvent mixture were estimated by means of the UNIFAC group interactions method.[13] $(\mu_\beta^E)_i^{res}$ 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

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

In the AR model,[12] the solubility φ_β of solute β is described by the volume fraction of the solute

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

where $(\Delta\bar{G}_\beta^{\mathrm{fh}})_{x_i=1} = RT\ \ln(a_\beta^{\mathrm{st}}/x_\beta^{(i)}) - 1 + V_\beta^0/V_i^0$ 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 qualitatively well the β-carotene solubility in the systems formed by *tert*-butyl methyl ether and *tert*-amyl methyl ether with cyclohexane and hexane and toluene as shown in Figures 1 and 2. For the ether + saturated hydrocarbon, both models predict a slight, insignificant maximum shifted toward the solvent, showing better solubility of β-carotene. The maximums appear despite low values of the excess Gibbs energy, G_{12}^{E}, (see Table 3, (at its maximum it is in range of 220−300 J mol^{-1} at $T = 293.15$ K) due to low differences in the solubility of pure solvents $|x_\beta^{(1)} - x_\beta^{(2)}|$. Moreover, the shift of the maximum depends on this difference. For systems formed by toluene with *tert*-butyl methyl ether and *tert*-amyl methyl ether, the FH and AR models predict concave-downward solubility curves and negative x_β^{M} values over the whole concentration range as shown in Figures 1 and 2. This can be explained by the large difference $|x_\beta^{(1)} - x_\beta^{(2)}|$ in the solubilities of β-carotene in pure solvents[11] as well as by the low values of the excess Gibbs energy, G_{12}^{E} (see Table 3, at its maximum it is in range of 100−130 J mol^{-1} at $T = 293.15$ K).

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Received for review December 15, 2004. Accepted March 22, 2005.

JE0495583