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Solubility of β-Carotene in Binary Solvents Formed by Some Hydrocarbons with Ketones

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Experimental results are reported for the solubility of β-carotene in six binary mixed solvents formed by 2-propanone or 2-butanone with cyclohexane, hexane, and toluene at 293.15 K. A spectrocolorimeter was used for analysis of the β-carotene concentration. The solubility of β-carotene in pure solvents increases in the order 2-propanone < hexane < 2-butanone < cyclohexane < toluene. In the mixed solvents studied a maximum of β-carotene solubility is observed, except for the toluene + 2-propanone binary solvent.

Introduction

This study of β-carotene solubility in mixed binary solvents[1,2] formed by a hydrocarbon with a ketone at 293.15 K is a continuation of our earlier studies on the distribution coefficient of β-carotene between the mentioned mixed solvents and water.[3,4] Currently, limited solubility data of crystalline solid nonelectrolytes in binary mixed solvents are known but not for any biologically active substances such as β-carotene. The measurements of β-carotene solubility in pure organic solvents were made recently by Craft and Soares.[5]

Experimental Section

Materials. β-Carotene from Sigma (started purity 95 mol %) was used as supplied. The analysis of the β-carotene samples by liquid chromatography showed that the purity was better than 95 mol % of the trans isomer. Organic solvents—hexane (99.95 mol %) standard, by Chemipan, Poland; toluene (99 mol %) analytical reagent grade, by the Płock Refinery Industry R & D Center; and cyclohexane (99 mol %) standard, by Ubichem Ltd.—were distilled; 2-propanone analytical reagent grade (99 mol %), supplied by the Płock Refinery Industry R & D Center, was twice distilled. All reagents were stored over molecular sieves type 4A. Refractive indices n_D for the reagents studied, at $T = 298.15$ K, are listed in Table 1 together with values from the literature.

Procedure. Determination of β-carotene solubility in both pure and mixed solvents was carried out measuring percent transmission of light v at a selected wavelength. The transmission was measured at (293.1 ± 0.1) K using a Specol, DDR colorimeter.[8] Prior to the measurements, reference curves were drawn up for the dependence of β-carotene molar concentration c_β (mol L^{-1}) in a solvent (pure or mixed, of a known composition) with respect to the absorbance $D = \log(100/\nu)$ according to the Beer and Lambert law:

$$c_\beta = a_1 \log D \tag{1}$$

The concentrations c_β of β-carotene for the reference curve were calculated from β-carotene mass fractions using eq 2. The parameter a_1 in eq 1 was calculated as an average $a_1 = \sum a_{1,i}/n$ over each series of n measurements, where $a_{1,i} = c_{\beta,i}/\log(100/\nu_i)$ is the result for the i-th experimental point. The results, whose deviation $|a_{1,i} - a_1|$ exceeds the value of the mean standard deviation twice, were rejected.[9] Reference curves were set up at three selected wavelengths for different β-carotene concentrations in pure solvent, and for all of the compositions of the mixed solvent examined.

Table 1. Physicochemical Properties of the Solvents Studied: M = Molecular Mass; ρ = Density at 293.15 K; n_D = Refractive Index at 298.15 K

solvent	M_i^a (g/mol)	ρ^a (g/cm^3)	n_D exp	n_D lit.^{a}
2-propanone	58.080	0.790 79	1.3561	1.356 09
2-butanone	72.107	0.804 9	1.3767	1.376 85
cyclohexane	84.162	0.778 55	1.4236	1.423 54
hexane	86.178	0.659 37	1.3722	1.372 26
toluene	92.141	0.866 93	1.4941	1.494 13
β-carotene^b	536.85	1.00		

[a] Riddick et al.[6] [b] Lenfant and Thyrion.[7]

To obtain saturated solutions of β-carotene, a solution containing β-carotene in excess was stirred 24 h at constant temperature $T = (293.1 \pm 0.1)$ K. The sample was kept at constant temperature an additional period to enable any dispersed solids to settle down. This procedure was always found sufficient. The bottles (8 mL volume) were filled with a silicone-rubber diaphragm to prevent solvent evaporation from the samples and reference solutions as well as to avoid contact with oxygen from air. Hypodermic syringes were used to sample the solutions and to add the solution being diluted.

To find the β-carotene concentration in the saturated solution, a sample was taken and then diluted such that the final mixture transmission value was in the middle of the range of the reference curve. For each of the saturated

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Table 2. Solubility of β-Carotene in Pure Solvents at 293.15 K, in Molar Concentrations c_β together with Mean Standard Deviation σ_n (in parentheses) and s_β (mg L^{-1}) in Comparison with the Literature Data

		s_β (mg L^{-1})	
solvent	$10^3 c_\beta$ (mol L^{-1})	this work[a]	lit.[b]
2-propanone	0.222 (0.025)	120	200
2-butanone	1.02 (0.13)	550	
cyclohexane	2.65 (0.10)	1430	2000
hexane	0.663 (0.037)	360	600
toluene	10.1 (1.1)	5420	4000

[a] $s_\beta = 10^3 M_\beta c_\beta$. [b] Craft and Soares[5] data at ambient temperature and β-carotene purity > 90%.

solutions studied, at least three samples of dilute solutions were prepared, which differed in concentration. The β-carotene concentration c_β was determined in a diluted sample from the reference curve given by eq 1 and then recalculated on mass fractions by means of eq 2. The saturated solution mass fractions w_β were calculated using the known values of the masses of the solvent and of the saturated solution sample.

The mean value of the β-carotene mass fraction w_β in the saturated solution was calculated from the formula as an average $w_\beta = \sum w_{\beta,i}/n$ where the summation extends over all n of experimental data, $w_{\beta,i}$. Similarly as before, the Chauvenet criterion was used to eliminate results $w_{\beta,i}$, when the deviation $|w_{\beta,i} - w_\beta|$ exceeded the value of the standard deviation twice.

Conversion of β-carotene mass fractions (in both pure and mixed solvents) into molar concentrations c_β (mol L^{-1}) and mole fractions x_β can be made by using the following formulas:

$$c_\beta = 10^3 w_\beta / [w_\beta V_\beta^\circ + (1 - w_\beta) V_{12}^{\mathrm{id}} M_\beta / M_{12}] \tag{2}$$

$$x_\beta = w_\beta / [w_\beta + (1 - w_\beta) M_\beta / M_{12}] \tag{3}$$

where $V_{12}^{\mathrm{id}} = V_1^\circ x_1^\circ + V_2^\circ x_2^\circ$ is the ideal molar volume of the mixed solvent and the term $w_\beta V_\beta^\circ$ is negligible in this case, $M_{12} = M_1 x_1^\circ + M_2 x_2^\circ$ and M_1, M_2, and M_β are the molecular masses of the pure solvents 1, 2, and β-carotene, respectively, and V_1°, V_2°, and V_β° are the molar volumes of the solvents 1, 2, and β-carotene, respectively, whereas w_β is the β-carotene mass fraction and x_1° and $x_2^\circ = 1 - x_1^\circ$ are the mole fractions of the components of the binary mixed solvent. Equation 2 is derived assuming an ideal molar volume of the three-component mixture. The molar volumes of the pure solvents and solute were calculated from the density and molecular mass listed in Table 1.

Results and Discussion

In Table 2 reported β-carotene solubilities in the pure solvents are compared with the literature data.[5] The differences in solubilities for experimental and literature data can be explained by the purities of solute and solvents, the character of the impurities, as well as the difference between the temperature 293.15 of these measurements and the ambient temperature of Craft's and Soares measurements.

The β-carotene solubility increases in the order 2-propanone < hexane < 2-butanone < cyclohexane < toluene. Similarly, it was observed for the distribution coefficient of β-carotene between the above-mentioned hydrocarbons and water.[8]

Table 3. Solubility of β-Carotene in the Mixed Solvents Hydrocarbon (1) + Ketone (2) at 293.15 K: x_1° = Hydrocarbon Mole Fraction in Binary Solvent; c_β = Molar Concentrations of β-Carotene and Mean Standard Deviation σ_n (in Parentheses); x_β = Solubility of β-Carotene in Mole Fraction; x_β^M Is from Eq 4

x_1°	$10^3 c_\beta$ (mol L^{-1})	$10^4 x_\beta$	$10^4 x_\beta^M$
	Cyclohexane (1) + 2-Propanone (2)		
0	0.222 (0.025)	0.163 (0.018)	0
0.2516	1.51 (0.13)	1.28 (0.11)	0.4
0.5030	4.26 (0.34)	3.88 (0.31)	2.4
0.7597	5.53 (0.29)	5.53 (0.29)	3.3
	5.25 (0.50)[a]	5.25 (0.49)	3.0
1	2.66 (0.11).	2.87 (0.11)	0
	Hexane (1) + 2-Propanone (2)		
0	0.222 (0.025)	0.163 (0.018)	0
0.2455	0.664 (0.041)	0.58 (0.04)	0.2
0.5094	1.34 (0.09)	1.38 (0.09)	0.9
0.7528	1.72 (0.09)	2.01 (0.10)	1.3
	1.66 (0.10)[a]	1.94 (0.12)	1.2
1	0.663 (0.037)	0.87 (0.05)	0
	Toluene (1) + 2-Propanone (2)		
0	0.222 (0.025)	0.163 (0.018)	0
0.2429	1.02 (0.08)	0.83 (0.06)	−1.9
0.4960	3.22 (0.39)	2.90 (0.35)	−2.6
0.7501	6.31 (0.25)	6.21 (0.25)	−2.0
	6.45 (0.32)[a]	6.35 (0.31)	−1.8
1	10.1 (1.1)	10.8 (1.1)	0
	Cyclohexane (1) + 2-Butanone (2)		
0	1.02 (0.13)	0.91 (0.12)	0
0.2441	4.31 (0.45)	4.06 (0.42)	2.7
0.4832	9.40 (0.30)	9.30 (0.29)	7.4
0.5013	9.47 (0.80)	9.40 (0.79)	7.5
0.7542	8.89 (0.37)[a]	9.24 (0.38)	6.9
0.7591	9.02 (0.50)	9.39 (0.52)	6.6
	8.67 (0.37)[a]	9.02 (0.38)	7.0
1	2.66 (0.10)	2.87 (0.11)	0
	Hexane (1) + 2-Butanone (2)		
0	1.02 (0.13)	0.91 (0.12)	0
0.2531	2.82 (0.25)	2.82 (0.25)	1.9
0.4978	3.36 (0.13)	3.71 (0.15)	2.8
0.7535	2.88 (0.13)	3.47 (0.15)	2.6
1	0.663 (0.037)	0.87 (0.05)	0
	Toluene (1) + 2-Butanone (2)		
0	1.02 (0.13)	0.91 (0.12)	0
0.2530	3.39 (0.28)	3.18 (0.26)	−0.2
0.5071	6.36 (0.70)	6.26 (0.69)	0.3
0.7700	15.3 (0.7)	15.8 (0.7)	7.3
1	10.1 (1.1)	10.8 (1.1)	0

[a] Separate run.

In Table 3 are reported results of the β-carotene solubility in the mixed binary solvents expressed in molar concentrations c_β and in mole fractions x_β together with the mean standard deviation σ_n and deviation function x_β^{M}. The deviation function x_β^{M} was applied for better representation of the behavior of the solute in mixed solvents.[10] The deviations are those from the linear dependence of β-carotene solubility on solvent compositions:

$$x_\beta^{\mathrm{M}} = x_\beta - \sum_{i=1}^{n=2} x_i^\circ x_\beta^{(i)} \tag{4}$$

where x_β, $x_\beta^{(1)}$, and $x_\beta^{(2)}$ are the solubilities in the mixed and pure solvents 1 and 2, respectively.

The β-carotene solubility data x_β are illustrated in Figure 1a for binary mixed solvents formed by 2-propanone with hydrocarbons and in Figure 1b for 2-butanone with hydrocarbons. In mixed solvents formed by 2-propanone with cyclohexane and hexane as well as by 2-butanone with cyclohexane, hexane, and toluene, maximum solubilities of β-carotene are observed. For a mixed solvent formed by

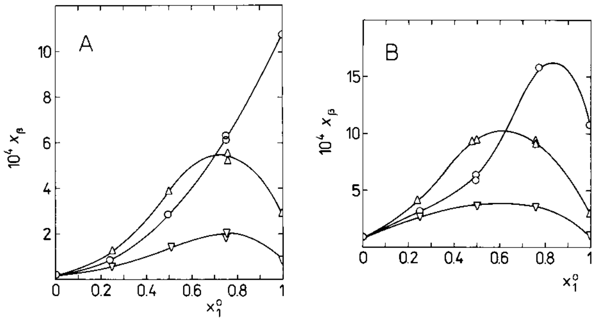

Figure 1. Solubility of β-carotene in the mixed solvents hydrocarbon (1) + ketone (2) at 293.15 K expressed in mole fractions x_β versus mole fraction of hydrocarbon x_1° in a binary mixed solvent formed by a ketone with (△) cyclohexane (1), (▽) hexane (1), and (○) toluene (1): (A) 2-propanone (2) and (B) 2-butanone (2). A solid line is drawn through the experimental points.

toluene with 2-propanone, the concave solubility curve x_β is observed in Figure 1a and negative values of the x_β^M function were obtained (see Table 3).

These results can be interpreted by means of Acree models of solubility[11] as well as the Flory and Huggins theory of nonathermal mixtures.[12] The preliminary calculations[1,2] indicate an important role of the large, positive excess Gibbs energy, G_{12}^E, of the binary mixed solvent formed by saturated hydrocarbon and ketone[13] on the appearance of the maximum solubility of β-carotene. The different behavior of the toluene + 2-propanone mixed solvent, that is, lack of a maximum and negative x_β^M function (cf. Table 3 and Figure 1a), is interpreted by means of the above-mentioned models as a result of the much lower excess Gibbs energy G_{12}^E for this system.[13] However, the β-carotene solubility curve for the toluene + 2-butanone system shows a maximum at the 2-butanone diluted region and a positive−negative x_β^M function (cf. Table 3 and Figure 1b). Such behavior can be interpreted on the basis of the above-mentioned models as a result of a shift of the G_{12}^E maximum toward the toluene rich region or higher curvature of the G_{12}^E curve in the toluene rich region. Such effects are manifested by a higher value activity coefficient of the 2-butanone in toluene system at infinite dilution.[1,2]

The maximum solubility of the β-carotene in mixed solvents formed by 2-propanone with saturated hydrocarbons explains the appearance of a maximum observed for the distribution coefficient of β-carotene between water and mixed solvents[3,4] as a function of 2-propanone concentration in the organic phase.

The fact of a markedly increased solubility of β-carotene in mixed solvents is of great impact in the selection of the best mixed solvent in the commercial processes of the β-carotene production by extraction.

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