970 *J. Chem. Eng. Data* **1999,** *44,* 970−973

Distribution Coefficient of β-Carotene in Systems Composed of Hexane, Water, and 2-Propanone and Toluene, Water, and 2-Propanone

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The distribution coefficient of β-carotene between water and a mixed organic solvent was measured at $T = 298.15$ K. Binary solvent systems formed by 2-propanone with either hexane or toluene were used as the mixed solvent. The liquid−liquid equilibria (LLE), along with the tie lines, were determined for two ternary aqueous systems, hexane + water + 2-propanone and toluene + water + 2-propanone. These systems exhibit a parabolic miscibility gap. The coexistence curves were measured by a titration method, and results were smoothed by means of either three- or four-parameter equations.

1. Introduction

This work is an extension of the previous studies on the distribution coefficient of β-carotene between an organic solvent and water (Treszczanowicz et al., 1998) and mixed organic solvent and water (Treszczanowicz et al., 1999). The need for use of low-boiling extractants resulted in an attempt to use mixed solvents exhibiting large positive deviations from Raoult's law, which have a lower boiling point, compared with pure solvents. The application of an inexpensive and volatile component such as 2-propanone allows one to reduce the hydrocarbon and energy consumption. In our previous paper (Treszczanowicz et al., 1999) mixed solvents composed of 2-propanone and hydrocarbons such as cyclohexane and methylcyclohexane were examined. Here results of investigations are reported for two ternary aqueous systems: hexane (1) + water (2) + 2-propanone (3) and toluene (1) + water (2) + 2-propanone (3) at $T = 298.15$ K.

2. Experimental Section

Materials. β-Carotene, of 95% purity, was supplied by Sigma. Hexane (99.95%) standard, from Chemipan, Warsaw, and toluene analytical reagent grade (99%), by Plock Refinery Industry R & D Centre, were used without additional purification. 2-Propanone analytical reagent grade (99%), by Plock, was twice distilled. The 2-propanone and water used were twice distilled. Refractive index values of the materials measured at $T = 298.15$ K agree well with the literature values (cf. Table 1).

Table 1. Physicochemical Properties of the Solvents Studied: M, Molecular Weight;[a] t_b, Boiling Point at Standard Pressure;[a] d, Density;[a] and n_D, Refractive Index at 298.15 K

				n_D		
i	solvent	M_i/(g/mol)	d/(g/cm^3)	expt	lit.[a]	t_b/°C
1	H_2O	18.01	0.997 05	1.3330	1.33287	100.0
2	$(CH_3)_2CO$	58.080	0.785 08	1.3561	1.35609	56.0
3	C_6H_{14}	86.177	0.654 84	1.3722	1.37226	68.7
4	$C_6H_5CH_3$	92.140	0.862 19	1.4941	1.49413	110.6

[a] Riddick et al. (1986).

Table 2. Mole Fractions of the Coexistence Curve for a Hydrocarbon (1) + Water (2) + 2-Propanone (3) at 298.15 K

x_1	x_3	x_1	x_3	x_1	x_3
		Hexane (1)			
0.000003	0.0000[a]	0.1257	0.6261	0.1895	0.6395
0.0111	0.3102	0.1339	0.6302	0.2508	0.6218
0.0321	0.5400	0.1463	0.6338	0.3350	0.5676
0.0413	0.5214	0.1617	0.6361	0.3737	0.5535
0.0503	0.5557	0.1651	0.6355	0.5657	0.3984
0.0592	0.5747	0.1860	0.6364	0.999394	0.0000[a]
0.0885	0.6019	0.1888	0.6365		
		Toluene (1)			
0.000106	0.0000[a]	0.0595	0.4412	0.1837	0.5806
0.0039	0.2001	0.0599	0.4404	0.1867	0.5800
0.0176	0.3083	0.0605	0.4404	0.1882	0.5965
0.0348	0.3731	0.0621	0.4465	0.1894	0.5952
0.0389	0.3915	0.0626	0.4602	0.1935	0.5905
0.0413	0.3907	0.0791	0.4797	0.1985	0.5860
0.0413	0.3923	0.0815	0.4918	0.2960	0.5755
0.0425	0.4060	0.0854	0.4959	0.3957	0.5176
0.0437	0.4046	0.0904	0.5065	0.4619	0.4695
0.0449	0.4031	0.1040	0.5227	0.4933	0.4475
0.0455	0.4042	0.1299	0.5559	0.5588	0.3930
0.0523	0.4210	0.1448	0.5621	0.5772	0.3808
0.0571	0.4380	0.1497	0.5772	0.6631	0.3047
0.0586	0.4401	0.1510	0.5899	0.7741	0.2067
0.0590	0.4298	0.1665	0.5809	0.9976	0.0000[a]

[a] Verified data by Sorensen and Arlt (1979) for hydrocarbon + water binary systems.

Measuring Procedure. Liquid−liquid equilibria were determined by the titration method described by Letcher et al. (1986) using the apparatus described by Treszczanowicz and Cieslak (1993). For most of the mixtures the concentration measurements were limited to the organic layer as a result of the calculation procedure. The concentration of components in each of the phases was determined

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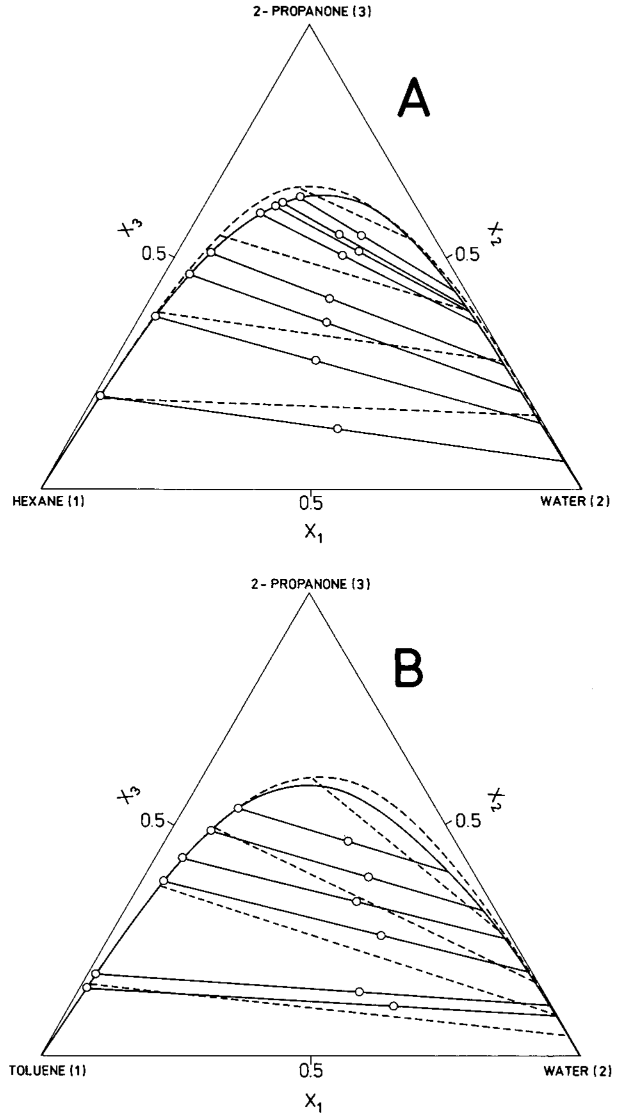

Figure 1. Liquid−liquid equilibrium at $T = 298.15$ K in ternary systems: (A) hexane (1) + water (2) + 2-propanone (3) and (B) toluene (1) + water (2) + 2-propanone (3). The continuous line corresponds to the experimental data smoothed with eq 1 and parameters given in Table 3. The straight lines denote tie lines, continuous lines represent the experimental data given in Table 4, and dashed lines and curves represent the literature data (see text) calculated using the UNIQUAC model and parameters given by Sorensen and Arlt (1979).

by GLC method using a Hewlett-Packard model 6890G, except for β-carotene which was determined by a HPLC method (using 2-propanone as solvent). The relative accuracy of the concentration was ±0.5% for the hexane and toluene and ±1% for 2-propanone and β-carotene. The temperature of measurements $T = 298.15$ K was kept within ±0.02 K. The procedure for the measurement of the liquid−liquid coexistence curve, the tie line and calculation of the distribution coefficient have been detailed elsewhere (Treszczanowicz et al., 1999).

Table 3. Coefficients a_i in Equations 1−3 for Systems Formed by a Hydrocarbon (1) + Water (2) + 2-Propanone (3) at 298.15 K and Standard Deviation (σ) and Maximum Deviation (mx) with Respective to Mole Fraction x_1

quantity	eq 1	eq 2	eq 3
	Hexane (1)		
a_1	53.103	3.8301	3.3865
a_2	78.776	1.3325	1.2677
a_3	1.1548	1.2578	1.7438
a_4	2.4466	−	−
σ	0.0130	0.0056	0.0054
mx	0.0395	0.0135	0.0123
x_1	0.0321	0.0321	0.0321
	Toluene (1)		
a_1	598.99	3.2098	2.8819
a_2	3004.4	1.2264	1.1735
a_3	6.8369	1.2338	1.6868
a_4	7.7794	−	−
σ	0.0075	0.0085	0.0097
mx	0.0200	0.0281	0.0348
x_1	0.1510	0.0039	0.0039

3. Results and Discussion

Results of the measurement of the liquid−liquid equilibria at $T = 298.15$ K are given in Table 2 and illustrated in Figure 1. The coexistence (binodal) curve coordinates, mole fraction of the 2-propanone x_3 and hydrocarbon x_1, were smoothed by means of a four-parameter equation

$$x_3 = (x_1 - x_1^{(2)})(x_1^{(1)} - x_1)\left(\frac{a_1}{1 + a_2x_1} + \frac{a_3}{1 + a_4x_1}\right) \qquad (1)$$

and by means of two three-parameter equations proposed by Letcher et al. (1992),

$$x_3 = a_1(1 - x_A)^{a_2}x^{a_3}{}_A \qquad (2)$$

$$x_3 = a_1(-\ln x_A)^{a_2}x^{a_3}{}_A \qquad (3)$$

where $x_A = (x_1 + 0.5x_3 - x_1^{(2)})/(x_1^{(1)} - x_1^{(2)})$ and $x_1^{(1)}$, $x_1^{(2)}$ are mole fractions of components 1 (hydrocarbon) in phase 1 (nonaqueous, left in Figure 1) and phase 2 (aqueous, right in Figure 1) for the binary water + hydrocarbon systems. The parameters in eqs 1−3 were calculated by the Levenberg−Marquardt nonlinear least-squares method (Press et al., 1988) and are reported in Table 3 along with the standard deviation σ and maximum deviation $\max|x_{3,j}^{(\mathrm{calc})} - x_{3,j}^{\mathrm{expt}}|$ values. The standard deviation σ is defined by formulas

$$\sigma = [\sum_{i=1}^{n}(x_{3,i}^{(\mathrm{calc})} - x_{3,i}^{(\mathrm{expt})})^2/(n - m)]^{1/2} \qquad (4)$$

where n is number of data points and m is the number of parameters.

The results of liquid−liquid equilibria were compared in Figure 1A,B with literature data smoothed by Sorensen and Arlt (1979) by means of UNIQUAC model using the data of Treybal and Vondrak (1949) from op cit, p 487, for the hexane + 2-propanone + water system and Hackl et al. (1978) from op cit, p 495, for the toluene + 2-propanone + water system.

Studies on the coexistence curve and the tie lines of solutions with β-carotene show that the presence of β-carotene has no effect on the liquid−liquid equilibrium as compared with the experimental error in the composition determination. This allowed a significant simplification in the method for the measurement of the distribution coefficient and of the method of determination of concentrations in the coexisting mixtures (the tie lines). The mole fraction

Table 4. Compositions of the Conjugate Solutions of the Tie Lines, Experimental ($x_1^{(1)}$,$x_3^{(1)}$) and Calculated ($x_1^{(2)}$,$x_3^{(2)}$) and Initial Mixture ($x_1^{(0)}$,$x_3^{(0)}$), Experimental Concentrations of β-Carotene $c_\beta^{(1)}$,$c_\beta^{(2)}$ in Both Liquid Phases for the Quaternary System a Hydrocarbon (1) + Water (2) + 2-Propanone (3) + β-Carotene (β), and Distribution Coefficient k_c at 298.15 K

organic phase			initial mixture		aqueous phase			
$x_1^{(1)}$	$x_3^{(1)}$	$c_\beta^{(1)}$/(g L^{-1})	$x_1^{(0)}$	$x_3^{(0)}$	$x_1^{(2)}$	$x_3^{(2)}$	$c_\beta^{(2)}$/(g L^{-1})	k_c
				Hexane (1)				
0.204	0.630	9.327	0.132	0.550	0.0200	0.425	0.2765	34.
0.241	0.618	5.636	0.174	0.551	0.0167	0.395	0.0130	434.
0.260	0.611	4.593	0.155	0.511	0.0150	0.376	0.0075	612.
0.296	0.594	7.062	0.187	0.505	0.0139	0.362	0.0133	531
0.431	0.510	5.453	0.260	0.412	0.0080	0.268	0.0070	779.
0.491	0.465	7.136	0.292	0.360	0.0048	0.189	0.0082	870.
0.602	0.374	6.606	0.351	0.281	0.0036	0.152	0.0085	777
0.790	0.204	4.377	0.386	0.132	0.0013	0.064	0.0072	608.
				Toluene (1)				
0.364	0.538	3.402	0.198	0.465	0.0423	0.396	0.0071	479.
0.442	0.489	5.159	0.199	0.386	0.0212	0.311	0.0070	737.
0.526	0.427	6.374	0.252	0.331	0.0094	0.246	0.0072	885.
0.584	0.380	4.856	0.242	0.265	0.0026	0.185	0.0080	607.
0.813	0.177	6.189	0.343	0.140	0.0006	0.113	0.0089	695.
0.844	0.148	4.074	0.295	0.108	0.0004	0.086	0.0069	590.

ratio for the nonaqueous phase can be found from the concentration ratio of $c_3^{(1)}/c_1^{(1)}$:

$$x_3^{(1)}/x_1^{(1)} = c_3^{(1)}M_1/c_1^{(1)}M_3 \tag{5}$$

where $c_3^{(1)}$ and $c_1^{(1)}$ are concentrations (g/L) of components 3 and 1 in organic phase (1) determined by GLC technique; M_1 and M_3 are their molar masses. The x_3 vs x_1 function for the coexistence curve defined by eq 1 can be used to evaluate mole fractions $x_3^{(1)}$ and $x_1^{(1)}$ for various values of their ratio $x_3^{(1)}/x_1^{(1)}$. The tie line coordinates for the aqueous layer, $x_3^{(2)}$ and $x_1^{(2)}$, were obtained as a results of intersection of a straight line drawn through point ($x_1^{(1)}$, $x_3^{(1)}$) and point ($x_1^{(0)}$, $x_3^{(0)}$) corresponding to the composition of the starting mixture with this part of the coexistence curve described by eq 1 which relates to the aqueous layer. Results of calculations of composition of the mixture at equilibrium, $x_1^{(1)}$, $x_3^{(1)}$ and $x_1^{(2)}$, $x_3^{(2)}$ together with the composition of the starting mixtures $x_1^{(0)}$, $x_3^{(0)}$ are collected in Table 4. Results of measurements of the β-carotene concentrations in the organic and aqueous layers, $c_\beta^{(1)}$ and $c_\beta^{(2)}$, and calculations of the distribution coefficient values, $k_c = c_\beta^{(1)}/c_\beta^{(2)}$, are also reported in Table 4. In Figure 1 are compared the tie lines found in this study with literature data (Sorensen and Arlt, 1979).

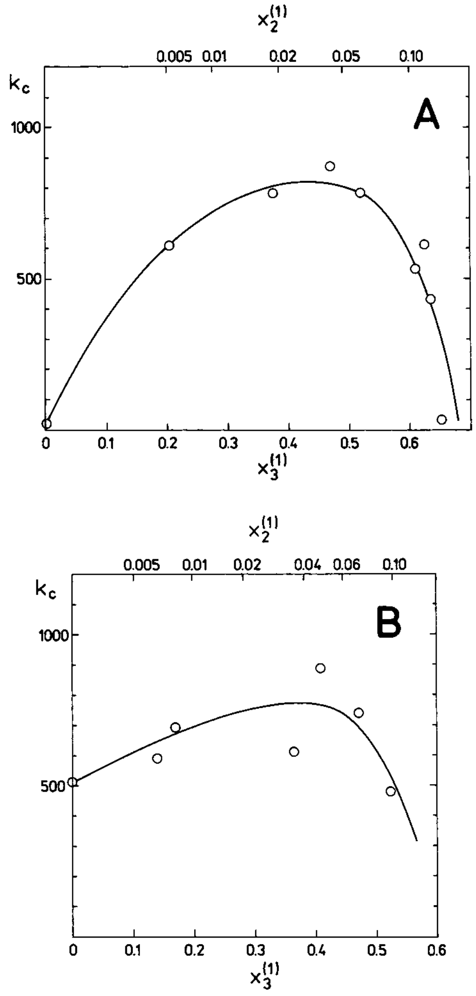

Figure 2. Distribution coefficient k_c of β-carotene at T = 298.15 K vs mole fraction of 2-propanone, $x_3^{(1)}$, and water $x_2^{(1)}$, in the nonaqueous (organic) phase: (A) hexane (1) + water (2) + 2-propanone (3) and (B) toluene (1) + water (2) + 2-propanone (3). The k_c value for composition $x_3^{(1)}$ = 0 was taken from the paper by Treszczanowicz et al. (1998).

Presumably, the solubility of β-carotene in hydrocarbon + 2-propanone mixtures is larger than in the each of the pure solvents studied (Treszczanowicz, 1999). Hence, as shown in Figure 2A,B, the distribution coefficient for the mixed solvent of hexane + 2-propanone as well as toluene + 2-propanone initially increases with 2-propanone concentration at a low water content in the nonaqueous phase. However, with increasing water concentration in the nonaqueous layer, the distribution coefficient value k_c decreases both due to the diminishing solubility of β-carotene in the nonaqueous phase and its concomitant higher solubility in the aqueous phase (cf. the coexistence curve in Figure 1). A maximum occurs on the curve that depicts the 2-propanone concentration effect on the distribution coefficient k_c for β-carotene in the hexane (1) + water (2) + 2-propanone (3) system. The maximum appears approximately at $x_3^{(1)}$ = 0.45, which corresponds to $x_2^{(1)} \cong$ 0.03. For the mixed solvent containing hexane the increase in distribution coefficient the k_c with the 2-propanone concentration is greater, as compared with the solvent containing toluene. For the hexane system this increase is exceptionally significant (cf. Figure 2) compared with the extraction using the hydrocarbon only. Both the hexane system and the toluene system demonstrate significant positive deviations from Raoult's law. The system toluene

+ acetone has a nearly tangent zeotrope (Horsley, 1973 (cf. Swietoslawski (1963)), whereas in the hexane + 2-propanone system there is an azeotrope with a boiling point by nearly 6 K lower than the boiling point of 2-propanone at atmospheric pressure (Horsley, 1973). This could possibly justify the use of this mixed solvent instead of the hydrocarbon only and hexane in the mixed solvent with 2-propanone rather than toluene.

The comparison of the results obtained in the previous paper (Treszczanowicz et al., 1999) for distribution coefficient k_c in systems formed by cyclohexane + 2-propanone + water and methylcyclohexane + 2-propanone + water shows similar behavior. The mixed solvent containing hexane or cyclohexane exhibits a high k_c maxima as a function of 2-propanone concentration. The higher k_c values for the cyclohexane + 2-propanone mixed solvent are observed. However, the hexane + 2-propanone system exhibits two times lower minima on the boiling temperature curve than the cyclohexane + 2-propanone system in comparison to the lower boiling component. The results observed for the toluene as well as methylcyclohexane systems do not show such large increases of k_c. Therefore, the reagent cost seems to be the controlling factor in choosing between the mixed solvent containing 2-propanone and hexane or cyclohexane.

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