mean of ΔH_{vap} for each compound are listed in Tables II and III.

Discussion

The previously reported values for the enthalpies of combustion of 3-methylisoxazole and 5-methylisoxazole, -541.96 and -540.57 kcal mol^{-1} (*9*), respectively, differ by nearly 1% from the values reported here. We observed in the course of this investigation that the value of $\Delta E_c°/M$ for both these compounds is sensitive to atmospheric moisture.

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Received for review November 7, 1977. Accepted February 17, 1978. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Phase Equilibria Behavior of the Ternary Systems Carbon Dioxide–*trans*-Decalin–*n*-Eicosane and Carbon Dioxide–*trans*-Decalin–2-Methylnaphthalene

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The phase equilibria behavior of the two ternary systems carbon dioxide–*trans*-decalin–2-methylnaphthalene and carbon dioxide–*trans*-decalin–*n*-eicosane was investigated in both the liquid–vapor (L–V) and liquid–liquid–vapor (L_1–L_2–V) regions. Three mixtures of approximately 25, 50, and 75 CO_2-free mol % *trans*-decalin were studied for each ternary system. Pressure, liquid-phase composition, and liquid-phase molar volume data were measured at several temperatures for all mixtures of both ternary vapor–liquid systems. Pressure, liquid-phase compositions, and molar volumes of the two coexisting liquid phases are presented as a function of temperature for the same ternary systems along their liquid 1–liquid 2–vapor loci. The termination of these loci are located and characterized. CO_2-free selectivities between the liquid phases in the L_1–L_2–V region are presented, in view of the possible use of CO_2 as a selective solvent in separation processes.

Introduction

CO_2 can be used as a selective solvent for the separation of a mixture of hydrocarbons by taking advantage of the formation of two liquid phases upon pressurization of the mixture with CO_2. Furthermore, there is growing interest in CO_2–hydrocarbon phase equilibria behavior as pertains to enhanced oil recovery processes.

The authors have for some time been engaged in studying the phase equilibria behavior of CO_2–hydrocarbon systems, with a view to providing data which would be useful for the design of separational processes, using CO_2 as a selective solvent, and could as well be relevant to the understanding of enhanced oil recovery processes. Huie and co-workers (*1*) studied the ternary system CO_2–*n*-decane–*n*-eicosane and showed that the CO_2-rich phase (L_2) selectively extracts the lower alkane from the higher alkane. Kulkarni et al. (*2*) studied the ternary system CO_2–*n*-decane–2-methylnaphthalene (where 2-methylnaphthalene and *n*-eicosane have similar melting points) and found that the L_2 phase once again selectively extracts the *n*-decane. Zarah et al. (*6*) studied the ternary system CO_2–*n*-butylbenzene–*n*-eicosane and Yang et al. (*5*) studied the ternary system CO_2–*n*-butylbenzene–2-methylnaphthalene. Both found that the L_2 phase selectively extracts the lighter aromatic *n*-butylbenzene from both the *n*-eicosane and the 2-methylnaphthalene.

Studies have been performed previously on the CO_2–hydrocarbon binary systems which serve as limits to the CO_2–hydrocarbon ternary system results to be reported herein. Kulkarni (*2*) studied the CO_2–2-methylnaphthalene system, Huie et al. (*1*) studied the CO_2–*n*-eicosane system, and Tiffin et al. (*4*) studied the CO_2–*trans*-decalin system. The binary system studies focused on L–V and L_1–L_2–V phase behavior.

This present investigation of the phase equilibria behavior and separability of these two CO_2–hydrocarbon systems will complement the aforementioned studies and help elucidate the phase behavior of CO_2–hydrocarbon studies in general. The systems were chosen to provide information on a typical naphthenic hydrocarbon, such as *trans*-decalin in the presence of other hydrocarbon types.

Experimental Section

A detailed description of the experimental equipment and procedure is given elsewhere (*1*, *3*). Briefly, for the L–V isotherms, a known amount of the desired hydrocarbon was placed in a 10-mL glass equilibrium cell. During the experimental runs, measured amounts of pure CO_2 gas were added to the thermostated equilibrium cell from a high-pressure bomb, through the use of a positive displacement mercury pump. By a mass balance, the moles of CO_2 added to the liquid phase were then determined.

In the case of the L_1–L_2–V runs, the moles of CO_2 in an individual liquid phase were determined by making a run in which

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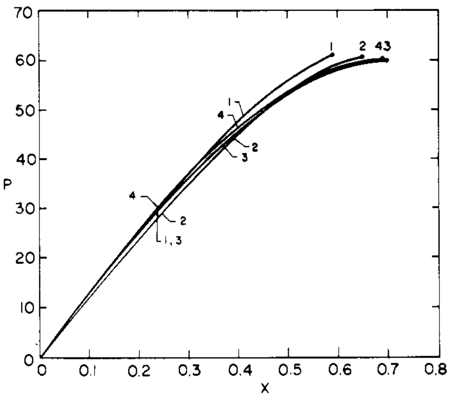

Figure 1. Smoothed pressure (atm) vs. composition (mole fraction CO_2) curves for the ternary vapor–liquid system carbon dioxide–*trans*-decalin–2-methylnaphthalene at T = 25.0 °C. The liquid–liquid–vapor terminal points are indicated by a heavy dot (●): curve 1, mole ratio tD/2MN = 0.3123; curve 2, mole ratio tD/2MN = 0.8450; curve 3, mole ratio tD/2MN = 2.509; curve 4, CO_2–tD binary system (*4*).

the other liquid phase was present in a trace amount. Thus, two runs were required to obtain the properties of both L_1 and L_2. Procedures for determining the termination points of the L_1–L_2–V loci (Q, UCST, and K points) are rather routine and are discussed elsewhere (*1*, *3*).

The hydrocarbon selectivities for the L_1–L_2–V region were obtained through the use of a Jerguson cell. There are two sampling ports on the cell, one being used to sample the upper liquid phase, the other used to sample the lower liquid phase. Temperature was controlled to ±0.10 °C by immersing the cell in a constant-temperature bath. During the sampling, the CO_2 was evaporated into the air and the CO_2-free compositions of the two liquid phases were determined by measuring the refractive indices of the samples with a Valentine Model 450A refractometer. The refractive index was accurate to ±0.0001, equivalent to compositional accuracies of ±0.001 mass fraction for mixtures of *trans*-decalin and 2-methylnaphthalene and ±0.004 mass fraction for mixtures of *trans*-decalin and *n*-eicosane.

Temperature was measured with a Pt-resistance thermometer to an estimated accuracy of ±0.02 °C for the L–V isotherms and measured to an estimated accuracy of ±0.10 °C for the L_1–L_2–V data. Pressure was measured with Bourdon tube gauges, which were frequently calibrated against an accurate dead-weight gauge, to an estimated accuracy of ±0.07 atm. The viewable glass cell was marked, carefully calibrated and judged to give volumetric readings to an accuracy of ±0.01 cm³.

Materials

The CO_2 used in this study was obtained from the Matheson Co. as "Coleman Grade" material with a stated minimum purity of 99.99%. Oxygen, carbon monoxide, and hydrogen were the major impurities.

The 2-methylnaphthalene used was the product of Aldrich Chemical Co.; the *n*-eicosane was obtained from the Humphrey Chemical Co.; the *trans*-decalin was manufactured by Columbia Organic Chemicals Co. All hydrocarbons stated a minimum purity of 99% and were used without further purification.

Results

Tables S1–S10 in the supplementary material present the smoothed and raw liquid-phase composition and liquid molar volume in the V–L region for mixtures of the ternary system CO_2–*trans*-decalin–2-methylnaphthalene at 0, 25, 50, and 75 °C. Tables S11–S17 present similar data on isotherms for mixtures of the ternary system CO_2–*trans*-decalin–*n*-eicosane at 25, 50, and 75 °C. For Tables S1–S17, the standard deviations of the raw data from the smoothed values of composition and molar volume were ±0.002 mole fraction and ±0.5 mL/g-mol, respectively. Figures 1–5 are plots of some of these

Table I. Smoothed Three-Phase Vapor-Liquid 1-Liquid 2 Behavior in the Carbon Dioxide-*trans*-Decalin-2-Methylnaphthalene System[a]

Temp, °C	Pressure, atm	Mole fraction CO_2		Molar volume, mL/g-mol	
		L_1	L_2	L_1	L_2
5.0	38.2	0.551	0.969	88.3	50.4
10.0	43.1	0.562	0.967	87.8	51.6
15.0	48.45	0.572	0.966	87.5	53.0
20.0	54.4	0.582	0.966	87.3	54.7
25.0	60.85	0.587	0.969	87.2	56.8
30.0	68.0	0.589	0.974	87.0	59.5
35.0	75.8	0.594	0.979	86.6	63.1
38.73[b]	82.24	0.601		85.8	

[a] L_1 mole ratio of tD/2MN = 0.3423. [b] Type K singular point.

Table II. Smoothed Three-Phase Vapor-Liquid 1-Liquid 2 Behavior in the Carbon Dioxide-*trans*-Decalin-2-Methylnaphthalene System[a]

Temp, °C	Pressure, atm	Mole fraction CO_2		Molar volume, mL/g-mol	
		L_1	L_2	L_1	L_2
−5.0	29.2	0.562	0.958	88.6	49.3
0.0	33.3	0.585	0.956	87.0	50.3
5.0	37.8	0.605	0.953	85.7	51.4
10.0	42.6	0.621	0.951	84.7	52.6
15.0	48.1	0.635	0.949	83.9	53.8
20.0	54.0	0.645	0.949	83.5	55.3
25.0	60.4	0.650	0.952	83.4	57.0
30.0	67.3	0.655	0.957	82.9	59.2
35.0	75.1	0.664	0.966	81.0	62.1
40.0	83.2	0.678	0.980	77.3	67.3
40.55[b]	84.44	0.680		76.5	

[a] L_1 mole ratio of tD/2MN = 0.9194. [b] Type K singular point.

Table III. Smoothed Three-Phase Vapor-Liquid 1-Liquid 2 Behavior in the Carbon Dioxide-*trans*-Decalin-2-Methylnaphthalene System[a]

Temp, °C	Pressure, atm	Mole fraction CO_2		Molar volume, mL/g-mol	
		L_1	L_2	L_1	L_2
−10.0	25.4	0.548	0.956	90.9	48.0
−5.0	29.2	0.581	0.951	88.3	49.6
0.0	33.2	0.607	0.946	86.0	51.1
1.74[c]	34.73	0.616	0.945	85.3	51.6
5.0	37.7	0.633	0.941	83.9	52.7
10.0	42.5	0.658	0.937	82.1	54.1
15.0	47.8	0.679	0.934	80.4	55.6
20.0	53.7	0.696	0.933	78.9	57.1
25.0	60.0	0.706	0.934	77.9	58.6
30.0	66.8	0.713	0.939	77.3	59.6
35.0	74.4	0.716	0.951	77.3	61.4
40.0	82.8	0.721	0.971	75.9	66.3
42.26[b]	86.65	0.730		71.0	

[a] L_1 mole ratio of tD/2MN = 3.016. [b] Type K singular point. [c] L_1-L_2 density inversion point.

Table IV. Experimental Pressure-Temperature Locus of Quadruple (Q) Points (Vapor-Liquid 1-Liquid 2-Vapor Coexistence) for the Ternary System Carbon Dioxide-*trans*-Decalin-2-Methylnaphthalene

Temp, °C	Pressure, atm	Temp, °C	Pressure, atm
−38.7[a]	10.4	3.5	36.5
−24.4	16.7	9.1[b]	42.35
−14.0	33.2		

[a] CO_2-tD binary Q point (*4*). [b] CO_2-2MN binary Q point (*2*).

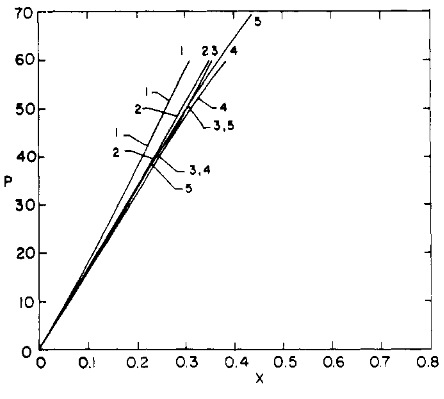

Figure 2. Smoothed pressure (atm) vs. composition (mole fraction CO_2) curves for the ternary vapor-liquid system carbon dioxide-*trans*-decalin-2-methylnaphthalene at T = 50.0 °C: curve 1, CO_2-2MN binary system (*2*); curve 2, mole ratio tD/2MN = 0.3459; curve 3, mole ratio tD/2MN = 0.8382; curve 4, mole ratio tD/2MN = 2.906; curve 5, CO_2-tD binary system (*4*).

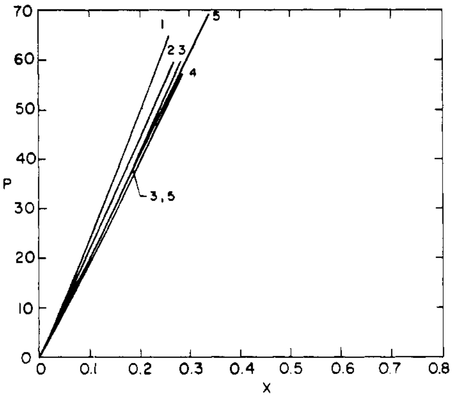

Figure 3. Smoothed pressure (atm) vs. composition (mole fraction CO_2) curves for the ternary vapor-liquid system carbon dioxide-*trans*-decalin-2-methylnaphthalene at T = 75.0 °C: curve 1, CO_2-2MN binary system (*2*); curve 2, mole ratio tD/2MN = 0.3141; curve 3, mole ratio tD/2MN = 0.8450; curve 4, mole ratio tD/2MN = 2.906; curve 5, CO_2-tD binary system (*4*).

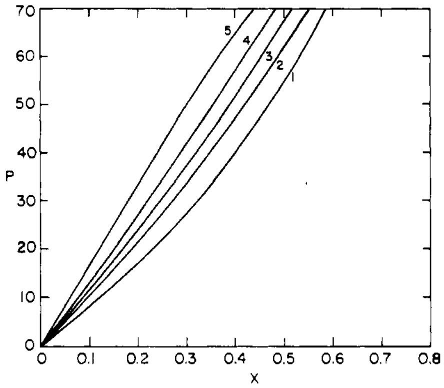

Figure 4. Smoothed pressure (atm) vs. composition (mole fraction CO_2) curves for the ternary vapor-liquid system carbon dioxide-*trans*-decalin-*n*-eicosane at T = 50.0 °C: curve 1, CO_2-nC_{20} binary system (*3*); curve 2, mole ratio tD/nC_{20} = 0.332; curve 3, mole ratio tD/nC_{20} = 0.908; curve 4, mole ratio tD/nC_{20} = 2.876; curve 5, CO_2tD binary system (*4*).

vapor-liquid data, including the "bounding" binary isotherms, at several temperatures and hydrocarbon ratios for the two ternary systems studied.

The results of the L_1-L_2-V studies are presented on Tables I-VII. The data for the ternary system CO_2-*trans*-decalin-2-methylnaphthalene are presented in Tables I, II, and III, which give the compositions and liquid molar volumes of both liquid phases, as well as the pressure, as a function of temperature for a given ratio of hydrocarbons. The hydrocarbon ratios are approximately 1:3, 1:1, and 3:1 in these three tables. Similar information is presented in Tables V, VI, and VII for the ternary system CO_2-*trans*-decalin-*n*-eicosane. Table IV gives a pressure-temperature locus of Q points (V-L_1-L_2-S) for the ternary system in which pure 2-methylnaphthalene is the S phase. The raw data for Tables I-III and V-VII are given in Tables S18-S23 of the supplementary material.

The standard deviations of the raw data from the smoothed values of composition and molar volume are ±0.002 mol fraction and ±0.5 mL/g-mol, respectively, for the L_1 and L_2 values. Of special interest in these tables, besides the Q-point and K-point loci, is the inversion point in Table III. Phase inversions have been previously observed by the authors in L_1-L_2-V systems and are discussed in detail elsewhere (*4*, *6*). Briefly, below the inversion temperature, the CO_2-rich phase L_2, which forms second upon pressurization of the initial L-V system with CO_2,

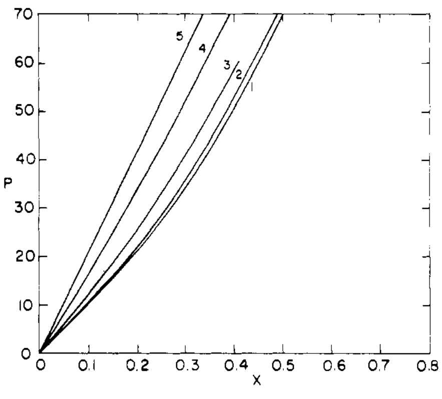

Figure 5. Smoothed pressure (atm) vs. composition (mole fraction CO_2) curves for the ternary vapor-liquid system carbon dioxide-*trans*-decalin-*n*-eicosane at T = 75.0 °C: curve 1, CO_2-nC_{20} binary system (*3*); curve 2, mole ratio tD/nC_{20} = 0.339; curve 3, mole ratio tD/nC_{20} = 0.908; curve 4, mole ratio tD/nC_{20} = 2.876; curve 5, CO_2-tD binary system (*4*).

Table V. Smoothed Three-Phase Vapor-Liquid 1-Liquid 2 Behavior in the Carbon Dioxide-*trans*-Decalin-*n*-Eicosane System[c]

Temp, °C	Pressure, atm	Mole fraction CO_2 L_1	Mole fraction CO_2 L_2	Molar volume, mL/g-mol L_1	Molar volume, mL/g-mol L_2
23.8[a]	61.25	0.686	0.9937	128.8	59.1
26.0	64.50	0.689	0.9955	127.3	60.7
28.0	67.60	0.694	0.9969	125.1	62.9
30.0	70.60	0.701	0.9975	123.0	66.2
32.0	73.85	0.709	0.9982	120.8	71.9
33.05[b]	75.55	0.714		119.5	

[a] Quadruple point (L_1-L_2-V-S). [b] Type K singular point. [c] L_1 mole ratio of tD/nC_{20} = 0.3405.

Table VI. Smoothed Three-Phase Vapor-Liquid 1-Liquid 2 Behavior in the Carbon Dioxide-*trans*-Decalin-*n*-Eicosane System[c]

Temp, °C	Pressure, atm	Mole fraction CO_2 L_1	Mole fraction CO_2 L_2	Molar volume, mL/g-mol L_1	Molar volume, mL/g-mol L_2
17.5[a]	52.3	0.642	0.9835	120.7	54.2
20.0	55.6	0.648	0.9850	120.2	55.7
22.0	58.3	0.653	0.9861	119.7	57.0
24.0	61.05	0.659	0.9875	119.0	58.5
26.0	63.8	0.664	0.9887	118.1	60.2
28.0	66.7	0.668	0.9904	117.0	62.2
30.0	69.75	0.673	0.9922	115.6	64.5
32.0	73.0	0.677	0.9940	114.5	68.0
34.0	76.2	0.680	0.9954	113.7	73.4
34.75[b]	77.4	0.681		113.5	

[a] Quadruple point (L_1-L_2-V-S). [b] Type K singular point. [c] L_1 mole ratio of tD/nC_{20} = 0.9724.

Table VII. Smoothed Three-Phase Vapor-Liquid 1-Liquid 2 Behavior in the Carbon Dioxide-*trans*-Decalin-*n*-Eicosane System[c]

Temp, °C	Pressure, atm	Mole fraction CO_2		Molar volume, mL/g-mol	
		L_1	L_2	L_1	L_2
12.5[a]	46.2	0.623	0.9775	103.9	52.5
14.0	47.9	0.628	0.976	103.6	53.1
16.0	50.1	0.634	0.975	103.2	53.9
18.0	52.4	0.640	0.974	102.6	54.8
20.0	54.85	0.646	0.9735	102.1	55.8
22.0	57.4	0.652	0.974	101.5	56.8
24.0	60.05	0.657	0.975	100.8	58.0
26.0	62.8	0.661	0.977	100.0	59.3
28.0	65.6	0.664	0.980	99.2	60.7
30.0	68.5	0.668	0.982	98.3	62.1
32.0	71.5	0.673	0.9845	97.2	63.8
34.0	74.7	0.678	0.987	96.1	65.8
36.0	78.0	0.685	0.989	94.9	71.4
37.6[b]	80.75	0.691		93.8	

[a] Quadruple point (L_1-L_2-V-S). [b] Type K singular point. [c] L_1 mole ratio of tD/nC_{20} = 2.984.

Table VIII. Smoothed Values of Selectivity β of CO_2 for *trans*-Decalin in 2-Methylnaphthalene as a Function of Temperature and L_1 Mole Ratio $(N_{tD}/N_{2MN})_{L_1}$

L_1 mole ratio $(N_{tD}/N_{2MN})_{L_1}$	Temp, °C			
	5.0	15.0	25.0	35.0
0.333	1.51	1.55	1.60	1.67
0.429	1.41	1.45	1.52	1.61
0.667	1.27	1.32	1.38	1.48
1.000	1.17	1.21	1.28	1.38
1.500	1.09	1.13	1.18	1.29
2.333	1.03	1.05	1.10	1.20

appears beneath the L_1 phase in the cell. Above the inversion temperature, the L_2 phase forms above the L_1 phase. In the CO_2–*trans*-decalin binary system, an inversion point is reported at 9.8 °C (*4*). For both ternary system studies herein, the inversion point locus runs from the CO_2–*trans*-decalin inversion point over to the Q locus.

Both ternary system L_1–L_2–V loci are bounded by Q points at the low-temperature end and K points at the upper end. This is reasonable since all pertinent binary limits show similar phase equilibria behavior.

It was necessary to list the Q points of the CO_2–*trans*-decalin-2-methylnaphthalene system separately in Table IV for several reasons. The first is that the Q-point locus is separated from the CO_2–*trans*-decalin binary L_1–L_2–V locus in P–T space by only about 0.1 atm at 0 °C; the two loci gradually get closer and coincide (within experimental error) at the CO_2–*trans*-decalin Q point at −38.7 °C.

The results of the sampling experiments conducted with the Jerguson cell are shown in the form of selectivity as a function of temperature and $(N_{td}/N_{HC})_{L_1}$ in Table VIII for the ternary system CO_2–*trans*-decalin-2-methylnaphthalene and in Table IX for the ternary system CO_2–*trans*-decalin–*n*-eicosane. Selectivity β is defined as

$$\beta = \frac{(N_{td}/N_{HC})_{L_2}}{(N_{td}/N_{HC})_{L_1}}$$

where HC refers to 2-methylnaphthalene or *n*-eicosane depending upon the ternary system. The standard deviations of the raw selectivity data from the smoothed values was ±0.011 for the CO_2–*trans*-decalin-2-methylnaphthalene system and ±0.25 for the CO_2–*trans*-decalin–*n*-eicosane system. Raw sampling data for Tables VIII and IX are given in Supplementary Tables S24 and S25, respectively.

Table IX. Smoothed Values of Selectivity β of CO_2 for *trans*-Decalin in *n*-Eicosane as a Function of Temperature and L_1 Mole Ratio $(N_{tD}/N_{nC_{20}})_{L_1}$

L_1 mole ratio $(N_{tD}/N_{nC_{20}})_{L_1}$	Temp, °C		
	26.0	28.5	31.0
0.250	2.77	3.59	4.31
0.429	3.14	3.90	4.50
0.667	3.42	4.10	4.63
1.000	3.62	4.21	4.67
1.500	3.78	4.23	4.63
2.333	3.88	4.23	4.53

Remarks

The above results on the two ternary CO_2–hydrocarbon systems, when compared wth the four previously studied ternary systems (*1*, *2*, *5*, *6*), seem to suggest that CO_2 selectively extracts the more volatile component. However, data on the ternary system carbon dioxide-*trans*-decalin–*n*-eicosane and both pertinent CO_2–hydrocarbon binaries clearly show that CO_2 does not necessarily selectively extract the hydrocarbon showing greater solubility of CO_2 in a binary system.

One also finds that the low selectivities for the ternary system CO_2–*trans*-decalin-2-methylnaphthalene might be attributable to the similarities in the two double-ringed hydrocarbons.

Glossary

K point	critical point of the two phases L_2 and V
L_1	CO_2-lean liquid phase
L_2	CO_2-rich liquid phase
N	moles
P	pressure (atm)
Q point	quadruple point (coexistence of the four phases V-L_1-L_2-S)
T	temperature

Greek

β	solvent (CO_2)-free extractive selectivity

Subscripts

HC	hydrocarbon
2MN	2-methylnaphthalene
nC_{20}	*n*-eicosane
tD	*trans*-decalin

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Received for review June 6, 1977. Accepted February 10, 1978. The authors are grateful for support provided by the National Science Foundation (Grant No. ENG 75-06533).

Supplementary Material Available: Smoothed and raw data on 17 ternary system isotherms, labeled Tables S1–S17, as well as raw data for Tables I–III and V–IX, labeled Tables S18–S25 (31 pages). Ordering information is given on any current masthead page.