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Phase-Equilibria Behavior of the System Carbon Dioxide–*n*-Butylbenzene–2-Methylnaphthalene

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The phase-equilibria behavior of the ternary system CO_2–*n*-butylbenzene–2-methylnaphthalene was studied in the liquid–vapor, solid–liquid–vapor, and liquid–liquid–vapor regions. Detailed pressure, temperature, molar volume and composition data for each region and also the selectivities of CO_2 in the ternary liquid–liquid–vapor region are presented. The liquid–liquid–vapor coexistence region for the ternary system was found to be bounded by a Q-point locus, a K-point locus, and a UCST locus. Also presented are the data on the depression in the melting point of 2-methylnaphthalene upon the addition of *n*-butylbenzene under atmospheric pressure.

Phase equilibria behavior of CO_2–hydrocarbon(s) systems have been studied by many investigators. Partial miscibility behavior has been observed for some of the systems (*2, 5, 6, 7*) and suggests the use of CO_2 as a selective solvent. Its potential use in this respect is supported by its availability, nontoxicity, and noncorrosiveness. The studies of CO_2 selectivity with respect to different hydrocarbons between liquid phases are needed to evaluate the use of CO_2 as a selective solvent.

Huie and co-workers (*3*) studied the ternary system CO_2–*n*-decane–*n*-eicosane and examined the selectivity of CO_2 for lower vs. higher alkanes. The results show that CO_2 selectively extracts the lower alkane from the higher alkane.

The Huie study was extended to systems of CO_2 with alkanes and aromatics by Kulkarni (*4*) and Zarah (*9*). Kulkarni studied the ternary system of CO_2–*n*-decane–2-methylnaphthalene, where the aromatic 2-methylnaphthalene has a similar melting point to that of *n*-eicosane. Zarah studied the system CO_2–*n*-butylbenzene–*n*-eicosane, where the aromatic *n*-butylbenzene has the same carbon number as *n*-decane. In both systems, CO_2 selectively extracts the compound with lower carbon number.

The systems of CO_2 with aromatic compounds have been studied only by Francis (*1*); all those studies were done at 25 °C. There has been no detailed work ever done on CO_2–aromatic systems. Therefore, our earlier work (*3, 4, 9*) was extended to a ternary system of CO_2–*n*-butylbenzene–2-methylnaphthalene. The relevant phase behavior for this system was studied. The selectivity of CO_2 in this ternary three-phase system, as well as the compositional and volumetric data, are reported. These data could be used for correlative purposes.

Experiments Performed

The following experiments were performed in this study: (a) The melting point depression of 2-methylnaphthalene upon the addition of *n*-butylbenzene was measured at several compositions at atmospheric pressure. (b) The liquid–vapor isotherms of the ternary system CO_2–*n*-butylbenzene–2-methylnaphthalene were studied at different temperatures at certain mole ratios of the two hydrocarbons in the system. (c) The solid–liquid–vapor equilibria were studied for the same ternary system at certain mole ratios of the two hydrocarbons in the liquid phase. (d) The liquid–liquid–vapor region of the same ternary system was studied in detail, both by stoichiometric techniques and by sampling techniques.

Experimental Section

Most of the experiments involved in this study were done with a P-V-T apparatus which featured a glass equilibrium cell of about 10 cm^3 in volume and a constant temperature bath. The detailed description of this apparatus and the experimental procedure is elsewhere (*8*). This apparatus was used for stoichiometric experiments.

The sampling study for the ternary liquid–liquid–vapor phase behavior was done by means 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.

For the stoichiometric experiments, the procedure is briefly described as follows: a measured amount of CO_2 is pressurized into the glass equilibrium cell which is initially loaded with a measured mass of the hydrocarbon components and the amount of CO_2 dissolved into the liquid solution is directly calculated by means of a material balance.

In the case of the two-phase liquid–vapor behavior study, the compositional and volumetric data are calculated straightforward. In the case of the solid–liquid–vapor system, the solid in the solution is kept in a trace account during the experiment, so that the amount of solid is negligible (the solid phase can be assumed to be pure 2-methylnaphthalene). Therefore the composition and molar volume of the liquid phase can be calculated.

In the case of ternary three-phase liquid–liquid–vapor behavior, the composition and molar volume of the two liquid phases cannot be calculated with a single set of experimental data. Two separate runs were done to provide the data needed for property determination. In each run, the temperature and pressure were the same while one or the other of the liquid phases was kept in small amount.

The terminations (boundaries) for the ternary liquid–liquid–vapor loci with given mole ratios of the two hydrocarbons in the L1 phase are Q points (coexistence of the four phases V–L1–L2–S) at the lower temperature end, and K points (critical point

Table I. Experimental Data on the Melting Point Depression of 2-Methylnaphthalene upon Additon of *n*-Butylbenzene

Temp (°C)	Mole fraction of 2-methylnaphthalene
34.09	1.0000
28.15	0.9129
23.83	0.8512
15.44	0.7361
8.95	0.6502

Table II. Smoothed Values of Pressure, Composition, and Molar Volume for a Liquid–Vapor Isotherm at 35 °C for the Ternary System CO_2–*n*-Butylbenzene –2-Methylnaphthalene with $(N_{nBB}/N_{2MN})_L$ = 0.3296

Pressure (atm)	Mole fraction of CO_2	Liquid molar volume ($cm^3/(g\ mol)$)
5	0.037	144.10
10	0.073	140.35
15	0.110	136.75
20	0.145	133.25
25	0.181	129.50
30	0.217	125.70
35	0.252	121.85
40	0.288	118.20
45	0.323	114.40
50	0.358	110.70
55	0.398	106.85
60	0.437	99.50

Table III. Smoothed Values of Pressure, Composition, and Molar Volume for a Liquid–Vapor Isotherm at 35 °C for the Ternary System CO_2–*n*-Butylbenzene–2-Methylnaphthalene with $(N_{nBB}/N_{2MN})_L$ = 1.7269

Pressure (atm)	Mole fraction of CO_2	Liquid molar volume ($cm^3/(g\ mol)$)
5	0.040	149.00
10	0.079	144.45
15	0.119	139.80
20	0.162	135.20
25	0.208	130.70
30	0.253	126.05
35	0.298	121.50
40	0.343	117.00
45	0.387	111.95
50	0.435	106.75
55	0.487	101.35
60	0.540	95.20

Table IV. Smoothed Values of Pressure, Composition, and Molar Volume for a Liquid–Vapor Isotherm at 50 °C for the Ternary System CO_2–*n*-Butylbenzene–2-Methylnaphthalene with $(N_{nBB}/N_{2MN})_L$ = 0.3296

Pressure (atm)	Mole fraction of CO_2	Liquid molar volume ($cm^3/(g\ mol)$)
5	0.032	144.90
10	0.062	141.80
15	0.093	138.75
20	0.123	135.70
25	0.154	132.55
30	0.186	129.45
35	0.216	126.40
40	0.240	123.50
45	0.274	120.50
50	0.303	117.60
55	0.333	114.50
60	0.362	111.55

of L2 and V) or UCST (upper critical solution temperature of L1 and L2) at the higher temperature end, depending upon the mole ratio of the two hydrocarbons in the L1 phase.

The melting point depression study measured the melting temperature of mixtures of *n*-butylbenzene and 2-methylnaphthalene under atmospheric pressure. The melting temperature is that point at which only a trace amount of solid existing in the solution does not disappear after vigorous stirring.

In all computations performed, it was assumed that there was negligible hydrocarbon present in the vapor phase, as the hydrocarbons exhibit very little volatility at the conditions of the study.

In the sampling experiments, the Jerguson cell was immersed 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 are evaluated by measuring the refractive indexes of the samples. A Valentine Model 450A refractometer was used.

A Pt-resistance thermometer was used for measuring temperatures with an estimated accuracy of ±0.03 °C. Pressures were measured with Bourdon tube gauges frequently calibrated against an accurate dead weight gauge. The maximum error in measuring pressures was estimated to be ±0.07 atm. Liquid volumes in the glass equilibrium cell were measured by means of a cathetometer and judged to be accurate to ±0.005 ml. The compositions were determined to an estimated accuracy of ±0.002 mole fraction, and the maximum error in the reported molar volume is estimated to be ±0.05 ml/(g mol).

Smoothed compositional and volumetric data were obtained by plotting data on large scale graph paper. The error introduced during smoothing of the data is less than the experimental error. The actual raw data are reported elsewhere (*8*).

Materials

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

The CO_2 was prepared for use by distillation from the cylinder at room temperature to a 1000-cm^3 storage bomb maintained at 0 °C. Later about one-third of the condensate in the storage bomb was vented to the atmosphere by redistillation to the atmosphere.

The *n*-butylbenzene and the 2-methylnaphthalene used were the products of Aldrich Chemical Co., and were labeled as having 99% minimum purity. Both the *n*-butylbenzene and the 2-methylnaphthalene were used without further purification.

Results

(a) Melting Point Depression. Table I shows the experimental data on the melting point depression of 2-methylnaphthalene upon the addition of *n*-butylbenzene. All data were obtained under atmospheric pressure.

(b) Liquid–Vapor Isotherms for the CO_2–n-Butylbenzene–2-Methylnaphthalene System. Liquid-vapor isotherms were performed on this ternary system at 35 °C with two different $(N_{nBB}/N_{2MN})_L$, which is the mole ratio of *n*-butylbenzene to 2-methylnaphthalene in the liquid phase and at 50 °C with four different $(N_{nBB}/N_{2MN})_L$. The smoothed values of pressure, liquid phase composition, and molar volume are presented in Tables II–VII.

Table V. Smoothed Values of Pressure, Composition, and Molar Volume for a Liquid–Vapor Isotherm at 50 °C for the Ternary System CO_2–*n*-Butylbenzene–2-Methylnaphthalene with $(N_{nBB}/N_{2MN})_L = 0.3587$

Pressure (atm)	Mole fraction of CO_2	Liquid molar volume (cm³/(g mol))
5	0.031	143.90
10	0.062	140.80
15	0.093	137.70
20	0.124	134.65
25	0.155	131.55
30	0.187	128.50
35	0.218	125.45
40	0.248	122.35
45	0.278	119.30
50	0.309	116.30
55	0.339	113.30
60	0.370	110.30

Table VI. Smoothed Values of Pressure, Composition, and Molar Volume for a Liquid–Vapor Isotherm at 50 °C for the Ternary System CO_2–*n*-Butylbenzene–2-Methylnaphthalene with $(N_{nBB}/N_{2MN})_L = 1.5289$

Pressure (atm)	Mole fraction of CO_2	Liquid molar volume (cm³/(g mol))
5	0.035	145.40
10	0.068	142.05
15	0.102	138.75
20	0.134	135.45
25	0.167	132.25
30	0.200	129.00
35	0.233	125.45
40	0.265	122.40
45	0.298	119.20
50	0.332	115.80
55	0.365	112.65
60	0.398	109.40

Table VII. Smoothed Values of Pressure, Composition, and Molar Volume for a Liquid–Vapor Isotherm at 50 °C for the Ternary System CO_2–*n*-Butylbenzene–2-Methylnaphthalene with $(N_{nBB}/N_{2MN})_L = 1.7269$

Pressure (atm)	Mole fraction of CO_2	Liquid molar volume (cm³/(g mol))
5	0.035	152.50
10	0.069	148.55
15	0.105	144.70
20	0.137	140.70
25	0.155	136.75
30	0.205	133.05
35	0.240	129.50
40	0.277	125.95
45	0.312	120.45
50	0.347	118.90
55	0.380	115.50
60	0.414	112.05

(c) CO_2–n-Butylbenzene–2-Methylnaphthalene Solid–Liquid–Vapor System. Mixtures with two different $(N_{nBB}/N_{2MN})_L$ were studied along the solid–liquid–vapor equilibrium line. Shown in Tables VIII and IX are the smoothed temperature, pressure, CO_2 mole fraction in the liquid phase, and the liquid molar volume. Each solid–liquid–vapor equilibrium line terminates with a Q point at the high pressure end.

Table VIII. Smoothed Values of Pressure, Temperature, Composition, and Molar Volume of the Solid–Liquid–Vapor Locus for the System CO_2–*n*-Butylbenzene–2-Methylnaphthalene with $(N_{nBB}/N_{2MN})_L = 0.2533$

Pressure (atm)	Temp (°C)	Mole fraction of CO_2	Liquid molar volume (cm³/(g mol))
10	15.20	0.096	131.00
15	12.65	0.149	126.13
20	10.20	0.209	120.00
25	7.40	0.282	112.90
30	4.20	0.382	105.25
35	2.90	0.550	92.75
35.47[a]	2.87	0.561	87.44

[a] Q-point.

Table IX. Smoothed Values of Pressure, Temperature, Composition, and Molar Volume of the Solid–Liquid–Vapor Locus for the System CO_2–*n*-Butylbenzene–2-Methylnaphthalene with $(N_{nBB}/N_{2MN})_L = 0.4350$

Pressure (atm)	Temp (°C)	Mole fraction of CO_2	Liquid molar volume (cm³/(g mol))
10	7.40	0.117	128.80
15	5.05	0.175	123.40
20	2.30	0.242	117.00
25	−0.60	0.335	109.25
29.50[a]	−3.20	0.599	97.50

[a] Q-point.

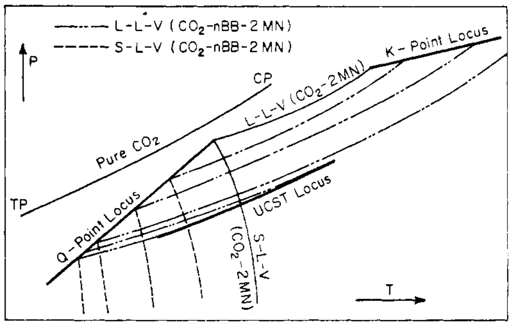

Figure 1. Schematic phase diagram for the ternary system carbon dioxide–*n*-butylbenzene–2-methylnaphthalene on the *P*–*T* space.

(d) CO_2–n-Butylbenzene–2-Methylnaphthalene Liquid–Liquid–Vapor System. (1) Stoichiometric Experiments. Figure 1 shows the schematic phase diagram for this ternary system on a *P*–*T* space, including the liquid–liquid–vapor region, solid–liquid–vapor region, the K-point curve, the Q-point curve, and the UCST point curve.

The unsmoothed data for the boundaries of the liquid–liquid–vapor coexistence region are given in Table X. Within these boundaries, the liquid–liquid–vapor equilibrium lines with certain $(N_{nBB}/N_{2MN})_{L1}$ were studied. At the lower values of $(N_{nBB}/N_{2MN})_{L1}$ the termination points for the liquid–liquid–vapor equilibrium line are Q point at the lower end, and K point at the upper end of the locus; whereas, at higher values of $(N_{nBB}/N_{2MN})_{L1}$, a UCST termination at the upper end of the liquid–liquid–vapor locus was observed. The transition from K-point termination to UCST termination occurs for a value of $(N_{nBB}/N_{2MN})_{L1}$ between 0.9462 and 0.9659.

Table X. Experimental Data for the Boundaries of the Liquid–Liquid–Vapor Coexistence Region for the System CO_2–*n*-Butylbenzene–2-Methylnaphthalene

	Temp (°C)	Pressure (atm)	$(N_{nBB}/N_{2MN})_{L1}$
Q-Point	−3.202	29.504	0.4533
	2.867	35.472	0.2533
	3.886	36.898	0.2393
	4.133	36.767	0.2221
	6.044	38.749	0.1471
K-point	38.081	80.717	0.1169
	38.154	80.986	0.1471
	38.925	82.005	0.2221
UCST	2.475	34.727	1.1362
	10.786	43.165	0.9883
	11.643	43.973	0.9883[a]
	15.693	47.984	0.9777
	16.851	49.276	0.9777[a]

[a] Reappearance of two liquid phases.

Table XI. Experimental Values of Temperature, Pressure, Mole Fractions of CO_2, and Molar Volumes of the Two Liquid Phases in Liquid–Liquid–Vapor Equilibria for the System CO_2–*n*-Butylbenzene–2-Methylnaphthalene with $(N_{nBB}/N_{2MN})_{L1}$ = 0.1117

Temp (°C)	Pressure (atm)	Mole fraction of CO_2		Liquid molar volume (cm^3/(g mol))	
		L1	L2	L1	L2
5	38.200	0.5017	0.9661	93.95	51.20
10	43.089	0.5107	0.9663	94.39	52.50
15	48.532	0.5175	0.9672	94.53	54.44
20	54.654	0.5203	0.9696	95.13	56.70
25	61.049	0.5221	0.9719	95.67	59.20
30	68.130	0.5187	0.9759	96.30	62.96
35	76.000	0.5275	0.9818	94.97	70.09

Table XII. Experimental Values of Temperature, Pressure, Mole Fractions of CO_2, and Molar Volumes of the Two Liquid Phases in Liquid–Liquid–Vapor Equilibrium for the System CO_2–*n*-Butylbenzene –2-Methylnaphthalene with $(N_{nBB}/N_{2MN})_{L1}$ = 0.2565

Temp (°C)	Pressure (atm)	Mole fraction of CO_2		Molar volume (cm^3/(g mol))	
		L1	L2	L1	L2
5	37.981	0.5260	0.9714	90.56	46.19
10	42.878	0.5574	0.9604	89.55	47.65
15	48.117	0.5541	0.9623	91.59	48.07
20	54.150	0.5566	0.9647	92.32	49.30
25	60.498	0.5480	0.9678	94.90	50.85
30	67.504	0.5419	0.9733	96.77	51.50
35	75.240	0.5360	0.9829	98.19	48.50

Five liquid–liquid–vapor systems with different $(N_{nBB}/N_{2MN})_{L1}$ were studied in detail. Tables XI–XV show the unsmoothed temperature, pressure, and the calculated CO_2 mole fractions and the molar volumes of the liquid 1 and liquid 2 phases.

Since the liquid–liquid–vapor equilibria loci on the *P–T* space are crowded with respect to pressure, a plot of ΔP vs. T along fixed $(N_{nBB}/N_{2MN})_{L1}$ is shown in Figure 2, where ΔP is defined as the difference between the pressure of the ternary system in liquid–liquid–vapor equilibrium and that of the binary system CO_2–2-methylnaphthalene in the liquid–liquid–vapor equilibrium. This binary liquid–liquid–vapor locus on the *P–T* space was studied previously (*4*) and is shown in Figure 3. For the K-point and Q-point terminations, the extrapolation of the binary liquid–liquid–vapor curve on the *P–T* space is used as a reference.

Table XIII. Experimental Values of Temperature, Pressure, Mole Fractions of CO_2, and Molar Volumes of the Two Liquid Phases in Liquid–Liquid–Vapor Equilibrium for the System CO_2–*n*-Butylbenzene–2-Methylnaphthalene with $(N_{nBB}/N_{2MN})_{L1}$ = 0.4155

Temp (°C)	Pressure (atm)	Mole fraction of CO_2		Molar volume (cm^3/(g mol))	
		L1	L2	L1	L2
5	37.645	0.5757	0.9468	90.22	52.25
10	42.475	0.5825	0.9482	90.77	53.24
15	47.917	0.5823	0.9484	92.60	54.36
20	53.699	0.5807	0.9511	94.23	55.73
25	60.094	0.5771	0.9547	96.17	57.27
30	66.695	0.5826	0.9602	95.01	58.70
35	74.516	0.5723	0.9694	97.39	59.45

Table XIV. Experimental Values of Temperature, Pressure, Mole Fraction of CO_2, and Molar Volumes of the Two Liquid Phases in Liquid–Liquid–Vapor Equilibrium for the System CO_2–*n*-Butylbenzene–2-Methylnaphthalene with $(N_{nBB}/N_{2MN})_{L1}$ = 0.6446

Temp (°C)	Pressure (atm)	Mole fraction of CO_2		Molar volume (cm^3/(g mol))	
		L1	L2	L1	L2
5	37.378	0.6478	0.9227	82.65	56.86
10	42.140	0.6602	0.9210	82.39	58.16
15	47.582	0.6663	0.9197	83.27	59.94
20	53.297	0.6663	0.9238	84.79	60.81
25	59.691	0.6582	0.9312	87.48	62.05
30	66.562	0.6523	0.9410	88.95	64.00
35	74.113	0.6437	0.9554	90.51	61.80

Table XV. Experimental Values of Temperature, Pressure, Mole Fraction of CO_2, and Molar Volumes of the Two Liquid Phases in Liquid–Liquid–Vapor Equilibrium for the System CO_2–*n*-Butylbenzene–2-Methylnaphthalene with $(N_{nBB}/N_{2MN})_{L1}$ = 0.9460

Temp (°C)	Pressure (atm)	Mole fraction of CO_2		Molar volume (cm^3/(g mol))	
		L1	L2	L1	L2
5	37.219	0.7443	0.8920	73.01	57.27
10	42.049	0.7672	0.8824	71.62	59.35
15	47.355	0.7798	0.8775	71.61	60.80
20	53.069	0.7765	0.8825	73.48	61.03
25	59.192	0.7606	0.8952	75.33	61.54
30	66.063	0.7413	0.9102	78.26	63.69
35	73.478	0.7276	0.9320	80.15	59.05

(*2*) ***Sampling Experiments.*** The results of experiments conducted with the Jerguson cell are shown in the form of selectivity as a function of temperature and $(N_{nBB}/N_{2MN})_{L1}$ in Tables XVI–XVIII, where selectivity β is defined as

$$\beta = \frac{(N_{nBB}/N_{2MN})_{L2}}{(N_{nBB}/N_{2MN})_{L1}}$$

The selectivities at three temperatures, 20, 30, and 38 °C, are

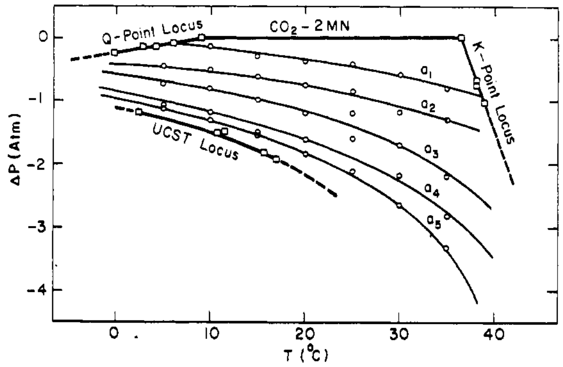

Figure 2. Plot of pressure difference between ternary system carbon dioxide-*n*-butylbenzene-2-methylnaphthalene, and binary system carbon dioxide-2-methylnaphthalene, vs. temperature in the liquid-liquid-vapor coexistence region along certain $(N_{nBB}/N_{2MN})_{L1} = a_i$: $a_1 = 0.1117$, $a_2 = 0.2565$, $a_3 = 0.4155$, $a_4 = 0.6446$, $a_5 = 0.9460$.

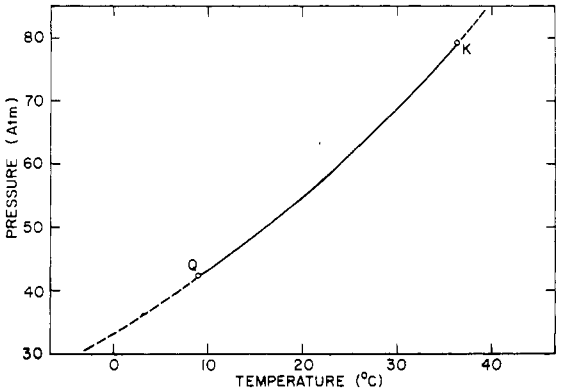

Figure 3. Plot of pressure vs. temperature for the binary system carbon dioxide-2-methylnaphthalene in liquid-liquid-vapor equilibrium.

Table XVI. Smoothed Values of Selectivity of CO_2 and Equilibrium Pressure as a Function of $(N_{nBB}/N_{2MN})_{L1}$ for the System CO_2-*n*-Butylbenzene-2-Methylnaphthalene in the Liquid-Liquid-Vapor Region at 20 °C

$(N_{nBB}/N_{2MN})_{L1}$	β	Pressure (atm)
0.20	2.112	54.30
0.30	1.953	54.01
0.40	1.812	53.80
0.50	1.673	53.57
0.60	1.572	53.38
0.70	1.491	53.23
0.80	1.431	53.14

reported. Also shown in these tables are the corresponding equilibrium pressures.

The experimental data show that in the temperature range (20-38 °C) and pressure range (53-81 atm), the selectivity of CO_2 in this ternary system ranges between 1.4 and 2.3, and the selectivity increases with both temperature and pressure. The probable error in the reported selectivity values is estimated to be ±0.18.

Remarks

Table XVII. Smoothed Values of Selectivity of CO_2 and Equilibrium Pressure as a Function of $(N_{nBB}/N_{2MN})_{L1}$ for the System CO_2-*n*-Butylbenzene-2-Methylnaphthalene in the Liquid-Liquid-Vapor Region at 30 °C

$(N_{nBB}/N_{2MN})_{L1}$	β	Pressure (atm)
0.20	2.181	67.74
0.30	2.018	67.37
0.40	1.894	67.03
0.50	1.786	66.76
0.60	1.689	66.58
0.70	1.602	66.45
0.80	1.525	66.29

Table XVIII. Smoothed Values of Selectivity of CO_2 and Equilibrium Pressure as a Function of $(N_{nBB}/N_{2MN})_{L1}$ for the System CO_2-*n*-Butylbenzene-2-Methylnaphthalene in the Liquid-Liquid-Vapor Region at 38 °C

$(N_{nBB}/N_{2MN})_{L1}$	β	Pressure (atm)
0.20	2.360	80.68
0.30	2.140	80.07
0.40	2.027	79.57
0.50	1.939	79.11
0.60	1.863	78.77
0.70	1.796	78.61
0.80	1.737	78.54

The above results reinforce our earlier conjecture (*4*) that CO_2 selectivity extracts from mixtures those hydrocarbons (either paraffinic or aromatic) which exhibit greater miscibility with CO_2 in a binary sense.

The phase behavior complexity (and variety) of the four ternary CO_2-hydrocarbon systems studied to date presents a challenge to one wishing to correlate such information. In turn, the authors reemphasize the value of studying and understanding the relevant binary systems specific to the ternary systems of interest. The binary systems CO_2-*n*-butylbenzene and CO_2-2-methylnaphthalene were extensively studied earlier in ref 9 and 4, respectively.

The authors are presently engaged in the study of the systems CO_2-*n*-butylbenzene and CO_2-*trans*-decalin at cryogenic conditions, as well as ternary liquid-liquid-vapor systems containing CO_2 with naphthenic components.

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Nomenclature

K-point = critical point of the two phases L2 and V
L1 = CO_2 lean liquid phase
L2 = CO_2 rich liquid phase
N = moles
P = pressure (atm)
Q-point = quadruple point, coexistence of the four phases V-L1-L2-S
T = temperature (°C)
UCST = upper critical solution temperature of L1 and L2

Greek

β = solvent (CO_2) free extractive selectivity

Subscript

2MN = 2-methylnaphthalene
nBB = *n*-butylbenzene

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The Solubility of Potassium Chloride in Ordinary and Heavy Water

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Using the sealed tube method the solubility of KCl has been redetermined in D_2O in the temperature range 21–88 °C and compared with new determinations in ordinary water. The present work confirms earlier work published about 40 years ago; however, many more determinations have been made and a higher precision has been obtained. Both of these sets of data have been subjected to least-squares treatment, and polynominal equations have been obtained.

For several years after the discovery of heavy water its solubility relations with a number of substances were studied. Experimental work was hampered due to the difficulty in procuring D_2O and the lack of knowledge of its fundamental properties. The passage of considerable time has resulted in marked changes in both respects; it therefore seemed desirable to redetermine the solubility of one salt in both ordinary and heavy water and compare the results with what seemed the best of earlier work. Potassium chloride was chosen largely because it could be obtained in a relatively high state of purity fairly easily.

Experimental Section

Chemicals. The heavy water was purchased from The Stuart Oxygen Co. who claimed a 99.7% D_2O content; it was used without further purification. Care was taken to avoid unnecessary contact with the atmosphere or ordinary water. The solvent ordinary water was laboratory deionized water. The KCl was the best grade of J. T. Baker; it was twice recrystallized from deionized water and fused.

Appartus and Method. All of the determinations were made using the sealed tube method which involves introducing weighed quantities of solute and solvent into a tube and sealing. Then the tube is heated slowly with shaking to determine the temperature at which the last small crystal remains. Mercury in glass thermometers were employed throughout this work. No important change has been made from that described earlier (*2*, *3*).

Results. In Table I will be found the contents of the 16 tubes containing KCl and ordinary water. The third column gives the solubility in moles of KCl per 55.51 mol of ordinary water. The last column gives the temperature at which the last small crystal remained. Corresponding results for 15 runs with 99.7% D_2O are given in Table II.

The values in the third column of Table II were calculated with the aid of the apparent molecular weight of the 99.7% D_2O, 20.028; this value is very close to that of pure D_2O, 20.029. Shearman and Menzies (*1*) expressed their results on the basis of pure D_2O. To do this required a short linear extrapolation from 98.2% D_2O to 100.0% D_2O. This slight difference in the

Table I. Observed Solubility of KCl in Ordinary Water

Wt KCl (g)	Wt H_2O (g)	M	Temp, °C
0.3343	1.0174	4.407	16.13
0.2559	0.7360	4.668	21.97
0.3009	0.8556	4.716	23.50
0.3803	1.0622	4.803	26.32
0.3856	1.0307	5.018	30.80
0.3679	0.9663	5.050	31.59
0.3850	0.9817	5.264	37.62
0.4528	1.1233	5.406	41.00
0.3023	0.7116	5.698	48.12
0.4013	0.9178	5.903	53.27
0.3212	0.7313	5.891	53.82
0.4310	0.9378	6.164	62.88
0.4534	0.9619	6.322	66.23
0.5565	1.1630	6.418	69.12
0.5860	1.1759	6.684	77.07
0.6816	1.3145	6.955	85.26

Table II. Observed Solubility of KCl in D_2O

Wt KCl (g)	Wt D_2O (g)	M	Temp, °C
0.2746	0.9843	4.160	21.51
0.3248	1.1182	4.331	25.78
0.3202	1.0644	4.486	28.99
0.3709	1.1279	4.904	39.48
0.3372	0.9880	5.089	43.16
0.4027	1.1744	5.113	44.53
0.3841	1.0800	5.304	49.19
0.3105	0.8394	5.516	55.54
0.3464	0.9225	5.600	56.87
0.3142	0.8245	5.683	58.72
0.3627	0.9269	5.835	63.00
0.3571	0.8751	6.085	70.06
0.4055	0.9862	6.132	71.45
0.4570	1.0667	6.389	79.36
0.4062	0.9048	6.695	88.42

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