Enthalpy of Ternary Mixtures of *m*-Cresol/1-Methylnaphthalene/*trans*-Decalin between 291 and 650 K at Pressures of 207, 690, and 10342 kPa

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Experimental enthalpy measurements were made on three ternary mixtures of *m*-cresol, 1-methylnaphthalene, and *trans*-decalin at temperatures between 291.5 and 650 K and pressures of 206.8, 689.5, and 10342.1 kPa using a reference fluid boil-off calorimeter. As the *m*-cresol concentration increased, enthalpy values predicted by the Soave–Redlich–Kwong equation of state became worse.

Introduction

As part of a continuing effort (*1–5*) to obtain enthalpies for coal-derived liquid model compounds, enthalpy measurements have been obtained on three ternary mixtures of *m*-cresol/1-methylnaphthalene/*trans*-decalin. Enthalpy measurements are importnt not only to provide basic data for use in engineering design and analysis, but also to check thermodynamic property correlations.

The present study considers a system consisting of a acidic oxygen compound present with an aromatic and a naphthenic compound. Such a system simulates the kinds of interactions likely to be present in coal-derived liquids. Enthalpy measurements have been completed on each of the three pure fluids (*1*, *4*, *5*, *6*); however, no enthalpy measurements have to date been reported for mixtures of *m*-cresol/1-methylnaphthalene/*trans*-decalin. These multicomponent system data can also be useful in studying the common assumption of characterizing actual undefined mixtures, such as coal-derived liquids, in terms of lumped compound types.

Experimental Section

The experimental data were obtained with a Freon-11 ($CFCl_3$) reference fluid boil-off calorimeter system, which was discussed in detail in previous papers (*1*, *3*) and will not be repeated. In summary, energy is transferred from the flowing test fluid to boiling Freon-11. The quantity of energy transferred is determined from the mass of Freon-11 that is boiled off. Based on tests using water and *n*-heptane as standard fluids, the accuracy of the calorimeter was determined to be ±1% of the measured enthalpy difference or 3 kJ/kg whichever is greater (*1*, *3*). The *m*-cresol purchased from Sigma Chemical Co. and the 1-methylnaphthalene purchased from Aldrich Chemical Co. were certified as 99+ mol %. It was not possible to obtain significant quantities of high-purity *trans*-decalin, and thus the *trans*-decalin was produced chemically from a mixture of *cis*- and *trans*-decalin purchased from Fischer Chemical Co. An anhydrous aluminum chloride catalyst was used to convert the *cis*-decalin until a mixture composition of from 0.93 to 0.96 mole fraction *trans*-decalin was obtained. Details of this process are reported elsewhere (*7*). All three of the pure fluids were further distilled in a Perkin-Elmer spinning band distillation column. The final chemicals, after distillation, were always greater than 99% pure, as determined by gas chromatography.

The compositions of each of the three mixtures as obtained from direct weighing of the samples are reported in Table I.

Table I. Compositions and Analyses of Ternary Mixtures

Ternary 1
- *60.33 mol % m-cresol*, 99.8 mol % *m*-cresol, with the major impurity assumed to be one of the cresol isomers, Sigma Chemical Co.
- *29.33 mol % 1-methylnaphthalene*; 99.4 mol % 1-methylnaphthalene, 1 major impurity unknown, Aldrich Chemical Co.
- *10.34 mol % trans-decalin*, 99.0 mol % *trans*-decalin, the one major impurity assumed to be *cis*-decalin, Fisher Chemical Co.

Ternary 2
- *20.00 mol % m-cresol*; 99.9 mol % *m*-cresol, with the major impurity assumed to be one of the cresol isomers. Sigma Chemical Co.
- *40.00 mol % 1-methylnaphthalene*; 99.4 mol % 1-methylnaphthalene, 1 major impurity unknown, Aldrich Chemical Co.
- *40.00 mol % trans-decalin*, 99.2 mol % *trans*-decalin, the one major impurity assumed to be *cis*-decalin, Fisher Chemical Co.

Ternary 3
- *40.00 mol % m-cresol*; 99.9 mol % *m*-cresol, with the major impurity assumed to be one of the cresol isomers, Sigma Chemical Co.
- *10.00 mol % 1-methylnaphthalene*; 99.4 mol % 1-methylnaphthalene, 1 major impurity unknown, Aldrich Chemical Co.
- *50.00 mol % trans-decalin*, 99.1 mol % *trans*-decalin, the one major impurity assumed to be *cis*-decalin, Fisher Chemical Co.

[a] The data are given in the following order: *amount of compound in mixture*, purity of the compound used, number and identification of impurities, where purchased.

These compositions neglect impurities in each of the pure fluids. Also reported in the table are the purities of each of the compounds that were added to form each mixture, as determined by gas chromatography. During the course of the experimental runs for each mixture the sample composition was periodically checked by gas chromatography. Samples were taken during liquid, vapor, and two-phase runs to ensure constant composition. Compositions determined by gas chromatography varied less than 0.1 mol % of each component; therefore, the mixture composition was assumed to be constant.

Results and Discussion

Results for the enthalpy of the 60.33% *m*-cresol/29.33% 1-methylnaphthalene/10.34% *trans*-decalin are presented in Table II and illustrated in Figure 1. Comparable results for the 20.00% *m*-cresol/40.00% 1-methylnaphthalene/40.00% *trans*-decalin and for the 40.00% *m*-cresol/10.00% 1-methylnapthalene/50.00% *trans*-decalin are respectively presented in Tables III and IV and illustrated in Figures 2 and 3. Measurements for all three systems were obtained along isobars of 206.8 and 10342.1 kPa (30 and 1500 psia) over a temperature range of 291.5–650 K (65–710 °F). For the 60.33% *m*-cresol/29.33% 1-methylnaphthalene mixture and the 20.00% *m*-cresol/40.00% 1-methylnaphthalene mixture, data were also obtained at 689.5 kPa (100 psia).

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Table II. Enthalpy Data for the Ternary Mixture of 60.33% *m*-Cresol/29.33% 1-Methylnaphthalene/10.34% *trans*-Decalin

inlet temp		inlet press.		outlet press.		exptl enthalpy		press. correction		cor enthalpy	
K	°F	kPa	psia	kPa	ksia	kJ/kg	Btu/lb	kJ/kg	Btu/lb	kJ/kg	Btu/lb
439.1	330.8	213.7	31.0	137.9	20.0	307.5	132.2	0.03	0.01	307.6	132.2
450.7	351.6	208.6	30.3	137.9	20.0	335.2	144.1	0.03	0.01	335.3	144.1
466.5	380.0	206.8	30.0	137.9	20.0	372.4	160.1	0.03	0.01	372.5	160.1
485.0	413.4	208.6	30.3	137.9	20.0	423.1	181.9	0.03	0.01	423.2	181.9
495.6	432.4	206.8	30.0	131.0	19.0	481.0	206.8	0.02	0.01	481.0	206.8
491.5	425.1	213.7	31.0	137.9	20.0	462.9	199.0	0.03	0.01	462.9	199.0
494.3	430.1	208.6	30.3	137.9	20.0	479.6	206.2	0.03	0.01	479.6	206.2
501.7	443.4	210.3	30.5	137.9	20.0	543.8	233.8	0.03	0.01	543.8	233.8
505.0	449.3	210.3	30.5	131.0	19.0	615.3	264.5	0.02	0.01	615.3	264.5
510.0	458.3	210.3	30.5	110.3	16.0	767.8	330.1	0.01	0.00	767.8	330.1
517.3	471.5	208.6	30.3	110.3	16.0	846.4	363.9	0.01	0.00	846.4	363.9
523.6	482.8	210.3	30.5	103.4	15.0	861.2	370.2	0.00	0.00	861.2	370.2
528.3	491.3	212.0	30.8	103.4	15.0	872.7	375.2	0.00	0.00	872.7	375.2
543.5	518.6	208.6	30.3	96.5	14.0	903.7	388.5	0.00	0.00	903.7	388.5
558.8	546.2	206.8	30.0	96.5	14.0	936.1	402.5	0.00	0.00	936.1	402.5
573.7	573.0	210.3	30.5	96.5	14.0	965.3	415.0	0.00	0.00	965.3	415.0
588.9	600.3	208.6	30.3	96.5	14.0	1002.6	431.0	0.00	0.00	1002.6	431.0
603.4	626.4	206.8	30.0	96.5	14.0	1031.0	443.3	0.00	0.00	1031.0	443.3
617.8	652.3	213.7	31.0	96.5	14.0	1066.4	458.5	0.00	0.00	1066.4	458.4
634.8	683.0	210.3	30.5	96.5	14.0	1108.7	476.6	0.00	0.00	1108.7	476.6
650.4	711.1	213.7	31.0	96.5	14.0	1135.9	488.3	0.00	0.00	1135.9	488.3
375.0	215.3	689.5	100.0	517.1	75.0	160.0	68.8	0.32	0.14	160.3	68.9
385.1	233.4	687.8	99.8	510.2	74.0	183.4	78.8	0.32	0.14	183.7	79.0
395.9	253.0	689.5	100.0	524.0	76.0	214.9	92.4	0.33	0.14	215.2	92.5
408.3	275.3	687.8	99.8	620.5	90.0	240.8	103.5	0.40	0.17	241.2	103.7
423.9	303.3	689.5	100.0	592.9	86.0	272.0	116.9	0.38	0.16	272.4	117.1
377.5	219.8	701.5	101.8	541.2	78.5	169.0	72.7	0.34	0.15	169.4	72.8
362.9	193.5	687.8	99.8	537.8	78.0	136.1	58.5	0.34	0.15	136.5	58.7
362.0	192.0	696.4	101.0	579.2	84.0	128.6	55.3	0.37	0.16	128.9	55.4
465.1	377.6	10335.2	1499.0	10266.3	1489.0	355.8	153.0	7.92	3.40	363.8	156.4
466.0	379.1	10342.1	1500.0	10266.3	1489.0	359.7	154.6	7.92	3.40	367.6	158.0
486.7	416.4	10345.6	1500.5	10280.1	1491.0	407.8	175.3	7.93	3.41	415.8	178.7
510.9	460.0	10328.3	1498.0	10245.6	1486.0	471.9	202.9	7.90	3.40	479.8	206.3
530.6	495.4	10349.0	1501.0	10245.6	1486.0	512.4	220.3	7.90	3.40	520.3	223.7
537.4	507.6	10355.9	1502.0	10259.4	1488.0	542.0	233.0	7.91	3.40	549.9	236.4
553.2	536.1	10362.8	1503.0	10280.1	1491.0	578.7	248.8	7.93	3.41	586.6	252.2
575.8	576.8	10355.9	1502.0	10273.2	1490.0	638.7	274.6	7.92	3.41	646.6	278.0
598.9	618.3	10328.3	1498.0	10231.8	1484.0	685.8	294.9	7.89	3.39	693.7	298.2
600.5	621.2	10328.3	1498.0	10231.8	1484.0	698.2	300.2	7.89	3.39	706.0	303.5
620.9	658.0	10328.3	1498.0	10231.8	1484.0	759.1	326.4	7.89	3.39	767.0	329.8
640.5	693.3	10335.2	1499.0	10238.7	1485.0	810.4	348.4	7.90	3.39	818.3	351.8

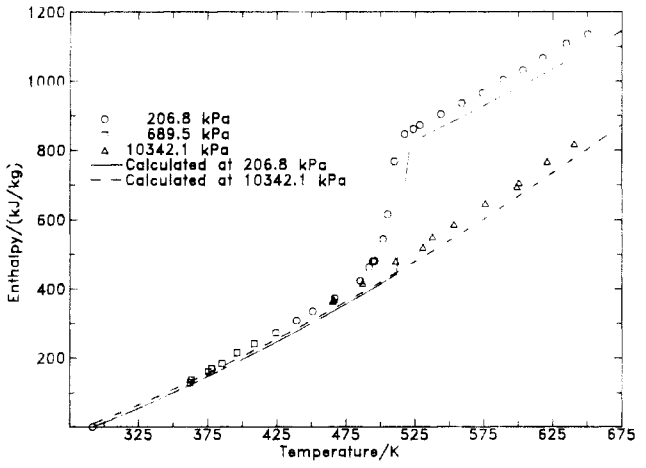

Figure 1. Enthalpy of the (mol %) 60.33% *m*-cresol/29.33% 1-methylnaphthalene/10.34% *trans*-decalin.

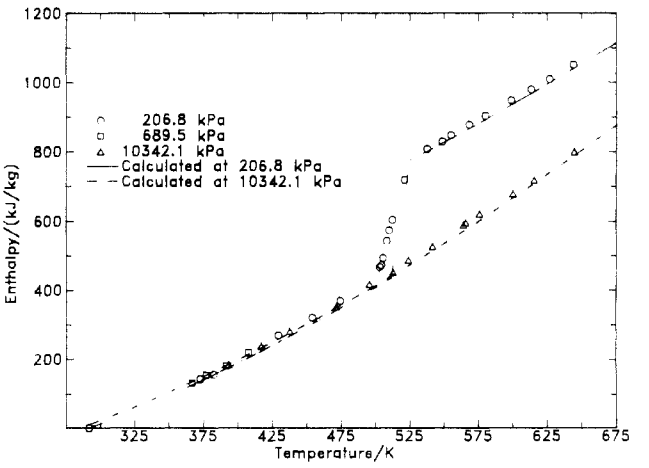

Figure 2. Enthalpy of the (mol %) 20.00% *m*-cresol/40.00% 1-methylnaphthalene/40.00% *trans*-decalin.

The values labeled "experimental enthalpy" are enthalpies based on a reference of $H = 0$ at 291.5 K and the outlet pressure of the calorimeter. The pressure of the boiling reference fluid is not controlled but varies with the barometric pressure and thus the outlet temperature of the calorimeter varies slightly from run to run. The values labeled "experimental enthalpy" in Tables II, III, and IV have been corrected to a reference temperature of 291.5 K by using the heat capacity of the liquid obtained by extrapolating the liquid curve of Figures 1, 2, and 3 to 291.5 K and taking the slope of the curve at 291.5 K. Temperature corrections were very small and never amounted to more than 1 kJ/kg.

The values labeled "corrected enthalpy" are the experimental values corrected to a reference $H = 0$ at 291.5 K and 0.1013 MPa by using the correlation of Kesler and Lee (*8*, *9*) and the pseudocritical parameters for the mixture. These are computed by using the pure fluid critical properties in Table V obtained from ref *10* and *11* by applying the mixing rules proposed by

Table III. Enthalpy Data for the Ternary Mixture of 20.00% *m*-Cresol/40.00% 1-Methylnaphthalene/40.00% *trans*-Decalin

inlet temp		inlet press.		outlet press.		exptl. enthalpy		press. correction		cor enthalpy	
K	°F	kPa	psia	kPa	psia	kJ/kg	Btu/lb	kJ/kg	Btu/lb	kJ/kg	Btu/lb
372.4	210.6	213.7	31.0	96.5	14.0	143.3	61.6	0.00	0.00	143.3	61.6
382.2	228.2	208.6	30.3	96.5	14.0	156.0	67.1	0.00	0.00	156.0	67.1
429.2	312.9	212.0	30.8	96.5	14.0	269.2	115.7	0.00	0.00	269.2	115.7
454.0	357.5	210.3	30.5	96.5	14.0	320.8	137.9	0.00	0.00	320.8	137.9
474.0	393.6	206.8	30.0	93.1	13.5	368.9	158.6	−0.01	0.00	368.9	158.6
500.3	440.8	206.8	30.0	96.5	14.0	457.7	196.8	0.00	0.00	457.7	196.8
502.8	445.3	213.7	31.0	96.5	14.0	467.1	200.8	0.00	0.00	467.1	200.8
504.1	447.8	213.7	31.0	96.5	14.0	472.5	203.2	0.00	0.00	472.5	203.2
505.2	449.6	212.0	30.8	93.1	13.5	493.5	212.2	−0.01	0.00	493.5	212.2
507.9	454.6	210.3	30.5	93.1	13.5	542.8	233.4	−0.01	0.00	542.8	233.4
509.8	458.0	208.6	30.3	96.5	14.0	573.9	246.7	0.00	0.00	573.9	246.7
512.2	462.3	210.3	30.5	96.5	14.0	604.4	259.8	0.00	0.00	604.4	259.8
521.2	478.5	215.5	31.3	96.5	14.0	718.8	309.0	0.00	0.00	718.8	309.0
537.6	508.1	208.6	30.3	96.5	14.0	808.2	347.5	0.00	0.00	808.2	347.5
548.6	527.9	206.8	30.0	96.5	14.0	829.0	356.4	0.00	0.00	829.0	356.4
554.9	539.2	274.1	29.8	89.6	13.0	847.5	364.4	−0.01	0.00	847.5	364.4
568.1	562.9	212.0	30.8	87.9	12.8	877.5	377.3	−0.01	0.00	877.5	377.2
579.7	583.8	213.7	31.0	86.2	12.5	903.5	388.4	−0.01	−0.01	903.5	388.4
598.9	618.4	210.3	30.5	86.2	12.5	948.2	407.6	−0.01	−0.01	948.2	407.6
613.4	644.4	210.3	30.5	86.2	12.5	979.7	421.2	−0.01	−0.01	979.7	421.2
626.7	668.3	206.8	30.0	87.9	12.8	1009.0	433.8	−0.01	0.00	1009.0	433.8
644.2	699.9	213.7	31.0	84.5	12.3	1051.4	452.0	−0.01	−0.01	1051.4	452.0
366.5	200.1	689.5	100.0	289.6	42.0	131.8	56.7	0.15	0.07	132.0	56.8
376.6	218.1	682.6	99.0	303.4	44.0	154.8	66.5	0.16	0.07	154.9	66.6
391.3	244.6	687.8	99.8	303.4	44.0	181.2	77.9	0.16	0.07	181.3	78.0
407.6	274.0	689.5	100.0	306.8	44.5	219.8	94.5	0.17	0.07	220.0	94.6
393.0	247.7	10321.5	1497.0	9962.9	1445.0	176.8	76.0	7.97	3.43	184.8	79.5
416.9	290.8	10293.9	1493.0	9962.9	1445.0	230.5	99.1	7.97	3.43	238.4	102.5
437.5	327.8	10287.0	1492.0	9976.7	1447.0	272.9	117.3	7.99	3.43	280.9	120.8
471.1	388.4	10328.3	1498.0	9997.4	1450.0	343.1	147.5	8.00	3.44	351.1	150.9
495.1	431.5	10314.6	1496.0	9969.8	1446.0	409.5	176.0	7.98	3.43	417.4	179.5
512.6	463.1	10307.7	1495.0	9969.8	1446.0	443.3	190.6	7.98	3.43	451.2	194.0
523.7	483.0	10342.1	1500.0	10162.9	1474.0	478.5	205.7	8.14	3.50	486.7	209.2
541.3	514.6	10321.5	1497.0	9997.4	1450.0	519.3	223.3	8.00	3.44	527.3	226.7
563.9	555.3	10342.1	1500.0	10162.9	1474.0	580.9	249.7	8.14	3.50	589.0	253.2
565.6	558.3	10183.6	1477.0	10059.5	1459.0	587.5	252.6	8.05	3.46	595.5	256.0
575.6	576.4	10342.1	1500.0	10149.1	1472.0	612.3	263.2	8.13	3.49	620.4	266.7
599.9	620.1	10342.1	1500.0	10152.5	1472.5	669.9	288.0	8.13	3.49	678.0	291.5
615.5	648.1	10342.1	1500.0	10149.1	1472.0	709.3	305.0	8.13	3.49	717.5	308.4
644.5	700.4	10342.1	1500.0	10152.5	1472.5	790.8	340.0	8.13	3.49	798.9	343.5

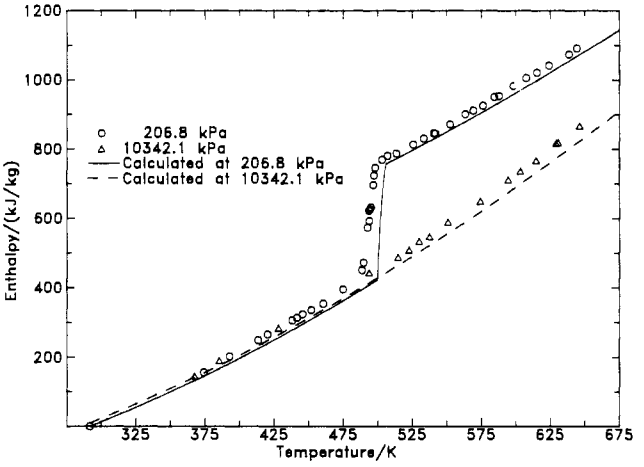

Figure 3. Enthalpy of the (mol %) 40.00% *m*-cresol/10.00% 1-methylnaphthalene/50.00% *trans*-decalin.

Kesler and Lee (*8*, *9*). These values are listed in Table VI. Since these pressure corrections are quite small even a substantial error in the values obtained from the generalized correlation will have an insignificant effect on the values reported here.

The high-pressure results in Figures 1–3 illustrate the effect of temperature on the liquid enthalpy, while the low-pressure data show the effect of vaporization on the sample. The data in the two-phase region, where the change in enthalpy with temperature is the greatest, are enthalpy values for a two-phase mixture with overall composition equal to that of the sample. This curve differs from results for pure fluids, where the two-phase line should be vertical. An estimated precision of ±0.5% is also illustrated on these figures, which is consistent with our estimated accuracy of ±1%. Due to energy effects resulting from hydrogen bonding, the mixtures containing greater percentages of *m*-cresol have the greater enthalpy. Considering these mixtures to be model coal–liquid systems, the weight percent oxygen of each of these samples is also reported in Table VI. Thus, it can be seen that a relatively low percent of phenolic oxygen concentration can have a substantial effect on the total enthalpy of a coal-derived liquid. Also, the mixture containing the least 1-methylnaphthalene has the steepest two-phase region since the mixture consists of 90% *m*-cresol + *trans*-decalin, which have similar boiling temperatures at these conditions.

Shown in the figures are the calculated results by use of the Soave (*12*) equation of state in conjunction with reported ideal gas enthalpies (*10*, *13*). In all calculations, interaction parameters were set equal to zero. As can be seen, the calculated enthalpies are lower than the experimental values. Furthermore, the equation of state predicts a two-phase region at significantly higher temperatures than were obtained experimentally. In the two-phase region, enthalpy values were determined by using a flash calculation to determine the vapor–liquid equilibrium and by calculating enthalpies from the resulting vapor/liquid mixture.

The Soave equation of state has been developed for nonpolar fluids and is in error when used to estimate enthalpies of polar, associating fluids, such as *m*-cresol. One would also

Table IV. Enthalpy Data for the Ternary Mixture of 40.00% *m*-Cresol/10.00% 1-Methylnaphthalene/50.00% *trans*-Decalin

inlet temp		inlet press.		outlet press.		exptl enthalpy		press. correction		cor enthalpy	
K	°F	kPa	psia	kPa	psia	kJ/kg	Btu/lb	kJ/kg	Btu/lb	kJ/kg	Btu/lb
373.9	213.4	214.4	31.1	103.2	15.0	156.5	67.3	0.00	0.00	156.5	67.3
392.6	247.0	206.6	30.0	96.3	14.0	202.7	87.2	0.00	0.00	202.7	87.2
413.4	284.5	208.4	30.2	96.3	14.0	248.6	106.9	0.00	0.00	248.6	106.9
420.2	296.8	210.1	30.5	96.3	14.0	265.4	114.1	0.00	0.00	265.4	114.1
438.1	328.9	213.5	31.0	96.3	14.0	305.6	131.4	0.00	0.00	305.6	131.4
441.6	335.3	208.4	30.2	102.4	14.9	313.6	134.8	0.00	0.00	313.6	134.8
445.7	342.6	216.6	31.4	96.7	14.0	323.5	139.1	0.00	0.00	323.5	139.1
451.9	353.7	210.5	30.5	96.7	14.0	335.5	144.3	0.00	0.00	335.5	144.3
460.4	369.1	210.5	30.5	96.7	14.0	353.4	151.9	0.00	0.00	353.4	151.9
474.7	394.8	203.2	29.5	110.1	16.0	395.5	170.0	0.01	0.00	395.5	170.0
488.3	419.2	208.4	30.2	95.5	13.9	450.4	193.6	0.00	0.00	450.4	193.6
489.5	421.4	205.8	29.8	123.1	17.8	472.5	203.1	0.02	0.01	472.5	203.1
492.5	426.8	204.1	29.6	123.1	17.8	573.5	246.5	0.02	0.01	573.5	246.6
493.4	428.4	204.1	29.6	130.0	18.8	622.3	267.5	0.02	0.01	622.3	267.5
493.7	429.0	206.7	30.0	123.1	17.8	592.8	254.9	0.02	0.01	592.8	254.9
494.0	429.6	204.1	29.6	130.0	18.8	625.7	269.0	0.02	0.01	625.7	269.0
494.8	431.0	209.3	30.3	102.4	14.9	631.3	271.4	0.00	0.00	631.3	271.4
496.6	434.2	206.8	30.0	96.5	14.0	695.6	299.1	0.00	0.00	695.6	299.1
497.1	435.2	206.8	30.0	103.4	15.0	722.9	310.8	0.00	0.00	722.9	310.8
497.9	436.5	204.3	29.6	103.4	15.0	745.3	320.4	0.00	0.00	745.3	320.4
503.0	445.7	209.8	30.4	130.5	18.9	768.6	330.5	0.02	0.01	768.7	330.5
507.0	452.9	206.8	30.0	110.3	16.0	780.1	335.4	0.01	0.00	780.1	335.4
513.4	464.5	208.6	30.3	110.3	16.0	786.9	338.3	0.01	0.00	786.9	338.3
525.6	486.4	208.6	30.3	110.3	16.0	813.0	349.5	0.01	0.00	813.0	349.5
533.1	499.8	208.6	30.3	110.3	16.0	830.0	356.9	0.01	0.00	830.1	356.9
540.5	513.1	206.8	30.0	110.3	16.0	845.9	363.7	0.01	0.00	845.9	363.7
541.5	514.9	206.4	29.9	116.8	16.9	845.1	363.3	0.01	0.01	845.1	363.3
552.3	534.6	208.6	30.3	110.3	16.0	871.2	374.5	0.01	0.00	871.2	374.5
563.2	554.0	206.8	30.0	110.3	16.0	901.3	387.5	0.01	0.00	901.3	387.5
568.9	564.4	209.9	30.4	89.2	12.9	911.6	391.9	−0.01	0.00	911.6	391.9
575.9	576.9	210.3	30.5	110.3	16.0	925.4	397.9	0.01	0.00	925.4	397.9
584.2	592.0	208.6	30.3	110.3	16.0	950.3	408.5	0.01	0.00	950.3	408.5
587.6	598.0	206.4	29.9	89.2	12.9	953.5	409.9	−0.01	0.00	953.4	409.9
598.1	616.9	215.0	31.2	89.2	12.9	982.6	422.4	−0.01	0.00	982.6	422.4
607.4	633.6	204.7	29.7	89.2	12.9	1005.3	432.2	−0.01	0.00	1005.3	432.2
615.2	647.6	206.4	29.9	89.2	12.9	1021.0	438.9	−0.01	0.00	1021.0	438.9
624.0	663.5	203.0	29.4	89.2	12.9	1041.4	447.7	−0.01	0.00	1041.4	447.7
638.6	689.9	206.4	29.9	89.2	12.9	1074.2	461.8	−0.01	0.00	1074.1	461.8
644.1	699.7	209.9	30.4	89.2	12.9	1091.7	469.3	−0.01	0.00	1091.6	469.3
367.0	201.0	10293.7	1493.0	10217.9	1482.0	137.3	59.0	8.02	3.45	145.4	62.5
385.0	233.3	10390.3	1507.0	10328.2	1498.0	181.8	78.2	8.11	3.49	189.9	81.6
428.1	311.0	10362.7	1503.0	10300.6	1494.0	275.4	118.4	8.09	3.48	283.4	121.9
493.5	428.7	10362.7	1503.0	10300.6	1494.0	434.6	186.9	8.09	3.48	442.7	190.3
514.4	466.3	10369.6	1504.0	10300.6	1494.0	479.5	206.2	8.09	3.48	487.6	209.6
522.4	480.7	10369.6	1504.0	10307.5	1495.0	500.4	215.1	8.09	3.48	508.5	218.6
529.7	493.8	10362.7	1503.0	10300.6	1494.0	526.1	226.2	8.09	3.48	534.2	229.7
537.3	507.4	10362.7	1503.0	10307.5	1495.0	539.2	231.8	8.09	3.48	547.3	235.3
550.7	531.6	10355.8	1502.0	10300.6	1494.0	581.1	249.8	8.09	3.48	589.2	253.3
574.0	573.5	10355.8	1502.0	10300.6	1494.0	641.2	275.7	8.09	3.48	649.3	279.1
594.3	610.0	10355.8	1502.0	10300.6	1494.0	702.8	302.2	8.09	3.48	710.9	305.6
603.2	626.0	10348.9	1501.0	10293.7	1493.0	727.7	312.8	8.08	3.47	735.7	316.3
614.5	646.5	10355.8	1502.0	10300.6	1494.0	758.6	326.1	8.09	3.48	766.7	329.6
629.1	672.6	10348.9	1501.0	10286.8	1492.0	808.1	347.4	8.08	3.47	816.1	350.9
630.7	675.6	10355.8	1502.0	10286.8	1492.0	810.1	348.3	8.08	3.47	818.2	351.8
646.2	703.4	10355.8	1502.0	10286.8	1492.0	859.0	369.3	8.08	3.47	867.1	372.8

Table V. Critical Constants

name	formula	T_c, K	P_c, atm	acentric factor	ref
m-cresol	$C_6H_4CH_3OH$	705.80	45.05	0.464	*10, 11*
1-methylnaphthalene	$C_{10}H_7CH_3$	772.00	35.20	0.334	*10*
trans-decalin	$C_{10}H_{16}$	687.10	31.00	0.294	*10*

Table VI. Pseudoacentric and Pseudocritical Properties for the Mixtures

mixture	T_c, K	P_c, atm	acentric factor	av mol wt	wt % oxygen
ternary 1	724.90	39.98	0.408	121.23	7.8
ternary 2	724.74	34.93	0.344	133.81	2.4
ternary 3	702.55	36.02	0.366	126.60	5.1

expect nonzero interaction parameters for *m*-cresol with the other components of the ternary system. The calculated results are in best agreement with the experimental data for the mixture containing the lowest fraction (20 mol %) *m*-cresol as shown in Figure 2; however, the results show that a relatively low concentration of oxygen (< 8.0%) can cause the equation of state to differ substantially from the experimental data.

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Registry No. *m*-Cresol, 108-39-4; 1-methylnaphthalene, 90-12-0; *trans*-decalin, 493-02-7.

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Mutual Binary Solubilities: Perfluorodecalin/Hydrocarbons

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Mutual solubility data for perfluorodecalin + *n*-hexane, + *n*-heptane, + *n*-octane, + *n*-nonane, + 1-hexene, and + 1-heptene are reported. The NRTL and UNIQUAC equations were used to correlate the data. UNIFAC group parameters for the interactions CH_2/CF_2(c) and $CH{=}CH_2/CF_2$(c) can also be obtained.

Introduction

Perfluorocarbon/hydrocarbon systems are particularly adequate to test the applicability of the activity coefficient models as multicomponent mixtures change swiftly from type to type of equilibrium pattern over a small temperature range.

As part of a program to study multicomponent mixtures containing perfluorodecalin (PFD) and hydrocarbons, this paper reports the results of measurements on liquid–liquid equilibrium for perfluorodecalin + *n*-hexane, + *n*-heptane, + *n*-octane, + *n*-nonane, + 1-hexene, and + 1-heptene. These experimental data are analyzed by the NRTL and UNIQUAC equations. UNIFAC group parameters for the interactions CH_2/CF_2(c) and $CH{=}CH_2/CF_2$(c) were obtained and published elsewhere (*1*). CF_2(c) refers to a cyclic molecule.

Experimental Section

The experimental work was carried out using a thermostated miniature cell similar to that described by Soares et al. (*2*). Temperature was controlled and was measured by means of a precision thermometer within an accuracy of 0.01 K. The mixtures were stirred with a magnetic stirrer for at least 30 min and allowed to settle for a period of 4 h. Once the equilibrium had been reached, samples of two conjugate phases were carefully withdrawn by using microsyringes and injected directly into the column of a gas–liquid chromatograph (Pye Unicam) combined with an electronic integrator (Varian CDS 111). Special care was taken with the measurements above the room temperature to avoid phase splitting due to cooling.

Calibration curves were obtained by using at least 10 mixtures of known concentration, of which four to six chromatograms were obtained. Four to six samples of both phases were

Table I. Mutual Solubility of PFD (1) and *n*-Hexane (2)

	solubility, wt %			solubility, wt %	
temp, K	x_1	x_{12}	temp, K	x_1	x_{12}
277.55	28.48	92.65	288.75	44.55	88.82
278.45	29.48	92.53	290.85	48.91	87.35
279.15	30.48	92.47	293.25	54.05	85.09
281.15	33.16	91.79	293.65	55.85	84.49
283.15	35.72	91.12	294.05	58.07	83.59
286.15	40.35	89.82	294.35	59.63	83.06
288.15	43.45	89.18	295.05	66.10	81.35

Table II. Mutual Solubility of PFD (1) and *n*-Heptane (2)

	solubility, wt %			solubility, wt %	
temp, K	x_{11}	x_{12}	temp, K	x_{11}	x_{12}
278.45	18.78	96.36	299.95	37.07	92.38
282.45	21.51	95.76	300.65	37.80	92.21
286.65	24.41	95.08	301.95	39.60	91.81
288.15	25.59	94.78	303.15	41.20	91.40
289.15	26.12	94.56	304.25	42.49	91.02
291.15	27.95	94.35	306.75	46.68	89.79
293.15	29.72	93.98	308.15	49.30	88.99
295.75	32.30	93.49	310.55	56.49	87.08
297.65	34.35	92.97	311.25	60.48	85.68
298.15	34.80	92.88	311.75	65.03	83.78

Table III. Mutual Solubility of PFD (1) and *n*-Octane (2)

	solubility, wt %			solubility, wt %	
temp, K	x_{11}	x_{12}	temp, K	x_{11}	x_{12}
278.55	13.58	97.02	316.35	39.61	90.66
287.75	17.57	96.32	324.05	50.81	84.57
298.15	23.48	94.98	325.65	54.08	82.67
298.55	24.01	94.87	326.45	55.84	82.00
307.85	30.09	93.44	327.25	58.22	81.35
313.15	36.22	91.53			

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