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High-Pressure Phase Diagrams of Methane + Decahydronaphthalene and Methane + Acenaphthene Mixtures

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Liquid vapor equilibrium data on the methane + decahydronaphthalene (decalin) mixture at (294, 323, 373, and 423) K and on the methane + acenaphthene mixture at (398, 423, and 453) K and pressures up to 160 MPa are reported. The data have been obtained with a high-pressure cell and an infrared absorption method, coupled with a suitable mathematical treatment of the spectra.

Introduction

The results presented in this paper are a continuation of our investigative program on phase diagrams of light + heavy hydrocarbon binary mixtures. Such data are needed in order to develop calculation models for more complex mixtures such as crude oils and natural gases. Models, including equations of state, group contribution methods, or molecular simulations, need binary mixtures' experimental data in order to fit their parameters. High-pressure data are especially scarce in the literature because they are difficult to measure. However, they are useful because deep oil fields are at high pressures.

For these measurements, we use a spectroscopic method with a high-pressure variable-volume cell. Such an in situ method is particularly well suited for high pressure and permits fast and easy measurements.

We have already published data for the following mixtures: methane + 1-methylnaphthalene;[1] methane + hexane and methane + benzene;[2] methane + squalane and methane + hexatriacontane;[3] methane + tetralin (1,2,3,4-tetrahydronaphthalene) and methane + 9,10-dihydrophenanthrene;[4] and propane + tetralin and propane + 1-methylnaphthalene.[5] In this paper, two other mixtures are investigated: methane. + decalin and methane + acenaphthene.

Experimental Section

Chemicals. The purity of methane was 99.9%. Acenaphthene and *cis*-decalin, supplied by Aldrich with a purity of 99%, were used without further purification.

Apparatus and Procedures. The apparatus and experimental procedure have been previously described.[1] A more detailed description of the treatment of spectra, namely the elimination of the baseline, has been given previously.[6] Concentration measurements of each component in the gas and liquid phases have been obtained with an accuracy of less than 1%, as mentioned in the preceding papers. The concentration of methane, which remains high in both phases, is easily measured with this accuracy. As for the other substance, its concentration may be very low in the gas phase. Therefore, concentration measurements in the gas phase at low pressure are not reported because of very low infrared absorption by the solute. Although a measurable absorption could be obtained by increasing the absorption path-length, it has not been done because measurements in this pressure range can be easily obtained using more classical methods. The relative uncer-

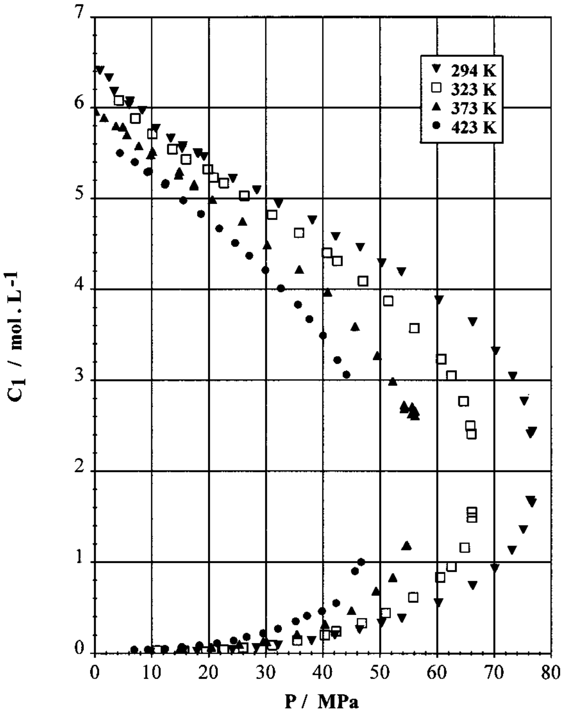

Figure 1. Concentration of decalin as a function of pressure in the gas and liquid coexisting phases for the mixture methane + decalin at four temperatures: ▼, 294 K; □, 323 K; ▲, 373 K; ●, 423 K.

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Table 1. Vapor−Liquid Equilibrium Data for Methane + Decalin at (294, 323, 373, and 423) K (C_1 = Decalin Concentration; C_2 = Methane Concentration)

	gas phase		liquid phase			gas phase		liquid phase	
P/MPa	C_1/mol·L^{-1}	C_2/mol·L^{-1}	C_1/mol·L^{-1}	C_2/mol·L^{-1}	P/MPa	C_1/mol·L^{-1}	C_2/mol·L^{-1}	C_1/mol·L^{-1}	C_2/mol·L^{-1}
					T = 294 K				
0.9			6.41	0.16	28.4	0.06	13.09	5.09	4.17
2.5			6.33	0.46	32.2	0.09	14.03	4.94	4.65
3.4			6.18	0.62	38.1	0.14	15.20	4.76	5.26
6.0			6.03	1.21	42.2	0.20	15.80	4.58	5.80
6.2			6.07	1.2	46.5	0.26	16.33	4.46	6.23
8.3			5.97	1.54	50.3	0.33	16.63	4.29	6.77
10.3	0.01	4.57	5.77	2.00	53.8	0.38	16.93	4.19	7.19
13.3			5.66	2.36	60.3	0.55	17.14	3.88	8.23
15.3			5.55	2.67	66.2	0.74	17.19	3.64	9.07
15.4	0.02	7.84	5.58	2.64	70.2	0.93	16.92	3.32	10.11
18.0	0.02	9.13	5.50	2.93	73.2	1.13	16.57	3.04	10.98
18.1			5.49	2.89	75.2	1.36	16.00	2.77	11.87
19.1			5.46	2.98	76.3	1.68	15.17	2.41	12.99
24.2	0.04	11.69	5.22	3.71	76.7	1.65	15.23	2.44	12.97
					T = 323 K				
4.2			6.08	0.65	40.5	0.20	14.19	4.40	5.71
7.1			5.88	1.16	42.4	0.24	14.40	4.31	5.95
10.5	0.03	4.68	5.71	1.63	46.9	0.33	14.97	4.09	6.65
13.6			5.54	2.14	51.2	0.44	15.40	3.87	7.38
15.8	0.03	6.84	5.43	2.46	55.9	0.61	15.54	3.57	8.26
19.7	0.02	8.42	5.32	2.86	60.6	0.83	15.5	3.23	9.36
20.8	0.04	8.87	5.23	3.01	62.5	0.95	15.15	3.05	9.92
22.6	0.04	9.54	5.17	3.25	64.7	1.16	14.96	2.77	10.75
26.1	0.06	10.83	5.03	3.71	66.0	1.49	14.19	2.50	11.48
31.1	0.09	12.32	4.82	4.40	66.1	1.55	13.99	2.41	11.52
35.7	0.14	13.30	4.62	5.01					
					T = 373 K				
0.1			5.96	0.04	29.5	0.13	9.51		
1.6			5.89	0.31	30.2	0.13	9.40	4.49	4.12
3.7			5.80	0.57	35.6	0.21	10.75	4.22	5.00
4.9			5.79	0.72	40.6	0.32	11.70	3.97	5.81
5.6			5.70	0.83	45.3	0.47	12.32	3.59	6.80
7.7			5.58	1.11	49.4	0.68	12.57	3.27	7.70
9.8			5.48	1.39	52.2	0.83	12.79	2.99	8.46
10.1	0.02	3.46	5.52	1.39	54.4	1.18	12.38	2.73	9.12
14.7	0.03	5.09	5.26	2.07	54.5	1.19	12.32	2.69	9.22
14.8			5.30	2.04	55.5			2.63	9.40
17.4			5.16	2.43	55.6			2.71	9.31
17.4			5.14	2.40	56.1			2.61	9.45
20.5	0.07	6.90	4.99	2.80	56.1			2.66	9.36
25.6	0.10	8.44	4.75	3.56					
					T = 423 K				
4.4			5.50	0.51	26.9	0.18	7.55	4.37	3.49
7.0	0.04	2.11	5.40	0.83	29.7	0.22	8.16	4.21	4.00
9.3	0.04	2.89	5.29	1.13	32.4	0.27	8.72	4.01	4.46
9.5			5.30	1.17	35.4	0.35	9.36	3.83	4.98
12.3	0.05	3.74	5.15	1.57	37.4	0.41	9.65	3.67	5.33
12.4			5.17	1.52	39.9	0.46	10.32	3.49	5.79
15.4	0.07	4.64	4.98	1.93	42.4	0.55	10.61	3.22	6.34
18.5	0.09	5.50	4.83	2.33	44.1			3.06	6.80
21.6	0.11	6.24	4.67	2.74	45.6	0.90	10.47		
24.5	0.14	7.08	4.51	3.14	46.7	1.00	10.55		

tainty on the mole fraction may be computed by

$$\frac{\Delta y}{y} = 2\frac{\Delta c}{c}(1 - y) \qquad (1)$$

where $\Delta c/c$ is the relative uncertainty for concentration measurements. As a result, $\Delta y/y$ is always less than $2\Delta c/c$ even if the concentration of the minor component goes to zero.

The most important source of uncertainty is the pressure gauge with an accuracy of 0.4 MPa. The estimated uncertainty of temperature is 0.5 °C.

Results

Methane + Decalin Mixture. Molar concentrations of decalin (C_1) and methane (C_2) are reported in Table 1. Other quantities such as mole fraction and molar volume may be determined from these data. C_1 and C_2 are plotted against pressure at the different temperatures in Figures 1 and 2, respectively. The pressure−mole fraction plot of the coexistence curves at different temperatures is given in Figure 3. It is interesting to note the trend of critical pressure to situate the data relative to the classical phase diagrams described by Van Konynenburg and Scott.[7] Again, as seen for other methane + heavy hydrocarbon mixtures,[4] the critical pressure decreases with increasing temperature in this temperature range.

Two sources of data were available in the literature for comparison with this work. Stepanova and Vassilieva[8] reported high-pressure data at 373 an 423 K. Unfortunately they do not mention which configuration (cis or

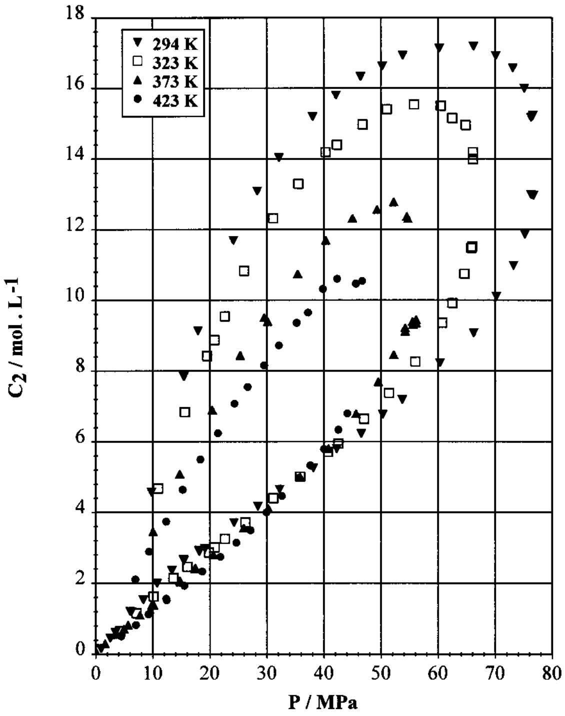

Figure 2. Concentration of methane as a function of pressure in the gas and liquid coexisting phases for the mixture methane + decalin at four temperatures: ▼, 294 K; □, 323 K; ▲, 373 K; ●, 423 K.

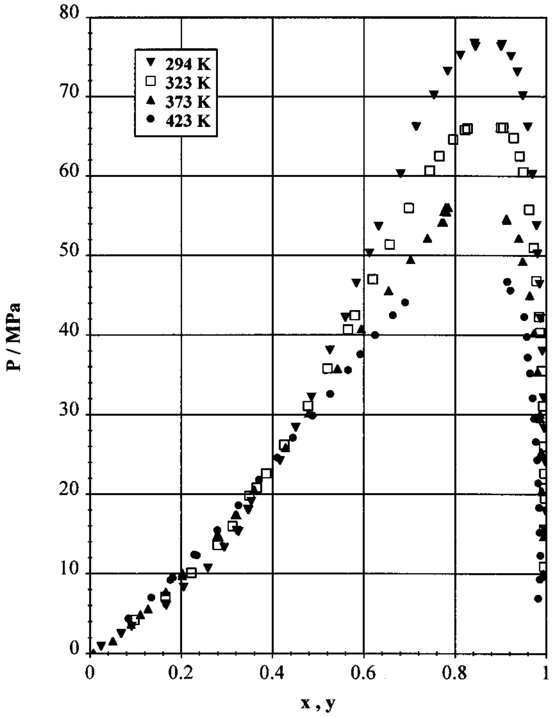

Figure 3. Phase diagrams of methane + decalin at four temperatures: ▼, 294 K; □, 323 K; ▲, 373 K; ●, 423 K. $x, y = C_2/(C_1 + C_2)$ = mole fractions of methane.

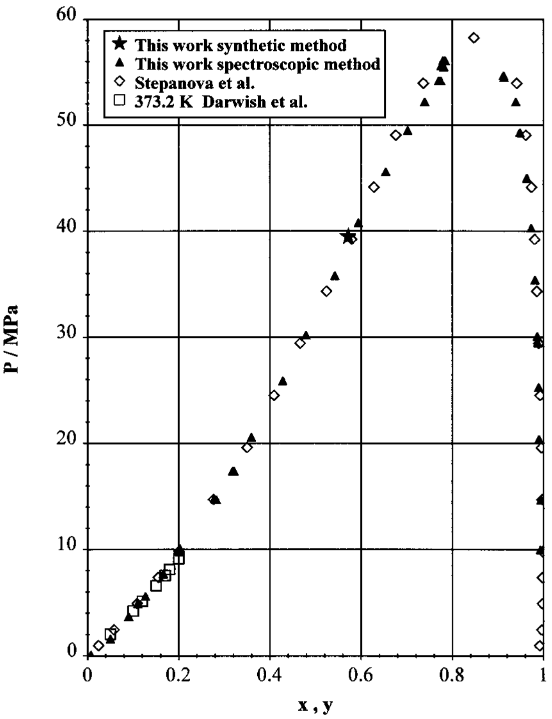

Figure 4. Comparison with literature data. Phase diagram of methane + decalin at 373 K: ▲, this work; ◇, 373 K, Stepanova et al.;[8] □, Darwish et al.;[9] ★, this work synthetic method. x, $y = C_2/(C_1 + C_2)$ = mole fractions of methane.

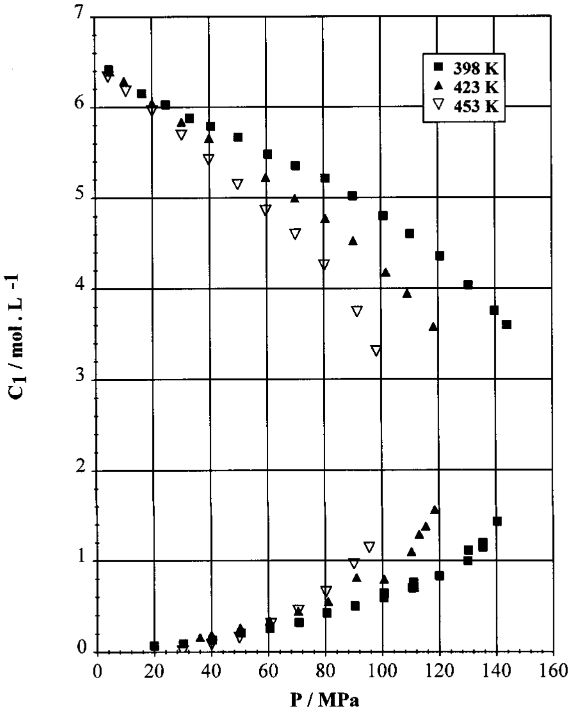

Figure 5. Concentration of acenaphthene as a function of pressure in the gas and liquid coexisting phases for the mixture methane + acenaphthene: ■, 398 K; ▲, 423 K; ▲, 463 K.

trans) was used in their experiments. Most likely, they used an undefined mixture. More recently, low-pressure data on methane + *trans*-decalin at 323, 373, and 423 K have been reported by Darwish et al.[9] Although the solute compounds differ in configuration, it is still possible to make a comparison as long as *cis*-decalin and *trans*-decalin are assumed to have similar solubilities in methane. These data were obtained by a synthetic method with a variable volume equilibrium cell. Our data are consistent with those of Stepanova and Vassilieva in the whole range at 373 and 423 K. However, the agreement is not as good near the critical point. Our data are also consistent with the low-pressure data reported by Darwish et al. at 323, 373, and 423 K. Figure 4 shows an example of the agreement at 373 K.

Table 2. Vapor−Liquid Equilibrium Data for Methane + Acenaphthene at (398, 423, and 453) K (C_1 = Acenaphthene Concentration; C_2 = Methane Concentration)

	gas phase		liquid phase	
P/MPa	C_1/mol·L^{-1}	C_2/mol·L^{-1}	C_1/mol·L^{-1}	C_2/mol·L^{-1}
		T = 398 K		
4.9			6.484	0.281
16.4			6.207	1.210
19.9	0.070	6.077		
24.7			6.063	1.803
30.1	0.093	8.792		
33.1			5.920	2.114
40.4	0.134	10.927	5.818	2.542
50.3	0.210	12.587	5.685	3.038
60.5	0.258	13.886	5.478	3.818
70.5	0.321	14.948	5.336	4.395
80.5	0.426	15.690	5.185	5.002
90.2	0.501	16.318	4.984	5.706
100.5	0.590	16.871		
100.7	0.641	16.784	4.756	6.476
110.3	0.698	17.185	4.554	7.195
110.9	0.765	16.996		
111.1	0.705	17.213		
120.3	0.830	17.386	4.305	8.122
129.9	0.994	17.391		
130.4	1.112	17.196	3.989	9.071
135.2	1.145	17.050		
135.2	1.199	17.265		
140.0	1.430	16.666	3.696	10.168
144.1			3.545	10.657
		T = 423 K		
5.3			6.393	0.260
10.2			6.292	0.663
20.0			6.044	1.476
30.3			5.837	2.250
36.0	0.161	9.196		
40.0	0.190	9.981	5.657	2.936
50.0	0.266	11.629		
60.1	0.340	12.937	5.223	4.444
70.2	0.445	13.975	4.996	5.216
80.8	0.550	14.898	4.771	6.075
90.6	0.814	15.387	4.526	6.931
101.2	0.795	15.811	4.179	8.068
109.7	1.097	15.795	3.948	8.865
112.9	1.288	15.572		
115.2	1.380	15.439		
118.4	1.563	15.209	3.579	9.967
		T = 453 K		
4.6			6.337	0.156
10.8			6.180	0.743
20.0			5.962	1.565
21.9	0	5.997		
30.1	0.010	7.902	5.692	2.479
39.9	0.081	9.839	5.420	3.366
49.9	0.157	11.418	5.146	4.230
60.3	0.308	12.755	4.858	5.180
70.3	0.451	13.715	4.597	6.085
80.2	0.654	14.253	4.256	7.183
90.0	0.962	14.528		
91.6			3.742	8.701
95.4	1.143	14.548		
98.3			3.308	9.959

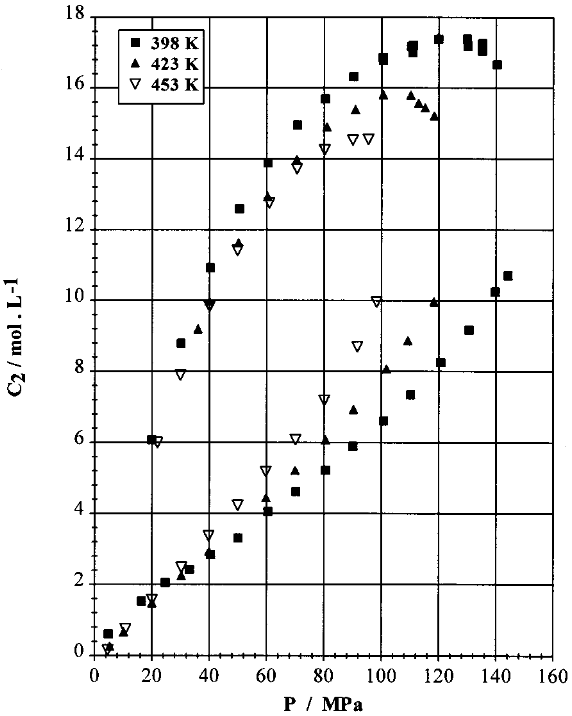

Figure 6. Concentration of methane as a function of pressure in the gas and liquid coexisting phases for the mixture methane + acenaphthene: ■, 398 K; ▲, 423 K; ▽, 453 K.

Table 3. Comparison with Literature Data for the Methane + Decalin Mixture: Average Absolute Deviations

reference	temp/phase	pressure range/MPa	avg ΔY
Darwish et al.[9]	323 K/liquid	4.2	0.0169
Stepanova and Vassilieva[8]	373 K/liquid	1.6−56.1	0.0072
Stepanova and Vassilieva[8]	373 K/gas	10.1−54.5	0.0051
Darwish et al.[9]	373 K/liquid	3.7−10.1	0.0077
Stepanova and Vassilieva[8]	423 K/liquid	4.4−44.1	0.0075
Stepanova and Vassilieva[8]	423 K/gas	7.0−46.7	0.0108
Darwish et al.[9]	423 K/liquid	4.4−9.5	0.0156

To compare more precisely with the existing data, and since the reported data are not at the same pressures, a fourth-degree polynomial fit was performed through each set of these authors' data. Then, the absolute deviation between our data and this polynomial was calculated for the points lying in the same range. Average absolute deviations are reported in Table 3 for each set of data. The deviations are typically on the order of 0.01 for the mole fractions and in many cases are lower. However, near the critical point the discrepancy is significantly greater. For example, the greatest observed discrepancy is 0.021 for the mole fraction at 150 °C and 45.6 MPa. It should be noted that only one value was in the same range of pressure as that of the Darwish et al. data at 50 °C.

One point of the bubble curve we obtained with the synthetic method is also plotted in Figure 4. This point shows a fair agreement with the results obtained from the spectroscopic method. We find a difference in mole fraction of 0.003, while the uncertainty of the synthetic method is 0.005 mole fraction. The experimental procedure for the synthetic method is similar to that used by Darwish et al.[10] in which measured amounts of decalin and methane are inserted in the cell so that the mole fraction is well-known. The temperature is regulated at the value of interest (373 K). The volume of the cell is varied, and the corresponding pressure is recorded. The bubble pressure is then determined as the pressure corresponding to a discontinuous change in the slope of the pressure−volume plot.

Methane + Acenaphthene Mixture. Vapor−liquid equilibrium data for the methane + acenaphthene mixture are reported in Table 2. Acenaphthene (C_1) and methane (C_2) concentrations in each phase are given at various pressures. Figures 5 and 6 show a plot of acenaphthene and methane concentrations as a function of pressure along the coexistence lines. Mole fractions are computed from C_1

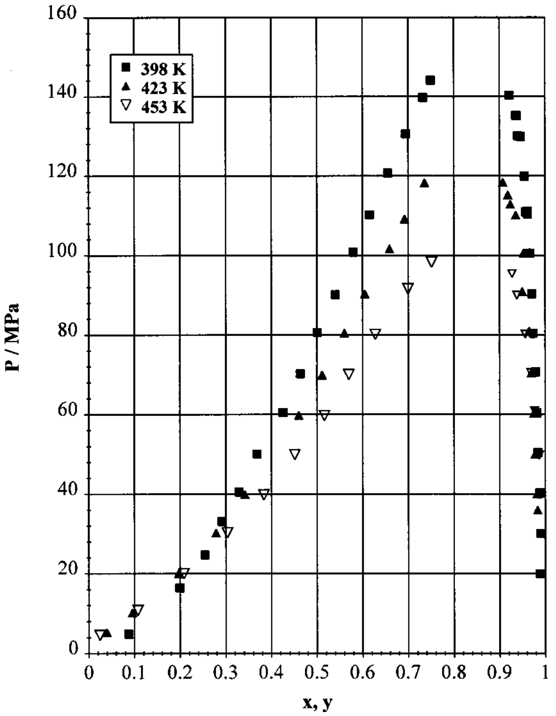

Figure 7. Phase diagram of methane + acenaphthene at three temperatures: ■, 398 K; ▲, 423 K; △, 453 K. x, $y = C_2/(C_1 + C_2)$ = mole fractions of methane.

and C_2. Pressure−mole fraction plots at (398, 423, and 453) K including the critical vicinity are shown in Figure 7. We note that the trend of the critical line is the same as that above in this temperature range. No data on this mixture were available in the literature for comparison.

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