Vapor–Liquid Equilibrium in the Methane–Carbonyl Sulfide Binary System

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The phase behavior of the methane–carbonyl sulfide binary system was studied at 25, 50, 75, and 100 °C and at pressures from the vapor pressure of carbonyl sulfide to near the critical pressure for the system. The experimental phase composition data were used to calculate equilibrium ratios for each component in the binary system. Experimental refractive index measurements of the equilibrium phases were used together with the measured phase compositions to calculate the phase densities according to the Lorentz–Lorenz refractivity relationship.

The occurrence of sulfur compounds during the processing of fossil fuels is a matter of increasing concern because of the environmental problems created by plant effluents and because of the increasingly stringent specifications being placed on the sulfur content of plant products. The proper design of facilities for the removal and control of these compounds requires a knowledge of their thermodynamic properties and their equilibrium phase relationships with other compounds.

Carbonyl sulfide is one of the more commonly occurring sulfur compounds on which data of the above type are required. Miranda et al. (7) have presented data on the equilibrium phase properties of the carbonyl sulfide–propane binary system. More recently, Robinson and Senturk (11, 12) have studied the vapor pressure and density of pure carbonyl sulfide. As a continuation of this work, this paper presents the results of a study of the phase behavior of the carbonyl sulfide–methane binary system.

Experimental Section

The experimental equipment and procedures used for this work were essentially the same as those described by Miranda et al. (7) and earlier in more detail by Besserer and Robinson (2, 3). The mixture of methane and carbonyl sulfide under investigation was confined in a stainless steel cell between two movable pistons. The pressure of the cell contents was varied by altering the relative position of the pistons with a Ruska double-acting two-cylinder pump. The interface between phases could be brought into view at a bull's-eye observation port by moving both pistons up or down simultaneously. The refractive index of each phase was calculated from measurements made by using an autocollimating telescope, a helium–neon laser, and a special window and mirror arrangement.

Experiments were carried out at 25, 50, 75, and 100 °C and at pressures from the vapor pressure of carbonyl sulfide to the critical region at each temperature. The temperature was measured with a calibrated iron–constantan thermocouple referenced to an ice bath. The temperatures are believed known to ±0.05 K. The pressures were measured with a 0–3000 psi Heise gage calibrated against a Ruska dead-weight gage and are believed known to within ±3 psia (20.7 kPa).

The phase compositions were determined by using a Hewlett-Packard Model 700 gas chromatograph with a thermal conductivity cell detector. The column used was a 6 ft by $^1/_8$ in. diameter stainless steel tube packed with Porapak QS maintained at a temperature of 50 °C. A ten-port single loop sample injection valve with backflush was used to elute the

Table I. Equilibrium Phase Compositions in the Methane–Carbonyl Sulfide System

pressure, MPa	y_{CH_4}	x_{CH_4}	K_{CH_4}	$K_{CO's}$
		$T = 25$ °C		
2.47	0.4318	0.0446	9.68	0.595
3.59	0.5637			
3.65		0.0884		
5.57	0.6630	0.1850	3.58	0.413
7.27	0.6867	0.2653	2.59	0.426
9.16	0.6823	0.3660	1.86	0.501
10.72	0.6172	0.4866	1.27	0.746
		$T = 50$ °C		
3.37	0.2644	0.0411	6.43	0.767
4.62	0.4167	0.0915	4.55	0.642
6.21	0.5063	0.1613	3.14	0.589
7.57	0.5370	0.2240	2.40	0.597
8.73	0.5400	0.2878	1.88	0.646
9.62	0.5278	0.3438	1.54	0.720
10.16	0.4989	0.3889	1.28	0.820
		$T = 75$ °C		
4.53	0.1242	0.0276	4.50	0.901
5.38	0.2123	0.0610	3.48	0.839
6.28	0.2739	0.0962	2.85	0.803
7.40	0.3245	0.1502	2.16	0.795
8.33	0.3344	0.2026	1.65	0.835
8.62	0.3289	0.2208	1.49	0.861
		$T = 100$ °C		
6.06	0.0205	0.0102	2.01	0.990
6.50	0.0549	0.0313	1.75	0.976
6.71	0.0574	0.0421	1.36	0.984

methane in the forward and the carbonyl sulfide in the backflush mode. Two samples of the equilibrium vapor and liquid phases were taken at each condition and triplicate analyses were run on each sample. Peak areas were determined by using a mechanical integrator.

The chromatograph was calibrated by using pure components in a 0.5-cm³ sample loop at pressures less than about 20 kPa. The response was linear under these conditions and the factor for converting area fraction to mole fraction for methane relative to carbonyl sulfide was 1.8123.

In view of the toxic nature of carbonyl sulfide, appropriate safety precautions were observed when handling or transferring the material to or from the equilibrium apparatus.

Materials

The methane used in this work was ultra high purity grade obtained from Matheson, and it had a concentration of 99.97 mol % methane. The carbonyl sulfide was obtained on a special order from Matheson and the liquid phase which was used for all experiments contained 99.7 mol % carbonyl sulfide. The major impurities were hydrogen sulfide 0.03%, carbon disulfide 0.05%, and carbon dioxide 0.21%. There were traces of nitrogen and carbon monoxide.

Results

The experimentally measured equilibrium-phase compositions and the calculated equilibrium ratios at each of the four ex-
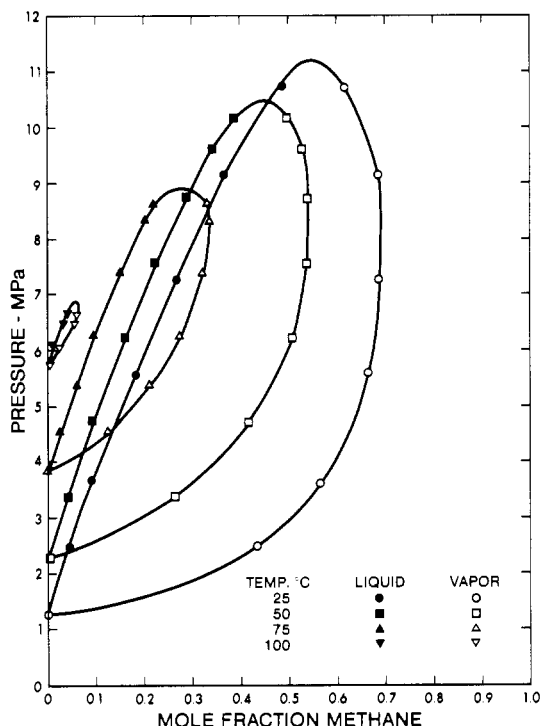
Figure 1. Pressure–equilibrium phase composition diagram for the methane–carbonyl sulfide system.
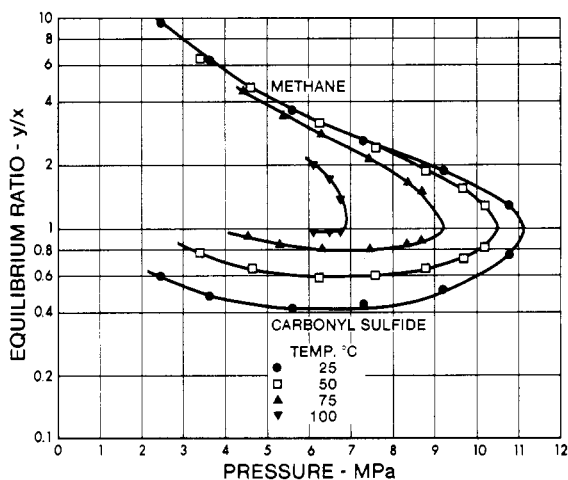

Figure 2. Equilibrium ratios for methane and carbonyl sulfide in the methane–carbonyl sulfide binary system.

perimental temperatures are presented in Table I and are plotted against pressure in Figures 1 and 2. The experimentally measured refractive indices of the vapor and liquid phases and the calculated molal volumes are also given at 25, 50, and 75 °C in Table II. No refractive index measurements were made at 100 °C because this condition was so close to the critical region that it was not always possible to adjust the amount of each phase to the point where a reading could be taken. Furthermore the instability of the refractive index line at this condition results in large inaccuracies in the measurements.

Data Reduction

The molal volumes of the equilibrium phases were calculated by using the measured refractive index data and the Lorentz–Lorenz molar refractivity relationship which is given as

$$R_{LL} = \frac{n^2 - 1}{n^2 + 2}\left(\frac{1}{\rho_m}\right) \quad (1)$$

Table II. Experimental Refractive Indices and Calculated Molar Volumes for the Methane–Carbonyl Sulfide Equilibrium Phases

pres-sure, MPa	$n_V{}^a$	$n_L{}^a$	R_{LL_V}, cm³/ mol	R_{LL_L}, cm³/ mol	V_V, cm³/ mol	V_L, cm³/ mol
		$T = 25\,°C$				
2.41	1.0220	1.3444	10.650	13.377	728.90	63.08
3.58	1.0293	1.3314	9.644	13.034	496.21	63.64
5.46	1.0437	1.3097	8.972	12.408	310.34	64.45
7.27	1.0579	1.2860	8.784	11.763	229.94	65.74
9.13	1.0834		8.814		160.99	
10.12	1.1074		9.052		129.03	
10.75		1.2030		10.237		77.11
		$T = 50\,°C$				
3.37	1.0302	1.3117	11.787	13.386	588.54	69.12
4.61	1.0389	1.2991	10.761	13.043	417.80	69.94
6.20	1.0527	1.2821	10.082	12.536	289.68	70.96
7.57	1.0680	1.2612	9.859	12.060	220.19	73.32
8.66	1.0849		9.821		176.26	
8.76		1.2387		11.613		76.81
9.57	1.1068	1.2146	9.922	11.252	142.22	82.28
10.13	1.1370	1.1920	10.123	10.940	113.85	88.92
		$T = 75\,°C$				
4.55	1.0487	1.2742	12.790	13.500	397.36	78.45
5.35	1.0565	1.2642	12.195	13.277	327.06	79.86
6.24	1.0668	1.2515	11.723	12.989	266.47	81.81
7.36	1.0837	1.2336	11.375	12.625	207.04	85.21
8.30	1.1064	1.2062	11.298	12.239	162.52	92.95
8.63	1.1156	1.1913	11.348	12.090	150.55	98.61

^{a} Relative to vacuum at 6328 A.

The molar refractivity of the mixture was calculated as the molar average of the pure component molar refractivities, that is

$$R_{LL_M} = \sum_i z_i R_{LL_i} \quad (2)$$

where R_{LL_M} is the molar refractivity of the mixture, z_i the mole fraction of component i in any phase and R_{LL_i} the molar refractivity of component i.

It is well-known that R_{LL} is a weak function of temperature and density and is not a constant as originally defined by the Lorentz–Lorenz relationship. Eisenberg et al. (*5, 8, 9*) have proposed an empirical relation which describes the dependence of the refractive index on temperature and density. The relationship is

$$f(n) = \frac{n^2 - 1}{n^2 + 2} = A\rho_m{}^B e^{-CT} \quad (3)$$

where *A*, *B*, and *C* are characteristic constants of the material and depend on the wavelength of light. Eisenberg and his associates used the above expression successfully to describe the refractive indices of liquids like H_2O, D_2O, CH_3OH, C_6H_6, CCl_4, etc. and later Hadrich (*6*) used it to describe the behavior of hydrocarbon gases and liquids over wide ranges of temperature and pressure.

Refractive index measurements for methane obtained at –37.3, –73.2, and –101.2 °C during an earlier investigation (*10*) were used together with predicted values of the molar density using the Benedict–Webb–Rubin (*1*) equation of state to prepare a plot of –ln f(n) against –ln ρ_m which according to eq 3 is a straight line. This plot is shown in Figure 3. A linear least-squares fit of the data gives the slope *B* and the intercept gives Ae^{-CT}. The values obtained were 1.008 for *B* and 6.86 cm³/mol for Ae^{-CT}. Since all of the data for all of the temperatures fell on the same linear plot, it was concluded that Ae^{-CT} was temperature independent.

The above values of *B* and Ae^{-CT} were then used in eq 3 together with densities of methane calculated by the Benedict–Webb–Rubin (*1*) equation at the pressures and temperatures of each binary data point to evaluate R_{LL} for the methane for
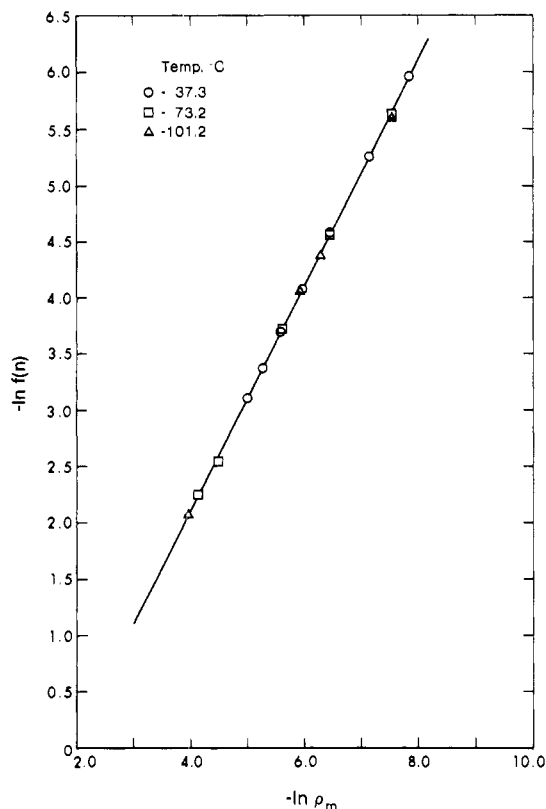
Figure 3. Graphical determination of constants in refractive index–density functional relationship.

use in eq 2. The improved constants for use in the Benedict–Webb–Rubin equation which were determined by Bishnoi et al. (4) were used for calculating the properties of pure methane. The corresponding values of R_{LL} for carbonyl sulfide were determined by using the same approach but with the experimental refractive index and density data for pure carbonyl sulfide reported by Robinson and Senturk (11). The values of B and Ae^{-CT} for carbonyl sulfide obtained from the graphical treatment of the data were 0.991 and 13.17 cm³/mol, respectively. The values of R_{LL} for the mixture obtained from eq 2 together with the refractive index data for the binary equilibrium phases were used to calculate the molar volumes reported in Table II.

The reliability of the values reported in Table II depends on the accuracy of the experimental phase compositions and refractive index measurements. The phase compositions are generally believed known to within ±0.003 mol fraction, although in the critical region this might decrease to ±0.005 mol fraction. The refractive index measurements are within ±0.0001. The molal refractivity of the pure components is thought to be within ±1.3% for the liquid and ±1.1% for the vapor. Thus the reliability of the molal volumes of the saturated liquids is thought to be within ±1.3% and of the saturated vapors within ±1.1%. In cases where the refractive index of the vapor becomes close to unity the error could be as high as 5%.

Glossary

A, B, C	characteristic constants in equation describing effect of density and temperature on refractive index
n	refractive index
R_{LL}	Lorentz–Lorenz molar refractivity, cm³/mol
T	absolute temperature, K
Z	mixture composition, mole fraction
ρ	density, mol/cm³

Subscripts

i	any component in a mixture
L	liquid
m	molar
M	mixture
V	vapor

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