VAPOR-LIQUID EQUILIBRIA FOR THE NITROGEN-METHANE-CARBON DIOXIDE SYSTEM*

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Vapor-liquid equilibrium data for the nitrogen-methane-carbon dioxide system were measured by static method at −40°C to 0°C and up to 100 atm. The applicability of the BWR equation for this ternary system was examined. A marked improvement in the equilibria was obtained by introducing correction factors determined from the data of each prediction of vapor-liquid binary system.

In a previous paper[2], we showed that vapor-liquid equilibrium relations for systems consisting of carbon dioxide and light hydrocarbon could not be well predicted by the BWR equation[1]. In such a case, the BWR equation was sufficiently improved by introducing a correction factor, m_{cj} into the constant, A_0. According to Stotler and Benedict[4], the constant, A_0, for a multicomponent system is formulated as follows[2,3]

$$A_0 = \sum_i^N x_i^2 A_{0i} + 2 \sum_{\substack{i \\ j \neq i \\ j>i}}^{N} \sum_j^N x_i x_j m_{ij} \sqrt{A_{oi} A_{oj}} \qquad (1)$$

where m_{ij} is the correction factor and has been shown to be less than unity in general[2,3]. The usefulness of m_{ij} is recognized for several binary systems containing carbon dioxide[2,3,5] and hydrogen sulfide[3]. However, application of m_{ij} to ternary systems seems to have been slight.

The purpose of the present work is to check the usefulness of m_{ij} for the nitrogen-methane-carbon dioxide system, whose vapor-liquid equilibrium data have been determined by static method. The equilibrium cell used here was the same one described in a previous paper[2]. Gas chromatography was adopted to analyse equilibrium composition. The experimental results at various pressures and temperatures are listed in **Table 1** and are compared with predicted K-values by the BWR equation in **Table 2**. The correction factors used in this calculation were determined based on the vapor-liquid equilibrium data of each binary system[2,4] and are presented in **Table 3**. As shown in Table 2, the original BWR equation predicts erroneous K-values for this ternary system. However, the modified BWR equation containing m_{ij} is shown to be successful.

Table 1 Vapor-liquid equilibrium data for the N_2-CH_4-CO_2 system

y_{N_2}	y_{CH_4}	x_{N_2}	x_{CH_4}
0°C		60 atm	
0.229	0.046	0.037	0.013
0.169	0.116	0.032	0.033
0.124	0.170	0.023	0.052
0.072	0.237	0.015	0.075
0°C		80 atm	
0.306	0.064	0.079	0.026
0.253	0.120	0.071	0.050
0.205	0.169	0.060	0.077
0.182	0.196	0.057	0.091
0.149	0.237	0.049	0.112
0.100	0.290	0.038	0.146
0.075	0.315	0.030	0.165
0.061	0.334	0.024	0.179
0.047	0.344	0.020	0.190
0°C		100 atm	
0.381	0.007	0.141	0.004
0.316	0.070	0.132	0.039
0.247	0.123	0.126	0.082
0.220	0.149	0.125	0.103
0.200	0.158	0.120	0.115
−20°C		60 atm	
0.342	0.195	0.052	0.038
0.174	0.374	0.032	0.110
0.113	0.439	0.024	0.131
−20°C		80 atm	
0.525	0.062	0.102	0.022
0.439	0.144	0.094	0.046
0.372	0.210	0.086	0.072
0.289	0.297	0.075	0.117
0.259	0.324	0.071	0.135
0.230	0.348	0.065	0.153
0.169	0.409	0.054	0.206
0.127	0.456	0.047	0.240
0.092	0.494	0.035	0.282
0.066	0.510	0.028	0.312
−20°C		100 atm	
0.393	0.182	0.136	0.097
0.331	0.239	0.131	0.143
0.301	0.259	0.127	0.163
0.277	0.280	0.123	0.178

(continued)

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−40°C		60 atm	
0.561	0.168	0.063	0.044
0.444	0.279	0.059	0.080
0.286	0.439	0.046	0.126
0.205	0.521	0.034	0.174
0.124	0.610	0.024	0.223
−40°C		80 atm	
0.682	0.060	0.104	0.023
0.574	0.176	0.100	0.064
0.464	0.279	0.086	0.108
0.332	0.406	0.086	0.197
0.285	0.449	0.083	0.228
0.247	0.486	0.066	0.236
0.185	0.541	0.064	0.318
0.121	0.589	0.059	0.398
−40°C		100 atm	
0.486	0.244	0.144	0.127
0.399	0.316	0.139	0.174
0.368	0.339	0.140	0.206
0.361	0.349	0.148	0.224
0.345	0.357	0.156	0.246

Table 3 Correction factor, m, for binary systems

System	0°C and 80 atm	−40°C and 60 atm
N_2—CH_4	0.966[4]	0.966[4]
CH_4—CO_2	0.945	0.910
N_2—CO_2	1	1

Table 2 Comparison of predicted and experimental K-values for the N_2-CH_4-CO_2 system

K_{N_2}			K_{CH_4}			K_{CO_2}		
Exp.	Calc. 1*	Calc. 2**	Exp.	Calc. 1	Calc. 2	Exp.	Calc. 1	Calc. 2
				0°C and 80 atm				
3.873	3.127	3.266	2.462	1.757	2.029	0.704	0.734	0.727
3.563	3.010	3.172	2.400	1.724	1.992	0.713	0.742	0.733
3.417	2.844	3.034	2.195	1.678	1.940	0.725	0.756	0.744
3.193	2.787	2.986	2.154	1.662	1.921	0.730	0.760	0.748
3.041	2.647	2.875	2.116	1.621	1.876	0.732	0.771	0.755
2.632	2.469	2.706	1.986	1.567	1.809	0.748	0.785	0.769
2.500	2.342	2.591	1.909	1.526	1.761	0.758	0.796	0.778
2.542	2.253	2.506	1.866	1.497	1.726	0.759	0.805	0.785
2.350	2.185	2.442	1.810	1.475	1.700	0.771	0.812	0.790
				−40°C and 60 atm				
8.905	6.302	7.546	3.818	2.048	3.189	0.303	0.341	0.322
7.525	5.949	7.278	3.488	2.005	3.112	0.322	0.348	0.326
6.217	5.065	6.416	3.484	1.869	2.858	0.332	0.373	0.342
6.029	4.500	5.711	2.994	1.780	2.642	0.346	0.393	0.358
5.167	4.083	5.219	2.735	1.714	2.486	0.353	0.410	0.372

* Calculated by the original BWR equation
** Calculated by the modified BWR equation

Nomenclature

A_o = constant of the BWR equation
i, j = component i and j
K = K-value (y/x)
m_{ij} = correction factor for $i-j$ pair interaction
N = number of component
x = mole fraction of liquid phase
y = mole fraction of vapor phase

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