

Isothermal vapor-liquid equilibria for the binary system of dimethyl ether (CH_3OCH_3)+methanol (CH_3OH)

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(Received 31 December 2010 • accepted 24 April 2011)

Abstract—Isothermal vapor-liquid equilibrium data for the binary mixture of dimethyl ether (CH_3OCH_3)+methanol (CH_3OH) were measured within the temperature range of 308.15-328.15 K. The data in the two-phase region were measured by using a circulation-type equilibrium apparatus in which both vapor and liquid phases are continuously recirculated. The experimental data were correlated with the Peng-Robinson equation of state (PR-EoS) using the Wong-Sandler mixing rules combined with the NRTL excess Gibbs free energy model. The values calculated by the PR-EoS with the W-S mixing rules show good agreement with our experimental data.

Key words: Dimethyl Ether (CH_3OCH_3), Methanol (CH_3OH), Vapor-liquid Equilibria (VLE), Peng-Robinson Equation of State (PR-EoS)

INTRODUCTION

Dimethyl ether (DME), also known as methyl ether, methyl oxide, and wood ether is a colorless liquid or compressed gas. It resists autoxidation unlike other alkyl ethers. DME is also relatively non-toxic, although it is highly flammable. In fact, it is one of the most promising alternative fuels in mobile process from simple adaptations because its high cetane number is more than 55 compared to diesel's, which is 40-55 [1]. Also, NO_x , CO emission is very low in a DME combustion system owing to straightforward of C-C bonds. Hence, interest in process from methanol to DME is rising along with the expansion of the clean energy trend these days.

DME is primarily produced via gasification of coal by converting hydrocarbons, generally sourced from natural gas to synthesis gas [2]. And there are predominantly two kinds of DME production methods: either the conventional process via methanol or directly in one step [3]. First, in indirect synthesis process, DME is produced by methanol dehydration under the presence of catalyst. Second, it is requires a dual catalyst system that acts as a methanol synthesis catalyst and a methanol dehydration catalyst via direct DME synthesis from natural gas without having to first produce and purify methanol [3,4].

Accordingly, vapor-Liquid equilibrium data for dimethyl ether (CH_3OCH_3)+methanol (CH_3OH) binary system are necessary to design the appropriate process and to maximize advantages of efficient process for converting methanol into dimethyl ether. However, there are few experimental data reported in the literature for dimethyl ether (CH_3OCH_3)+methanol (CH_3OH) system [4-8].

In this work, isothermal VLE data for binary mixture of dimethyl ether (CH_3OCH_3)+methanol (CH_3OH) at five equally spaced temperatures from 308.15 K to 328.15 K were measured by using a circulation-type equilibrium apparatus in which both phases were

continuously recirculated. The experimental data were correlated with the Peng-Robinson equation of state (PR-EoS) [9] using the Wong-Sandler mixing rule [10] combined with the nonrandom two-liquid (NRTL) excess Gibbs free energy model. In the range of experimental temperature, the average absolute deviations of pressure and vapor phase compositions between experimental and calculated values were determined and the relevant parameters were presented.

EXPERIMENTAL

1. Chemicals

High-grade chemicals of dimethyl ether and methanol were used for VLE measurement. Dimethyl ether was purchased from Sigma Aldrich (USA) with 99+% purity. Methanol was purchased from J. T. Baker (USA) with the purity higher than 99%. They were used without any further purification.

2. Apparatus

The experimental apparatus used in this study was a circulation type equilibrium apparatus, where both liquid and vapor phases were recirculated continuously. This apparatus was explained well in our previous works [11-14], so the explanation was omitted here.

3. Procedure

Experiments to measure vapor-liquid equilibrium data for the binary system of DME (1)+MeOH (2) were performed by the following procedures. The system was first evacuated to remove all inert gases. A certain amount of MeOH was supplied to the cell, and then the temperature of the entire system was held constant by controlling the temperature of the water bath. After the desired temperature was attained, the pressure of the pure component was measured. A certain amount of DME was introduced into the cell from a sample reservoir. Both the vapor and liquid phases were recirculated by the dual-head circulation pump until an equilibrium state was established. It was observed that 2 hours are sufficient to obtain thermal equilibrium between the cell fluid and the thermostatic bath as well as the vapor and liquid phases. After equilibration, the pres-

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sure in the equilibrium cell was measured and then vapor and liquid samples were withdrawn from the recycling lines by the vapor and liquid sampling valves, respectively. The compositions of the samples were measured by immediately injecting them into the GC, which was connected online to the vapor and liquid sampling valves. The GC was calibrated with pure components of known purity and with mixtures of known composition that were prepared gravimetrically. At least five analyses were performed for each phase, and the average values were considered to correspond to the equilibrium values. Considering the margin of error and the reproducibility of the GC, we generally estimated an overall uncertainty in the measurements of the composition of 0.002 in the mole fraction for both the liquid and the vapor phases.

CORRELATION

The experimental VLE data were correlated with the Peng-Robinson equation of state (PR-EoS) [9] using the Wong-Sandler mixing rule [10].

PR-EoS

$$P = \frac{RT}{v_M - b} - \frac{a(T)}{v_M(v_M + b) + b(v_M - b)} \quad (1)$$

with

$$a(T) = \left(0.457235 \frac{R^2 T_c^2}{P_c}\right) \alpha(T) \quad (2)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (3)$$

$$\alpha(T) = [1 + k(1 - \sqrt{T/T_c})]^2 \quad (4)$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (5)$$

where the parameter a is a function of temperature, b is constant, k is a constant characteristic of each substance, ω is the acentric factor, P (MPa) is the pressure, P_c (MPa) is the critical pressure, T (K) is the absolute temperature, T_c (K) is the critical temperature, and v_M is the molar volume of the mixture.

The Wong-Sandler mixing rules [10] were used in this work to obtain EoS parameters for a mixture from those of the pure components. These mixing rules for a cubic equation of state can be written as

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - a/RT)_{ij}}{\left(1 - A_{\infty}^E / CRT - \sum_i x_i a_i / RT b_i\right)} \quad (6)$$

with

$$(b - a/RT)_{ij} = \frac{1}{2} [(b - a/RT)_i + (b - a/RT)_j] (1 - k_{ij}) \quad (7)$$

and

$$\frac{a_m}{b_m} = \sum_i x_i \frac{a_i}{b_i} + \frac{A_{\infty}^E}{C} \quad (8)$$

where C is a numerical constant equal to $\ln(\sqrt{2}-1)/\sqrt{2}$ for the PR-EoS used in this work. The single adjustable parameter (k_{ij}) for each

Table 1. Thermodynamic properties of components [17]

Chemical	Chemical formula	T_c /K	P_c /MPa	ω
Dimethyl ether (1)	CH ₃ OCH ₃	400.0	5.240	0.200
Methanol (2)	CH ₃ OH	512.6	8.090	0.556

binary pair is referred to as the Wong-Sandler mixing rule parameter. Also, A_{∞}^E is an excess Helmholtz free energy model at infinite pressure that can be equated to a low-pressure excess Gibbs energy model [15]. In this study, we used the NRTL model [16] given by

$$\frac{A_{\infty}^E}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_r x_r G_{ri}} \quad (9)$$

with

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad \text{and} \quad \tau_{ji} = (g_{ji} - g_{ij}) / (RT) \quad (10)$$

The critical temperature (T_c), critical pressure (P_c), and acentric factor (ω) for both dimethyl ether and methanol used to calculate the parameters for the PR-EoS are provided in Table 1. We have set the non-randomness parameter, α_{ij} equal to a fixed value of 0.3 for all of the binary mixtures studied here. The parameters of the PR EoS were obtained by minimizing the following objective function.

$$\text{objective function} = \frac{1}{N} \sum_j \left[\left(\frac{P_{j, \text{exp}} - P_{j, \text{cal}}}{P_{j, \text{exp}}} \right) \times 100 \right]^2 \quad (11)$$

RESULTS AND DISCUSSION

In this work, the equilibrium compositions for the DME (1)+MeOH (2) binary systems were measured at five equally spaced temperatures from 308.15 to 328.15 K. To verify the consistency of our experimental data, we compared our experimental data at 313.15 K with literature data already reported by Chang et al. [5]

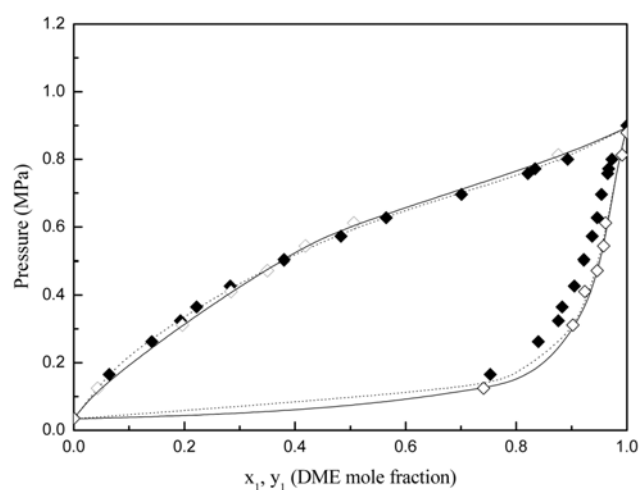


Fig. 1. Comparison of our experimental data with literature data for the DME (1)+MeOH (2) system at 313.15 K: (◇), experimental, our work; (◆), experimental, Chang et al. [5]; (—) calculated with k_{ij} adjusted with our data ($k_{ij}=0.4900$); (---) calculated with k_{ij} adjusted with Chang et al. data ($k_{ij}=0.3736$).

Table 2. Comparison of the measured pure component vapor pressures with the database McGraw-Hill [17]

Component	T/K	P_{exp}/MPa	P_{ref}/MPa	ΔP	$\Delta P/P_{exp}$
Dimethyl ether (1)	308.15	0.7703	0.7829	-0.0126	0.0164
	313.15	0.8786	0.8944	-0.0158	0.0180
	318.15	1.0003	1.0173	-0.0170	0.0170
	323.15	1.1311	1.1525	-0.0214	0.0189
	328.15	1.2748	1.3006	-0.0258	0.0202
					Ave 0.0181
Methanol (2)	308.15	0.0273	0.0265	0.0008	0.0297
	313.15	0.0355	0.0340	0.0015	0.0425
	318.15	0.0464	0.0432	0.0032	0.0692
	323.15	0.0550	0.0544	0.0006	0.0011
	328.15	0.0678	0.0679	0.0001	0.0013
					Ave 0.0476

Table 3. Vapor-liquid equilibrium measurements for the DME (1)+ MeOH (2) system

Experimental data			PR-EoS			
P_{exp}/MPa	$x_{1,exp}$	$y_{1,exp}$	P_{cal}/MPa	$y_{1,cal}$	$\Delta P/\text{Mpa}$	Δy_1
T/K=308.15						
0.0273	0.0000	0.0000	0.0265	0.0000	0.0008	0.0000
0.1233	0.0701	0.7903	0.1251	0.7985	-0.0018	-0.0082
0.1911	0.1295	0.8786	0.1839	0.8690	0.0072	0.0096
0.2635	0.2213	0.9233	0.2705	0.9180	-0.0070	0.0053
0.3410	0.2945	0.9436	0.3402	0.9397	0.0008	0.0039
0.3913	0.3584	0.9502	0.3991	0.9523	-0.0078	-0.0021
0.4678	0.4300	0.9587	0.4596	0.9621	0.0082	-0.0034
0.5011	0.4784	0.9624	0.4960	0.9669	0.0051	-0.0045
0.7146	0.8763	0.9872	0.7003	0.9892	0.0144	-0.0020
0.7703	1.0000	1.0000	0.7829	1.0000	-0.0126	0.0000
T/K=313.15						
0.0355	0.0000	0.0000	0.0340	0.0000	0.0015	0.0000
0.1241	0.0430	0.7408	0.1241	0.7338	0.0000	0.0070
0.3115	0.1964	0.9022	0.3117	0.9055	-0.0002	-0.0033
0.4106	0.2840	0.9240	0.4080	0.9336	0.0026	-0.0096
0.4724	0.3498	0.9462	0.4768	0.9470	-0.0044	-0.0008
0.5431	0.4190	0.9578	0.5421	0.9568	0.0010	0.0010
0.6113	0.5064	0.9614	0.6103	0.9651	0.0010	-0.0037
0.8124	0.8761	0.9915	0.8016	0.9865	0.0108	0.0050
0.8786	1.0000	1.0000	0.8944	1.0000	-0.0158	0.0000
T/K=318.15						
0.0464	0.0000	0.0000	0.0432	0.0000	0.0032	0.0000
0.1156	0.0319	0.6385	0.1138	0.6283	0.0018	0.0102
0.1967	0.0957	0.7928	0.2029	0.8007	-0.0062	-0.0079
0.3263	0.1917	0.8829	0.3222	0.8847	0.0041	-0.0018
0.4319	0.2716	0.9203	0.4291	0.9208	0.0028	-0.0005
0.4833	0.3025	0.9333	0.4711	0.9306	0.0122	0.0027
0.5718	0.3815	0.9433	0.5735	0.9484	-0.0017	-0.0051
0.6604	0.4768	0.9565	0.6764	0.9611	-0.0160	-0.0046
0.7510	0.5860	0.9714	0.7594	0.9694	-0.0084	0.0020
0.9386	0.8751	0.9837	0.9123	0.9853	0.0263	-0.0016
1.0003	1.0000	1.0000	1.0173	1.0000	-0.0170	0.0000

Table 3. Continued

Experimental data			PR-EoS			
P_{exp}/MPa	$x_{1,exp}$	$y_{1,exp}$	P_{cal}/MPa	$y_{1,cal}$	$\Delta P/\text{Mpa}$	Δy_1
T/K=323.15						
0.0550	0.0000	0.0000	0.0544	0.0000	0.0006	0.0000
0.1496	0.0447	0.6554	0.1511	0.6508	-0.0015	0.0046
0.2484	0.1000	0.7844	0.2450	0.7935	0.0034	-0.0091
0.3381	0.1586	0.8543	0.3343	0.8558	0.0038	-0.0015
0.4477	0.2397	0.8881	0.4525	0.9011	-0.0048	-0.0130
0.5052	0.2841	0.9031	0.5152	0.9170	-0.0100	-0.0139
0.6061	0.3527	0.9293	0.6071	0.9345	-0.0010	-0.0052
0.7014	0.4196	0.9533	0.6876	0.9462	0.0138	0.0071
1.0457	0.8722	0.9811	1.0286	0.9833	0.0171	-0.0022
1.1311	1.0000	1.0000	1.1525	1.0000	-0.0214	0.0000
T/K=328.15						
0.0678	0.0000	0.0000	0.0679	0.0000	-0.0001	0.0000
0.1705	0.0357	0.6119	0.1689	0.6062	0.0016	0.0057
0.2640	0.0896	0.7565	0.2680	0.7607	-0.0040	-0.0042
0.3710	0.1558	0.8440	0.3722	0.8363	-0.0012	0.0077
0.5208	0.2440	0.8916	0.5155	0.8915	0.0053	0.0001
0.5994	0.2880	0.9064	0.5887	0.9096	0.0107	-0.0032
0.6892	0.3538	0.9173	0.6954	0.9292	-0.0062	-0.0119
0.8623	0.4856	0.9498	0.8743	0.9518	-0.0120	-0.0020
1.1898	0.8722	0.9851	1.1640	0.9811	0.0258	0.0040
1.2748	1.0000	1.0000	1.3006	1.0000	-0.0258	0.0000

$$^a \Delta P = P_{exp} - P_{cal}$$

$$^b \Delta y_1 = y_{exp} - y_{cal}$$

at the same temperature. In Fig. 1 both sets of experimental data are shown, and results of correlation by using the PR-EoS are given as an example. It can be seen that, despite excellent agreement between the two sets of data for the bubble curve, there is a small discrepancy in the vapor phase especially at the higher composition of dimethyl ether. The same discrepancy to the Chang et al. [5] data appears in the Holldorff and Knapp paper [7] and in the Teodorescu and Rasmussen paper [8] when the same type of comparison

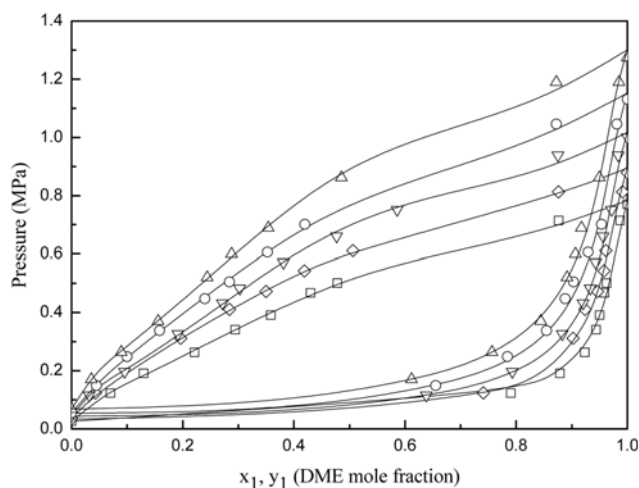


Fig. 2. P-x-y diagram for the DME (1)+MeOH (2) system. Experimental data at 308.15 K (\square); 313.15 K (\diamond); 318.15 K (∇); 323.15 K (\circ); 328.15 K (\triangle); calculated with the PR-EoS using W-S mixing (—).

was made for the 293.15 K and 353.15 K isotherm, respectively.

Table 2 shows the comparison of measured vapor pressures of pure dimethyl ether and methanol with those calculated from the database McGraw-Hill [17], which are considered to be reliable for the pure compounds considered and consistent with literature data. The absolute average relative deviation ($\sum|\Delta P/P|/N(\%)$) between measured and calculated values from the data of McGraw-Hill [17] was 1.81% for dimethyl ether and 4.76% for methanol. The experimental vapor-liquid equilibrium data and the results of the correlation are reported in Table 3. This table lists the measured mole fractions of the liquid and vapor phases, the pressures and temperatures in equilibrium and the deviations between measured and calculated pressures (ΔP) and vapor compositions (Δy).

Fig. 2 shows the comparison of measured and calculated values with the PR-EoS for the binary system of the DME (1)+MeOH (2) at various temperatures of (308.15, 313.15, 318.15, 323.15 and 328.15) K. Also, the calculated values were well matched with experimental data. The interaction parameters of the binary mixtures for each isotherm, the binary parameters k_{ij} , and the absolute average deviations of pressure (AAD-P(%)) and the absolute average deviation of vapor-phase composition (AAD-y) between measured and calculated values are reported in Table 4. Fig. 3 plots the binary parameters, k_{ij} , vs. temperature. As can be seen in this figure and

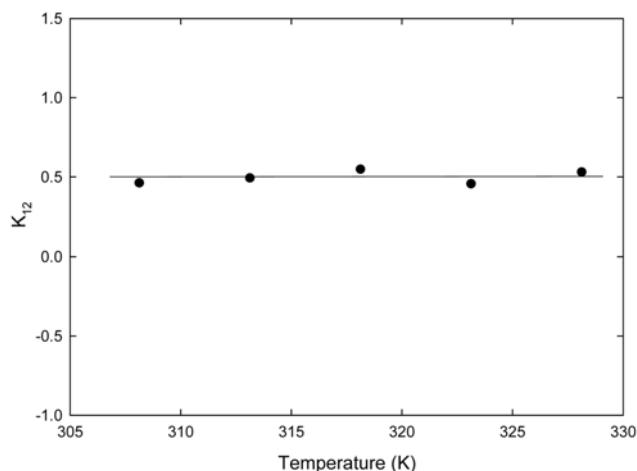


Fig. 3. Parameter k_{ij} obtained by using the PR-EoS with W-S mixing rule. The equation of the fitting line is $k_{ij}=0.002 T/K+0.1384$ ($308.15 K \leq T \leq 328.15 K$).

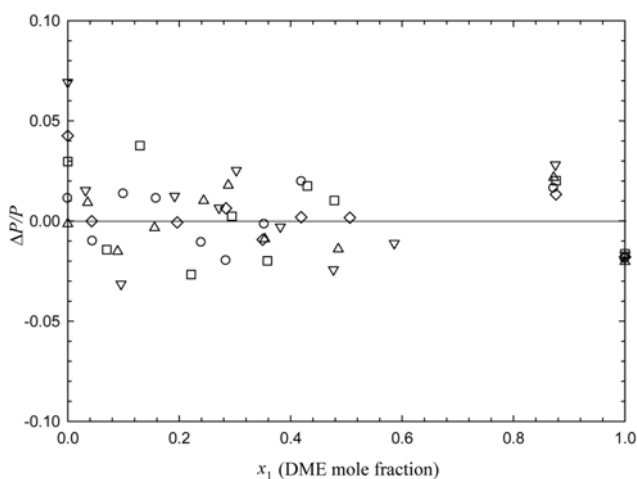


Fig. 4. Deviation of pressure for the system DME (1)+MeOH (2) from the PR-EoS using W-S mixing rule at 308.15 K (\square); 313.15 K (\diamond); 318.15 K (∇); 323.15 K (\circ); 328.15 K (\triangle).

Table 4, the binary parameters, k_{ij} show temperature independency and they have almost the same value of 0.5.

In Figs. 4 and 5, the average absolute deviations of pressure ($\Delta P/P_{exp}$ %) and the vapor phase compositions (Δy_i) were plotted with the liquid phase compositions (x_i), point by point. The overall aver-

Table 4. Values of binary parameters and average absolute deviations of P and y

T/K			308.15	313.15	318.15	323.15	328.15
PR-EoS	Binary parameter	^a k ₁₂	0.4589	0.4900	0.5446	0.4533	0.5270
		^a τ ₂₁	3.6358	3.6420	4.0959	3.2178	0.3984
		^a τ ₁₂	−1.9637	−1.8991	−2.1258	−1.8585	−2.0589
	^b AAD-P (%)		1.9477	1.0426	2.2143	1.3310	1.2200
	^c AAD-y		0.0039	0.0034	0.0033	0.0057	0.0039

^aThe unit of k_{12} , τ_{21} and τ_{12} is dimensionless

^bAAD-P (%) = $(1/N) \sum |(P_{exp} - P_{cal})/P_{exp}| \times 100$

^cAAD-y = $(1/N) \sum |(y_{exp} - y_{cal})|$

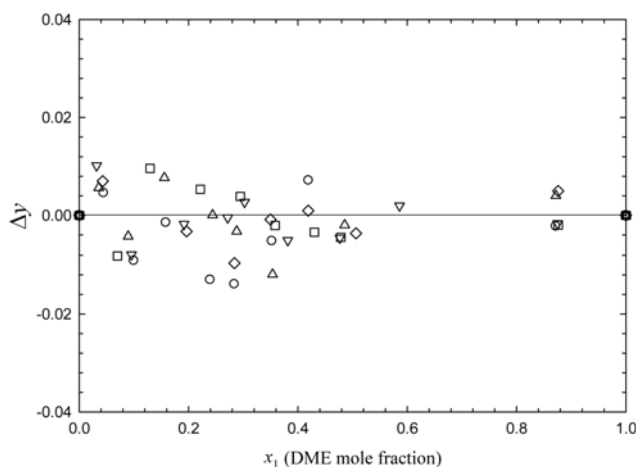


Fig. 5. Deviation of vapor composition for the system DME (1)+MeOH (2) from the PR- EoS using W-S mixing rule at 308.15 K (□); 313.15 K (◇); 318.15 K (▽); 323.15 K (○); 328.15 K (△).

age values of AAD-P (%) and AAD-y through the temperature range from 308.15 to 328.15 K were 1.551% and 0.004, respectively. All values are small and acceptable. From these figures and the low average deviations of P and y, we conclude that the calculated values with the PR-EoS using the W-S mixing rules gives good agreements with the experimental data.

CONCLUSIONS

The isothermal vapor-liquid equilibrium data for the binary systems of DME (1)+MeOH (2) were measured at five equally spaced temperatures of (308.15, 313.15, 318.15, 323.15 and 328.15) K using a circulation-type equilibrium apparatus. The experimental VLE data were correlated with the PR-EoS using the Wong-Sandler mixing rules. Calculated results with these equations show good agreement with our experimental data.

ACKNOWLEDGEMENT

This work was supported by the Special Research Grant of Sogang University.

LIST OF SYMBOLS

a(T) : temperature-dependent constant of EoS
 A : adjustable parameters of NRTL model [kJ/g-mol]
 b : molecular volume [l/g-mol]
 g : an energy parameter [kJ/g-mol]
 k : PR-EoS parameter
 N : the number of components in mixture
 P : pressure [MPa]

R : gas constant, 8.3144 [J/mol·K]
 T : temperature [K]
 V : molar volume [l/g-mol]
 x : liquid mole fraction
 y : vapor mole fraction

Greek Letters

α : attraction parameter
 Δ : deviation
 τ : dimensionless form of A/RT
 ω : acentric factor

Subscripts

c : critical property
 cal : calculated
 exp : experimental
 i, j : ith and jth components of the mixture
 m : mixtures

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