High pressure isothermal vapor-liquid equilibria for the binary system of carbon dioxide (CO₂)+1,1,1-trifluoroethane (R-143a)

Seol A Kim, Ki-Pung Yoo, and Jong Sung Lim[†]

Department of Chemical and Biomolecular Engineering, Sogang University, C.P.O. Box 1142, Seoul 100-611, Korea
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Abstract−Isothermal vapor-liquid equilibrium data for the binary mixture of carbon dioxide (CO_2)+1,1,1-trifluoro-ethane (HFC-143a) were measured within the temperature range of 273.15-333.15 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: Carbon Dioxide (CO_2), HFC-143a, Vapor-liquid Equilibria (VLE), Peng-Robinson Equation of State (PR EOS)

INTRODUCTION

For many years, chlorofluorocarbons (CFCs) were extensively used as refrigerants due to their non-toxicity, non-flammability, thermodynamic properties and so on. However, their use has been restricted by the Montreal Protocol (1989) because of their harmfulness to the ozone layer [1,2]. So, many researchers investigated CFCs alternatives such as hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). However, the use of HCFCs has also been banned by the Kyoto Protocol (2005) because of their high global warming potential (GWP). HFCs are synthetic refrigerants which consist of hydrogen, fluorine, and carbon. They are considered as alternative refrigerants for CFCs and HCFCs because they have zero ozone depletion potential (ODP) [3]. HFC-143a (1,1,1-Trifluoroethane, $C_2H_3F_3$) is the halogenated aliphatic group. It has zero ODP; thus HFC-143a is used as a refrigerant either by itself or more commonly as a component of blended mixtures [4]. Unlike CFCs used as refrigerants, it has no chlorine atoms, and thus is not a potent ozone-depleting chemical [1,4]. It is also used as a propellant in canned air products used to clean electronic equipment. On the other hand, Carbon Dioxide (CO_2) is a representative compound of the carbon cycle. It is natural refrigerant and often used in air conditioners and other cooling processes. To develop optimal alternative refrigerants for CFCs and HCFCs, many mixtures have been investigated. These mixtures satisfy the properties of original refrigerant conditions such as flammability and toxicity but with less environmental impact (ozone depletion and global warming). Vapor-liquid equilibrium (VLE) data are necessary to design appropriate refrigeration process and determine optimal process conditions [5,6]; however, there are few experimental data reported in the literature for CO_2 (1)+HFC-143a system [4].

In this work, isothermal VLE data for binary mixture of Carbon dioxide (CO_2)+1,1,1-trifluoroethane (HFC-143a) at seven equally spaced temperatures from 273.15 K to 333.15 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) [7] using the Wong-Sandler mixing rule [8] combined with the 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 carbon dioxide and HFC-143a were used for VLE measurement. Carbon dioxide was purchased from Dong-A special gas co. (Korea) with 99.9% purity. HFC-143a was purchased from Sogno international co. (Korea) with the purity higher than 99.9%. 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 [2,9-12], so the explanation of this was omitted here.

3. Procedure

Experiments to measure vapor-liquid equilibrium data for the binary system of CO_2 (1)+HFC-143a (2) were performed by the following procedure. The system was first evacuated to remove all inert gases. A certain amount of HFC-143a 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 CO_2 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 pressure 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.

4. Correlation

The experimental VLE data were correlated with the Peng-Robinson equation of state (PR-EoS)[7] using the Wong-Sandler mixing rule [8].

PR-EoS

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

with

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

$$b = 0.077796 \frac{RT_c}{P_c} \tag{3}$$

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

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{5}$$

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 [8] 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

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

with

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

and

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

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 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 [13]. In this study, we used the nonrandom two-liquid (NRTL)

Table 1. Thermodynamic properties of components [15]

Chemical	Chemical formula	T_c/K	P_c/MPa	ω
Carbon dioxide (1)	CO_2	304.21	7.384	0.2239
HFC-143a (2)	CH_3CF_3	346.04	3.776	0.2611

model [14] given by

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

with

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

The critical temperature (T_c), critical pressure (P_c), and acentric factor (ω) for both carbon dioxide and HFC-143a that were 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.

$$\text{objective function} = \frac{100}{N}\left[\sum_j^N \left(\frac{P_{exp} - P_{cal}}{P_{exp}}\right)^2 + \sum_j^N \left(\frac{y_{exp} - y_{cal}}{y_{cal}}\right)^2\right] \tag{11}$$

RESULTS AND DISCUSSION

Table 2 shows the comparison of measured vapor pressures of pure CO_2 and HFC-143a with those calculated from the database REFPROP 6.01 [15], 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 REFPROP 6.01 [15] was 0.0001% for CO_2 and 0.016% for HFC-143a. 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

Table 2. Comparison of the measured pure component vapor pressures with the database REFPROP 6.01 [15]

Component	T/K	P_{exp}/MPa	P_{ref}/MPa	ΔP	$\Delta P|/P_{exp}$
CO_2 (1)	273.15	3.482	3.482	0.000	0.0000
	283.15	4.495	4.497	−0.002	0.0004
	293.15	5.722	5.722	0.000	0.0000
	303.15	7.205	7.205	0.000	0.0000
					Ave 0.0001
HFC-143a (2)	273.15	0.614	0.620	−0.006	0.0100
	283.15	0.827	0.837	−0.010	0.0120
	293.15	1.089	1.106	−0.017	0.0156
	303.15	1.413	1.435	−0.022	0.0156
	313.15	1.779	1.832	−0.053	0.0298
	323.15	2.275	2.308	−0.033	0.0145
	333.15	2.827	2.874	−0.047	0.0166
					Ave 0.016

Table 3. Vapor-liquid equilibrium measurements for the CO₂ (1)+ HFC-143a (2) system

Experimental data			PR EoS			
P_{exp}/MPa	$x_{1, exp}$	$y_{1, exp}$	P_{cal}/MPa	$y_{1, cal}$	$^a\Delta P$/MPa	$^b\Delta y_1$
T/K=273.15						
0.614	0.000	0.000	0.621	0.000	−0.007	0.000
0.883	0.116	0.325	0.896	0.349	−0.014	−0.024
1.220	0.237	0.540	1.211	0.560	0.009	−0.021
1.600	0.367	0.685	1.578	0.703	0.021	−0.019
1.944	0.493	0.776	1.951	0.795	−0.007	−0.019
2.268	0.599	0.836	2.268	0.851	0.000	−0.015
2.510	0.679	0.872	2.504	0.885	0.006	−0.013
2.758	0.760	0.906	2.742	0.916	0.016	−0.009
2.937	0.823	0.931	2.927	0.937	0.010	−0.006
3.027	0.843	0.939	2.987	0.944	0.040	−0.006
3.241	0.911	0.963	3.190	0.967	0.050	−0.004
3.482	1.000	1.000	3.476	1.000	0.006	0.000
T/K=283.15						
0.827	0.000	0.000	0.839	0.000	−0.012	0.000
1.110	0.096	0.262	1.124	0.282	−0.014	−0.020
1.386	0.174	0.418	1.373	0.437	0.013	−0.019
1.689	0.268	0.551	1.689	0.572	0.000	−0.022
2.075	0.375	0.658	2.071	0.683	0.004	−0.025
2.434	0.474	0.743	2.441	0.759	−0.007	−0.016
2.779	0.565	0.800	2.785	0.813	−0.007	−0.013
3.110	0.648	0.845	3.104	0.855	0.005	−0.009
3.468	0.743	0.888	3.468	0.896	0.000	−0.007
3.758	0.811	0.916	3.726	0.922	0.032	−0.006
4.040	0.885	0.947	4.017	0.951	0.023	−0.004
4.495	1.000	1.000	4.504	1.000	−0.008	0.000
T/K=293.15						
1.089	0.000	0.000	1.113	0.000	−0.022	0.000
1.448	0.096	0.240	1.444	0.254	0.004	−0.015
1.655	0.162	0.355	1.689	0.382	−0.034	−0.027
2.062	0.244	0.498	2.014	0.507	0.047	−0.009
2.441	0.344	0.607	2.441	0.622	0.000	−0.015
2.751	0.409	0.667	2.729	0.681	0.022	−0.014
3.172	0.504	0.737	3.172	0.752	0.000	−0.015
3.620	0.593	0.793	3.598	0.806	0.022	−0.013
4.061	0.683	0.845	4.039	0.852	0.022	−0.007
4.564	0.782	0.894	4.533	0.897	0.032	−0.003
4.971	0.858	0.923	4.926	0.930	0.045	−0.007
5.722	1.000	1.000	5.741	1.000	−0.019	0.000

Table 3. Continued

Experimental data			PR EoS			
P_{exp}/MPa	$x_{1, exp}$	$y_{1, exp}$	P_{cal}/MPa	$y_{1, cal}$	$^a\Delta P$/MPa	$^b\Delta y_1$
T/K=303.15						
1.413	0.000	0.000	1.444	0.000	−0.031	0.000
1.834	0.106	0.242	1.877	0.249	−0.044	−0.008
2.310	0.203	0.409	2.316	0.414	−0.006	−0.005
2.779	0.297	0.528	2.772	0.534	0.007	−0.007
3.282	0.390	0.619	3.257	0.628	0.025	−0.009
3.661	0.466	0.679	3.671	0.690	−0.010	−0.011
4.399	0.592	0.764	4.399	0.774	0.000	−0.011
5.240	0.726	0.838	5.219	0.847	0.021	−0.009
5.757	0.805	0.878	5.729	0.886	0.028	−0.008
6.109	0.858	0.900	6.090	0.913	0.018	−0.012
6.640	0.936	0.943	6.669	0.956	−0.030	−0.012
7.205	1.000	1.000	7.217	1.000	−0.012	0.000
T/K=313.15						
1.779	0.000	0.000	1.847	0.000	−0.068	0.000
2.199	0.086	0.182	2.237	0.184	−0.038	−0.003
2.744	0.184	0.348	2.732	0.348	0.012	0.000
3.330	0.283	0.476	3.297	0.477	0.033	−0.001
4.020	0.394	0.586	3.987	0.587	0.032	−0.002
4.578	0.482	0.656	4.573	0.656	0.005	0.000
5.288	0.584	0.722	5.290	0.722	−0.002	0.000
5.757	0.652	0.762	5.783	0.758	−0.026	0.004
6.247	0.717	0.789	6.260	0.790	−0.013	0.000
6.778	0.787	0.806	6.773	0.804	0.005	0.001
T/K=323.15						
2.275	0.000	0.000	2.328	0.000	−0.053	0.000
2.806	0.100	0.187	2.845	0.184	−0.038	0.003
3.482	0.203	0.342	3.464	0.336	0.018	0.006
4.220	0.314	0.468	4.212	0.461	0.008	0.007
4.999	0.421	0.561	4.999	0.551	0.000	0.011
5.440	0.480	0.598	5.447	0.588	−0.007	0.010
5.833	0.533	0.621	5.835	0.614	−0.002	0.007
6.226	0.590	0.619	6.225	0.626	0.001	−0.007
T/K=333.15						
2.827	0.000	0.000	2.897	0.000	−0.070	0.000
3.668	0.135	0.214	3.720	0.204	−0.052	0.010
4.116	0.197	0.293	4.132	0.278	−0.016	0.015
4.737	0.281	0.375	4.709	0.360	0.028	0.015
5.033	0.322	0.407	4.995	0.393	0.039	0.014
5.323	0.383	0.417	5.413	0.431	−0.013	−0.013

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

equilibrium and the deviations between measured and calculated pressures (ΔP) and vapor compositions (Δy).

Fig. 1 shows the comparison of measured and calculated values with the PR-EOS for the binary system of the CO₂ (1)+HFC-143a (2) at various temperatures of (273.15, 283.15, 293.15, 303.15, 313.15, 323.15 and 333.15) K. As can be seen in this figure, this system showed slightly negative deviation from the Raoult's law and no azeotropes for all the temperature ranges studied here. Also, the calculated values well matched the experimental data. The interaction parameters of the binary mixtures for each isotherm, the binary par-

ameters 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. 2 plots the binary parameters, k_{ij}, vs. temperature. As can be seen in this figure and Table 4, the binary parameters, k_{ij} show temperature dependency and they can be fitted with 1st order polynomial equations for the temperature and k_{ij} is given by Eq. (12).
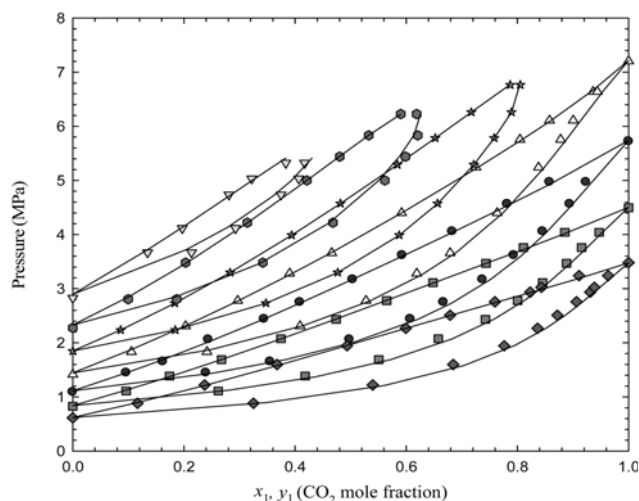
Fig. 1. P-x-y diagram for the CO_2 (1)+HFC-143a (2) system. Experimental data at 273.15 K (◆); 283.15 K (■); 293.15 K (●); 303.15 K (▲); 313.15 K (★); 323.15 K (⬢); 333.15 K (▼); calculated with the PR- EoS using W-S mixing (—).
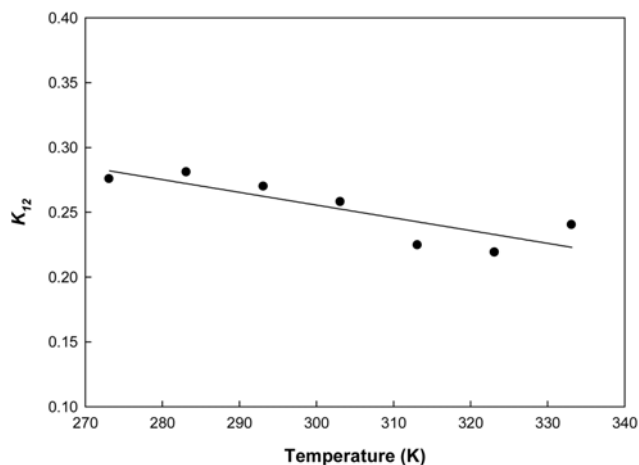

Fig. 2. Parameter k_{ij} obtained by using the PR-EOS with W-S mixing rule. The equation of the fitted line is $k_{ij}=-0.0010$ T/K$-$0.5505 (333.15 K$\geq$T$\geq$273.15 K).

$$k_{ij}=-0.0010 \text{ T/K}-0.5505 \qquad (12)$$

In Figs. 3 and 4, the average absolute deviations of pressure (ΔP/
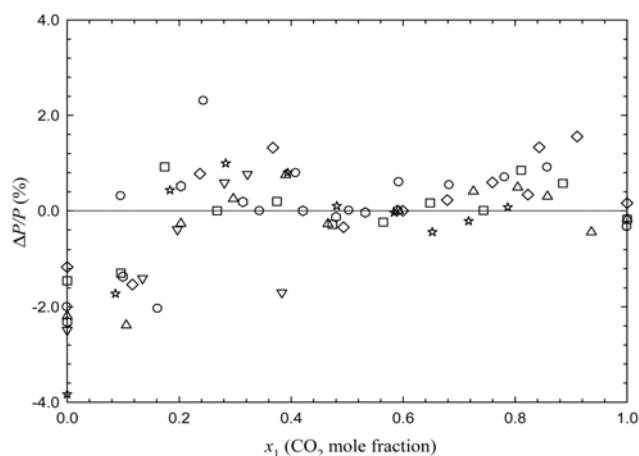

Fig. 3. Deviation of pressure for the system CO_2 (1)+HFC-143a (2) from the PR- EoS using W-S mixing rule at 273.15 K (◇); 283.15 K (□); 293.15 K (○); 303.15 K (△); 313.15 K (☆); 323.15 K (⬡); 333.15 K (▽).
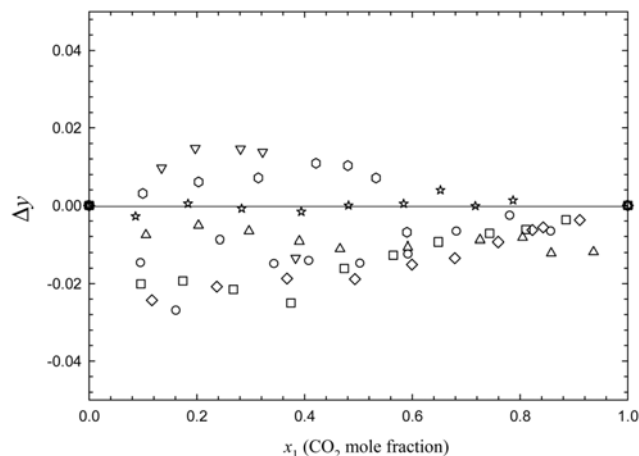

Fig. 4. Deviation of vapor composition for the system CO_2 (1)+ HFC-143a (2) from the PR- EoS using W-S mixing rule at 273.15 K (◇); 283.15 K (□); 293.15 K (○); 303.15 K (△); 313.15 K (☆); 323.15 K (⬡); 333.15 K (▽).

P_{exp} %) and the vapor phase compositions (Δy_1) were plotted with the liquid phase compositions (x_1), point by point. The overall average values of AAD-P (%) and AAD-y through the temperature range from 273.15 to 333.15 K were 0.786% and 0.0084, respectively.

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

		T/K	273.15	283.15	293.15	303.15	313.15	323.15	333.15
PR-EoS	Binary parameter	[a]k_{12}	0.2755	0.2807	0.2697	0.2578	0.2244	0.2188	0.2401
		[a]τ_{21}	0.1973	0.3328	0.5280	0.1002	−0.1233	−0.1291	−0.1028
		[a]τ_{12}	−0.2610	−0.3504	−0.5228	−0.1394	0.2420	0.3353	0.1868
	[b]AAD-P (%)		0.779	0.514	0.877	0.661	0.866	0.570	1.237
	[c]AAD-y		0.011	0.012	0.010	0.008	0.001	0.006	0.011

[a]The unit of k_{12}, τ_{21} and τ_{12} is dimensionless
[b]AAD-P (%)=(1/N)$\Sigma|(P_{exp}-P_{cal})/P_{exp}|\times100$
[c]AAD-y=(1/N)$\Sigma|(y_{exp}-y_{cal})|$

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 agreement with the experimental data.

CONCLUSIONS

The isothermal vapor-liquid equilibrium data for the binary systems of CO_2 (1)+HFC-143a (2) were measured at seven equally spaced temperatures (273.15, 283.15, 293.15, 303.15, 313.15, 323.15 and 333.15) 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.

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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 : i^{th} and j^{th} components of the mixture
m   : mixtures

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