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DEVELOPING BINARY INTERACTION PARAMETERS FOR EQUATIONS OF STATE

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ABSTRACT

Binary interaction parameters are routinely developed to improve the accuracy of equation of state estimations for binary mixtures. For a given data set, the numerical value of the vapor-liquid equilibrium constant varies with the kind of equilibrium calculation used for the evaluation. For the same experimental data, a constant temperature bubble point calculation and a constant pressure bubble point calculation will not yield exactly the same value for the vapor-liquid equilibrium constant, K.

INTRODUCTION

Equations of state are widely used for calculation of physical and thermodynamic properties of pure components and mixtures. Initially equations of state were used for calculations as they were developed. In more recent years determination of "binary interaction parameters" has become increasingly common. The purpose of the binary interaction parameter is to force the calculated results from the equation of state to more closely match the experimentally determined vapor-liquid equilibrium constants. In order to determine binary interaction parameters experimental vapor-liquid equilibrium data for the binary pair must be available. Nonlinear regression techniques are then used to determine the value of the binary interaction parameter that will minimize the objective error function for the given set of experimental data.

Figure 1 shows the form of the binary interaction parameter equations for the Soave-Redlich-Kwong (SRK) equation of state. The binary interaction parameters enter into the equations in such a way that they change primarily the calculate value of the vapor-liquid equilibrium constant, but have only minor impact on other values calculated from the equation of state.

EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA

Experimental determinations of vapor-liquid equilibrium are normally recorded giving a liquid composition, a vapor composition, a measured temperature and

Fig. 1: Binary Interaction Parameter Equations

Soave-Redlich-Kwong

$$(a_c\alpha) = \sum_{ij}\sum x_i\ x_j\ (a_{ci}^{0.5})\ (a_{cj}^{0.5})\ (\alpha_i^{0.5})\ (\alpha_j^{0.5})\ (1-k_{ij})$$

$$(a_c\alpha)_i = \sum_{j=1} x_j\ (a_{ci}^{0.5})\ (a_{cj}^{0.5})\ (\alpha_i^{0.5})\ (\alpha_j^{0.5})\ (1-k_{ij})$$

pressure. In some cases the relative amounts of the equilibrium vapor and liquid phases will also be reported. The vapor-liquid equilibrium constants for the components are calculated from the measured vapor and liquid compositions. The measurements for one data point for binary mixtures of ethane and isobutane taken from Besserer and Robinson (1973) are shown in Table 1. The experimentally determined vapor and liquid compositions result in a vapor-liquid equilibrium constant of 3.100 for ethane and 0.5447 for isobutane at a temperature of 100.6°F (38.1°C) and 155 psia (1.07 MPa). One technique for determining the binary interaction parameter for ethane and isobutane from data like those shown in Table 1 would be to use those values of the vapor-liquid equilibrium constants in a nonlinear regression program. However, this procedure ignores the fact that the equations of state involve vapor and liquid compositions in their calculations and that, generally, the procedure for calculation is to have a given feed and use the equation of state to calculate the desired equilibrium condition. The types of equilibrium calculations that could be carried out would include:

Table 1
Typical Reported Experimental Equilibrium Data

Temperature	100.6°F (38.1°C)
Pressure	155 psia (1.07 MPa)
Mol Fraction Ethane in Vapor	0.5524
Mol Fraction Ethane in Liquid	0.1782
Ethane Equilibrium Constant	3.100
i-Butane Equilibrium Constant	0.5447

1. A bubble point calculation on the experimental liquid composition with temperature fixed.
2. A bubble point calculation on the experimental liquid composition with pressure fixed.

3. A dew point calculation on the experimental vapor composition with temperature fixed.
4. A dew point calculation on the experimental vapor composition with pressure fixed.

In cases where the relative amounts of vapor and liquid are also reported there could be additional equilibrium flash calculations. These calculations will not be considered further in this discussion because the parallel between bubble and dew point calculations and equilibrium flash calculations should be obvious.

Besserer and Robinson (1973) reported data for a total of 23 experimental determinations of the vapor-liquid equilibrium constants for ethane and isobutane in mixtures that ranged from 10 percent to 90 percent of each component. The results of the nonlinear regression analysis of these 23 data points are shown in Table 2. The types of equilibrium calculations carried out together with the objective functions used for minimizing the errors were:

Table 2

Comparison of Experimental and Calculated Equilibrium Parameters for Ethane-i Butane Binary Mixtures

Average Absolute Percent Deviation

Equilibrium Calculation Objective Function	Binary Interaction Parameter	Liquid Composition		Vapor Composition		Equilibrium Constant		Temperature
		x_{C2}	x_{iC4}	x_{C2}	x_{iC4}	K_{C2}	K_{iC4}	
Bubble Point, Pressure Fixed								
K values	0.00288			3.74	4.70	3.74	4.70	0.39
K values and temp.	0.00288			3.74	4.70	3.74	4.70	0.39
Temperature	0.00009			3.92	4.70	3.92	4.70	0.35
Dew Point, Pressure Fixed								
K values	0.00292	5.23	4.20			4.78	5.41	1.06
K values and temp.	0.00288	5.24	4.20			4.79	5.41	1.06
Temperature	0.00009	5.43	4.17			4.94	5.38	0.97
Bubble Point, temperature fixed								Pressure
K values	−0.00873			3.68	4.59	3.68	4.59	1.55
K values and press.	−0.00849			3.68	4.62	3.68	4.62	1.55
Pressure	−0.00857			3.77	4.61	3.77	4.61	1.55
Dew point, temperature fixed								
K values	−0.00893	7.89	5.87			7.00	7.36	3.74
K values and press.	−0.00849	7.89	5.92			7.01	7.43	4.15
Pressure	−0.00857	8.79	6.38			7.65	7.99	4.41

1. **Bubble point calculations using experimental liquid composition and measured pressure.**

   a. **Objective function for K values**

$$OF = \sum_{n=1}^{ND} \left\{ \sum_{m=1}^{NC} \left(\frac{K_E - K_C}{K_E} \right)_m^2 \right\}_n$$

   b. **Objective function for K values and temperature**

$$OF = \sum_{n=1}^{ND} \left\{ \sum_{m=1}^{NC} \left(\frac{K_E - K_C}{K_E} \right)_m^2 \right\}_n + \sum_{m=1}^{ND} \left\{ \frac{T_E - T_C}{T_E} \right\}_m^2$$

   c. **Objective function for temperature**

$$OF = \sum_{m=1}^{ND} \left\{ \frac{T_E - T_C}{T_E} \right\}_m^2$$

2. **Dew point calculations using experimental vapor composition and measured pressure have the same objective function as those presented for the bubble point calculation.**

3. **Bubble point calculations using experimental liquid composition and measured temperature**

   a. **Objective function for K values same as for bubble point, at measured pressure**

   b. **Objective function for K values and pressure**

$$OF = \sum_{n=1}^{ND} \left\{ \sum_{m=1}^{NC} \left(\frac{K_E - K_C}{K_E} \right)_m^2 \right\}_n + \sum_{n=1}^{ND} \left\{ \frac{P_E - P_C}{P_E} \right\}_n^2$$

   c. **Objective function for pressures**

$$OF = \sum_{n=1}^{ND} \left\{ \frac{P_E - P_C}{P_E} \right\}_n^2$$

4. **Dew point calculations using experimental vapor composition and measured temperature have the same objective function as those presented for the bubble point at measured temperature.**

The different methods of calculation and different objective functions used to determine 'goodness of fit' yield different values of the calculated parameters

(K-values, temperature and pressure) for mixtures of ethane and i-butane. This is evident from study of the overall percent errors shown in Table 2. As an example, the k_{ij} for a temperature fixed bubble point and dew point using the pressure objective function are the same. The calculated K-value error is different by almost a factor of 2, and the calculated pressure error differs by almost a factor of 3.

Table 3 shows a more detailed comparison for three data points using the same value of k_{ij} as in Table 2. The differences in error of the calculated values is not so large as in Table 2, but are still large enough to cause concern about just how one should achieve error minimization for the data set.

Table 3

Comparison of Calculated and Experimental Values Using Binary Interaction Parameters from Table 2 for Pressure
(measured temperature 100.6^{0}F, k_{ij} = −0.00857)

		Equilibrium Constant				**Pressure psia (MPa)**	
	Composition	**Ethane**		**i Butane**			
Equilibrium Calculation	**m.f. C_2**	**Exp.**	**Calc.**	**Exp.**	**Calc.**	**Exp.**	**Calc.**
Bubble point, temperature fixed	0.1782	3.100	3.133	0.5447	0.5375	155.0 (1.07)	160.7 (1.11)
Dew point, temperature fixed	0.5524	3.100	3.167	0.5447	0.5422	155.0 (1.07)	158.8 (1.09)
Bubble point, temperature fixed	0.4841	1.710	1.684	0.3339	0.3582	326.0 (2.25)	333.9 (2.30)
Dew point, temperature fixed	0.8277	1.710	1.617	0.3339	0.3529	326.0 (2.25)	351.5 (2.42)
Bubble point, temperature fixed	0.9135	1.050	1.046	0.4763	0.5148	664.0 (4.58)	668.9 (4.61)
Dew point, temperature fixed	0.9588	1.050	1.037	0.4763	0.5447	664.0 (4.58)	680.6 (4.69)

Table 4 compares calculated values for the same three data points using the k_{ij} for pressure fixed bubble point and dew points with the temperature objective function. Differences in calculated K-values range up to 6% with errors in calculated temperature from 2^{0}F to 6^{0}F.

Table 5 shows a comparison of calculated values with three experimental data points from Morris and McLinden (1986) for mixtures of Refrigerants R13B_1 and R152a. Table 5 shows, for three different data points, values calculated in three different ways:

Table 4

Comparison of Calculated and Experimental Values Using Binary Interaction Parameters from Table 2 for Temperature (measured temperature 100.6°F, k_{ij} = 0.00009)

			Equilibrium Constant					
		Composition	Ethane		i Butane		Temperature	
Equilibrium Calculation	Pressure	m.f. C_2	Exp.	Calc.	Exp.	Calc.	°F	°C
Bubble point, temperature fixed	155.0	0.1782	3.100	3.229	0.5447	0.5167	95.4	35.2
Dew point, temperature fixed	155.0	0.5524	3.100	3.295	0.5477	0.5377	98.6	37.0
Bubble point, temperature fixed	326.0	0.4841	1.710	1.697	0.3339	0.3456	96.3	35.7
Dew point, temperature fixed	326.0	0.8277	1.710	1.681	0.3339	0.3395	94.7	34.8
Bubble point, temperature fixed	664.0	0.9135	1.050	1.046	0.4763	0.5177	99.5	37.5
Dew point, temperature fixed	664.0	0.9588	1.050	1.041	0.4763	0.5197	98.3	36.8

1. A temperature fixed bubble point calculation using the k_{ij} determined from temperature fixed bubble point calculations.

2. A temperature fixed dew point calculation using the k_{ij} determined from temperature fixed dew point calculations.

3. A temperature fixed dew point calculation using the k_{ij} determined from temperature fixed bubble point calculations.

Differences in calculated values range to about 7% for K-values and 5% for pressure.

Table 6 shows the comparison for the same three data points when temperature rather than pressure is calculated. K-value differences are as high as 6% but temperatures differ by less than 3°F.

The differences shown in Tables 2 to 6 are based on calculations using the Soave-Redlich-Kwong equation of state, but are typical of the errors that would be found for any equation of state when analyzing good, consistent experimental vapor-liquid equilibrium data. The errors do not represent a weakness in the quality of the data, but are indicative of the fact that no experimental data can be perfectly consistent. Small errors in analysis, pressure and temperature measurement cause the magnitude of error in calculated values shown here.

Table 5

Comparison of Calculated and Experimental Bubble Point and Dew Point Pressures for Mixtures of $R13B_1$ and R152a at 8.33°F (−13.2°C)

Equilibrium Calculation	Composition m.f. C_2	Equilibrium Constant R13B$_1$ Exp.	Equilibrium Constant R13B$_1$ Calc.	Equilibrium Constant R152a Exp.	Equilibrium Constant R152a Calc.	Pressure psia (MPa) Exp.	Pressure psia (MPa) Calc.	Interaction Parameter k_{ij}
Bubble point, temperature fixed	0.100	4.465	4.093	0.6151	0.6564	42.14 (0.290)	41.85 (0.288)	0.09544*
Dew point, temperature fixed	0.4465	4.465	3.388	0.6151	0.6376	42.14 (0.290)	43.46 (0.300)	0.08228**
Dew point, temperature fixed	0.4465	4.465	3.762	0.6151	0.6281	42.14 (0.290)	44.10 (0.304)	0.09544*
Bubble point, temperature fixed	0.500	1.494	1.465	0.5064	0.5354	69.32 (0.478)	68.67 (0.473)	0.09544*
Dew point, temperature fixed	0.7468	1.494	1.403	0.5064	0.5412	69.32 (0.478)	66.66 (0.466)	0.08228**
Dew point, temperature fixed	0.7468	1.494	1.391	0.5064	0.5466	69.32 (0.478)	69.97 (0.482)	0.09544*
Bubble point, temperature fixed	0.900	1.024	1.023	0.781	0.794	80.53 (0.555)	79.76 (0.550)	0.09544*
Dew point, temperature fixed	0.9219	1.024	1.034	0.781	0.722	80.53 (0.555)	78.81 (0.543)	0.08228**
Dew point, temperature fixed	0.9219	1.024	1.022	0.781	0.796	80.53 (0.555)	79.79 (0.550)	0.09544*

* Based on bubble point calculations with temperature fixed for 33 experimental data point.

** Based on dew point calculations with temperature fixed for 33 experimental data points.

Table 6

Comparison of Calculated and Experimental Bubble Point and Dew Point Temperatures and K Values for Mixtures of $R13B_1$ and R152a (T = 8.33°F, k_{ij} = 0.10061*)

Equilibrium Calculation	Pressure psia (MPa)	Composition m.f. C_2	Equilibrium Constant R13B$_1$ Exp.	Equilibrium Constant R13B$_1$ Calc.	Equilibrium Constant R152a Exp.	Equilibrium Constant R152a Calc.	Temperature Calc. °F (°C)
Bubble point, pressure fixed	42.14 (0.290)	0.100	4.465	4.200	0.6151	0.6444	7.72 (−13.5)
Dew point, pressure fixed	42.14 (0.290)	0.4465	4.465	4.019	0.6151	0.6227	5.93 (−14.5)
Bubble point, pressure fixed	69.32 (0.478)	0.500	1.494	1.465	0.5064	0.5353	8.12 (−13.3)
Dew point, pressure fixed	69.32 (0.478)	0.7468	1.494	1.393	0.5064	0.5457	7.13 (−13.8)
Bubble point, temperature fixed	80.53 (0.555)	0.900	1.024	1.020	0.781	0.8212	8.64 (−13.0)
Dew point, temperature fixed	80.53 (0.555)	0.9219	1.024	1.018	0.781	0.8285	8.95 (−12.8)

* Based on bubble point calculations with pressure fixed for 33 experimental data points.

CONCLUSION

The binary interaction parameters calculated by regression analysis from a given set of vapor-liquid equilibrium measurements will differ depending upon the equilibrium calculation and the objective function used in selecting the binary interaction parameters. Different values of the interaction parameters will result in different calculated vapor-liquid equilibrium constants. Those responsible for developing binary interaction parameters should give considerable thought to the method of equilibrium calculation and the objective function that will be used to determine the "best" value of the binary interaction parameter to use in a general purpose equation of state.

NOMENCLATURE

a_c	Parameter in Peng-Robinson and Soave-Redlich-Kwong equation of state
K	Vapor-liquid equilibrium constant
k	Binary interaction coefficient
NC	Number of component in the system
ND	Number of data points
OF	Objective function
P	Pressure
T	Temperature
x	Mole fraction
α	Parameter in Peng-Robinson and Soave-Redlich-Kwong equation of state

SUBSCRIPTS

C	Calculated value	j	Component j
E	Experimentally measured value	m	Component m
i	Component i	n	Data point n

REFERENCES

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