

Correlation and evaluation of VLE data for light n-alkane binary mixtures

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Abstract - Combined data sets of all available VLE data for C₁ +, and C₂ + n-alkanes up to C₅ for each systems were correlated as a function of temperature using modified Redlich-Kwong-Soave and Peng-Robinson equations of state. The two EOS give a similar least-squares fit but the binary K_{ij} parameter is less temperature dependent for the Peng-Robinson EOS.

INTRODUCTION

The objective of the present work is to correlate and evaluate the VLE data for two series of binary mixtures, viz., methane +, and ethane + n-alkane up to C₅. The Redlich-Kwong-Soave (RKS) (ref. 1) and the Peng-Robinson (PR) (ref. 2) equations of state (EOS) were used for correlation. The two EOS were modified to ensure good reproduction of the saturated vapor pressures of mixture components over the temperature range of interest, this being an essential requirement for successful correlation. All literature data available for each binary were correlated as a combined data set in contrast to Knapp et al. (ref. 3) who have correlated each reported data set individually. The present results should, therefore, be more conclusive, especially that new data were included.

THE MODIFIED RKS AND PR EOS

The two EOS may be written as:

$$P = RT/(V-b) - a/M \quad (1)$$

where M is given by $V(V+b)$ and $v^2+2bv-b^2$ for the RKS and PR EOS, respectively, with

$$a = \Omega_a (RT_c)^2/P_c \cdot \alpha \quad (2)$$

and

$$b = \Omega_b RT_c/P_c \quad (3)$$

where Ω_a is equal to 0.42748 and 0.457236 and Ω_b equals 0.08664 and 0.07796 for the RKS and PR, respectively. The temperature relation for α was taken after Soave (ref. 1),

$$\alpha = |1 + K(1-T_R^{0.5})|^2 \quad (4)$$

but K was assumed in either EOS to be related to temperature as suggested originally by Stryjek and Vera (refs 4-6) for the PR equation:

$$K = K_0 + |K_1 + K_2(K_3 - T_R)(1 - T_R^{0.5})| (1 + T_R^{0.5})(0.7 - T_R) \quad (5)$$

K₀ being a universal function of the acentric factor:

$$K_0 = c_0 + c_1 \cdot \omega - c_2 \cdot \omega^2 + c_3 \cdot \omega^3 \quad (6)$$

Table 1 gives the values of coefficients in eq. (6).

The c_i for PR EOS were taken from Stryjek and Vera (ref. 5); the c_i for RKS EOS were found in this study by using the set of data reported herein. Coefficients K₁, K₂, and K₃ are characteristic for a given compound; they are determined from saturated vapor pressure data. Table 2 lists the K_{ij}-values obtained for the presently investigated compounds (at T_R > 0.7, K₂ = 0 is assumed).

TABLE 1. Coefficients c_i for the RKS and PR EOS in eq. (6)

| EOS | c_0 | c_1 | c_2 | c_3 |
|-----|----------|---------|----------|------------|
| RKS | 0.479794 | 1.57588 | 0.192078 | 2.46102E-2 |
| PR | 0.378818 | 1.48950 | 0.170913 | 1.93759E-2 |

TABLE 2. Coefficients K_i for n-alkanes in eq. (5)

| EOS Compound | RKS | | | PR | | |
|-----------------|---------|--------|--------|---------|--------|--------|
| | K_1 | K_2 | K_3 | K_1 | K_2 | K_3 |
| Methane | -.04754 | .20314 | .51647 | -.00127 | .14248 | .51588 |
| Ethane | -.02073 | .17486 | .42992 | .02698 | .12864 | .43070 |
| Propane | -.01820 | .37947 | .43346 | .03152 | .32093 | .43346 |
| n-Butane | -.01693 | .73204 | .46676 | .03476 | .63796 | .46676 |
| n-Pentane | -.01368 | .47277 | .45738 | .03966 | .38820 | .45738 |

c_i and K_i values reported in Tables 1 and 2 are internally consistent with the values of T_C , P_C and ω_1 for methane through n-butane (ref. 5) and with the new values of $T_C = 469.69$ K and $P_C = 3.3639$ MPa already published by Kratzke et al. (ref. 7). They give a new value of the acentric factor i.e. $\omega = 0.25143$; all these values should be used together.

The saturated vapor pressure data fit for n-alkanes from methane through n-pentane are given in Table 3. The PR EOS gives a better fit over the reduced temperature ranges covered.

The mixing rules used in this study were:

$$\text{with } a = \sum_i \sum_j x_i x_j a_{ij} \quad (7)$$

$$\text{and } a_{ij} = (a_{ii} \cdot a_{jj})^{0.5(1-K_{ij})} \quad (8)$$

$$b = \sum_i x_i b_i \quad (9)$$

The binary K_{ij} parameter (eq. 8) was assumed to be a linear function of temperature,

$$K_{ij} = K_{ij}^0 + K_{ij}^T \cdot (T-273.15) \quad (10)$$

The objective function Q,

$$Q = \sum (\Delta p/p)^2 \quad (11)$$

was minimized with equal statistical weight used for each point.

RESULTS AND DISCUSSION

The data processed in this study are summarized in Table 4. Generally, the methane + n-alkane VLE data are readily accessible from many sources; there is much less data available for the ethane + n-alkane (except + propane) systems.

TABLE 3. The average absolute deviations (AAD,%) in the saturated vapor pressure reproductions obtained for n-alkanes with the RKS and PR EOS

| Compounds | T/K | | $T_R < 0.7$ | | $T_R > 0.7$ | | ref. |
|-----------|--------|--------|-------------|-------|-------------|-------|------|
| | min | max | RKS | PR | RKS | PR | |
| Methane | 90. | 190. | 0.182 | 0.157 | 0.517 | 0.435 | 8 |
| Ethane | 120.95 | 293.15 | 0.088 | 0.098 | 0.733 | 0.607 | 9 |
| Propane | 143.95 | 363.15 | 0.316 | 0.279 | 0.929 | 0.781 | 9 |
| n-Butane | 182.15 | 413.15 | 0.184 | 0.159 | 0.699 | 0.544 | 9,10 |
| n-Pentane | 196.05 | 453.15 | 0.300 | 0.266 | 0.858 | 0.691 | 7,9 |

TABLE 4. Data included in this study

| System | Temperature range, K | | NR/NI/NP* |
|-------------|----------------------|---------|-----------|
| Methane | | | |
| + Ethane | 110.9 | 318.706 | 7/34/295 |
| + Propane | 114.1 | 360.93 | 5/22/281 |
| + n-Butane | 144.26 | 410.95 | 7/34/380 |
| + n-Pentane | 176.21 | 449.82 | 4/51/685 |
| Ethane | | | |
| + Propane | 127.57 | 369.18 | 6/29/294 |
| + n-Butane | 303.15 | 394.26 | 3/10/74 |
| + n-Pentane | 277.59 | 410.93 | 1/ 6/74 |

*The code specifies the numbers of References/Isotherms/Total data points.

Table 5 gives the least-square fit of combined set of VLE data for each data source.

TABLE 5 Results of correlation for the combined source data

| EOS | | RKS | | $\Delta p/p, \%$ | | PR | | Ref |
|------------------------------------|--------|------------|--------|------------------|--------|------------|--------|-----|
| $\Delta p/p, \%$ | | Δy | | $\Delta p/p, \%$ | | Δy | | |
| BIAS | AAD | BIAS | AAD | BIAS | AAD | BIAS | AAD | |
| Methane + ethane | | | | | | | | |
| -0.048 | 1.116 | 0.0053 | 0.0103 | 0.113 | 1.000 | 0.0087 | 0.0115 | 11 |
| 0.815 | 1.665 | -0.0131 | 0.0137 | 0.779 | 1.824 | -0.0105 | 0.0118 | 12 |
| 0.114 | 1.184 | -0.0028 | 0.0031 | -0.069 | 1.263 | -0.0026 | 0.0031 | 13 |
| -1.516 | 1.588 | 0.0001 | 0.0001 | -0.814 | 1.801 | 0.0002 | 0.0002 | 14 |
| 0.725 | 1.199 | 0.0027 | 0.0030 | 0.914 | 1.324 | 0.0054 | 0.0056 | 15 |
| 0.685 | 1.610 | 0.0005 | 0.0024 | 0.075 | 1.401 | 0.0000 | 0.0021 | 16 |
| 0.535 | 1.287 | 0.0051 | 0.0072 | 0.776 | 1.422 | 0.0084 | 0.0090 | 17 |
| Methane + propane | | | | | | | | |
| 0.000 | 1.078 | 0.0096 | 0.0107 | 1.301 | 1.568 | 0.0168 | 0.0169 | 18 |
| -0.125 | 1.661 | -0.0008 | 0.0009 | -1.414 | 1.991 | -0.0008 | 0.0010 | 13 |
| 5.056 | 5.319 | -0.0006 | 0.0006 | 4.066 | 4.450 | -0.0006 | 0.0006 | 19 |
| -0.785 | 0.972 | X | X | -2.092 | 2.093 | X | X | 20 |
| -1.457 | 2.448 | 0.0023 | 0.0024 | -2.505 | 2.686 | 0.0027 | 0.0027 | 21 |
| Methane + n-butane | | | | | | | | |
| -1.183 | 1.812 | -0.0019 | 0.0121 | 0.185 | 1.728 | 0.0058 | 0.0099 | 22 |
| -2.498 | 2.888 | -0.0107 | 0.0107 | -0.393 | 1.875 | 0.0002 | 0.0045 | 23 |
| 2.802 | 10.344 | -0.0219 | 0.0255 | 2.467 | 10.507 | -0.0197 | 0.0254 | 24 |
| -4.972 | 6.800 | -0.0100 | 0.0100 | -4.463 | 6.575 | -0.0100 | 0.0100 | 25 |
| 3.253 | 3.291 | -0.0022 | 0.0121 | 4.219 | 4.219 | 0.0074 | 0.0109 | 26 |
| -1.724 | 2.679 | -0.0023 | 0.0024 | -1.815 | 2.743 | -0.0014 | 0.0018 | 27 |
| 1.295 | 3.475 | -0.0002 | 0.0026 | 1.107 | 3.491 | 0.0001 | 0.0027 | 28 |
| Methane + n-butane (Selected data) | | | | | | | | |
| -0.756 | 1.771 | -0.0016 | 0.0126 | 0.587 | 1.955 | 0.0061 | 0.0105 | 22 |
| -2.043 | 2.710 | -0.0111 | 0.0111 | 0.034 | 2.015 | -0.0003 | 0.0046 | 23 |
| 1.629 | 3.400 | 0.0020 | 0.0129 | 1.818 | 3.884 | 0.0069 | 0.0168 | 24 |
| -2.588 | 4.847 | -0.0077 | 0.0077 | -2.385 | 4.882 | -0.0077 | 0.0077 | 25 |
| 3.624 | 3.627 | -0.0020 | 0.0124 | 4.587 | 4.587 | 0.0039 | 0.0080 | 26 |
| -1.654 | 2.647 | -0.0022 | 0.0024 | -1.923 | 2.637 | -0.0014 | 0.0018 | 27 |
| 1.095 | 3.279 | -0.0001 | 0.0028 | 0.704 | 3.188 | 0.0002 | 0.0029 | 28 |
| Methane + n-pentane | | | | | | | | |
| -0.165 | 1.150 | -0.0036 | 0.0086 | 0.446 | 1.438 | 0.0017 | 0.0080 | 29 |
| -0.030 | 2.015 | -0.0088 | 0.0130 | -0.007 | 1.814 | -0.0026 | 0.0103 | 30 |
| -0.467 | 4.053 | 0.0010 | 0.0015 | -0.160 | 4.692 | 0.0016 | 0.0016 | 31 |
| 0.752 | 6.283 | -0.0011 | 0.0011 | 0.605 | 6.642 | -0.0006 | 0.0006 | 32 |
| Ethane + propane | | | | | | | | |
| 0.080 | 0.365 | -0.0106 | 0.0122 | 0.435 | 0.435 | -0.0096 | 0.0116 | 12 |
| -0.095 | 0.961 | 0.0065 | 0.0068 | 0.169 | 0.934 | 0.0078 | 0.0078 | 33 |
| -1.706 | 4.709 | -0.0132 | 0.0137 | -1.539 | 4.629 | -0.0127 | 0.0132 | 34 |
| 1.164 | 1.364 | 0.0000 | 0.0033 | 1.355 | 1.484 | 0.0008 | 0.0034 | 35 |
| -1.237 | 2.223 | 0.0073 | 0.0083 | -0.836 | 2.069 | 0.0092 | 0.0096 | 36 |
| 0.228 | 0.261 | 0.0005 | 0.0012 | 0.288 | 0.311 | 0.0006 | 0.0012 | 37 |
| Ethane + n-butane | | | | | | | | |
| 2.136 | 2.448 | 0.0090 | 0.0090 | 2.156 | 2.489 | 0.0142 | 0.0142 | 38 |
| -0.258 | 1.702 | -0.0161 | 0.0167 | -0.313 | 1.748 | -0.0138 | 0.0151 | 39 |
| -0.167 | 0.186 | 0.0009 | 0.0009 | -0.140 | 0.170 | 0.0012 | 0.0012 | 37 |
| Ethane + n-pentane | | | | | | | | |
| 0.659 | 1.695 | -0.0027 | 0.0127 | 0.550 | 1.813 | -0.0007 | 0.0139 | 40 |

Footnote: $\Delta p = p_{\text{exp}} - p_{\text{calcd}}$; $\Delta y = y_{\text{exp}} - y_{\text{calcd}}$ through the paper

Table 6 gives the parameters of the two EOS.

TABLE 6. The binary parameters of the RKS and PR EOS

| System | RKS | | PR | |
|-------------|------------|------------|------------|------------|
| | K_{ij}^O | K_{ij}^T | K_{ij}^O | K_{ij}^T |
| Methane | | | | |
| + Ethane | -0.015817 | -0.00013 | 0.001201 | -0.00002 |
| + Propane | -0.004061 | -0.00017 | 0.016339 | -0.00004 |
| + n-Butane | -0.017360 | -0.000272 | 0.008617 | -0.000035 |
| + n-Butane* | -0.019039 | -0.000295 | 0.007406 | -0.00006 |
| + n-Pentane | -0.004764 | -0.000344 | 0.024 | 0. |
| Ethane | | | | |
| + Propane | 0.001213 | -0.000014 | 0.004335 | -0.000012 |
| + n-Butane | -0.011772 | 0.000396 | -0.007635 | 0.000403 |
| + n-Pentane | -0.004076 | 0.000155 | -0.002828 | 0.000238 |

Footnote: *- selected data set through the paper

Tables 7 and 8 give the results of the overall correlation for each binary and all studied systems, respectively.

TABLE 7. Overall results of the correlation for the binaries

| System | $\Delta p/p, \%$ | | | | $\Delta y*100$ | | | |
|-------------|------------------|------|------|------|----------------|------|------|------|
| | BIAS | | AAD | | BIAS | | AAD | |
| | RKS | PR | RKS | PR | RKS | PR | RKS | PR |
| Methane | | | | | | | | |
| + Ethane | 0.18 | 0.10 | 1.28 | 1.35 | -.15 | -.07 | 0.43 | 0.45 |
| + Propane | -.19 | 0.06 | 1.65 | 2.04 | 0.46 | 0.83 | 0.59 | 0.92 |
| + n-Butane | 0.13 | 0.31 | 4.31 | 4.32 | -.60 | -.31 | 0.99 | 0.90 |
| + n-Butane* | -.25 | -.10 | 2.80 | 2.87 | -.17 | 0.15 | 0.64 | 0.55 |
| + n-Pentane | -.14 | 0.12 | 2.38 | 2.48 | -.72 | -.14 | 1.09 | 0.89 |
| Ethane | | | | | | | | |
| + Propane | 0.03 | 0.22 | 1.84 | 1.87 | -.11 | -.03 | 0.63 | 0.65 |
| + n-Butane | 0.37 | 0.30 | 1.65 | 1.65 | -.69 | -.46 | 1.21 | 1.24 |
| + n-Pentane | 0.66 | 0.55 | 1.70 | 1.81 | -.27 | -.07 | 1.27 | 1.39 |

TABLE 8. Overall results of the correlation

| System | $\Delta p/p, \%$ | | | | $\Delta y*100$ | | | |
|------------|------------------|------|------|------|----------------|------|------|------|
| | BIAS | | AAD | | BIAS | | AAD | |
| | RKS | PR | RKS | PR | RKS | PR | RKS | PR |
| Methane | | | | | | | | |
| + n-alkane | -.02 | 0.15 | 2.55 | 2.67 | -.38 | 0.01 | 0.86 | 0.83 |
| Ethane | | | | | | | | |
| + n-alkane | 0.24 | 0.31 | 1.77 | 1.82 | -.24 | -.11 | 0.87 | 0.92 |
| overall | 0.04 | 0.19 | 2.37 | 2.48 | -.35 | -.10 | 0.86 | 0.85 |

EVALUATION OF THE VLE DATA

An analysis of error distribution in the system pressures and vapor phase composition along x_1 and temperature axis, as well as, a comparison of the deviations for the data from various sources and within the homologous series were the basis for evaluating both the VLE data and performance of the two EOS.

Methane + ethane

In general, errors are rather small and no marked systematic deviations along temperature are found. An increase of y_1 deviations at higher temperatures ($T > 255$ K) is evident, having, however, different sign for data coming from various sources. Relatively great deviations in y_1 were found for the Price (ref. 12) data at 255.37 K. A comparison of his results with those of Davalos et al. (ref. 15) at 250 K and Gupta et al. (ref. 17) at 260 K showed clearly that those of Price are dubious as they follow rather close the 260 K isotherm.

Methane + propane

In general, the data for that system seem to be accurate. Greater systematic (positive in $\Delta p/p$) deviations from the overall fit of the combined set of data are detected only at 122.200 K for the Poon and Lu (ref. 19) data being also less precise at other isotherms. Systematic deviations in vapor phase composition have been produced also by the two EOS for the Reamer et al. (ref. 18) data.

Methane + n-butane

Results of the fit showed great systematic deviations in $\Delta p/p$ and Δy_1 at 244.26 and 277.59 K of the Roberts et al. (ref. 24) data, especially at low x_1 , also some other four points (refs 24-25) showed clearly a great random error. Two results of the fit are reported for that system: for all data and selected data obtained after omitting points in doubt. An improvement of the fit is evident. Errors greater than in other data are evident also in the Wang and McKetta (ref. 25) and Wiese et al. (ref. 26) data. Data of Elliot et al. (ref. 27) and Kahre (ref. 28), covering almost the same temperature range showed different sign of the temperature dependence of $\Delta p/p$ deviations. Moreover, the former showed generally negative and the latter positive y_1 deviations.

Methane + n-pentane

Most numerous data comes from the Berry and Sage (ref. 30) evaluation and within the same temperature range from Sage et al. (ref. 29). The Berry and Sage data showed large negative Δy_1 values at low temperatures monotonously passing to large positive Δy_1 values at their upper temperature limit. Their data at the lowest temperatures barely overlap with the highest temperatures of the Kahre (ref. 31) and Chu et al. (ref. 32) data. At the common temperature range, the large negative Δy_1 produced by the two EOS for the Berry and Sage data are not confirmed for the Kahre and Chu et al. data whose vapor phase compositions are very well reproduced by the two EOS. Again, the system pressures at the highest temperatures of the Berry and Sage data are not well represented by the two EOS with eqs (8) and (10). The more recent Chu et al. data showed relatively large $\Delta p/p$ random errors also having a systematic contribution for each isotherm. The Kahre data for the same temperature range showed mostly random errors, but of the same order as Chu et al. data. The y_1 deviations are of opposite sign for these two sets of data.

Ethane + propane

A major contribution to overall $\Delta p/p$ errors comes from the Djordjevich and Budenholzer (ref. 34) data. In fact, some of these cover the lowest temperature limit of data availability. Their data were obtained using two experimental set-ups and, probably, some systematic errors come from the inconsistency of two sets of measurements. Relatively big negative (systematic) deviations in y_1 result rather from systematic errors in measurements than from models applied as these deviations are not observed for this temperature range in other systems under study. Comparison of the Matschke and Thodos (ref. 33) and Miksovsky and Wichterle (ref. 35) data for the close temperatures showed clearly systematic deviations in vapor phase composition produced by the data from the former source. The VLE data are available here also at temperatures close to $T_{C,1}$ and $T_{C,2}$. They are well represented with the two EOS with eqs (8) and (10) and deviations are not greater than average for the whole temperature range. For two points only, at $T = 367.660$ K of the Miksovsky and Wichterle (ref. 35) data, convergence to a non-trivial solution could not be achieved using the K_{12} parameters found from the all data fit and that isotherm was not considered. In fact, maximum Y_{exp} value for that isotherm is below 0.02. Examples of the fit for isotherms in the vicinity of the critical temperatures of both mixture constituents are presented in Figs. 1 and 2.

Ethane + n-butane

Quite a good fit in term of $\Delta p/p$ was obtained even though not many data sets were available. Comparison of data of Mehra and Thodos (ref. 38) at 366.483 K and Uchytíl and Wichterle (ref. 37) at 363.40 K gives $\Delta p/p$ and Δy_1 values similar in magnitude, but opposite in sign. Comparison of data at 338.706 K (ref. 38) with data for 323.15 and 343.15 K (ref. 37) gives similar results. Also, systematic (negative) deviations in y_1 of the Lhotak and Wichterle (ref. 39) data are not confirmed by the more recent Uchytíl and Wichterle (ref. 37) data. The distributions of deviations confirmed that the systematic errors originate from various sources than from the EOS used.

Ethane + n-pentane

Data exist from one (ref. 40) source only. The system pressure is well represented by the two EOS. VLE data at 277.594 and 446.261 K give large, unexpected systematic deviations in y_i .

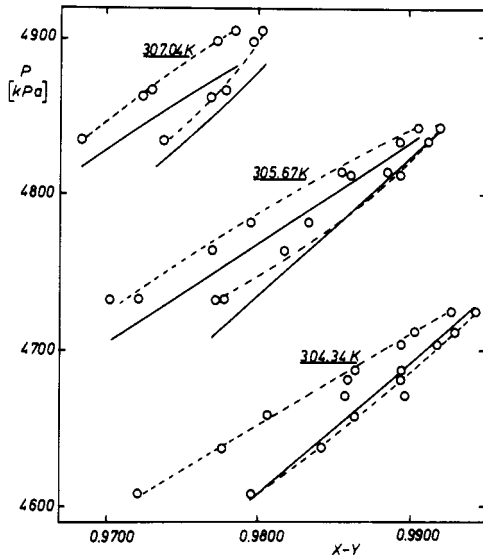


Fig. 1. VLE for ethane + propane with PR EOS at T close to $T_{C,1}$ in expanded scale; exptl. (o) (ref. $C,137$), graphically smoothed (---), and calcd. (—).

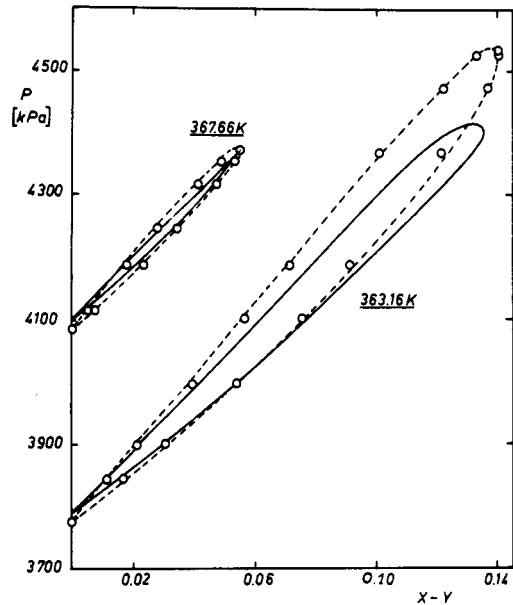


Fig. 2. VLE for ethane + propane with PR EOS at T close $T_{C,2}$ in expanded scale; exptl. (o) $C,2$ (ref. 35); graphically smoothed (---), and calcd. (—).

GENERAL REMARKS FROM THE DATA FIT AND EVALUATION

Majority of the available data for each system have similar precision. In the $T < T_{C,1}$ range the system pressures and vapor phase compositions are well represented by the two $C,1$ EOS with eq. (8) and these data seem to be accurate and mutually consistent. In the $T > T_{C,1}$ eq. (4) for K is extrapolated and the quality of prediction of vapor phase composition might be used as its rigorous test. Unfortunately, these data come mostly from the older sources and not from direct experiment but interpolation. Analysis of the $\Delta p/p$ and Δy_i values for all systems showed their overall random distribution confirming the applicability of eq. 5 in the $T > T_{C,1}$ range. But even when they seem to be smooth, relatively greater (especially in vapor phase composition) and systematic deviations for each data set suggest that the data should be treated as tentative.

As rule, with the two EOS, greater deviations in system pressures occur at lower temperatures and within the lower concentration range of the more volatile component. Differences in vapor phase compositions are smaller and random at lower temperatures, but as the temperature is raised they increase to produce moderate deviations at temperatures close to the critical temperature of the higher boiling component. Mostly they come from systematic errors of measurements as the absolute BIAS are close to ADD values and, even more, one sign of BIAS Δy_i values dominates for each data source. In addition, for the big set of data (more than 2000 points) positive and negative errors in $\Delta p/p$ and Δy_i values are almost cancelled (Table 8 and Figs. 3 and 4).

ON THE TEMPERATURE DEPENDENCE OF THE K_{ij} PARAMETER

Due to the wide temperature range (exceeding 200 K for most of the systems) of the VLE data eq. (10) has been postulated. The effectiveness of its use has been tested by the comparison

of the fit assuming $K_{ij}^T = 0$ and, K_{ij} being temperature independent. In terms of overall results given in Table 10 the improvement of the fit using real K_{ij} instead of $K_{ij}^T = 0$ is not so great for the systems with small differences in molecular parameters of constituents ($C_1 + C_2$ and $C_2 + C_3$); similarly small improvement has been found for the case where data cover a narrow temperature range ($C_3 + C_5$). In addition, most data are available at temperatures close to the average ones being not sensitive to the K_{ij}^T value. However, these differences are quite significant at low temperature boundary of i,j data (Tables 11 and 12). A comparison of the respective results showed that the errors may increase by the factor from 2 to 3 if $K_{ij}^T = 0$ instead of real K_{ij} is taken. (It is worth stating that here the minimum of objective function through i,j eq. (11) does not necessarily correspond to the minimum in the AAD value. These cases have been met twice, when slightly smaller AAD values have been obtained using $K_{ij}^T = 0$, but for these cases as well as for all others the RMS values were greater).

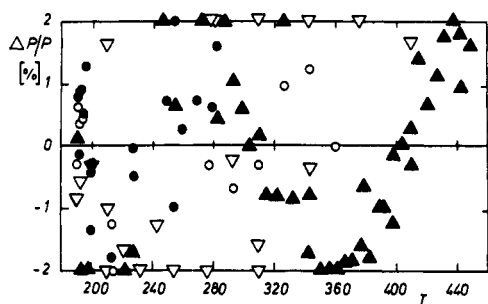


Fig. 3. Scatterdiagram of $\Delta p/p$ with PR EOS for isotherms of methane+n-alkane in the $T > T_{C,1}$ range; n-alkanes: ethane(●), propane(○), n-butane(▽), and n-pentane(▲).

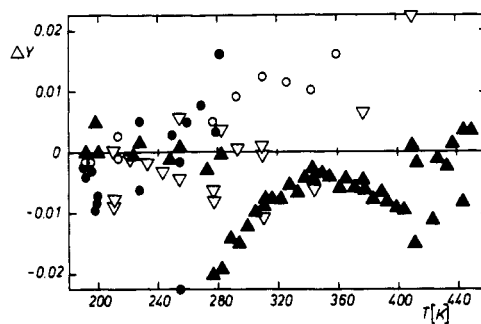


Fig. 4. Scatterdiagram of Δy with PR EOS for isotherms of methane+n-alkane in the $T > T_{C,1}$ range; n-alkanes: ethane(●), propane(○), n-butane(▽), and n-pentane(▲).

TABLE 9. The K_{ij} parameters of the two EOS for $K_{ij}^T = 0$

| System | RKS | PR |
|-------------|-----------|----------|
| Methane | | |
| + Ethane | -0.001039 | 0.002694 |
| + Propane | 0.015918 | 0.020417 |
| + n-Butane | -0.001645 | 0.011100 |
| + n-Butane* | -0.000489 | 0.011414 |
| + n-Pentane | -0.001045 | 0.026986 |
| Ethane | | |
| + Propane | 0.001678 | 0.001831 |
| + n-Butane | 0.012254 | 0.016397 |
| + n-Pentane | 0.005918 | 0.010655 |

Footnote: * - selected data set

TABLE 10. Overall results of the correlation for the binaries (with $K_{ij}^T = 0$)

| System | $\Delta p/p, \%$ | | | | $\Delta y * 100$ | | | |
|-------------|------------------|------|------|------|------------------|------|------|------|
| | BIAS | | AAD | | BIAS | | AAD | |
| | RKS | PR | RKS | PR | RKS | PR | RKS | PR |
| Methane | | | | | | | | |
| + Ethane | -.20 | -.18 | 1.48 | 1.38 | -.22 | -.06 | 0.43 | 0.45 |
| + Propane | -1.49 | 0.70 | 3.05 | 1.96 | 0.29 | 0.80 | 0.51 | 0.89 |
| + n-Butane | -1.17 | 0.00 | 5.57 | 4.28 | -.69 | -.32 | 0.87 | 0.88 |
| + n-Butane* | -1.70 | -.42 | 4.59 | 2.88 | -.27 | 0.14 | 0.47 | 0.53 |
| + n-Pentane | -2.11 | -.64 | 5.16 | 2.60 | -1.09 | -.20 | 1.14 | 0.86 |
| Ethane | | | | | | | | |
| + Propane | 0.06 | 0.15 | 1.88 | 1.87 | -.09 | -.02 | 0.62 | 0.65 |
| + n-Butane | 0.50 | 0.56 | 1.99 | 2.08 | -.75 | -.49 | 1.24 | 1.26 |
| + n-Pentane | 0.72 | 0.97 | 1.65 | 1.95 | -.20 | -.05 | 1.31 | 1.46 |

TABLE 11. Examples of low temperature VLE reproduction by the RKS and PR EOS with K_{ij}^P and real K_{ij}^T given in Table 6

| EOS: | RKS | | | | PR | | | | Ref |
|--------------------|-------|------|-------------------------|-------------------|-------|-------------------------|---------|-------------------|-----|
| | T | BIAS | $\Delta p/p, \%$ AAD | Δy AAD | BIAS | $\Delta p/p, \%$ AAD | BIAS | Δy AAD | |
| System $C_1 + C_2$ | | | | | | | | | |
| 130.372 | -0.05 | 1.87 | -0.0002 | 0.0002 | -0.05 | 1.85 | -0.0002 | 0.0002 | 13 |
| 144.261 | 1.21 | 1.70 | -0.0007 | 0.0007 | 0.92 | 1.39 | -0.0007 | 0.0007 | |
| 158.150 | -1.46 | 2.18 | -0.0031 | 0.0031 | -2.02 | 2.45 | -0.0033 | 0.0033 | |
| 110.928 | -1.52 | 1.59 | 0.0001 | 0.0001 | -0.81 | 1.80 | 0.0002 | 0.0002 | 14 |
| System $C_1 + C_3$ | | | | | | | | | |
| 114.100 | 2.74 | 3.36 | -0.0004 | 0.0004 | 2.03 | 2.81 | -0.0004 | 0.0004 | 19 |
| 118.300 | 2.60 | 2.80 | -0.0006 | 0.0006 | 1.70 | 2.13 | -0.0006 | 0.0006 | |
| System $C_1 + C_4$ | | | | | | | | | |
| 144.260 | -2.08 | 2.08 | 0.0000 | 0.0000 | 1.20 | 1.88 | 0.0000 | 0.0000 | 27 |
| 155.380 | -1.94 | 2.58 | 0.0000 | 0.0000 | 0.67 | 2.16 | 0.0000 | 0.0000 | |
| 166.500 | -0.87 | 1.98 | -0.0001 | 0.0001 | 0.42 | 2.02 | -0.0001 | 0.0001 | |
| 166.483 | 3.02 | 3.07 | 0.0000 | 0.0000 | 4.15 | 4.15 | 0.0000 | 0.0000 | 28 |
| 177.594 | 1.47 | 3.35 | 0.0000 | 0.0001 | 1.90 | 3.58 | 0.0000 | 0.0001 | |
| 185.928 | 3.29 | 4.31 | 0.0000 | 0.0002 | 3.35 | 4.22 | 0.0000 | 0.0002 | |
| System $C_1 + C_5$ | | | | | | | | | |
| 177.594 | -0.41 | 2.74 | 0.0000 | 0.0000 | -0.41 | 2.74 | 0.0000 | 0.0000 | 31 |
| 185.928 | -0.18 | 2.74 | 0.0000 | 0.0000 | -0.18 | 2.74 | 0.0000 | 0.0000 | |
| 190.928 | 0.11 | 3.79 | 0.0000 | 0.0000 | 0.11 | 3.79 | 0.0000 | 0.0000 | |
| 176.210 | 2.36 | 2.36 | 0.0000 | 0.0000 | 7.20 | 7.20 | 0.0000 | 0.0000 | 32 |
| 192.620 | -0.52 | 4.96 | -0.0001 | 0.0001 | 1.45 | 5.00 | -0.0001 | 0.0001 | |
| 194.170 | -2.44 | 5.76 | -0.0001 | 0.0001 | -0.62 | 4.88 | -0.0001 | 0.0001 | |

TABLE 12. Examples of low temperature VLE reproduction by the RKS and PR EOS with $K_{ij}^T = 0$ and K_{ij}^P given in Table 9

| EOS: | RKS | | | | PR | | | | Ref |
|--------------------|-------|-------|-------------------------|-------------------|-------|-------------------------|---------|-------------------|-----|
| | T | BIAS | $\Delta p/p, \%$ AAD | Δy AAD | BIAS | $\Delta p/p, \%$ AAD | BIAS | Δy AAD | |
| System $C_1 + C_2$ | | | | | | | | | |
| 130.372 | 0.52 | 2.41 | -0.0002 | 0.0002 | 0.16 | 2.05 | -0.0002 | 0.0002 | 13 |
| 144.261 | 1.85 | 2.29 | -0.0006 | 0.0006 | 1.28 | 1.71 | -0.0007 | 0.0007 | |
| 158.150 | -1.39 | 2.17 | -0.0031 | 0.0031 | -1.71 | 2.30 | -0.0032 | 0.0032 | |
| 110.928 | 1.23 | 3.53 | 0.0002 | 0.0002 | -0.03 | 2.42 | 0.0002 | 0.0002 | 14 |
| System $C_1 + C_3$ | | | | | | | | | |
| 114.100 | 4.94 | 5.18 | -0.0004 | 0.0004 | 2.93 | 3.51 | -0.0004 | 0.0004 | 19 |
| 118.300 | 4.23 | 4.23 | -0.0006 | 0.0006 | 2.42 | 2.67 | -0.0006 | 0.0006 | |
| System $C_1 + C_4$ | | | | | | | | | |
| 144.260 | 6.92 | 6.92 | 0.0000 | 0.0000 | 2.19 | 2.72 | 0.0000 | 0.0000 | 27 |
| 155.380 | 6.91 | 6.91 | 0.0000 | 0.0000 | 1.61 | 2.44 | 0.0000 | 0.0000 | |
| 166.500 | 5.10 | 5.13 | -0.0001 | 0.0001 | 1.02 | 2.19 | -0.0001 | 0.0001 | |
| 166.483 | 8.04 | 8.04 | 0.0000 | 0.0000 | 4.65 | 4.65 | 0.0000 | 0.0000 | 28 |
| 177.594 | 4.85 | 6.50 | 0.0000 | 0.0001 | 2.21 | 3.86 | 0.0000 | 0.0001 | |
| 185.928 | 5.88 | 6.48 | 0.0000 | 0.0002 | 3.55 | 4.39 | 0.0000 | 0.0002 | |
| System $C_1 + C_5$ | | | | | | | | | |
| 177.594 | 10.92 | 11.09 | 0.0000 | 0.0000 | 1.60 | 3.26 | 0.0000 | 0.0000 | 31 |
| 185.928 | 8.86 | 9.46 | -0.0001 | 0.0001 | 0.79 | 3.05 | 0.0000 | 0.0000 | |
| 190.928 | 9.94 | 11.19 | -0.0001 | 0.0001 | 0.68 | 4.08 | 0.0000 | 0.0000 | |
| 176.210 | 18.47 | 18.47 | 0.0000 | 0.0000 | 5.40 | 5.40 | 0.0000 | 0.0000 | 32 |
| 192.620 | 10.29 | 10.29 | -0.0001 | 0.0001 | -0.07 | 4.67 | -0.0001 | 0.0001 | |
| 194.170 | 8.32 | 8.32 | -0.0001 | 0.0001 | -2.17 | 5.55 | -0.0001 | 0.0001 | |

Much better description of the VLE using $K_{ij}^T = 0$ gives the PR EOS.

CONCLUSIONS

The RKS EOS allows to obtain a slightly better fit of system pressures (in terms of AAD). The temperature dependence of K_{ij} , even if slight, is clearly evident and must be allowed for when data covering a wide temperature range are correlated. It is sufficient, at least for the present systems composed of simple fluids, to adopt the linear temperature dependence of the binary parameter, even for the wide temperature ranges involved. The VLE close to

critical region is represented well by each EOS with the binary parameter assumed to be a linear function of temperature. The data correlation with $K_{ij}^T = 0$ showed evidently that better fit was obtained using the PR EOS and, thus, the PR^{1j}EOS is more recommended for the VLE prediction if available data are insufficient to determine the real K_{ij} value.

On the average, the two EOS used gave insignificant differences in the quality of the fits and error scatter diagrams, provided the expression for the "a" in eq. (1) parameter ensures a comparable accuracy of saturated vapor pressure reproduction of mixture constituents.

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REFERENCES

- G. Soave, *Chem. Eng. Sci.*, **39**, 1197-1203 (1972).
- D.Y. Peng and D.B. Robinson, *Ind. Eng. Chem. Fundam.*, **15**, 59-64 (1976).
- H. Knapp, R. Doring, L. Oerlich, U. Plockner and J.M. Prausnitz, *Vapor-Liquid Equilibria for Mixtures of Low Boiling Substances*, Chem. Data Series, Vol. VI, DECHEMA, Frankfurt/Main (1982).
- R. Stryjek and J.H. Vera, An Improved Cubic Equation of State, in *ACS Symp. Series, Equations of State - Theories and Applications* (eds. K.C. Chao and L.R. Robinson), **300**, 560 - 570 (1986).
- R. Stryjek and J.H. Vera, *Can. J. Chem. Eng.*, **64**, 323-333 (1986).
- R. Stryjek and J.H. Vera, *Can. J. Chem. Eng.*, **64**, 820-826 (1986).
- H. Kraztke, S. Muller, M. Bohn and R. Kohlen, *J. Chem. Thermodyn.*, **17**, 283-294 (1985).
- S. Angus, B. Armstrong and K.M. deReuck, *International Thermodynamics Tables of the Fluid State, Vol. 5, Methane*, Pergamon Press, Oxford (1979).
- API 44 Tables, Research project 44, Amer. Petr. Inst., Thermodynamic Research Center (Texas A&M University).
- J. Dykyj, M. Repas and J. Svoboda, *Tlak Nasytenej Pary Organickych Zlucenin (pokracovanie)*, Vydavatelstvo Slovenskej Akademie Vied, Bratislava (1984).
- O.T. Bloomer, D.C. Gami and J.D. Parent, *Institute of Gas Technology Res. Bull. No 17*, (1953) cf.: Price (ref. 12).
- A.R. Price, *Low Temperature Vapor-Liquid Equilibrium in Light Hydrocarbon Mixtures: Methane - Ethane - Propane System*, PhD Diss., Rice University, Houston, Texas (1957).
- I. Wichterle and R. Kobayashi, *Low Temperature Vapor-Liquid Equilibria in the Methane - Ethane - Propane Ternary and Associated Binary Methane Systems with Special Consideration of the Equilibria in the Vicinity of the Critical Temperature of Methane*, Monograph, Rice University, Houston, Texas (1970).
I. Wichterle and R. Kobayashi, *J. Chem. Eng. Data*, **17**, 1-8 (1972).
I. Wichterle and R. Kobayashi, *J. Chem. Eng. Data*, **17**, 13-18 (1972).
- G.M. Wilson, *Adv. Cryog. Eng.*, **20**, 164-171 (1975).
- J. Davalos, W.R. Anderson, R.E. Phelps and A.J. Kidnay, *J. Chem. Eng. Data*, **21**, 81-84 (1976).
- R.C. Miller, A.J. Kidnay and M.J. Hiza, *J. Chem. Thermodyn.*, **9**, 167-178 (1977).
- M.K. Gupta, G.C. Gardner, M.J. Hegarty and A.J. Kidnay, *J. Chem. Eng. Data*, **25**, 313-318 (1980).
- H.H. Reamer, P.H. Sage and W.N. Lacey, *Ind. Eng. Chem.*, **42**, 534-539 (1950).
- D.P.L. Poon and B.C.Y. Lu, *Adv. Cryog. Eng.*, **19**, 292-299 (1974).
- J.G.G. Calado, G.A. Garcia and L.A.K. Staveley, *Chem. Soc. Farad. Trans. I*, **70**, 1445-1451 (1974).
- H. Kalra and D.B. Robinson, *Cryogenic*, July, 409-412 (1975).
- B.H. Sage, B.L. Hicks and W.N. Lacey, *Ind. Eng. Chem.*, **32**, 1085-1092 (1940).
- T.J. Rigas, D.F. Mason and G. Thodos, *Ind. Eng. Chem.*, **50**, 1297-1300 (1958).
- L.R. Roberts and R.H. Wang, *J. Chem. Eng. Data*, **7**, 484-485 (1962).
- R.H. Wang and J.J. McKetta, *J. Chem. Eng. Data*, **9**, 30-35 (1964).
- H.C. Wiese, J. Jacobs and B.H. Sage, *J. Chem. Eng. Data*, **15**, 82-91 (1970).
- D.G. Elliot, R.J.J. Chen, P.S. Chappellear and R. Kobayashi, *J. Chem. Eng. Data*, **19**, 71-77 (1974).
- R.C. Kahre, *J. Chem. Eng. Data*, **19**, 67-71 (1974).
- B.H. Sage, H.H. Reamer, P.H. Olds and W.N. Lacey, *Ind. Eng. Chem.*, **34**, 1108-1117 (1942).
- V.M. Berry and B.H. Sage, *Phase Behavior in Binary and Multicomponent Systems at Elevated Pressures: n-Pentane and Methane - n-Pentane*, National Stand. Ref. Data Ser., Nat. Bur. Stand. **32** (1970).
- R.C. Kahre, *J. Chem. Eng. Data*, **20**, 363-367 (1975).
- T.C. Chu, R.J.J. Chen, P.S. Chappellear and R. Kobayashi, *J. Chem. Eng. Data*, **21**, 41-44 (1976).
- D.E. Matschke and G. Thodos, *J. Chem. Eng. Data*, **7**, 232-234 (1962).
- L. Djordjevic and R.A. Budenholzer, *J. Chem. Eng. Data*, **15**, 10-12 (1970).
- J. Miksovsky and I. Wichterle, *Czech. Chem. Commun.*, **40**, 365-370 (1975).
- H. Poll, H. Huemer and F. Moser, *Monatshefte fur Chemie*, **111**, 1159-1164 (1980).
- P. Uchytil and I. Wichterle, *Fluid Phase Equilibria*, **15**, 209-217 (1983).
- V.S. Mehra and G. Thodos, *J. Chem. Eng. Data*, **10**, 307-309 (1965).
- V. Lhotak and I. Wichterle, *Fluid Phase Equilibria*, **6**, 229-235 (1981).
- H.H. Reamer, V. Berry and B.H. Sage, *J. Chem. Eng. Data*, **6**, 184-191 (1961).