Short Communication

Can Quadruplet or Quintuplet Interactions Describe the Variation of the Critical Temperature with Composition of Gaseous Mixtures

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Recently, a simple model to account for the variation of various molar thermodynamic and other properties of ion exchange reactions has proved quite useful.[1–5] The model implies that the properties investigated can be related to the three kinds of pairs present: A–A, B–B and A–B=B–A. It seems tempting to try this approach also on other binary mixtures, and in this paper it is applied to critical temperatures of various gaseous mixtures. However, it is not sufficient to use pair interactions, and for that reason triplets, quadruplets and quintuplets have been tried. In the following, quintuplets are considered. However, in the various tables some statistical criteria for quadruplets are compared.

The model

The molar property Y is assumed to be related to the various kinds of quintuplets by

Table 1a. The system methane – propane. Methane, T^c = 190.7 K. Propane, T^c = 369.9 K. Data from Ref. 7. x = mole fraction of methane.

x	T^c		Some statistical criteria[a]	Quadruplets	Quintuplets
	Expt.	Eqn. (1)			
0.1400	360.9	360.90	Residual squares sum	1.389	0.3695
0.3228	344.3	344.03	Mean residual	0.4467	0.1950
0.4691	327.6	328.01	Residual mean	$3.333 \cdot 10^{-3}$	$-1.667 \cdot 10^{-3}$
0.5882	310.9	310.90	Standard deviation	0.527	0.272
0.6772	294.3	293.99	Percentage deviation	0.174	0.0861
0.7459	277.6	277.78	Hamilton R-factor/%	0.150	0.0774

[a]Ref. 9.

Table 1b. The system methane – propane. Methane, T^c = 190.7 K. Propane, T^c = 369.9 K. Data from Ref. 8. x = mole fraction of methane.

x	T^c		Some statistical criteria[a]	Quadruplets	Quintuplets
	Expt.	Eqn. (1)			
0.100	364.2	364.15	Residual squares sum	2.818	0.2572
0.200	354.4	354.54	Mean residual	0.5586	0.1543
0.300	344.1	343.79	Residual mean	$-2.714 \cdot 10^{-2}$	$8.571 \cdot 10^{-3}$
0.400	332.5	332.50	Standard deviation	0.685	0.207
0.500	319.5	319.80	Percentage deviation	0.219	0.0633
0.600	304.3	304.09	Hamilton R-factor/%	0.192	0.0581
0.700	283.6	283.67			

[a]Ref. 9.

Table 2. The system *n*-hexane – *n*-tridecane. *n*-Hexane, T^c = 507.3 K. *n*-Tridecane, T^c = 677.0 K. Data from Ref. 10. x = mole fraction of *n*-hexane.

x	T^c		Some statistical criteria[a]	Quadruplets	Quintuplets
	Expt.	Eqn. (1)			
0.100	666.2	666.29	Residual squares sum	1.788	0.3179
0.200	657.2	656.98	Mean residual	0.3889	0.1700
0.300	647.3	647.52	Residual mean	$2.222 \cdot 10^{-3}$	$2.333 \cdot 10^{-2}$
0.400	637.0	636.89	Standard deviation	0.473	0.199
0.500	624.3	624.42	Percentage deviation	0.0762	0.0329
0.600	609.3	609.54	Hamilton *R*-factor/%	0.0722	0.0304
0.700	591.5	591.60			
0.800	570.0	569.67			
0.900	542.2	542.30			

[a]Ref. 9.

$$Y = y_1x^5 + 5y_{m_1}x_1^4x_2 + 10y_{m_2}x_1^3x_2^2 + 10y_{m_3}x_1^2x_2^3 + 5y_{m_4}x_1x_2^4 + y_2x_2^5. \quad (1)$$

Here, x_1,x_2 are the stoichiometric mole fractions of the two components, and y_1,y_2 are the property Y for the pure components. y_{m_i} (i = 1–4) are the property Y for each kind of mixed quintuplet.

Eqn. (1) corresponds to a random distribution of the various kinds of quintuplets. However, it is sufficient to assume that the amount of each kind is proportional to $x_1x_2^4$ etc., and the proportionality constant included in y_{m_4} etc. For most systems, the quantity Y for the pure components (i.e., y_1 and y_2) is known and the data can be rearranged to a third degree polynomial by

$$\Delta = \frac{Y - y_1x_1^5 - y_2x_2^5}{x_1x_2} = 5y_{m_1}x_1^3 + 10y_{m_2}x_1^2x_2 + 10y_{m_3}x_1x_2^2 + 5y_{m_4}x_2^3. \quad (2)$$

Expressions similar to eqns. (1) and (2) are easily derived for triplets, quadruplets and higher multiplets by using the binomial theorem.

Eqn. (2) can easily be rearranged to a third degree polynomial in either x_1 or x_2. By least-squares methods the four constants a,b,c and d of the third degree polynomial in x_1:

$$\Delta = a + bx_1 + cx_1^2 + dx_1^3 \quad (3)$$

can be obtained. For x_2 as independent variable a similar expression is obtained. From eqns. (2) and (3) we obtain:

$$5y_{m_1} = a + b + c + d$$
$$10y_{m_2} = 3a + 2b + c$$
$$10y_{m_3} = 3a + b$$
$$5y_{m_4} = a. \quad (4a–d)$$

Similar expressions are easily derived for triplets, quadruplets etc.

Results

The data for illustration of the model have been taken from the compilation of Hicks and Young.[6] The critical temper-

Table 3. The system *n*-pentane – ethylbenzene. *n*-Pentane, T^c = 469.5 K. Ethylbenzene, T^c = 617.1 K. Data from Ref. 11. x = mole fraction of *n*-pentane.

x	T^c		Some statistical criteria[a]	Quadruplets	Quintuplets
	Expt.	Eqn. (1)			
0.100	605.73	605.66	Residual squares sum	0.7738	0.0979
0.200	594.00	594.13	Mean residual	0.2600	0.0878
0.300	581.75	581.80	Residual mean	$-8.889 \cdot 10^{-3}$	$-1.222 \cdot 10^{-2}$
0.400	568.57	568.42	Standard deviation	0.311	0.111
0.500	554.17	554.02	Percentage deviation	0.0576	0.0201
0.600	538.78	538.76	Hamilton *R*-factor/%	0.0531	0.0189
0.700	522.83	522.82			
0.800	506.05	506.21			
0.900	488.72	488.67			

[a]Ref. 9.

Table 4. The system *n*-hexane – cyclopentane. *n*-Hexane, T^c = 507.3 K. Cyclopentane, T^c = 511.6 K. Data from Ref. 12. x = mole fraction of *n*-hexane.

x	T^c		Some statistical criteria[a]	Quadruplets	Quintuplets
	Expt.	Eqn. (1)			
0.100	511.60	511.55	Residual squares sum	0.1325	0.0373
0.200	511.14	511.16	Mean residual	0.0856	0.0500
0.300	510.54	510.59	Residual mean	$-4.111 \cdot 10^{-2}$	$1.444 \cdot 10^{-2}$
0.400	510.03	510.02	Standard deviation	0.129	0.0683
0.500	509.63	509.56	Percentage deviation	0.0253	0.0134
0.600	509.28	509.25	Hamilton *R*-factor/%	0.0238	0.0126
0.700	508.97	509.05			
0.800	508.70	508.84			
0.900	508.38	508.38			

[a]Ref. 9.

atures of the pure components have been taken from various handbooks and compilations in the literature (not specified here).

The system methane–propane. This system was studied by Reamer *et al.*[7] as well as by Sage *et al.*[8] In Table 1a the results of Reamer *et al.* as given in Ref. 6 are compared with values calculated from eqn. (1) using the parameters given in Table 5. Table 1a also gives some statistical criteria for the sake of comparison between quadruplets and quintuplets. As can be seen, an appreciable improvement is obtained by extending the calculations to quintuplets. Table 1b gives the same information for the data of Sage *et al.*[8] Again, a considerable improvement is obtained by using quintuplets.

The system n-*hexane* – n-*tridecane.* This system was studied by Pak and Kay.[10] In Table 2, data given in Ref. 6 are compared with those obtained with the model using the parameters given in Table 5. Again quintuplets give a considerable improvement.

The system n-*pentane* – *ethylbenzene.* This system was studied by Kay and Hissong.[11] In Table 3, data given in Ref. 6 are compared with those obtained with the model using the parameters given in Table 5. Results similar to those for the other systems are obtained.

The system n-*hexane* – *cyclopentane.* This system was studied by Hissong and Kay.[12] In Table 4, data given in Ref. 6 are compared with those obtained with the model using the parameters given in Table 5. Again, quintuplets improve the fit, although quadruplets give a satisfactory fit.

Discussion

The parameters obtained by a least-squares fit to eqn. (3) and using eqns. (4a–d) are given in Table 5. The values in parentheses are those for the same parameters calculated from those for the pure components assuming the system to behave ideally, i.e.

$$5y_{m_1} = 4y_1 + y_2$$

Table 5. Parameters obtained by a least-squares fit to eqn. (3). The parameters were then computed from eqns. (4a–d). The values within parentheses were obtained from eqns. (5a–d).

System	$5y_{m_1}$	$10y_{m_2}$	$10y_{m_3}$	$5y_{m_4}$
Methane – propane	1372	3359	3264	1819
[a]	(1133)	(2624)	(2982)	(1670)
[b]	1307	3385	3154	1827
	(1133)	(2624)	(2982)	(1670)
n-Hexane – *n*-tridecane	2934	6132	6467	3264
	(2706)	(5752)	(6091)	(3215)
n-Pentane – ethylbenzene	2551	5367	5756	2968
	(2495)	(5285)	(5581)	(2938)
n-Hexane – cyclopentane	2552	5079	5096	2560
	(2541)	(5090)	(5099)	(2554)

[a]Ref. 7. [b]Ref. 8.

$$10y_{m_2} = 2(3y_1 + 2y_2)$$

$$10y_{m_3} = 2(2y_1 + 3y_2)$$

$$5y_{m_4} = y_1 + 4y_2. \qquad (5a–d)$$

Since deviations from ideal behavior for most critical temperatures are positive, the experimental parameters are larger than those obtained from eqns. (5a–d). The only exception in this set of data is for the system *n*-hexane – cyclopentane, the behaviour of which is practically ideal over the small temperature range covered.

The standard deviations in temperature range from about 0.2 K down to 0.07 K for the systems treated. This is close to the experimental uncertainty given by Hicks and Young,[6] viz. about 0.05 K to 0.1 K. If a better fit is desired it is a simple matter to extend the treatment to sextuplets and higher multiplets.

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