Short Communication

# A Simple Approach to Binary Mixtures

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Recently an attempt was made to fit data for binary mixtures by using the binomial theorem.[1] However, in that paper the model was not fully developed. Various polynomials $\Sigma a_i x^i$ were tested in order to find an acceptable fit: this was to ask nature the wrong question. The polynomial corresponding to the model is given by the effective coordination number in the mixture (see below). In this paper the final model is given and tested on volumes and enthalpies of mixing as well as on the critical temperature of mixtures. The data of Ref. 1 are recalculated in order to check the values of the parameters of the model.

## The model

Consider a mixture of the two components A and B. In the mixture the average coordination number is $z$. For simplicity this number is taken as the nearest integer. At every moment in the dynamic equilibrium in the mixture a molecule of A or B is surrounded by $z$ other molecules, either A or B only or a mixture of both. Here several compositions and configurations exist. If the distribution is random their number is given by the binomial theorem, $(x_1 + x_2)^z$. This expression is dimensionless. In order to relate the various configurations in the mixture to a molar property $Y$, which varies with composition, one has to introduce weighting factors into the binomial expression with the same dimension as $Y$, giving eqn. (1) for $z = 5$ (the co-

$$Y = y_{5,0}x_1^5 + 5y_{4,1}x_1^4x_2 + 10y_{3,2}x_1^3x_2^2 + 10y_{2,3}x_1^2x_2^3$$
$$+ 5y_{1,4}x_1x_2^4 + y_{0,5}x_2^5 \qquad (1)$$

ordination number used in this paper) where $x_1$ and $x_2$ are stoichiometric mole fractions of the two components, $y_{5,0}$ and $y_{0,5}$ are values of the property $Y$ for the pure components, and $y_{2,3}, y_{3,2}$ etc. are values of the property $Y$ for the various mixed configurations. Observe that it is not necessary that the value of each configuration is equal to $10x_1^2x_2^3$ etc.; it is sufficient that it is proportional to it, the proportionality factor being included in $y_{2,3}$ etc.

In many cases $y_{5,0}$ and $y_{0,5}$ are known, and the parameters are obtained by a least-squares fit of eqn. (2), i.e. a third-

$$\Delta = (Y - y_{5,0}x_1^5 - y_{0,5}x_2^5)/x_1x_2 = 5y_{4,1}x_1^3 + 10y_{3,2}x_1^2$$
$$+ 10y_{2,3}x_1x_2^2 + 5y_{1,4}x_2^3 \qquad (2)$$

degree polynomial in $x_1$ or $x_2$, since $x_1 + x_2 = 1$.

## Examples

*Volume of mixing in the system* $CCl_4$–$C_6H_6$ *at 298 K.* Bottomley and Scott[2] measured the volume of mixing in the system $CCl_4$–$C_6H_6$ at various temperatures. Here the data at 298 K are used. In Fig. 1 experimental excess volumes $(\Delta V)$ are compared with those from the model. $\Delta V$ is defined by eqn. (3), where $v_1$ and $v_2$ are the molar volumes

$$\Delta V = V_{exp} - v_1x_1 - v_2x_2 \qquad (3)$$

of $CCl_4$ and $C_6H_6$, taken as 97.00 and 89.00 cm³, respectively. These values do not influence the fit to $\Delta V$: they are needed when computing the contribution to $V$ from each configuration. In Table 1 experimental and computed values of $\Delta V$ are compared, together with some quantities from a statistical analysis of the residuals. These quantities indicate the fit obtained and are denoted fitness parameters. Table 2 gives the parameters obtained by fitting to eqn. (2) above. The fit is the same as that obtained by
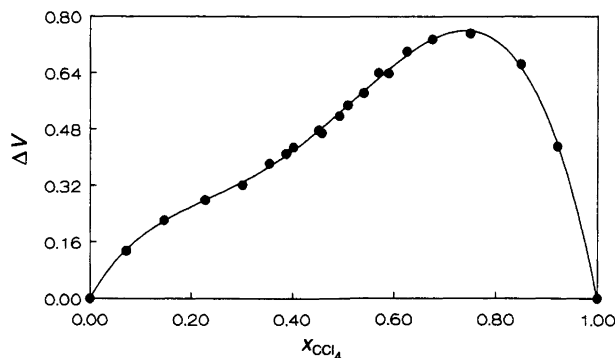


Fig. 1. $\Delta V$ plotted versus $x_{CCl_4}$ for the system $CCl_4$–$C_6H_6$ at 298 K. The curve has been computed with the parameters in Table 2. Data are taken from Ref. 2. ●, Experimental data.

Table 1. The system $CCl_4$–$C_6H_6$ at 298 K: experimental $\Delta V$ are compared with those computed from the model with the parameters in Table 2.[a]

| $x_{CCl_4}$ | $\Delta V_{exp}$ | $\Delta V_{calc}$ |
|---|---|---|
| 0.0722 | 0.001 35 | 0.001 38 |
| 0.1462 | 0.002 22 | 0.002 20 |
| 0.2278 | 0.002 79 | 0.002 79 |
| 0.3017 | 0.003 22 | 0.003 31 |
| 0.3544 | 0.003 83 | 0.003 74 |
| 0.3868 | 0.004 11 | 0.004 05 |
| 0.4010 | 0.004 29 | 0.004 20 |
| 0.4519 | 0.004 70 | 0.004 77 |
| 0.4584 | 0.004 70 | 0.004 85 |
| 0.4925 | 0.005 18 | 0.005 27 |
| 0.5091 | 0.005 49 | 0.005 48 |
| 0.5399 | 0.005 83 | 0.005 88 |
| 0.5694 | 0.006 41 | 0.006 25 |
| 0.5892 | 0.006 39 | 0.006 50 |
| 0.6247 | 0.007 01 | 0.006 90 |
| 0.6749 | 0.007 35 | 0.007 35 |
| 0.7499 | 0.007 52 | 0.007 59 |
| 0.8492 | 0.006 65 | 0.006 56 |
| 0.9202 | 0.004 32 | 0.004 40 |

Fitness parameters:

| | |
|---|---|
| Residual squares sum | $= 1.32 \times 10^{-7}$ |
| Mean residual | $= 6.90 \times 10^{-5}$ |
| Standard deviation | $= 9.70 \times 10^{-5}$ |
| Hamilton $R$-factor (%) | $= 1.60$ |

[a]Data from Ref. 2.



Fig. 2. The fraction $\alpha_{i,j}$ of each mixed configuration plotted versus $x_{CCl_4}$ for the system $CCl_4$–$C_6H_6$ at 298 K. The curves have been computed with the parameters in Table 2. Data are taken from Ref. 2. Values of $i,j$ as follows: +, 4,1; ▲, 3,2; +, 2,3; ●, 1,4.

the heat of mixing, $\Delta H$, is plotted versus $x_{hexadecane}$. In Table 3 experimental and computed values of $\Delta H$ are compared. The fitness parameters are also given. The fit is slightly better than that of Larkin et al., who fitted their data with two constants instead of four, as required by the model. Table 2 gives the parameters found by fitting to eqn. (2) above.

Bottomley and Scott, who also fitted $\Delta V$ to a third-degree polynomial. In order to illustrate the contribution of each configuration to the total volume, $V$, Fig. 2 gives the fraction, $\alpha_{i,j}$, of each mixed configuration as a function of $x_{CCl_4}$. The contributions from the pure components are excluded. No mixed configuration contributes more than about 40 % to the total.

Enthalpy of mixing in the system 2-methylpentane–n-hexadecane at 298 K. Larkin et al.[3] measured the heats of mixing of hexadecane with hexane isomers at 298 K. Here the system 2-methylpentane–n-hexadecane is chosen. In Fig. 3
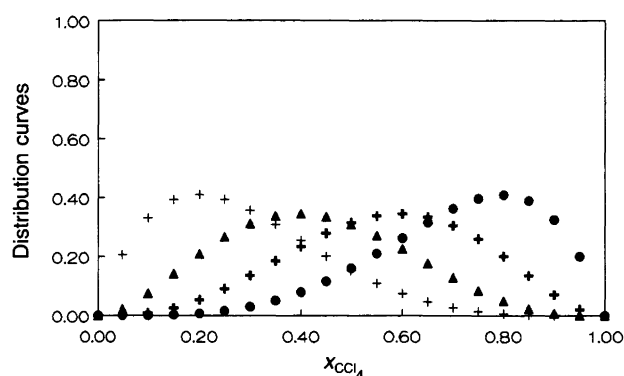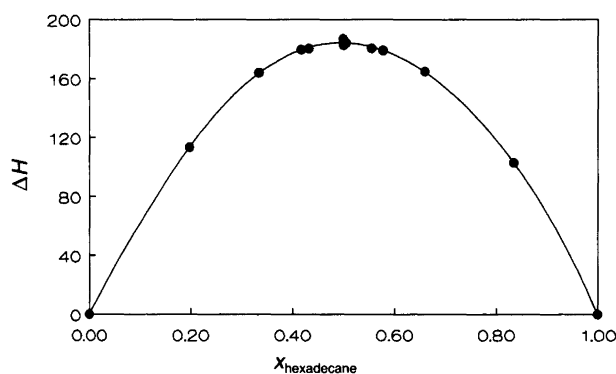


Fig. 3. Heat of mixing, $\Delta H$, plotted versus $x_{hexadecane}$ for the system 2-methylpentane–n-hexadecane at 298 K. The curve has been computed from eqn. (2) with the parameters in Table 2. Data are taken from Ref. 3. ●, Experimental data.

Table 2. Parameters obtained by a least-squares fit to eqn. (1) or (2).

| System | $Y$ | $y_{5,0}$ | $y_{4,1}$ | $y_{3,2}$ | $y_{2,3}$ | $y_{1,4}$ | $y_{0,5}$ |
|---|---|---|---|---|---|---|---|
| $CCl_4$–$C_6H_6$ | $V$ | 89.0 | 90.61 | 92.20 | 93.81 | 95.41 | 97.0 |
| $i$-$C_6H_{14}$–$C_{16}H_{34}$ | $\Delta H$ | 0 | 127.3 | 253.2 | 193.0 | 158.0 | 0 |
| $C_4H_{10}$–$C_7H_{16}$ | $T_c$ | 540.3 | 527.0 | 510.5 | 486.7 | 232.8 | 425.2 |
| $CH_4$–$C_3H_3$[a] | $T_c$ | 369.9 | 363.2 | 326.2 | 335.5 | 274.8 | 190.7 |
| $CH_4$–$C_3H_3$[b] | $T_c$ | 369.9 | 365.2 | 316.4 | 334.0 | 262.4 | 190.7 |
| $C_6H_{14}$–$C_{13}H_{28}$ | $T_c$ | 677.0 | 652.8 | 647.0 | 612.2 | 587.4 | 507.3 |
| $C_5H_{12}$–$C_6H_5C_2H_5$ | $T_c$ | 617.1 | 593.3 | 576.0 | 556.9 | 536.9 | 469.5 |
| $C_6H_{14}$–$C_5H_{10}$ | $T_c$ | 511.6 | 511.9 | 509.6 | 508.1 | 255.0 | 507.3 |

[a]Reamer. [b]Sage.

Table 3. The system 2-methylpentane–n-hexadecane at 298 K: experimental heats of mixing, $\Delta H_{exp}$, compared with values computed from eqn. (2) using the parameters in Table 2.[a]

| $x_{hexadecane}$ | $\Delta H_{exp}$ | $\Delta H_{calc}$ |
|---|---|---|
| 0.1972 | 113.5 | 113.59 |
| 0.3335 | 164.0 | 163.59 |
| 0.4166 | 179.6 | 179.36 |
| 0.4318 | 180.4 | 181.03 |
| 0.4996 | 186.9 | 184.03 |
| 0.5000 | 182.7 | 184.03 |
| 0.5050 | 184.2 | 184.03 |
| 0.5545 | 180.5 | 181.33 |
| 0.5769 | 179.1 | 178.96 |
| 0.6587 | 164.9 | 164.39 |
| 0.8336 | 102.9 | 102.96 |

Fitness parameters:

| | | |
|---|---|---|
| Residual squares sum | = | 11.64 |
| Mean residual | = | 0.662 |
| Standard deviation | = | 1.29 |
| Hamilton $R$-factor (%) | = | 0.613 |

[a]Data in J mol$^{-1}$ from Ref. 3.

Table 4. The critical temperature in the system n-butane–n-heptane: experimental $T_c$ values compared with values computed from eqn. (1) using the parameters in Table 2.

| $x_{butane}$ | $T_{c(exp)}$ | $T_{c(calc)}$ |
|---|---|---|
| 0 | 540.3 | 540.30 |
| 0.159 | 528.8 | 528.79 |
| 0.4249 | 504.8 | 504.78 |
| 0.6311 | 481.9 | 481.85 |
| 0.8010 | 459.8 | 459.25 |
| 0.9401 | 436.3 | 436.65 |
| 0.1 | 533.38 | 533.30 |
| 0.2 | 525.43 | 525.49 |
| 0.3 | 516.73 | 516.82 |
| 0.4 | 507.27 | 507.29 |
| 0.5 | 496.95 | 496.89 |
| 0.6 | 485.61 | 485.58 |
| 0.7 | 473.05 | 473.19 |
| 0.8 | 458.65 | 459.40 |
| 0.9 | 444.09 | 443.67 |
| 1 | 425.2 | 425.20 |

Fitness parameters:

| | | |
|---|---|---|
| Residual squares sum | = | 1.210 |
| Mean residual | = | 0.164 |
| Standard deviation | = | 0.348 |
| Hamilton $R$-factor (%) | = | 0.056 |

The critical temperature in n-butane–n-heptane mixtures. Kay[4] measured the critical temperature for the system n-butane–n-heptane. The data used in this paper are taken from Ref. 5. In Fig. 4 the critical temperature, $T_c$, is plotted versus $x_{butane}$. The curve is that of the model. In Table 4
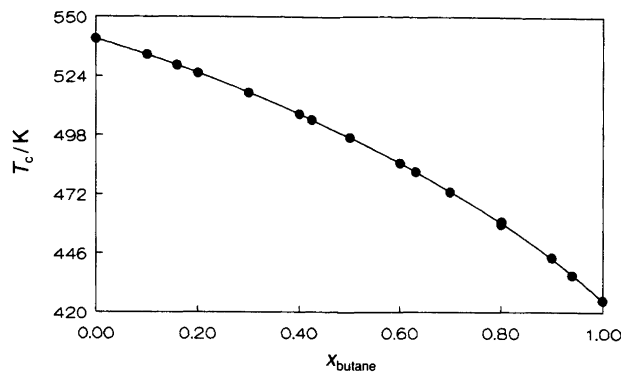


Fig. 4. The critical temperature, $T_c$, plotted versus $x_{butane}$ for the system n-butane–n-heptane. The curve has been computed from eqn. (1) with the parameters in Table 2. Data are taken from Ref. 4. ●, Experimental data.

experimental and computed values of $T_c$ are compared. The fit is acceptable, as seen from the fitness parameters. The critical temperatures of the pure components have been taken as 540.3 K for heptane and 425.2 K for butane. Table 2 gives the parameters found by fitting to eqn. (1).

Recalculation of the data in Ref. 1. The data in Ref. 1 have been recalculated using eqn. (1) in order to compare the results of the use of eqn. (2), which was used in Ref. 1. The results are given in Table 2. The difference from Ref. 1 is small.

## Discussion

The model outlined above gives some legitimacy to the power expansions used by many workers to fit data for mixtures, and is in keeping with the present conception of mixtures with $z$ being an experimentally available quantity. It is an (admittedly) simplifying assumption to choose the nearest integer $z$. Another simplifying assumption is that only nearest neighbours are taken into account. This implies the assumption that background effects vary negligibly with composition. On the other hand, there is no need to consider many-body interactions: the results are manifested in the various $y$ parameters, which are determined by least-squares methods. It is hoped that the parameters introduced in this paper may provide a helpful route towards a useful treatment of mixtures.

The extension to several components is obvious.

## References

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