CAPABILITY OF A GROUP CONTRIBUTION EQUATION OF STATE FOR DESCRIBING PHASE EQUILIBRIA IN HYDROCARBON SYSTEMS

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Abstract

Phase equilibrium calculations are performed for alkane-aromatics-naphtene ($+CO_2$) systems to test the ability of the earlier proposed Boublík-van der Waals group contribution equation of state. An important feature of the model is that it does not contain binary (or higher order) mixture parameters. It was found that the model fitted to pure component vapour pressure data performs poorly for mixtures, but if mixture data are also used to estimate model parameters the prediction is acceptable.

Keywords: equation of state group contribution phase equilibria, parameter estimation hydrocarbon systems.

1. The Model and Estimation Methods Used

A group contribution equation of state model has been proposed by FARKAS et al. [1]. In this paper the capability of this model is studied.

In a group contribution model the molecules are considered as composed of groups, and these groups take part in the interactions between molecules.

The pressure (P) is expressed through the compressibility factor (Z):

$$P = Z\frac{RT}{V} \tag{1}$$

R is the gas constant, T is the temperature, V is the molar volume.

The compressibility factor itself is the sum of two parts:

$$Z = Z_{rep} + Z_{attr} \tag{2}$$

The repulsive part depends on the reduced density $\tilde{\rho} = \frac{V^*}{V}$:

$$Z_{rep} = \frac{1 + (3\alpha - 2)\,\tilde{\rho} + \left(\frac{11}{2}\alpha^2 - \frac{9}{2}\right)\tilde{\rho}^2 - \left(\frac{17}{4}\alpha - \frac{13}{4}\right)\tilde{\rho}^3}{(1 - \tilde{\rho})^3} \tag{3}$$

where V^* is the hard core volume, V is the molar volume.

V^* is taken as temperature dependent:

$$V^* = \frac{\pi \sqrt{2}}{6} V^{00} \left[1 - C \exp \left(-\frac{3u^0}{kT} \right) \right]^3 \tag{4}$$

V^{00} and u^0/k are the parameters. C is constant and is taken as 0.12.

In the group contribution context the hard core volume is added from those of the groups:

$$V^* = \sum_i v_i V_i^* \tag{5}$$

where v_i is the number of groups i in the molecule, V_i^* is the hard core volume of group i.

The parameter α in *Eq.* (3) characterizes the non-sphericity of the molecule.

The attractive part contains the a cohesive energy parameter:

$$Z_{attr} = -\frac{a}{VRT} \tag{6}$$

In the group contribution context the cohesive energy is the sum of the interactions:

$$a = a_{DIS} = \frac{1}{2 \sum_k v_k Q_k} \sum_i \sum_j v_i Q_i v_j Q_j U_{ij} \tag{7}$$

Q_i is the number of contact points within a group of type i, v_i is the number of groups of type i in the molecule, and for certain types of contacts the U_{ij} interaction energy is the geometric mean of the $i - i$ and $j - j$ interaction energies (Berthelot's rule).

$$U_{ij} = \sqrt{U_{ii} U_{jj}} \tag{8}$$

If the Berthelot's rule holds, the model does not contain specific interaction parameters, neither for contacts between groups within a molecule nor for contacts between groups of different molecules. If the interactions are of non-specific nature Berthelot's rule is a good approximation. An example of case when it is not fulfilled is the hydrogen bonding.

The U_{ii} parameter is then considered temperature dependent:

$$U = U^0 \frac{T}{T^0} + H^0 \frac{T^0 - T}{T^0} + C^0 \left(\ln \frac{T}{T^0} - \frac{T^0}{T} + 1 \right) \tag{9}$$

Eq. (2) has been derived by Boublík [2], while *Eq.* (6) comes from van der Waals, the model is termed by the authors as BvdW.

As the molar volume to be substituted into *Eqs.* (1), (3) and (6) is not known, it should be sought as the root of *Eqs.* (2), (3) and (6). There are several roots, two of them correspond to the liquid and vapour phase in equilibrium, respectively.

These liquid and vapour molar volumes may also be compared with experimental (density) values, if they are available.

The α non-sphericity parameter is generally calculable from the geometry of the molecule. For hydrocarbon molecules appearing in this study it is approximated by linear function of the number of carbon atoms in the molecule:

$$\alpha = e^* n_c + d \tag{10}$$

The third parameter of the temperature dependence of interaction energies is taken as $C^0 = 0$.

E.g. in an alkane molecule there are two kinds of groups: CH_2 and CH_3.

The parameters to be estimated: V^{00} u^0/k U^0 and H^0 for the CH_2 and CH_3 groups, and e and d for the whole homologous series.

Substituting the (8) Berthelot's rule into $Eq.$ (7) the following expression is obtained:

$$a = \frac{1}{2} \frac{1}{\sum_j Q_j} \left(\sum_i Q_i \sqrt{U_{ii}} \right)^2 \tag{11}$$

Based on models proposed in the literature we compared the forms containing end neglecting the $\sum_j Q_j$ term in the denominator, and found better fit without the $\sum_j Q_j$ term [1]. The rearrangement results in (when applied to n-alkanes)

$$\sqrt{2a} = \sum_i Q_i \sqrt{U_{ii}} = 2Q^1_{CH_3} \sqrt{U_{CH_3 CH_3}} + (n-2)\, Q^1_{CH_2} \sqrt{U_{CH_2 CH_2}} \tag{12}$$

From pure component vapour pressure data or from mixture total pressure data the parameter estimation criterion used was the minimization of relative deviations, augmented with the term k for ridge regression [3] in certain cases:

$$\phi = \sum_i^N \left(\frac{P_i - \hat{P}_i}{P_i} \right)^2 + k \sum_j^p \frac{\hat{\beta}_j^2}{\beta_{j0}^2} = \min \tag{13}$$

where P_i is the measured vapour pressure, $\hat{P}_i$ is the estimated value, $\hat{\beta}$ denotes the estimated parameters.

It is usual to choose the minimization of relative deviations, as the relative error is constant. The last term contains a guessed value for the parameters in the denominator.

From mixture data, where measured vapour phase mole fractions were also available, the criterion was

$$\phi = \sum_i^N \left[\left(\frac{P_i - \hat{P}_i}{P_i} \right)^2 + \sum_j (y_{ji} - \hat{y}_{ji})^2 \right] = \min \tag{14}$$

(in some cases augmented with the ridge term as well), where y_{ji} is the vapour phase mole fraction of component j in the ith measurement point.
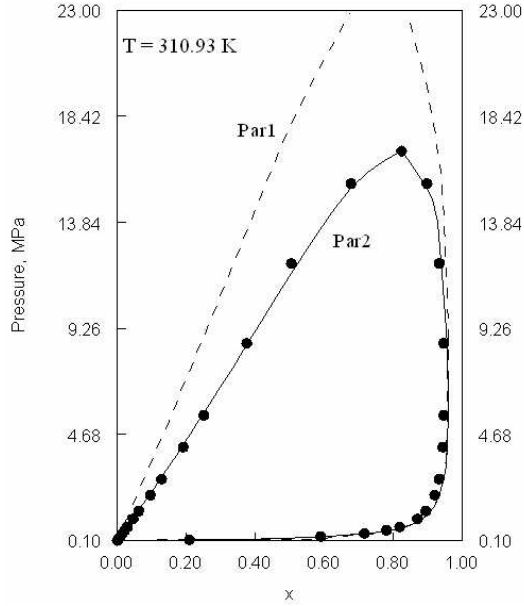

Fig. 1. P vs. x, y diagram for methane-pentane mixture, $\bullet$: experimental points

2. Estimation of Model Parameters, 1st Attempt

We found that the first few members of the homologous series may not be well described by building them from the basic groups, e.g. methane, ethane, propane, butane from the CH_2 and CH_3 groups, thus they were treated as entities themselves. The rest of the members of homologous series were taken as built from the basic groups, neglecting the effect of their environment. Carbon dioxide and nitrogen were also considered as specific compounds. The estimated parameter set obtained by the 1st attempt will be denoted as par1.

n-alkane Homologous Series

Building the molecules from the CH_2 and CH_3 groups the estimated α values in *Eq.* (3) were physically unacceptable ($\alpha < 1$) for C_5 and C_6. Thus the concept of building molecules was changed, instead of building the alkane molecules from CH_2 and CH_3 groups C_5H_{12} and CH_2 were used as bricks. Thus instead of *Eq.* (12)
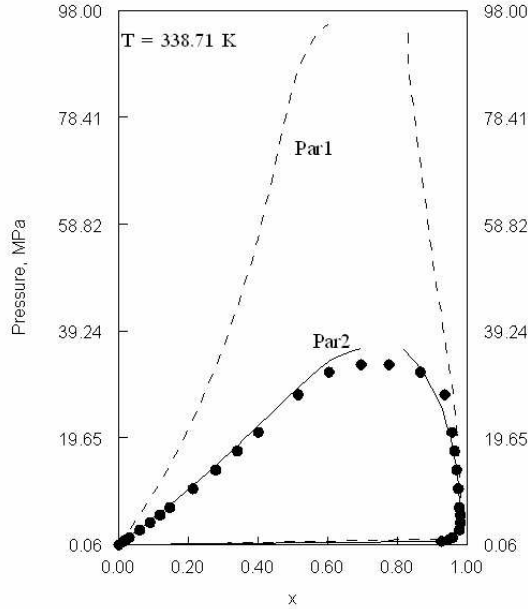
Fig. 2. P vs. x, y diagram for methane-benzene mixture, •: experimental points

the following one is valid:

$$\sqrt{2a} = \sum_m Q_m \sqrt{U_{mm}} = 2Q^1_{CH_3}\sqrt{U_{CH_3CH_3}} + (n-2)\,Q^1_{CH_2}\sqrt{U_{CH_2CH_2}} \quad (15)$$

Applying *Eq.* (5) to the case:

$$V^* = V^*_{C_5H_{12}} + (n-5)\,V^*_{CH_2}$$

with V^*_i parameters taken as temperature dependent. The parameters to be estimated were V^{00}, $u^0/k\,U^0$ and H^0 for the C_5H_{12} and CH_3 groups, and e and d for the whole homologous series, thus altogether 8+2 parameters.

Aromatic Homologous Series

The usual way of treating aromatic (alkyl-aromatic) compounds in group contribution context considers aliphatic CH_2 and CH_3 groups and aromatic CH and CH_2 groups. In order to reduce the number of groups (and thus the number of parameters), based on the experience gained with alkanes C_6H_6 and CH_2 groups were only considered, the number of parameters to be estimated was again 8+2. It is worth remarking that the estimated α values in *Eq.* (3) were physically unacceptable ($\alpha < 1$)
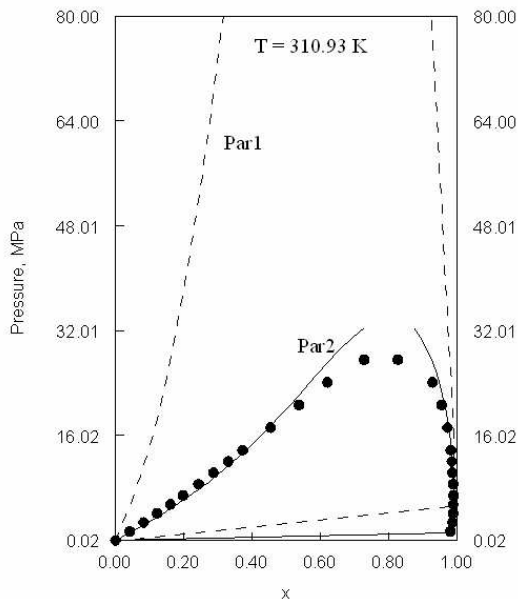
Fig. 3. P vs. x, y diagram for methane-cyclohexane mixture, •: experimental points

for benzene and toluene with least squares method, while ridge regression using $k = 4 \cdot 10^{-4}$ as ridge parameter gave reasonable values.

Cycloalkane (Naphtene) Homologous Series

Using an analogous approach as proved useful with aromatics the molecules were built up from cyclohexane (cC_6) and CH_2 groups. The methyl-cyclohexane data were neglected during parameter estimation as its normal boiling point does not fit to a smooth curve. Again the least squares regression gave physically unacceptable α values, those estimated through ridge regression were reasonable.

3. Prediction Results for the 1st Attempt

Here estimated parameter set par1 was used. The absolute difference between measured and predicted total pressure data (Pa) were in the range 0.3-1.6 for pentane-hexane, 1.9-10.0 for hexane-octane, 1.0-70.4 for ethane-hexane. This experience shows that the larger the difference in size of the molecules, the worse the prediction, while pure component vapour pressures (used in estimating parameters) are well predicted-interpolated. This offers the conclusion that the mixing rules are not appropriate. This type of weakness of equation of state models is usually cured by
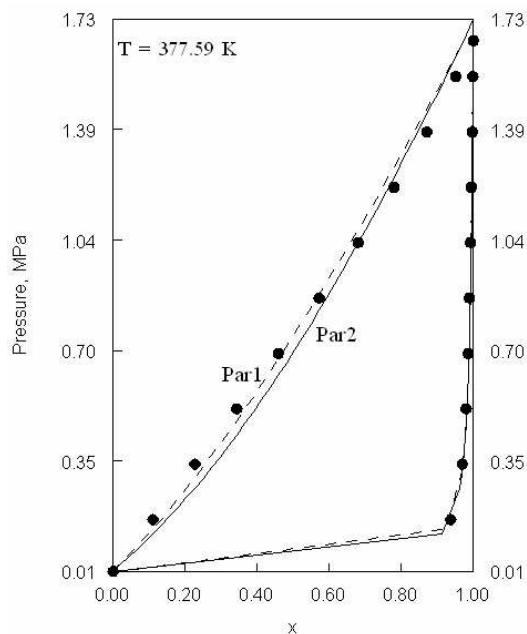
Fig. 4. P vs. *x*, *y* diagram for butane-decane mixture, •: experimental points

introducing empirical interaction parameters in *Eq.* (8) as deviation from Berthelot's rule, estimated from mixture (typically binary) data. We decided not to follow this route as our further aim was to use the model in continuous thermodynamics, where simpler models are preferable and all parameters should be expressed as function of carbon number or molecular mass. Experience gained during calculation hints that the estimated parameters are heavily correlated thus different parameter sets are able to give the same goodness of fit. Considering that pure component properties (used in estimating parameters) were described well, another parameter set is desired allowing good abilities for predicting mixture properties as well, keeping good description of pure component properties.

4. Improving Parameter Estimation 2nd Attempt

The parameter set of discrete components except methane (ethane, propane, butane, carbon dioxide and nitrogen) were kept from par1.

Methane, as its pure component vapour pressure measurement range (concerning temperature and pressure) is very far from the temperature and pressure range where it is in mixtures, caused special difficulties. The estimated parameter set obtained from pure component vapour pressure fit was not able to describe the mixture behaviour (methane-propane, methane-butane) of methane. Even the pa-

rameters estimated considering both pure component vapour pressure and mixture data were not useful. Thus we had to discard the pure component experimental data for methane and estimated the methane parameters from mixture data alone, using *Eq.* (12). These parameters then were not appropriate to calculate pure component vapour pressure for methane, but this was not the task. When estimating methane parameters from methane-propane, methane-butane mixture data, the parameters of the other component were not re-estimated, they were kept as fitted to the respective pure component data.

n-alkane Homologous Series

For obtaining a better parameter set experimental data 'orthogonal' to the pure component properties are to be used, certain binary data sets were selected for that purpose, namely C_1-C_5, C_1-C_7, C_1-C_{10}, C_2-C_5, C_2-C_{10} total pressure and vapour-liquid equilibrium composition data, in wide temperature range. This way the correlation between estimated parameters had been reduced, thus the least squares criterion was sufficient.

cycloalkane (naphtene) and aromatics homologous series

The same experience was gained for these compounds as for the alkanes: the parameters estimated by fitting the model to pure component data gave good prediction for pure component properties but the results for mixture properties were devastating. When CH_2 group parameters estimated from alkanes are kept for naphtenes and aromatics, the description of binary equilibria is much improved without using further binary data. This offered the additional advantage of having smaller number of parameters. If binary data sets (methane-cyclohexane and ethane-cyclohexane for naphtenes, methane-benzene, methane-toluene, ethane-benzene for aromatics) are also used to the parameter estimation, there is no further improvement. Thus par2 parameter set was obtained by using CH_2 group parameters estimated from alkanes and no binary information is utilized.

5. Prediction results for the 2nd attempt

Figs. 1,2,3 and *4* show the pressure-composition diagram for methane-pentane, methane-benzene, methane-cyclohexane and butane-decane mixture with both parameter sets (par1 and par2). The general conclusion is that the par2 parameter set gives much better results for mixtures containing lower carbon number (or smaller alkyl chain) molecules, while the difference disappears with increasing carbon number.
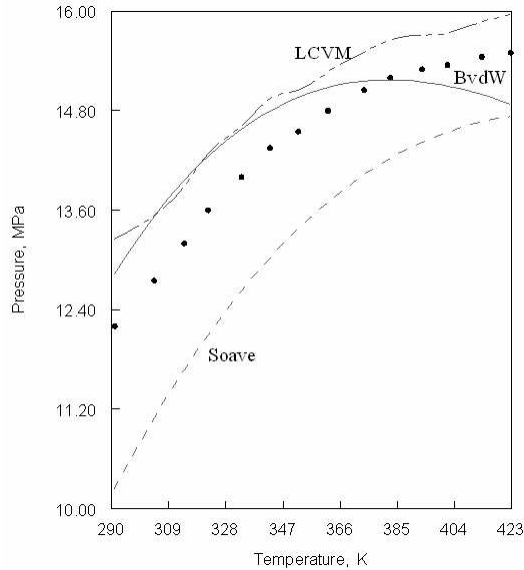
Fig. 5. Calculated bubble pressure versus temperature for Daridon's mixture A, •: experimental points

As the parameter set par2 proved to be superior, it was used exclusively for prediction. The values of estimated group parameters for homologous series are given in *Table 1*, those for the components treated as discrete compounds are given in *Table 2*.

Table 1. Parameters for the groups in three homologous series

	CH_2	Paraffins C_5H_{12}	Aromatics C_6H_6	Naphtenes C_6H_{12}
U^0	-0.6307	-0.4748	-0.9308	-0.5672
H^0	-0.7712	-0.5979	-1.1147	-0.6710
u^0/k	434.405	147.627	186.8572	217.5446
V^{00}	$1.5959 \cdot 10^{-5}$	$7.1887 \cdot 10^{-5}$	$6.3351 \cdot 10^{-5}$	$6.4741 \cdot 10^{-5}$
e		0.06766	0.07330	0.06458
d		0.88449	0.66766	0.92178

Using the parameter set in *Tables 1* and *2* predictions were made for synthetic multicomponent systems. *Fig. 5* shows the results for the bubble pressure of mixture containing methane (43.7%), decane (46.1%) and heavy fraction (10.2%), the latter

consisting of paraffins from C_{20} to C_{30} (A mixture) [4]. The results achieved by the LCVM equation of state model found in the literature [5] and those by the Soave [6] equation of state (our calculation) are also given for comparison.

Fig. 6 gives results for a mixture containing paraffin components from methane to tetra-decane and carbon dioxide up to 90% [7], D mixture+CO_2.

Fig. 7 shows the flash calculation results of a 24 components synthetic oil (mixture 3), [8] at 323.2 K. This oil contains CO_2, paraffins, aromatics and naphthenes.
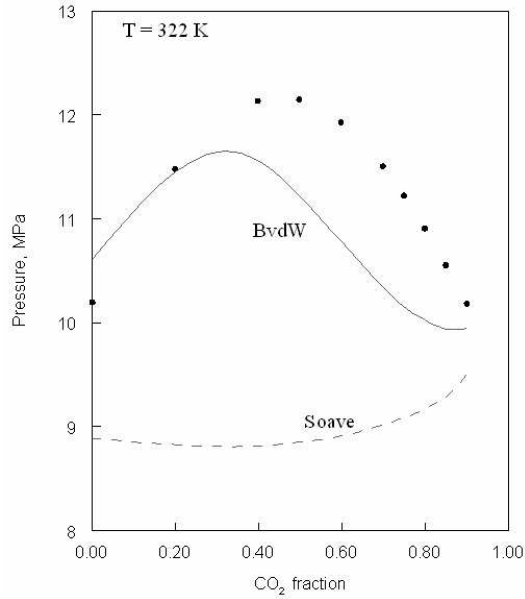

Fig. 6. Calculated bubble pressure versus concentration of CO_2 for Turek's mixture D, ·: experimental points

Table 2. Parameters for discrete compounds

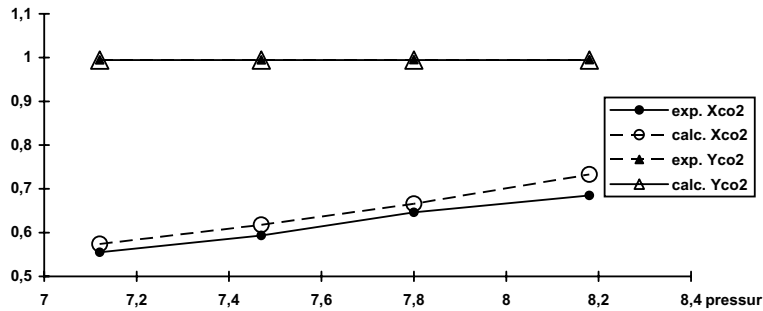|	methane	ethane	propane	butane	CO_2	N_2
u^0/k	0	58.2051	97.0991	122.8673	62.9862	0
U^0	−0.5146	−1.1939	−2.1329	−3.3406	−0.6760	−0.2626
H^0	−0.5799	−1.6166	−2.8342	−4.3361	−0.9272	−0.2867
V^{00}	$2.9141 \cdot 10^{-5}$	$3.5818 \cdot 10^{-5}$	$4.7010 \cdot 10^{-5}$	$5.9623 \cdot 10^{-5}$	$1.7290 \cdot 10^{-5}$	$2.2991 \cdot 10^{-5}$
α	1	1	1	1	1.1623	1

Fig. 7. Calculated and experimental concentration of CO_2 versus pressure from flashing

List of Symbols

a	cohesive energy parameter
H^0	parameter of temperature dependence of the interaction energy
P	pressure
Q_i	the number of contact points within a group of type i,
U_{ij}	interaction energy is the geometric mean of the $i-i$ and $j-j$ interaction energies
U^0	parameter of temperature dependence of theinteraction energy
u^0/k	parameter of temperature dependence of the hard core volume function
T	temperature
V	molar volume
V^{00}	parameter of the hard core volume function
V^*	hard core volume
y_{ji}	the vapour phase mole fraction of component j in the ith measurement point
Z	compressibility factor
α	non-sphericity parameter
$\hat{\beta}$	estimated parameters parameters
v_i	the number of groups of type i in the molecule.

Acknowledgements

References

[1] FARKAS, I. – KEMÉNY, S. – THURY É.– DEÁK, A., Hung. J. Ind. Chem., in press.

[2] BOUBLÍK, T., *Mol. Phys.* **68** (1989) pp. 191–198.

[3] NGO, S. H. – KEMÉNY, S. – DEÁK, A.: Chemometrics and Intelligent Chemical Laboratory Systems, **72** (2004) pp. 185–194.

[4] DARIDON, J. L. – XANS, P. – MONTEL, F.: Fluid Phase Equilibria **117** (1996) pp. 241–248.

[5] BOUKOUVALAS, C. J. – SPILIOTIS, N. – COUTSIKOS, PH. – TZOUVARAS, N.– TASSIOS, D., Fluid Phase Equilibria **92**, (1994) p. 75.

[6] SOAVE, G.: Chem. Eng. Sci. **27** (1972) 1197.

[7] TUREK, E. A. – METCALFE, R. S.– YARBOROUGH, L.– ROBINSON, R. L. JR., 1981. Phase Equilibria in Carbon Dioxide-Multicomponent Hydrocarbon System: Experimental Data and an Improved Prediction Technique, SPE Reprint Series N0. 15 – Phase Behavior, Soc. Of Pet. Engr., Dallas, Texas.

[8] ANGELOS, C. P. – BHAGWAT, S. V., *Fluid Phase Equilibria*, **72** (1992) pp. 189–209.