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Vapour Liquid Equilibrium in Asymmetric Mixtures of n-Alkanes with Ethane

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The paper presents a vapour liquid equilibria study in binary mixtures of n-alkanes with high dimensional asymmetry. Each mixture contains ethane and alkanes higher than eicosane. Calculations were done using two equations of state, Peng-Robinson (PR) and Soave (SRK), in combination with van der Waals mixing rules, corrected with two interaction parameters. A limited temperature dependence of the interaction parameters was found.

The correlations between the interaction parameters and the number of carbon atoms of the higher n-alkane led to equations valid for systems ethane + C_3 up to C_{44}.

The results of the prediction calculations were good, both with PR and SRK.

Key Words: Vapour liquid equilibrium, Interaction parameters, Asymmetric mixtures

Introduction

Fluid phase equilibrium in binary n-alkanes mixtures of very large size difference was studied in the last decade to find an answer to the practical problems arising in high depth hyperbaric reservoirs of oil and natural gas or in the gas-slurry processes in the Fischer-Tropsch synthesis. Experimental data are reported for systems of low alkanes in supercritical state (methane, ethane and propane) and high normal or branched alkanes, up to hexacontane.

Describing the vapour liquid equilibria (VLE) in these systems is a challenge for any given model, and different attempts are made mainly because the prediction capacities of the models are rather poor and empirical. For example, the molecular simulation based on a united-atom force field is considered in describing the VLE of the system ethane-tetracontane at constant pressure, [1]. Calculations based on the description of the liquid phase through Excess Gibbs Energy models, G^E, and the vapour phase using an equation of state, EOS, (G^E – EOS) are also reported to be successful considering the system ethane-eicosane at different temperatures [2]. More recently, the van der Waals equation of state has been successfully used with the thermodynamically consistent Wong-Sandler mixing rules to determine the critical properties of high alkanes, [3,4]. Equations of state (EOS) for long chain alkanes based on the statistical-mechanical perturbation theory have lately been reported, as is the case with the three parameters equation introduced by Eslami, [5], for n-alkanes up to eicosane. However, the prediction of the VLE is widely made using the cubic equations of state in combination with mixing rules including interaction parameters.

In this paper we examine the VLE of the binary systems of ethane and higher n-alkanes components (from eicosane to tetratetracontane). In the VLE calculations we use two phenomenological EOS: Peng-Robinson (PR, [6]) and Soave (SRK, [7]). We develop correlations between interaction parameters and the number of carbon atoms of the higher n-alkane and we use the estimated values in the VLE prediction calculations. Considering mediated values of the parameters on the investigated temperature range, prediction calculations are also made.

Review of the Models

The standard cubic EOS may be generalised using the following expression:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v^2 + uvb + wb^2} \tag{1}$$

The parameters u and w have certain values for each EOS:

PR: u = 2 w = -1   SRK : u = 1 w = 0

Both equations are mentioned in specialised studies as suitable for describing VLE of hydrocarbons, but both were originally developed for systems of short chain alkanes.

The temperature dependent parameter, a(T) and the parameter b are calculated using the critical parameters T_c, P_c and the acentric factor, ω:

$$\begin{aligned} a &= \tfrac{R^2 \cdot T_c^2}{P_c} \cdot \Omega_a \cdot \beta(T_r) \\ \beta(T_r) &= [1 + m(1 - T_r^{0.5})]^2 \\ m &= \alpha_1 + \alpha_2 \cdot \omega - \alpha_3 \cdot \omega^2 \end{aligned} \tag{2}$$

$$b = \frac{R \cdot T_c}{P_c} \cdot \Omega_b \tag{2a}$$

The parameters Ω_a , Ω_b, α_1, α_2 and α_3 depend on the EOS and are presented in Table 1 for the cubic equations that we used:

Table 1. Characteristic values of the parameters in EOS

EOS	Ω_a	Ω_b	α_1	α_2	α_3
SRK	0.42747	0.0866	0.48	1.574	0.176
PR	0.45724	0.0778	0.37464	1.5422	0.2699

For binary mixtures the following mixing rules are used:

$$a = \sum_{i=1}^{2}\sum_{j=1}^{2} X_i X_j a_{ij} \quad a_{ij} = (a_i a_j)^{1/2}(1-k_{ij}) \quad i,j=\overline{1,2} \tag{3}$$

$$b = \sum_{i=1}^{2}\sum_{j=1}^{2} X_i X_j b_{ij} \quad b_{ij} = \frac{1}{2}(b_i + b_j)(1-h_{ij}) \tag{4}$$

The mixing rules employ two interaction parameters, k_{ij} and h_{ij}.

The values of the interaction parameters are calculated by minimising an objective function in conjunction with a Bubble P isothermal algorithm:

$$FOBP = \sum_{i=1}^{NEXP}\left(\frac{P_i^{\exp} - P_i^{calc}}{P_i^{\exp}}\right)^2 \tag{5}$$

The average absolute deviation in pressure estimation, AADP, is used for estimating the quality of the VLE calculations. For a data set with NEXP experimental points, AADP is

$$AADP = \frac{1}{NEXP}\sum_{i=1}^{NEXP}\left|\frac{P_i^{\exp} - P_i^{calc}}{P_i^{\exp}}\right|100 \tag{6}$$

Database

Different specialised sources mention and use different values for the critical parameters of the components. In this paper the critical parameters of ethane are those given by Reid [8] and the values for the heavy components are calculated using the correlations of Magoulas and Tassios [9].

In the VLE calculations we used literature data, presented in Table 2.

Table 2. Experimental database for binary systems of ethane and n-alkanes

n-alkane	T / K	NEXP	Ref.
eicosane ($C_{20}H_{44}$)	323.2; 373.2; 400	6; 6; 7	[10]
	323.2; 373.2	9; 9	[10]+[11]
	300; 350; 423.2; 450; 473.2; 572.9	10; 14; 9; 6; 4; 4	[11]
docosan ($C_{22}H_{46}$)	310; 330; 350	5; 9; 7	[12]
tetracosane ($C_{24}H_{50}$)	330; 340; 350	7; 7; 4	[13]
octacosane ($C_{28}H_{58}$)	348.2; 373.2; 423.2	10; 7 ; 7	[10]
	373.2	11	[10]+[14]
	473.2; 573.2	4; 4	[14]
hexatriacontane ($C_{36}H_{74}$)	373.2; 423.2	7; 6	[10]
tetratetracontane ($C_{44}H_{90}$)	373.2; 423.3	9; 6	[10]

Results and Discussion

The VLE calculations were done using PR and SRK EOS coupled with mixing rules corrected first with one and then with two interaction parameters. The results are presented in Table 3.

Both equations of state provide good results, and the use of a second interaction parameter ($h_{ij} \neq 0$) leads to a significant improvement in the quality of the calculations; therefore, further prediction calculations were carried out by using only two interaction parameters.

Table 3. Results of the VLE calculations

T / K	EOS: PR			EOS: SRK		
	k_{ij}	h_{ij}	AADP/ %	k_{ij}	h_{ij}	AADP / %
ethane – n-eicosane						
300	0.0176	0	1.10	0.0188	0	1.18
	0.0247	0.0179	0.61	0.0231	0.0117	1.02
323.2	-0.0253	0	7.37	-0.0240	0	7.39
	0.0179	0.0209	0.67	0.0216	0.0211	0.77
323.2	-0.0167	0	8.44	-0.0139	0	8.37
	0.0324	0.0258	1.71	0.0316	0.0231	1.38
350	-0.0107	0	9.45	-0.0071	0	9.45
	0.0292	0.0237	1.26	0.0292	0.0237	1.26
373.2	-0.0379	0	9.34	-0.0290	0	9.53
	0.0148	0.0218	0.88	0.0260	0.0218	0.81
373.2	-0.0085	0	8.88	-0.0042	0	8.92
	0.0312	0.0271	2.07	0.0363	0.0266	2.01
400	-0.0034	0	9.04	-0.0002	0	8.66
	0.0314	0.0237	1.07	0.0329	0.0306	1.28
423.2	-0.0308	0	6.36	-0.0252	0	6.33
	0.0275	0.031	0.46	0.0346	0.0304	0.45
423.2	-0.0234	0	6.81	-0.0176	0	6.76
	0.0325	0.0328	0.95	0.0400	0.0323	0.94
450	-0.0060	0	8.11	-0.0040	0	7.67
	0.0408	0.0418	0.79	0.0441	0.0387	0.59
473.2	-0.0467	0	3.33	-0.0401	0	3.27
	0.0443	0.0346	0.84	0.0520	0.0330	0.85
572.9	0.0506	0	0.76	0.0635	0	0.73
	0.0649	0.0051	0.53	0.0742	0.0032	0.47
Overall	-0.0113	0	6.59	-0.0153	0	7.58
	0.0326	0.0263	0.91	0.0352	0.0279	0.99
ethane – n-docosane						
310	0.0245	0	3.38	0.0249	0	4.09
	0.0247	0.0019	3.37	0.0245	-0.0072	4.07
330	-0.0022	0	12.26	0.0005	0	12.21
	0.0320	0.0202	3.51	0.0346	0.0192	3.35
350	-0.0159	0	11.72	-0.0130	0	11.83
	0.0281	0.0220	2.27	0.0320	0.0215	2.25
Overall	0.0021	0	9.12	0.0041	0	9.36
	0.0283	0.0147	3.06	0.0304	0.0167	3.22

Table 3. Continued

ethane – n-tetracosane						
330	-0.0125	0	15.49	-0.0083	0	14.99
	0.0351	0.0231	6.02	0.0406	0.0225	5.12
340	-0.0136	0	15.74	-0.0093	0	15.22
	0.0351	0.0231	6.25	0.0350	0.0216	6.28
350	-0.0172	0	9.87	-0.0133	0	9.92
	0.0254	0.0244	3.41	0.0299	0.0234	3.37
Overall	-0.0144	0	13.70	-0.0103	0	13.38
	0.0319	0.0240	5.23	0.0352	0.0225	4.92
ethane – n-octacosane						
348.2	-0.0487	0	6.08	-0.0432	0	6.15
	0.0098	0.0198	0.94	0.0153	0.0188	0.90
373.2	-0.0534	0	6.81	-0.0481	0	6.86
	0.0018	0.0173	1.19	0.0120	0.0178	1.29
373.2	-0.0489	0	6.80	-0.0431	0	6.87
	0.0058	0.0178	1.81	0.0133	0.0173	1.85
423.2	-0.0971	0	3.81	-0.0656	0	5.93
	0.0034	0.0288	1.73	0.0125	0.0230	0.68
473.2	-0.0971	0	3.81	-0.0893	0	3.75
	0.0034	0.0288	1.73	0.0097	0.0264	1.71
573.2	-0.0896	0	2.13	-0.0693	0	1.79
	0.0030	0.0256	0.83	0.0103	0.0203	0.70
Overall	-0.0683	0	5.26	-0.0598	0	5.22
	0.0041	0.0219	1.66	0.0121	0.0210	1.21
ethane – n-hexatriacontane						
373.2	-0.0777	0	7.56	-0.0682	0	7.62
	0.0037	0.0183	0.65	0.0120	0.0166	0.70
423.2	-0.0745	0	7.85	-0.0650	0	7.81
	0.0207	0.0245	1.14	0.0308	0.0227	1.13
Overall	-0.0761	0	7.71	-0.0666	0	7.71
	0.0122	0.0214	0.90	0.0214	0.0196	0.91
ethane – n-tetratetracontane						
373.2	-0.1110	0	10.69	-0.0974	0	10.76
	0.0138	0.0234	1.04	0.0226	0.0203	1.09
423.2	-0.0551	0	1.88	-0.0370	0	1.51
	-0.0172	0.0162	0.74	-0.0117	0.0137	0.72
Overall	-0.0831	0	6.26	-0.0672	0	6.14
	-0.0017	0.0198	0.89	0.0054	0.0170	0.91

The values of the interaction parameter have weak temperature dependence. Considering this, we calculated temperature mediated values of k_{ij} and h_{ij} for each ethane + n-alkane system. These values were tested in VLE prediction calculations and the global results are presented in Table 4.

Based on the results presented in Fig. 1 and Fig. 2, we found correlations between the interaction parameters and the number of carbon atoms of the heavy component, n_C,shown by Eq. (6) and (7). Functions of second degree did not improve significantly the quality of the correlation.

Table 4. Results of the VLE prediction for binary systems of ethane - n-alkane with n_C carbon atoms

n_C	AADP $_{PR}$/ %		AADP $_{SRK}$ / %	
	*	**	*	**
20	3.46	4.76	5.6	5.81
22	5.06	3.50	6.23	3.71
24	5.31	6.94	5.66	6.26
28	3.79	5.19	3.15	3.64
36	1.54	1.73	1.48	1.95
44	1.85	1.97	1.86	1.85
Overall	3.50	4.01	4.00	3.87

*using interaction parameters mediated on the temperature interval (Table 2)
**using interaction parameters calculated with eq. (6) and (7)

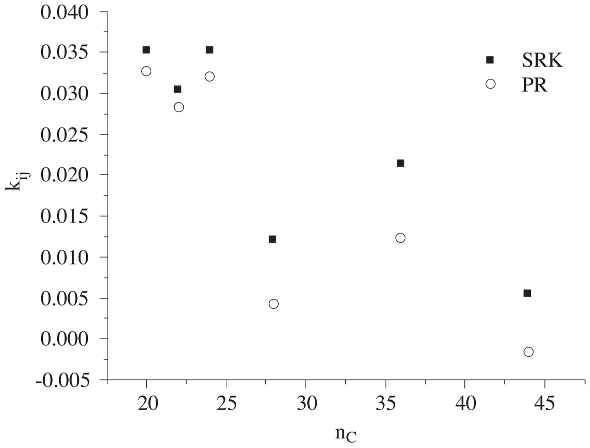

Figure 1. Temperature mediated values of k_{ij}. (Reference data from Table 3)

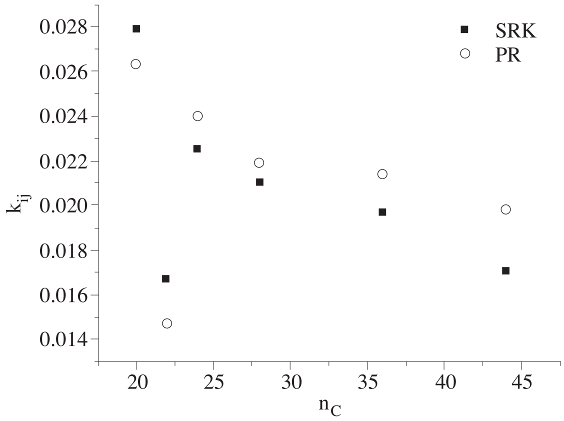

Figure 2. Temperature mediated values of h_{ij}. (Reference data from Table 3)

PR $k_{ij} = 0.05804 - 0.00138\, n_C$ (6a)

$h_{ij} = 0.0236 - 0.00008\, n_C$ (6b)

SRK $k_{ij} = 0.05601 - 0.00113\, n_C$ (7a)

$h_{ij} = 0.02647 - 0.00003\, n_C$ (7b)

The interaction parameters calculated from eq. (6) and eq. (7) can be used to predict the parameters of the EOS and the VLE in the systems ethane + n-alkane. The results are also tabulated in Table 4.

Using PR and SRK we obtained the same quality results and this work indicates that by neglecting the temperature dependence of the interaction parameters one can obtain only results of average quality.

For one temperature, T = 373.2K, we found a new set of correlations (far better results were obtained choosing polynomials of second degree):

$$\text{PR } k_{ij} = 0.1302 - 0.0076\, n_C + 1.44\ 10^{-4} n_C^2 \tag{8a}$$

$$h_{ij} = 0.0392 - 0.00226\, n_C + 4.41\ 10^{-5} n_C^2 \tag{8b}$$

$$\text{SRK } k_{ij} = 0.1619 - 0.0089\, n_C + 1.31\ 10^{-4} n_C^2 \tag{9a}$$

$$h_{ij} = 0.0665 - 0.00305\, n_C + 4.73\ 10^{-5} n_C^2 \tag{9b}$$

The average results of these prediction calculations are presented in Table 5. The results are good, better than those predicted using eq. (6) and eq. (7). This implies that even being weak, the temperature dependence of the interaction parameters is not to be neglected in highly accurate calculations.

Table 5. Results of VLE prediction (T = 373.2K) using eq. (8) and (9)

System ethane -	$AADP_{PR}$ / %	$AADP_{SRK}$ / %
- n-eicosane	2.18	1.42
- n-octacosane	1.37	3.28
-n –hexatriaconatene	0.75	4.68
-n –tetratetracosane	1.05	7.35
Overall	1.34	4.12

As an application, we present in Fig. 3, and Fig. 4 two VLE diagrams calculated for highly asymmetric mixtures, using predicted values of the interaction parameters and the experimental P-X data as reference.

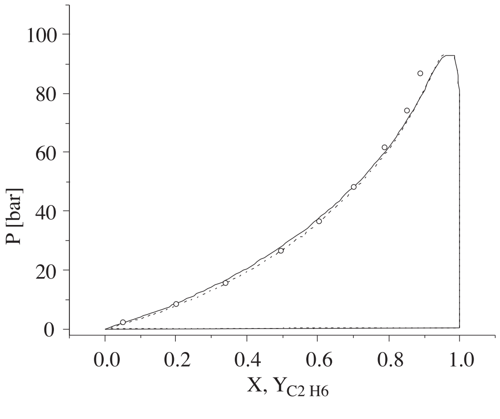

Figure 3. Phase equilibrium diagram. System ethane – docosane (T=330K) using PR-EOS and calculated interaction parameters: line – mediated on the temperature interval; dots –using eq. (6); circles - experimental data.

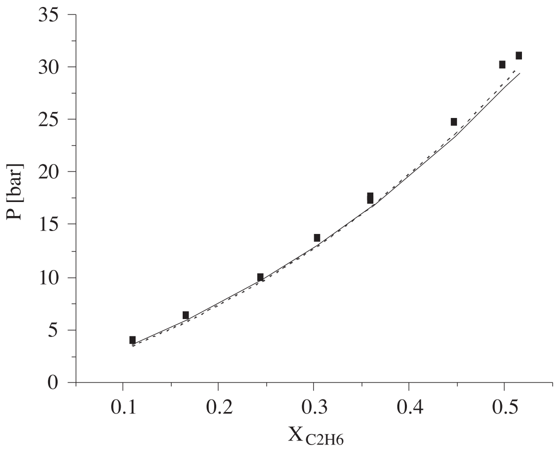

Figure 4. P-X equilibrium diagram. System ethane – n-tetratetracontane (T= 373.2K) using SRK and predicted interaction parameters: line –eq. (9); dots – eq. (7); squares - experimental data.

Many VLE calculations for binary systems ethane + n-alkanes up to eicosane are presented in specialised studies and were previously presented by the authors [15]. The next step in this work was to extend the investigated domain with respect to n_C considering all the binary mixtures of n-alkanes in which one component is ethane and the other ranges from propane to tetratetracontane. We developed correlations between the interaction parameters, k_{ij}, h_{ij} (temperature mediated) and n_C, for the systems $C_2 + C_{3...44}$:

$$\text{PR } k_{ij} = 0.001576 - 0.00218\, n_C + 5.25\, 10^{-5} n_C^2 \tag{10a}$$

$$h_{ij} = -\, 0.0091968 + 0.00196\, n_C - 2.97\, 10^{-5} n_C^2 \tag{10b}$$

$$\text{SRK } k_{ij} = 0.003633 - 0.00208\, n_C + 4.628\, 10^{-5} n_C^2 \tag{11a}$$

$$h_{ij} = 0.012255 + 0.000275\, n_C - 2.177\, 10^{-6} n_C^2 \tag{11b}$$

The quality of the correlations was tested in prediction calculations of the VLE. All the systems in the database were used in the calculations. Average AADP values were then calculated for each system and the results are tabulated in Table 6. The results of these calculations can be described as successful, considering the high asymmetry of the components.

Table 6. Results of the VLE prediction, using eq. (10) and (11)

System: Ethane -	$AADP_{PR}$/ %	$AADP_{SRK}$/ %
- n-eicosane	5.30	6.32
- n-docosane	3.72	4.19
- n-tetracosane	7.13	7.19
- n-octacosane	5.17	5.15
-n –hexatriaconatene	2.42	1.67
-n –tetratetracosane	1.82	5.26
Overall	4.26	4.79

Conclusions

Two cubic EOS (PR and SRK) used with standard mixing rules with two interaction parameters may describe the VLE in binary systems ethane + heavy n-alkanes from eicosane to tetratetracontane.

The interaction parameters slightly depend on temperature, and prediction calculations done with mediated values (on the temperature interval) are of average quality.

In this work we presented correlations between the interaction parameters and the number of carbon atoms in the heavy component molecule. The correlations are applicable for the systems ethane + $C_{20...44}$ and ethane + $C_{3...44}$. The prediction calculations done with these values led to good results.

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