MODELING OF THE PHASE BEHAVIOUR OF INDUSTRIALLY IMPORTANT MIXTURES FROM THE ASSOCIATED PERTURBED ANISOTROPIC CHAIN THEORY

Master thesis

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SUMMARY

In the last twenty years, the interest in the phase behavior of mixtures of polar, associating and ionic compounds has been grown and subsequently the interest in equations of state for these mixtures. A new field of equations of state has been developed, based on statistical thermodynamic grounds. The most successful thermodynamic theory for pure components and mixtures of components is perturbation theory. Donohue and co-workers developed a practical equation of state using perturbation theory for associating and polar components, the Associated Perturbed Anisotropic Chain Theory (APACT).

In this work, pure component molecular parameters for the APACT have been calculated. It is clear that APACT is able to describe the pure component properties with less than one percent error. Furthermore, it is clear that the molecular parameters for the APACT have a physical basis and are related to the size, dispersion energy and shape of the molecules.

Two systems have been described (ethanol-hexane and water-carbon dioxide) with the AP ACT. For the system ethanol-hexane the APACT was able to describe the entire phase behavior accurately and furthermore it predicts the azeotrope. This is in contrast to the Peng-Robinson (PR) equation of state, which is not able to describe the phase behavior of this system, even with a binary interaction parameter. For the system water-carbon dioxide, a binary interaction parameter was necessary for the APACT. In addition to Vapor-Liquid-Equilibria, also Liquid-Liquid-Equilibria have been calculated with the APACT.

Finally, the phase behavior for a number of freon mixtures has been calculated with the PACT and the predictions are compared with the PR equation of state and the Soave-Redlich-Kwong equation of state. The PACT was able to describe the mixtures approximately two times better than the PR equation of state. Introduction of a binary interaction parameter results in the same results for all the equations of state used.

It is clear that for systems that exhibit hydrogen bonding and polar interactions the APACT works better than the cubic equations of state and that for extrapolation or prediction purposes, the APACT should be used.

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1. INTRODUCTION

During the last two decades, the interest in the phase behavior of mixtures of polar, associating and ionic compounds has been grown and as a result the interest in equations of state for these mixtures. Understanding phase behavior is important since it can help to predict the separation of mixtures and almost every industrial process needs such a separation step. Knowing the phase behavior of mixtures can minimize the energy requirements of the process. Furthermore, the knowledge of phase behavior of mixtures has become more important for environmental reasons. Many process output streams are submitted to strong environmental regulations and therefore should be cleaned from any contamination.

The commonly used (cubic) equations of state, like the Peng-Robinson (PR) equation of state or the Soave-Redlich-Kwong (SRK) equation of state, are unable to describe the phase behavior of these non-ideal mixtures with high accuracy. As a result a new field of equations of state has been developed based on statistical thermodynamic grounds. The most successful thermodynamic theory for pure components and mixtures of components is perturbation theory. Prausnitz and co-workers were the first to develop a practical equation of state using perturbation theory, the Perturbed Hard Chain Theory (PHCT). In the last decade, the PHCT was extended to treat compounds that interact through dipolar and quadrupolar interactions (PACT), hydrogen bonding (APACT) and ionic forces. The Associated Perturbed Anisotropic Chain Theory (APACT) equation of state is especially designed for polar and associating systems. The success of PHCT and its extensions in describing the thermodynamic properties and phase behavior of complex systems is due to the fact that the equation accounts explicitly for all the molecular interactions exhibited in the system through expressions derived from fundamental principles.

In this work, the APACT equation of state is used to calculate industrially important mixtures, like freon mixtures. Because of the Montreal Protocol[1], all the chlorine atoms in the freons should be substituted by less harmful molecules. Research[1] has shown that the chlorine atoms in the freons are affecting and destructing the ozone layer. Routes of converting these chlorine freons (CFC's) to freons without chlorine atoms (HFC's) are developed and for process purposes the phase behavior of the mixtures should be predicted. These predictions can be done with the PACT equation of state. A comparison between the predictions from the PACT equation of state and from the PR equation of state is made.

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$Z = \frac{V}{V-b} - \frac{a}{RTV}$$

2. THEORY

2.0 Introduction

The first important correlation of thermodynamic properties was the ideal gas law, developed more than a century ago[2] :

$$Z^{ig} = \frac{PV}{RT} = 1 \qquad (2.1)$$

Deviations from this ideal gas law were tied to the fundamental nature of the molecules. Van der Waals[3] was the first to realize that there were two corrections necessary to the ideal gas law, one to account for molecular attractions and the other to account for repulsions. Based on these ideas he formulated his equation of state :

$1+\frac{b}{V}$

$$Z^{vdW} = \frac{V}{(V-b)} - \frac{a}{RTV} = Z^{rep} + Z^{att} \qquad (2.2)$$

Over the last 50 years, many cubic equations of state have been proposed based on van der Waals equation of state. The most famous equations of state are the Redlich-Kwong (RK)[4], Soave-Redlich-Kwong (SRK)[5] and Peng-Robinson (PR)[6] equation of state. The van der Waals equation of state was modified, based on empirical grounds.

1+

$$Z^{SRK} = \frac{RT}{(V-b)} - \frac{a}{RT(V+b)} = Z^{rep} + Z^{att} \qquad (2.3)$$

1+

$$Z^{PR} = \frac{V}{(V-b)} - \frac{a}{RT((V+b)+(b/V)(V-b))} = Z^{rep} + Z^{att} \qquad (2.4)$$

Equations 2.1-2.4 are given for the pure components. For mixtures the equations are the same, but this time mixing rules have to be used for the parameters a and b. The most commonly used mixing rules are given by[2] :

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad (2.5)$$

$$b = \sum_i x_i b_i \qquad (2.6)$$

$$a_{ij} = \sqrt{a_{ii} a_{jj}}\,(1-k_{ij}) \qquad (2.7)$$

One of the major drawbacks of the so-called cubic equations of state is that the only adjustable parameter is the binary (empirical) interaction parameter. For highly non-ideal mixtures, these equations of state produce large errors and unrealistic binary interaction parameters are needed. Because of the growing interest in systems of highly polar or associating compounds in the last two decades, new equations of state have been developed. These equations of state are developed especially to treat systems of polar, associating or ionic substances. Van der Waals (as well as Peng-Robinson and Soave-Redlich-Kwong) neglected the molecular rotation and vibration contributions to the equation of state, which exist in addition to the molecular attractions and repulsions.

Prausnitz and coworkers developed in the 1970s the Perturbed Hard Chain Theory (PHCT)[7,8], which is a combination of the perturbed hard sphere theory for small molecules and Prigogine's[9] theory for chain molecules. The PHCT is not an empirical equation of state, like the PR equation of state, but it has a strong physical background.

$$Z^{PHCT} = 1 + c\,(Z^{rep} + Z^{att}) \qquad (2.8)$$

where c is one third of the number of external degrees of freedom. The PHCT equation of state contains three adjustable parameters reflecting molecular size (repulsive forces), molecular potential energy (attractive forces) and the number of external degrees of freedom, that are those molecular motions which are affected by density. In 1985, Donohue and coworkers extended the PHCT to polar mixtures by adding a polar contribution to the equation of state, resulting in the Perturbed Anisotropic Chain Theory (PACT)[10].

$$Z^{PACT} = 1 + c\,(Z^{rep} + Z^{LJ} + Z^{polar}) \qquad (2.9)$$

In the PACT isotropic attractive forces are described by a Lennard-Jones potential, whereas in the PHCT the attractive forces are described by a square-well potential. Later on, Donohue and his coworkers superimposed an association model upon the PACT equation of state, resulting in the Associated Perturbed Anisotropic Chain Theory (APACT)[11].

Other equations of state, with physical backgrounds, have been developed in the last two decades. Most of them are based on statistical thermodynamics, like the Statistical Associating Fluid Theory (SAFT)[12] and the Sanchez-Lacombe (SL)[13] equation of state. Also an extension of the PHCT was developed for ionic fluids[14]. An overview of equations of state for polar, associating and ionic mixtures is given by Blindenbach[15].

2.1 The Associated Perturbed Anisotropic Chain Theory

The Associated Perturbed Anisotropic Chain Theory (APACT) equation of state is a closed form equation of state that accounts explicitly for hydrogen bonding, dispersion, polar and induced-polar forces. Hydrogen bonding is taken into account through chemical theory that assumes that hydrogen bonds result in the formation of new species. Repulsive interactions are calculated from the Carnahan-Starling[16] equation of state for spherical molecules and attractive forces are calculated as a perturbation over the reference fluid. Generalization of the equation of state to chain molecules was made by the introduction of a parameter c, which takes into account the non-spherical shape of the molecules. Originally, this generalization to chain molecules was made based on phenomenological arguments and, following Prigogine[9], the parameter c was referred to as one third of the total number of external degrees of freedom per molecule. However, recently, the generalized Flory equation of state[17], which is identical in form to the repulsive term in the PHCT equation of state and the PACT equation of state, showed that the parameter c can be related rigorously to the molecular geometry and the ratio of the excluded volume of a chain molecule to the excluded volume of a sphere.

The equation of state for a pure component can be written in terms of the compressibility factor Z as a sum of the contributions from these particular interactions :

$$Z^{APACT} = 1 + Z^{assoc} + c\,(Z^{rep} + Z^{LJ} + Z^{polar}) \qquad (2.10)$$

The isotropic attractive interactions (Lennard-Jones interactions) are calculated as a perturbation expansion over the hard-sphere potential whereas the polar interactions are calculated as a perturbation over the Lennard-Jones potential. The repulsive and attractive terms in equation 2.7 are association independent because of the assumptions made about the variation of the parameters of the associating species with the extent of association[11,18]. Since the expressions for the terms in equation 2.7 are quite lengthy, they are given in appendix A.

HS pert → LJ $\xrightarrow{\text{pert}}$ Polar ✓

3. PURE COMPONENTS

3.0 Introduction

In order to describe pure components with the APACT equation of state, five different molecular parameters (T^*, v^*, c, ΔH and ΔS/R) have to be fitted. These parameters represent the dispersion energy (T^*), characteristic volume (v^*), shape (c) and the hydrogen bonding capabilities (ΔH and ΔS/R) of the molecule and are fitted to experimental vapor pressure and liquid density data. The temperature range for the liquid density and vapor pressure data is usually between the triple point and the critical point of the component. Furthermore, the pressure range should be as large as possible, in order to calculate mixture properties over a large pressure range. For components that do not hydrogen bond, the APACT equation of state reduces to the PACT equation of state that has only three molecular parameters for each component. In the next paragraphs the fitting procedure is further explained and the results for the fitting of some components, mostly freons, are given.

3.1 Fitting procedure

The APACT software developed by Donohue and coworkers has a special program, which executes the fitting procedure. This program (purfit.for) has to be linked with the subroutines, which are in the files purreg.for, pursb1.for, pursb2.for and assoc.for. The program needs an input file as given in appendix C. Initial guesses for the five molecular parameters have to be given in the input file. When working with a component that does not hydrogen bond, the PACT equation of state has to be used and only three parameters have to be fitted. For a component that do hydrogen bond, T^*, v^* and c are fitted first. During this fitting, values for ΔH and ΔS/R are given in such a way that the equilibrium constant (K) is close to zero.

When creating the input file, initial guesses for the first three parameters are obtained from a component which has the same structure as the component for which the parameters have to be fitted. With a small number (5-10) of liquid density data added to the input file, the parameters are fitted. Every time the fitting procedure results in a different set of parameters, the values in the input file are changed. With the first 5-10 liquid density data, one tries to fit all three parameters in order to get a better initial guesses for them. After the first few liquid density data, more liquid density data are added and every time the parameters are refitted. Subsequently, the vapor pressure data are added until the entire temperature range (from the triple point to the critical point) and the desired pressure range is covered. At the end of this fitting, the percentage average absolute deviation (%AAD) between the equation of state predictions and the experimental values for the vapor pressure and liquid molar volume should be as low as possible. For a component that does not hydrogen bond the fitting procedure is then finished. Otherwise, the values of ΔH and $\Delta S/R$ are changed so that a non-zero value for the equilibrium constant is obtained and the fitting is redone. This until a minimum in the error between the calculated and the experimental data is accomplished. The easiest way to fit the last two parameters, is to keep ΔH constant and try to fit $\Delta S/R$. Then ΔH is changed by a small amount and fitting is repeated until the minimum in error is reached.

The entire fitting procedure is a state of art process that requires time and patience. Adding too many experimental data points at one stage can cause the program to create large errors or not to convert at all. Furthermore, it is important to have good initial guesses for the parameters.

3.2 Results

For many components, the molecular pure component parameters are already described in the literature[10,11,19-21]. But there are also some components, mostly freons, for which the parameters have not been reported in the literature. In this work, the molecular parameters for a few organic components (table 3.1) and for some freons have been fitted or sometimes refitted.

Table 3.1 molecular parameters for compounds used in this work

	T (K)	v^* (cm^3/mol)	c (-)	%AAD PVT T(K) P(bar)	%AAD VP T(K)	ref
n-heptane	339.1	83.97	1.9897	0.645 (277-623) (0.02-5000)	0.206 (213-540)	30
n-pentane	311.2	63.31	1.6435	0.483 (243-473) (0.05-500)	0.122 (243-453)	30
H_2	23.4	12.67	1.0	1.1 (50-300) (1-1000)	1.8 (20-32)	30

The thermodynamics properties needed for fitting the freons and the commonly used codes for freons are given in table 3.2.

Table 3.2 Thermodynamic properties of some freons[22]

	Formula	Dipole Moment (D)	M (g/mol)
R-10	CCl_4	0.0	152.82
R-11	CCl_3F	0.46	137.39
R-12	CCl_2F_2	0.51	120.92
R-13	$CCLF_3$	0.50	104.47
R-14	CF_4	0.0	88.01
R-20	$CHCl_3$	1.04	119.38
R-21	$CHCL_2F$	1.29	102.92
R-22	$CHCLF_2$	1.42	86.48
R-23	CHF_3	1.651	70.01
R-113	$C_2Cl_3F_3$	0.48	187.39
R-114	$C_2Cl_2F_4$	0.5	170.91
R-115	C_2ClF_5	0.52	154.47

The codes for the freons are based on a three digit scale where the first digit represents the number of carbon atoms in the freon minus one (when the first digit is zero, it is omitted), the second digit represents the number of hydrogen atoms plus one and the third digit is the number of fluoride atoms in the freon. With the thermodynamic properties from table 3.2, the molecular parameters for the PACT equation of state (the freons do not have hydrogen bonding capabilities) are calculated (table 3.3).

Table 3.3 Pure component parameters for the PACT equation of state

	T^* (K)	v^* (cm^3/mol)	c (-)	%AAD PVT T(K) P(bar)	%AAD VP T(K)	ref
R-11	322.1	51.17	1.4592	0.648 (213-373) (0-12)	0.0181 (243-403)	44
R-12	260.6	45.01	1.4747	0.639 (203-373) (0-33)	0.271 (203-363)	44
R-13	199.0	37.51	1.5618	0.922 (173-299) (0.3-36)	0.857 (173-299)	44
R-14	154.1	29.60	1.4736	0.439 (127-217) (0.2-28)	0.169 (138-222)	45
R-20	360.0	46.73	1.5398	0.541 (293-750) (10-200)	0.204 (239-531)	45
R-21	303.2	40.83	1.5083	0.408 (273-473) (1-200)	0.247 (213-433)	44
R-22	245.1	35.01	1.4921	0.853 (183-363) (0-44)	0.322 (173-333)	44
R-23	186.2	27.78	1.4871	1.31 (149-294) (0-42)	0.781 (172-277)	45
R-113	310.2	65.47	1.7875	0.431 (255-477) (0.06-30)	0.263 (255-477)	44
R-114	269.8	58.64	1.743	0.136 (238-328) (0.1-5.2)	0.0917 (233-333)	44
R-115	227.3	52.54	1.7369	0.489 (188-349) (0.07-29)	0.256 (188-349)	45

As can be seen from table 3.3, the PACT equation of state is able to fit the experimental data very well. The percentage average absolute deviation (%AAD) between the equation of state predictions and the experimental values for the vapor pressure and liquid molar volume are always less than one percent. In tables 3.4-3.6 the results for the molecular parameters are compared for each group of freons.

Table 3.4 Pure component molecular parameters for the PACT

component	T^* (K)	v^* (cm^3/mol)	c (-)	ϵ/k (-)	cT^* (K)
R10	377.8	57.98	1.4883	118	562.28
R11	322.1	51.17	1.4592	118	470.01
R12	260.6	45.01	1.4747	118	384.31
R13	199.0	37.51	1.5618	118	309.16
R14	154.1	29.60	1.4736	118	227.90

Table 3.5 Pure component molecular parameters for the PACT

component	T^* (K)	v^* (cm^3/mol)	c (-)	ϵ/k (-)	cT^* (K)
R20	360.0	46.73	1.5398	140	554.33
R21	303.2	40.83	1.5083	140	457.36
R22	245.1	35.01	1.4921	140	365.71
R23	186.2	27.78	1.4871	140	276.90

Table 3.6 Pure component molecular parameters for the PACT

component	T^* (K)	v^* (cm^3/mol)	c (-)	ϵ/k (-)	cT^* (K)
R113	310.2	65.47	1.7875	118	554.48
R114	269.8	58.64	1.743	118	470.26
R115	227.3	52.54	1.7369	118	394.80

The parameter ϵ/k is the characteristic energy per unit external surface area of the molecule and cT^* is a parameter which represent the dispersion energy per molecule. Following Vimalchand[20], a value of $\epsilon/k=118$ was used for all the non-polar and weakly polar CFC's and a value of $\epsilon/k=140$ was used for the highly polar HCFC's. When plotting the results from tables 3.4-3.6 versus the number of chlorine atoms in the freon-molecules, figures 3.1-3.4 are obtained. In these figures one parameter is plotted versus the number of chlorine atoms, to show the correlation between the plotted parameter and the number of chlorine atoms. From figure 3.1, it is clear that

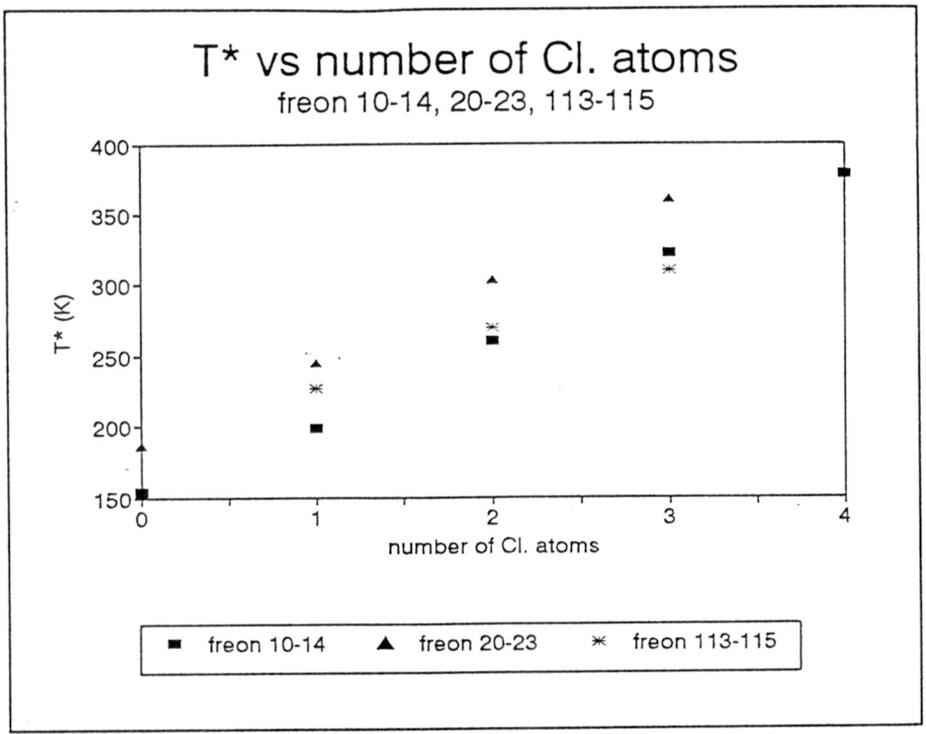

Figure 3.1 T^* vs number of Cl atoms for some freons

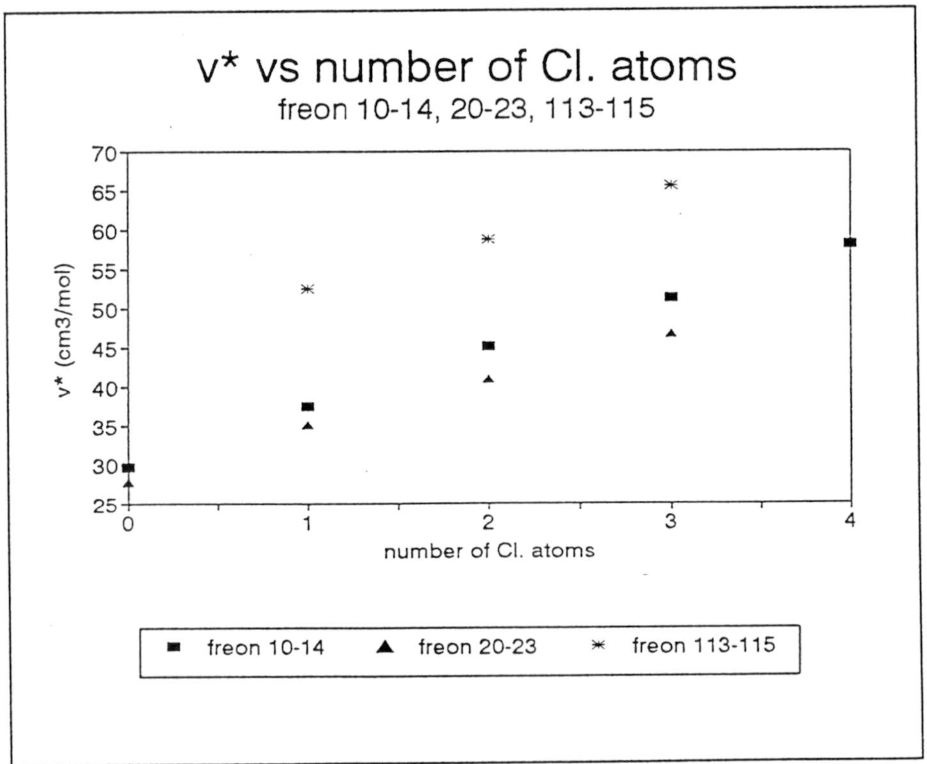

Figure 3.2 v^* vs number of Cl atoms for some freons

with increasing number of chlorine atoms in the freon (i.e. decreasing number of fluoride atoms in the freon) the T^* is increasing. This is due to the fact that the C-Cl bond has more energy than the C-F bond and therefore the entire dispersion energy of a molecule containing C-Cl bonds is higher than that of a molecule containing C-F bonds. From figure 3.2 it is clear that the parameter v^* is directly correlated to the molecular size. Replacing a fluoride atom by a (larger) chlorine atom results in a larger value for the parameter v^*. Furthermore, the freons based on ethane have a higher value for the parameter v^*, which is physically realistic since the volume of

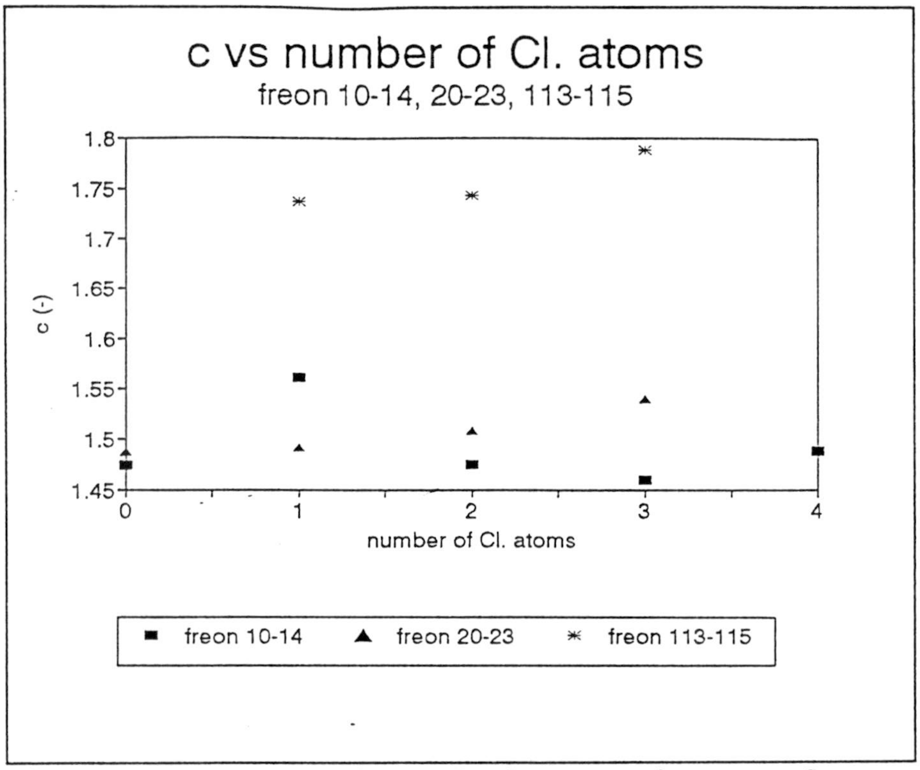

Figure 3.3 c vs number of Cl atoms in some freons

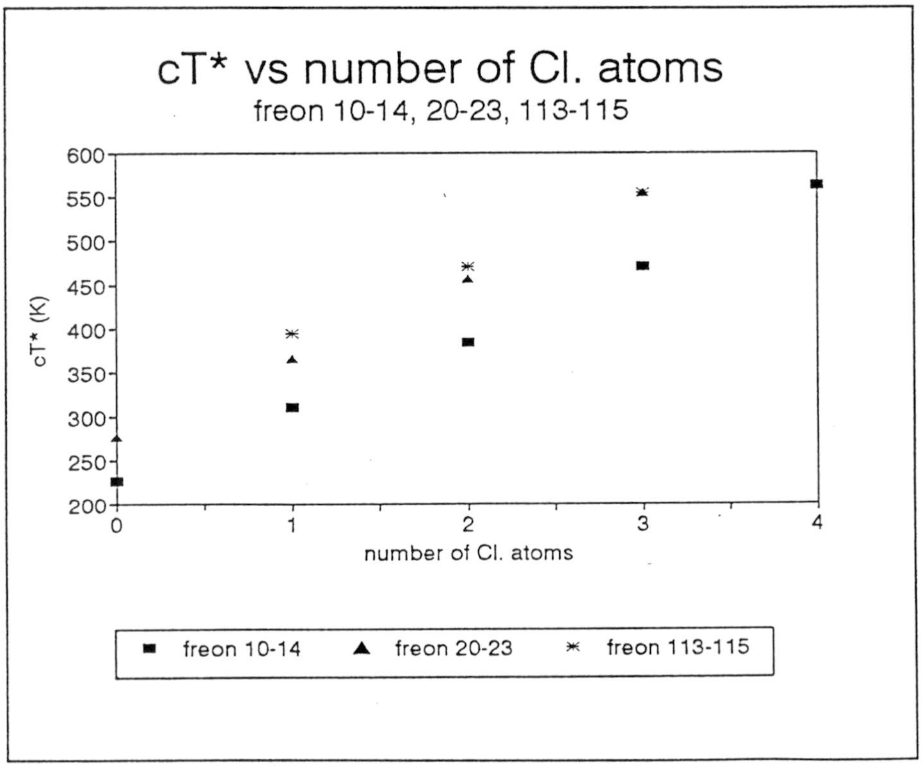

Figure 3.4 cT^* vs number of Cl atoms for some freons

ethane molecules are larger than the volume of methane molecules. Figure 3.3 gives a somewhat messy plot of the parameter c versus the number of chlorine atoms in the freon. The parameter c represents the shape of the molecule, or the deviation of the ideal (round) shape. When c has the value of one, the molecule is expected to be completely spherical. A more clear picture is obtained by plotting cT^* versus the number of chlorine atoms in the freon. When plotting cT^* versus the number of chlorine atoms in the freon straight lines are obtained (figure 3.4). The parameter cT^* is proportional to the dispersion energy per molecule and it is clear, from figure 3.4, that an increasing number of chlorine atoms in the freon molecule results in a higher dispersion energy per molecule. The reason for this is again that the C-Cl bond has more energy than the C-F bond.

3.4 Conclusion

The molecular parameters for some industrially used systems, like freons, have been fitted to experimental vapor pressures and liquid densities with the PACT equation of state. The PACT equation of state is able to describe the pure component properties with less than 1 percent error. The results for different groups of freons are compared and from these results, it can be seen that the molecular parameters are related to the size, energy and shape of the molecule and therefore have a clear physical meaning. The fitting procedure is described and can now be used easily and quickly.

4. MIXTURES

4.0 Introduction

With the pure component parameters calculated in chapter 3, the phase behavior of several mixtures has been calculated. The phase equilibria of ethanol-hexane is calculated with the APACT and compared with the Peng-Robinson (PR) equation of state. This calculation was performed to confirm the idea that for such a mixture the PR equation of state does not give satisfactory results and a more theoretical equation of state, like the APACT, should be used. Next, the phase equilibria of the system water-carbon dioxide has been calculated with the APACT, in order to investigate if the APACT is possible to describe such a highly non-ideal mixture. Further, the phase behavior of some binary and ternary freon mixtures has been calculated with the PACT equation of state. The results are compared with the PR equation of state and with the SRK equation of state. For these systems, also the optimal binary interaction parameter is determined and results are compared. In the next paragraphs all the results are given, explained and discussed.

4.1 Ethanol-hexane

Using the APACT equation of state, bubble and dewpoints of the mixture ethanol-n-hexane have been predicted at different temperatures. The ethanol-hexane system is chosen since it is a non-ideal system. Non-idealities arise from the dipole moment and the hydrogen bonding capabilities of ethanol and the chain-like structure of n-hexane. The calculations have been performed with the pure component parameters (obtained from Ikonomou et al.[11]), given in table 4.1. No binary interaction parameter was used in these calculations.

$\frac{\Delta H}{RT}$

ξ

Table 4.1 Pure component parameters[11] for ethanol and for n-hexane

	T^* (K)	v^* (cm^3/mol)	c (-)	ΔH (cal/mol)	$\Delta S/R$ (-)
ethanol	277.5	0.0342	1.22	-6.18	-11.57
n-hexane	326.4	0.07398	1.822		

In figure 4.1 the vapor-liquid equilibria (VLE) of ethanol-hexane is calculated with the APACT and with the PR equation of state and compared with experimental data[23]. For the PR equation of state, the binary interaction parameter is set equal to zero as well. From figure 4.1 it is clear that the APACT describes the system reasonably good over the entire composition range and predicts the azeotrope accurately. This is in contrast to the PR equation of state which does not describe the azeotrope. Furthermore the PR equation of state predictions for the VLE are not in agreement with the experimental data. The same calculations were done with a binary interaction parameter (figure 4.2 and figure 4.3). From figure 4.2 it can be seen that the introduction of a binary interaction parameter for the calculation with the APACT does not improve the results. Considerably better results in one composition range cause worse results in another composition range. From figure 4.1 it is clear that the introduction of a binary interaction parameter is not really necessary, and from figure 4.2, it can be seen that this introduction is superfluous. From the calculation with the PR equation of state (figure 4.3) it follows that the introduction of a binary interaction parameter results in better results, but it is clear that an accurate description of the phase behavior for this system with the PR equation of state is nearly impossible.

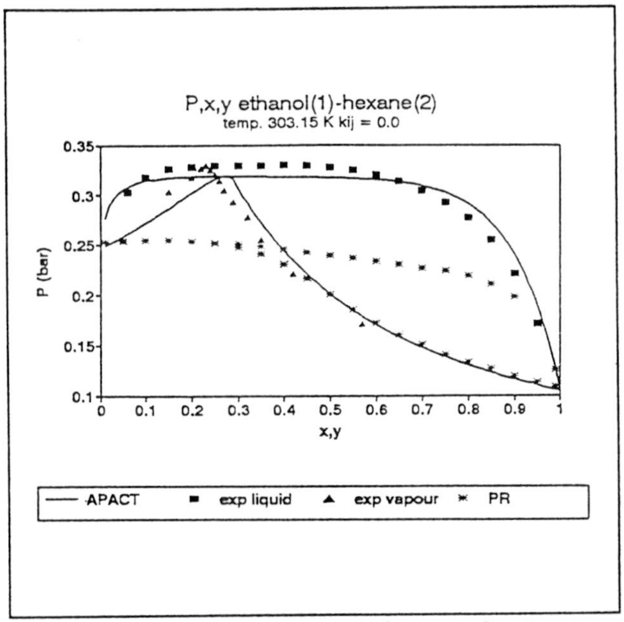

Figure 4.1 Comparison between the APACT EOS, the PR EOS and experimental data for the system ethanol-hexane at 303.15 K

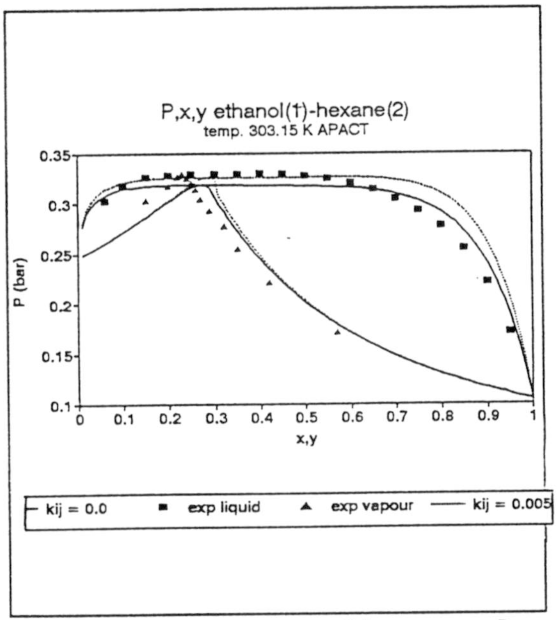

Figure 4.2 P,x,y diagram for ethanol-hexane at 303.15 K calculated with the APACT equation of state

The phase behavior of ethanol-hexane is also predicted at higher temperatures (figure 4.4).

These calculations were executed without the use of a binary interaction parameter. It is clear, from figure 4.4, that at higher temperatures the Vapor-Liquid-Equilibria are found at higher pressures, as was expected. Further, it can be seen that the azeotrope shifts to higher mole fractions of ethanol.

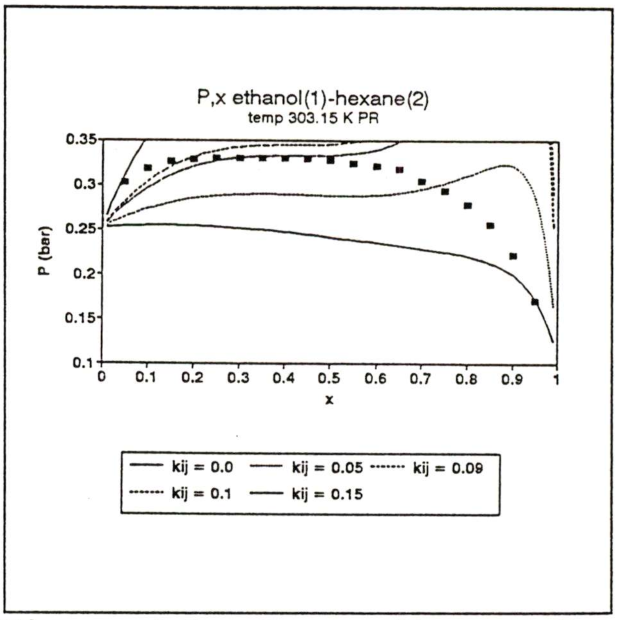

Figure 4.3 P,x,y diagram for the system ethanol-hexane at 303.15 K calculated with the PR equation of state

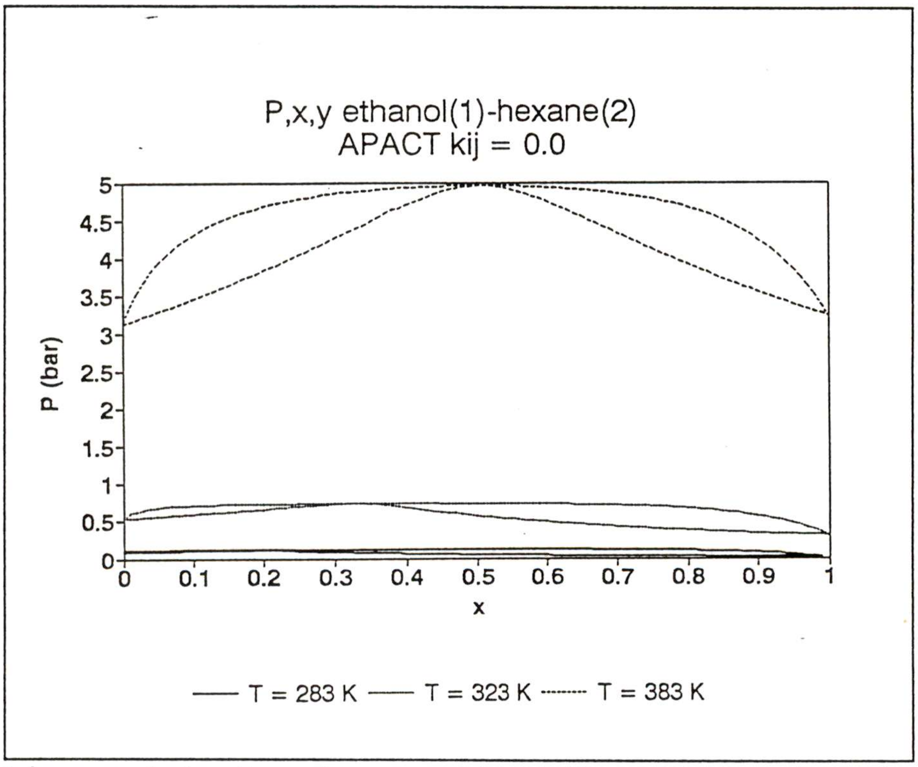

Figure 4.4 P,x diagram for the system ethanol-hexane at different temperatures calculated with the APACT equation of state without a binary interaction parameter

4.2 Water-carbon dioxide

The phase behavior of the system water-carbon dioxide was calculated at two different pressure ranges (0-44 bar and 100-1500 bar) with the APACT equation of state. The binary interaction parameter was correlated to experimental data at different temperatures. All the optimal binary interaction parameters were compared with the temperature to get the temperature dependence of this binary interaction parameter. Two versions of the APACT equation of state[18] were used. One version calculates the phase behavior of water with two association sites per water molecule, whereas the other version

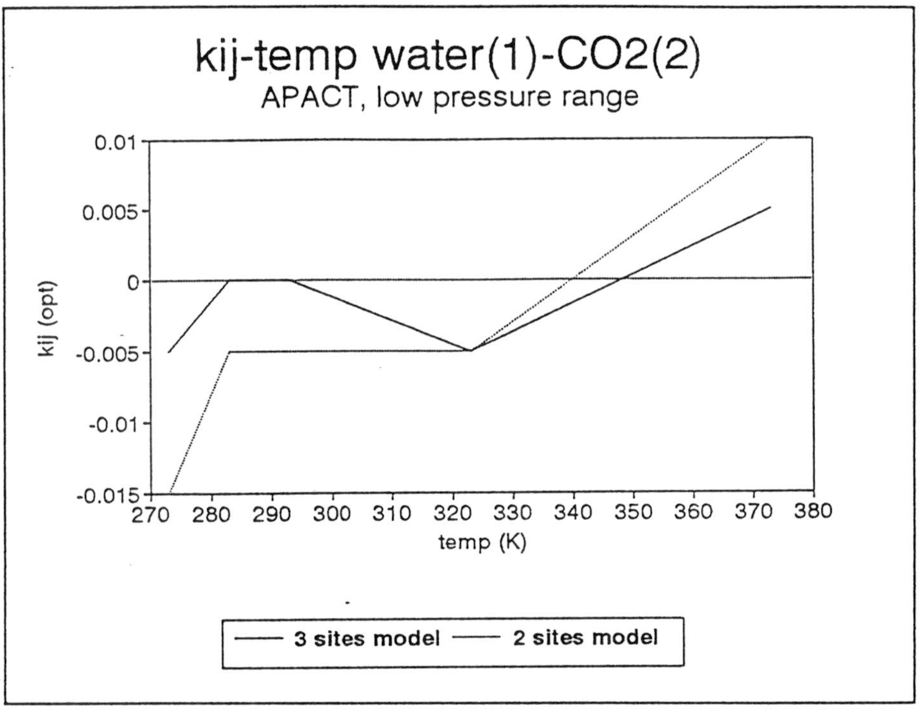

Figure 4.5 Optimal k_{ij} vs. temp. for water-CO_2 at low pressures with the APACT

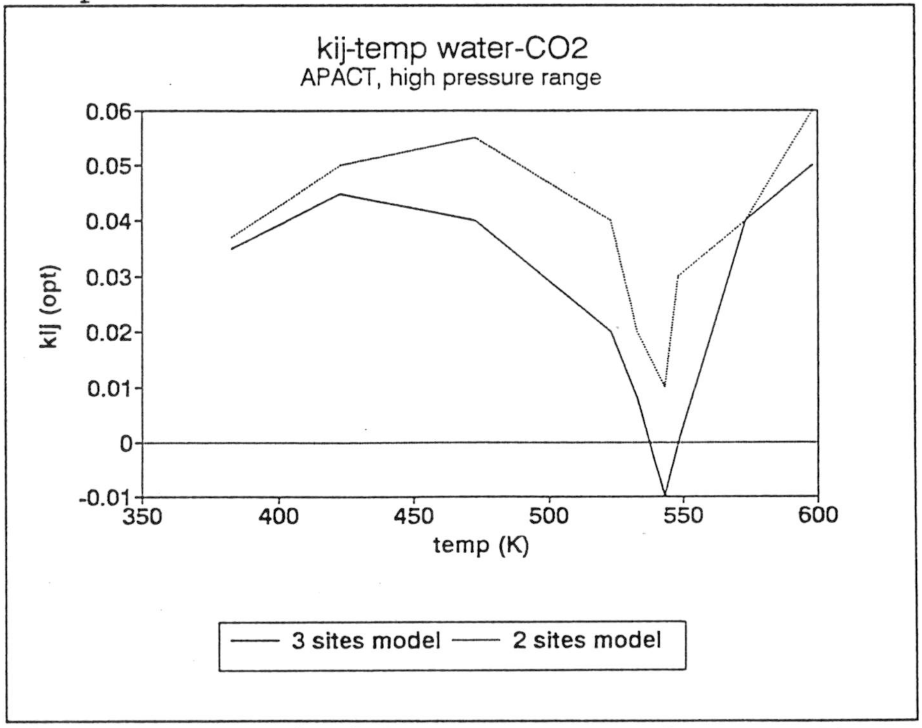

Figure 4.6 Optimal k_{ij} vs. temp. of water-CO_2 at high pressures with APACT

uses three association sites per water molecule. Better results would be expected with the three-sites model, because experiments showed that water in the liquid phase can have three (out of four) association sites bonded. In figure 4.5 and figure 4.6 the optimal binary interaction parameter is plotted versus the temperature for both low and high pressure range. Similar trends are seen from these figures. At higher temperatures the optimal binary interaction parameter decreases and then it increases. At higher temperatures the system becomes more ideal and so the binary interaction parameter would be expected

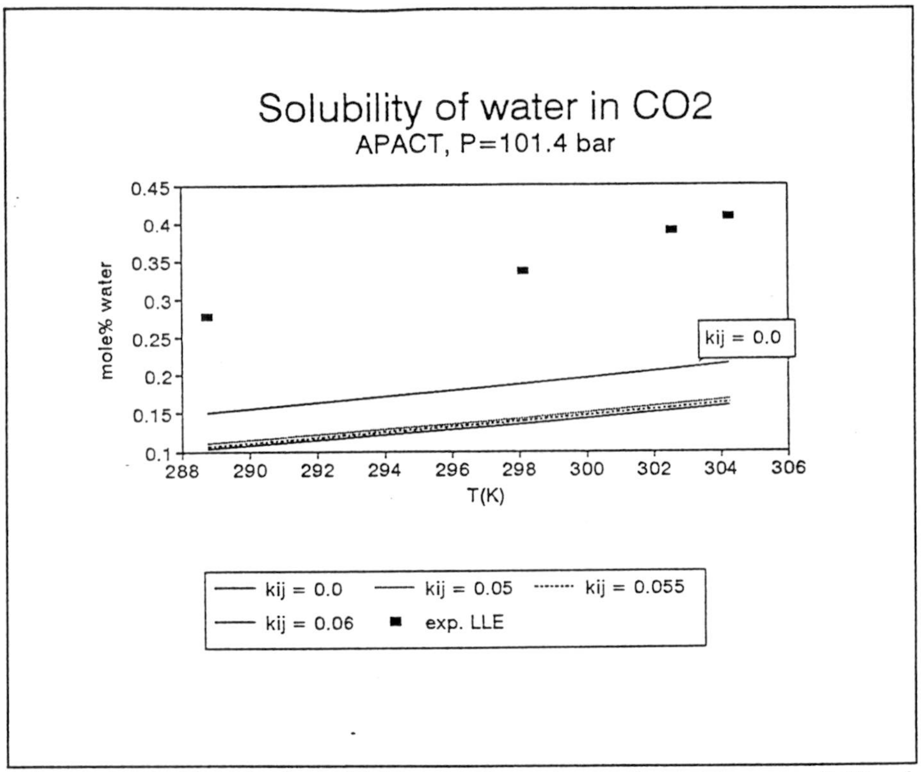

Figure 4.7 Solubility of water in CO_2 at 101.4 bar at different temperatures with APACT

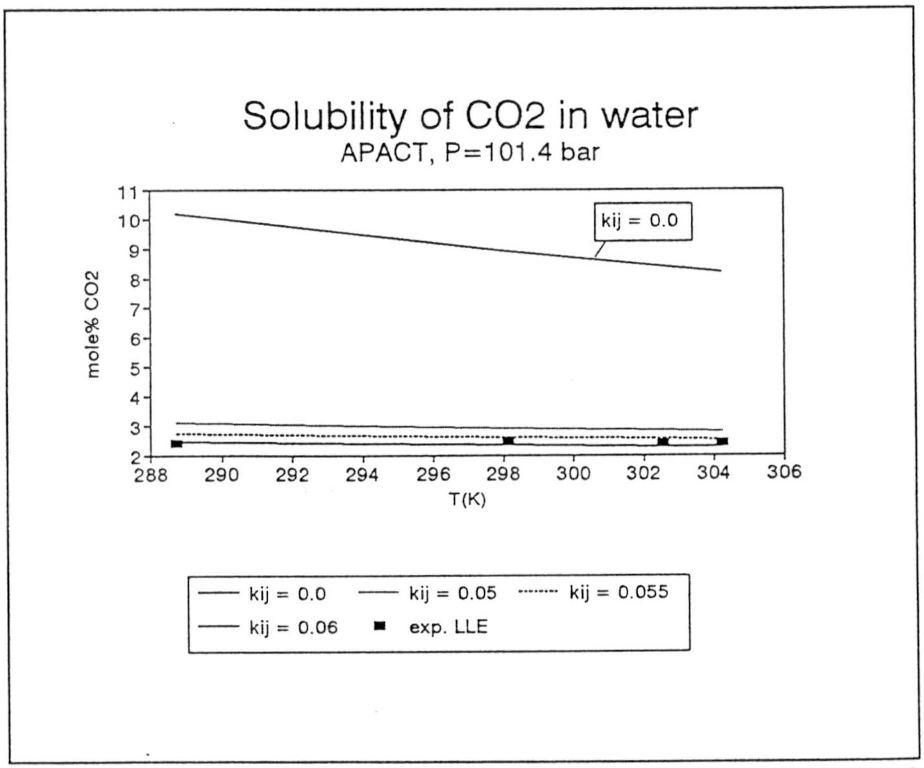

Figure 4.8 Solubility of CO_2 in water at 101.4 bar at different temperatures with APACT

to decrease. At the highest temperatures the optimal binary interaction parameter is again increased caused by the approach of the critical point. At the high pressure range the optimal binary interaction parameter is relatively high, due to the extreme non-ideality of this system.

Not only VLE have been calculated but also LLE. In figure 4.7 and figure 4.8 the results for these calculations are given. The calculations have been performed at two different pressures (100 and 200 bar) and compared to experimental data[24]. The results for the two different pressures were the same, so only one pressure is presented here. Because of the few experimental data points (4) it was relative easy to correlate the binary interaction parameter of the APACT equation of state to these data. However it was impossible to correlate with the same binary interaction parameter the solubility of water in CO_2 and the solubility of CO_2 in water at the same time.

4.3 Freon mixtures

4.3.0 Introduction

The phase behavior of several freon mixtures has been calculated at different temperatures and pressures (table 4.2).

Table 4.2 Temperature and pressure range of the calculated mixtures

System	Temperature (K)	Pressure (bar)	Ref.
H2-R13	135-220	20-120	25
H2-R14	95-165	20-120	26
R11-R22	298-373	3.1-44.2	26
R11-R23	298-372	1-77	27
R12-R13	255-290	1.5-30	28
R12-R22	295-329	10-14	29
R12-R114	277-372	3.5-14.5	29
R13-R14	200	1.5-15	30
R13-R14#	200-289	1.5-43	31
R13-R23	200-273	1.5-27.5	32
R13-R113	298-373	4.3-54	33
R14-R23	145-283	0.2-51.3	34
R22-R114	296-371	10-13.5	29
R22-R115	298-365	9-43.6	35
R23-R113	298-373	1-77	36
R13-nButane	310-400	4.3-45.5	37
R13-iButane	310-400	5.5-43	37
R20-nHexane	298-328	0.2-0.8	38
R20-nHeptane	298-323	0.06-0.7	38
R22-nPentane	304-384	5-40	39
R113-Benzene	278-308	0.1-0.6	40
R11-R22-R23	298-373	11.5-48	27
R22-R23-R114	298-373	6.4-41	27
R13-R14-R23	200	3.5-6.9	41

different data set

References in table 4.2 refer to the experimental data based on which calculations were performed. The phase equilibria are calculated with the PACT equation of state, since freons do not hydrogen bond. As it can be seen from table 4.2, two freon-hydrogen mixtures, thirteen binary freon-freon mixtures, six freon-hydrocarbon mixtures and three ternary freon-freon-freon mixtures have been calculated. The molecular parameters for the pure components are given in table 3.1 and tables 3.4-3.6. In the next paragraphs, results for every type of mixture are further explained.

4.3.1 Freon-hydrogen mixtures

Bubble points have been calculated for the system freon 13-H2 at temperatures between 134 K and 220 K. These calculations have been performed with different values for the binary interaction parameter. The idea was to get a correlation between the optimal binary interaction parameter and the temperature. The calculations were performed with the PACT equation of state (figure 4.9) and with the PR equation of state

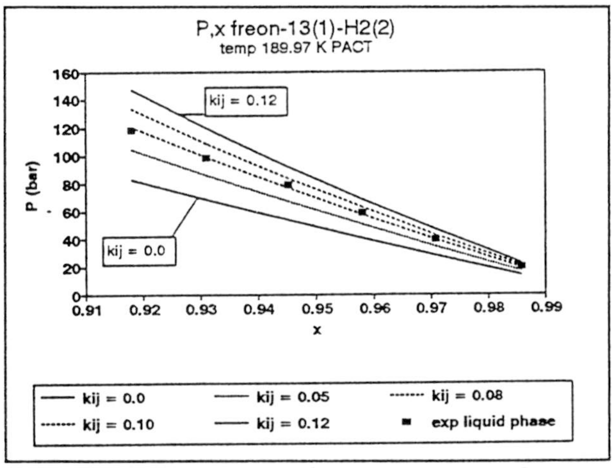

Figure 4.9 P,x diagram for freon 13-H2 at 190 K calculated with the PACT equation of state

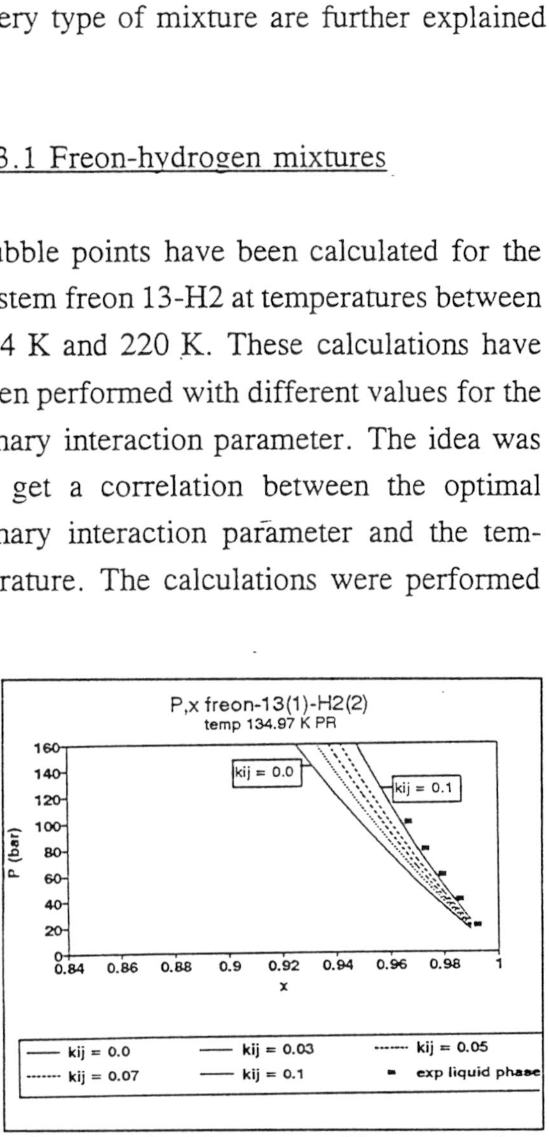

Figure 4.10 P,x diagram for freon 13-H2 at 135 K calculated with the PR equation of state

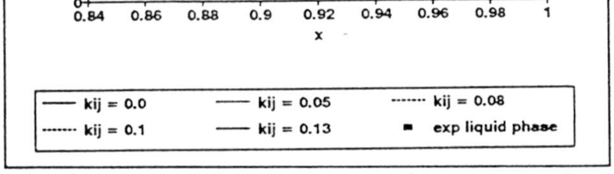

Figure 4.11 P,x diagram for freon 13-H2 at 160 K calculated with the PR equation of state

(figures 4.10 and 4.11). It can be seen from these figures that the PR equation of state requires a larger binary interaction parameter in comparison to the PACT. To develop the correlation between the optimal binary interaction parameter and the temperature, the values for the optimal binary interaction parameter were plotted versus the temperature and a straight line was drawn through the points (figures 4.12 and 4.13). From figures 4.12 and 4.13 it can be seen that it is possible to get a linear correlation between the optimal binary interaction parameter and the temperature. The coefficients for this linear correlation are given in table 4.3

Table 4.3 Coefficients for the linear correlation ($k_{ij}=A+B\cdot T$) between the binary interaction parameter and the temperature

System	A		B	
	PACT	PR	PACT	PR
Freon 13-H2	0.17901	-9.9496e-4	-4.911e-4	9.414e-4
Freon 14-H2	0.28928	0.1026	-1.8733e-3	8.6676e-4

From figures 4.12 and 4.13 it follows that the PACT equation of state requires a lower binary interaction parameter, whereas the PR equation of state requires a higher value for the binary interaction parameter with increasing temperature. One would expect that with increasing temperature the system becomes more ideal, so that the binary interaction parameter is expected to decrease with increasing

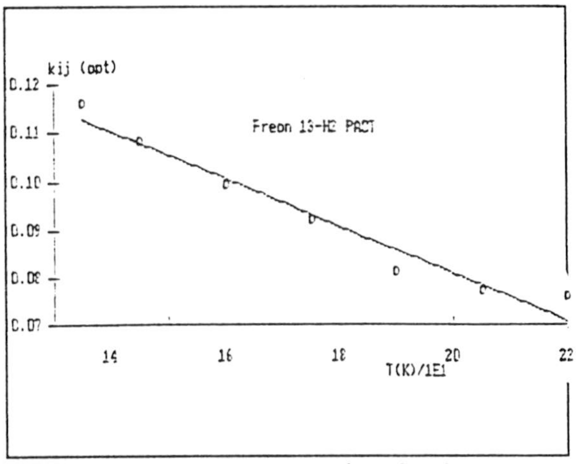

Figure 4.12 Optimal k_{ij} vs. temp. for freon 13-H2 for the PACT equation of state

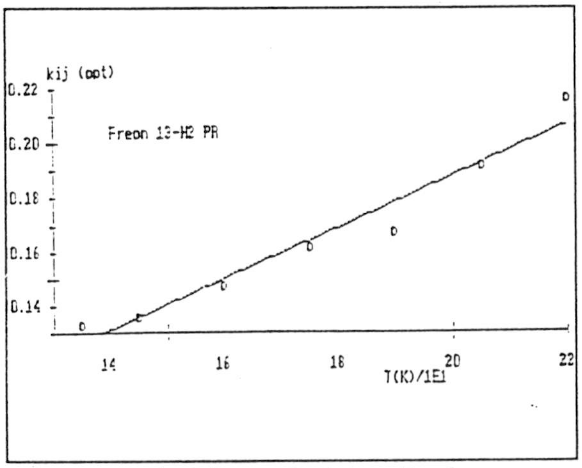

Figure 4.13 Optimal k_{ij} vs. temp. for freon 13-H2 for the PR equation of state

temperature. This trend is seen with the PACT. Furthermore, the binary interaction parameter for the PACT is lower than for the PR equation of state.

The same calculations have been done for the system freon 14-H2. Again, the optimal binary interaction parameter is plotted versus the temperature after correlating the calculated bubble pressures to the experimental data (figure 4.14 and 4.15 and table 4.3).

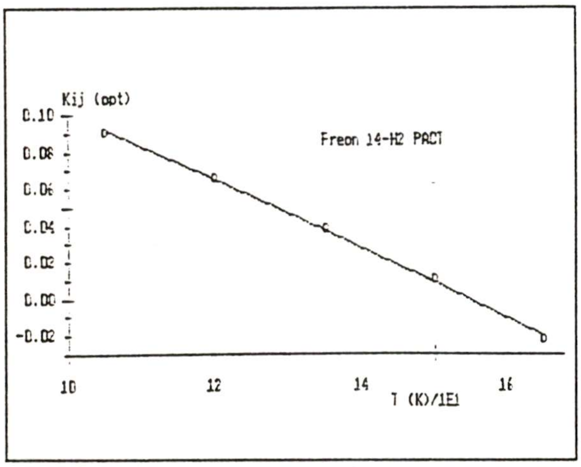

Figure 4.14 Optimal k_{ij} vs. temp. for the system freon 14-H2 for the PACT equation of state

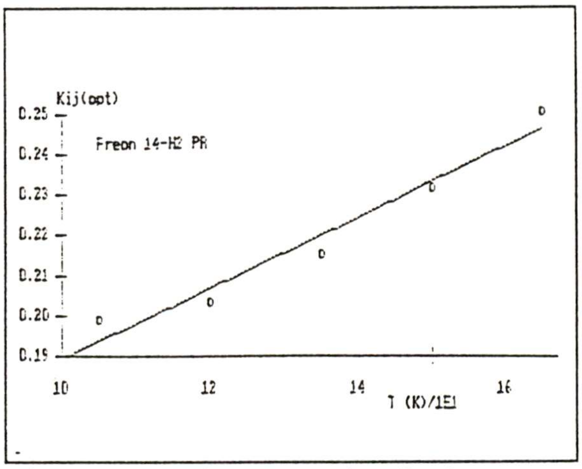

Figure 4.15 Optimal k_{ij} vs. temp. for the system freon 14-H2 for the PR equation of state

Again, the same trends are seen: for the PR equation of state the optimal binary interaction parameter is increasing with increasing temperature whereas for the PACT equation of state the optimal binary interaction parameter is decreasing with increasing temperature. Furthermore, it is clear that for this system, as well, the PR equation of state requires a much larger binary interaction parameter.

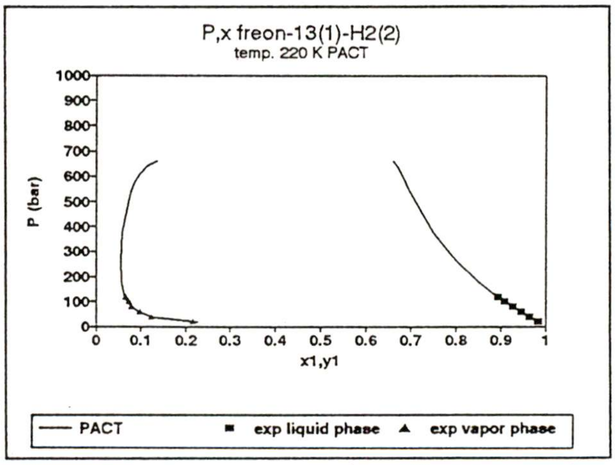

Figure 4.16 P,x diagram for the system freon 13-H2 at 220 K, calculated with the PACT equation of state and with k_{ij}=0.071

Finally, bubble points were predicted with the PACT equation of state for the system freon 13-H2 at 220 K over the entire composition range using the k_{ij} value calculated based on experimental data, resulting in higher bubble pressures (figure 4.16). In this system, a critical pressure is expected around 700 bar.

Experimental data in this region are not available, so this result can not be confirmed experimentally.

4.3.2 Binary freon mixtures

The phase behavior of 13 binary freon mixtures has been calculated with the PACT equation of state and with the PR equation of state. Calculated pressures are compared with experimental pressures[25-41]. Percentage average absolute deviation (%AAD) in bubble pressure between predictions and experiments has been calculated and compared. The %AAD is calculated from equation 4.1.

$$\%AAD = \frac{1}{N}\sum_{i}^{N} \frac{\left|P_i^{calc} - P_i^{\exp}\right|}{P_i^{\exp}} \qquad (4.1)$$

Where N is the number of experimental data points. The results of this comparison together with the results from the literature for the Soave-Redlich-Kwong (SRK) equation of state[42] are given in table 4.4.

Table 4.4 Binary freon-mixtures, comparison between PACT, PR and SRK

system	PACT			PR			SRK[42]	
	%AAD in Pressure		k_{ij}	%AAD in Pressure		k_{ij}	%AAD in Pressure	
	Pred.	Opt. k_{ij}		Pred.	Opt. k_{ij}		Pred.	Opt. k_{ij}
R11-R22	5.06	1.36	0.011	9.95	0.83	0.047	8.58	1.50
R11-R23	7.86	3.20	0.018	22.85	1.84	0.127	26.2	1.34
R12-R13	4.09	0.91	0.011	7.82	2.12	0.041	5.64	1.74
R12-R22	3.63	1.42	0.015	7.45	1.83	0.067	10.0	1.75
R12-R114	2.40	1.96	-0.005	2.17	2.17	0.00	1.98	1.89
R13-R14	5.94	1.68	0.022	8.40	2.03	0.036	4.30	1.14
R13-R14#	4.48	3.78	0.019	6.31	3.83	0.035	4.30	1.14
R13-R23	3.95	2.05	0.004	9.99	1.19	0.104	16.0	1.20
R13-R113	5.08	2.80	-0.003	7.41	2.64	0.025	5.14	2.0
R14-R23	5.64	3.82	0.007	22.32	4.43	0.104	23.7	4.9
R22-R114	5.65	3.17	0.013	8.14	2.77	0.055	7.57	0.74
R22-R115	4.21	0.79	0.016	6.56	1.01	0.054		
R23-R113	5.66	2.58	0.013	20.14	1.62	0.110	23.3	1.40

different temperature range

The results for the calculations without the use of a binary interaction parameter are referred to as pred. in table 4.4. In the next column, the %AAD with the optimal k_{ij} is given and in the third column the optimal value for k_{ij} is shown. From all these results, it is clear that the PACT equation of state describes these systems much better without the use of a binary interaction parameter than the other two cubic equations of state. The %AAD with the PACT equation of state is between two and eight percent, whereas for the PR equation of state and for the SRK equation of state the %AAD is between two and twenty-three percent.

Introducing a binary interaction parameter, results in an approximately the same %AAD (ca. two percent) for all equations of state. These results show that it is possible, for all three equations of state, to correlate the experimental data within a few percent when introducing a binary interaction parameter. The optimal binary interaction parameter is much lower for the PACT equation of state (0-0.022) than for the PR equation of state (0-0.127). Usually, when correlating the binary interaction parameter to the experimental data, it is impossible to extrapolate the results to conditions outside the boundaries of the experimental data. This is because the binary interaction parame-

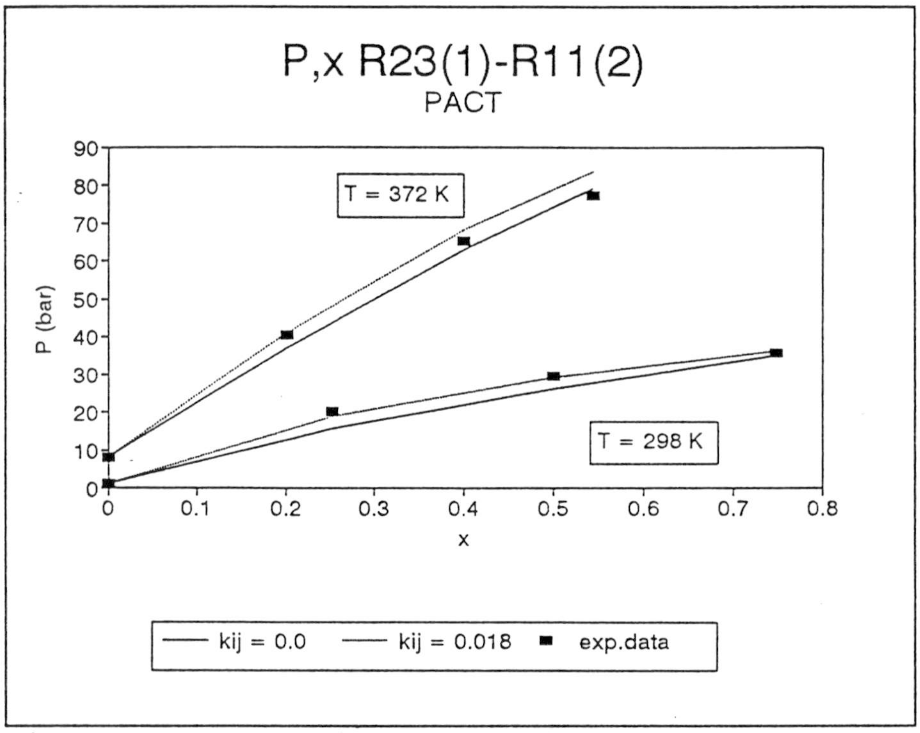

Figure 4.17 P,x diagram for freon 23-freon 11 at T=372 K and T=298 K calculated with the PACT equation of state

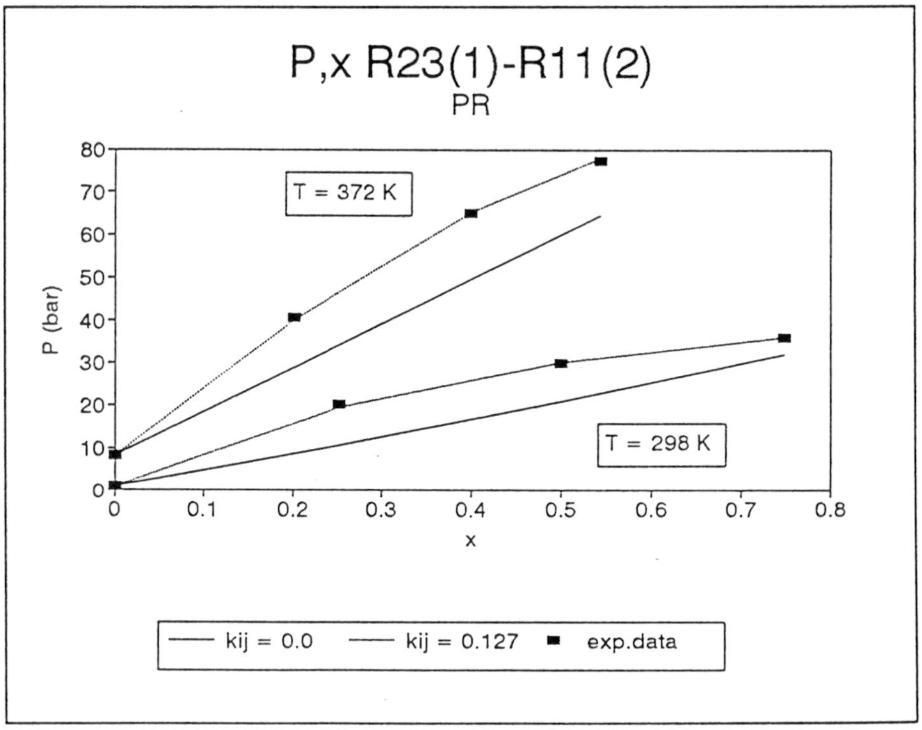

Figure 4.18 P,x diagram for freon 23-freon 11 at T=372 K and T=298 K calculated with the PR equation of state

ter is normally temperature and composition dependent. So for extrapolation purposes, the calculations should be carried out without the use of a binary interaction parameter. When doing so, the PACT equation of state gives the best results. The reason that the %AAD for binary systems containing HCFK's (freon 20-23) for the PR equation of state is relative high is caused by the more non-ideality of these systems. As can be seen from table 3.2, the dipole moments of these freons are much larger than the dipole moments for CFK's (freon 10-14). Binary systems of CFK's are relative simple systems and do not show too much non-ideality. This is the

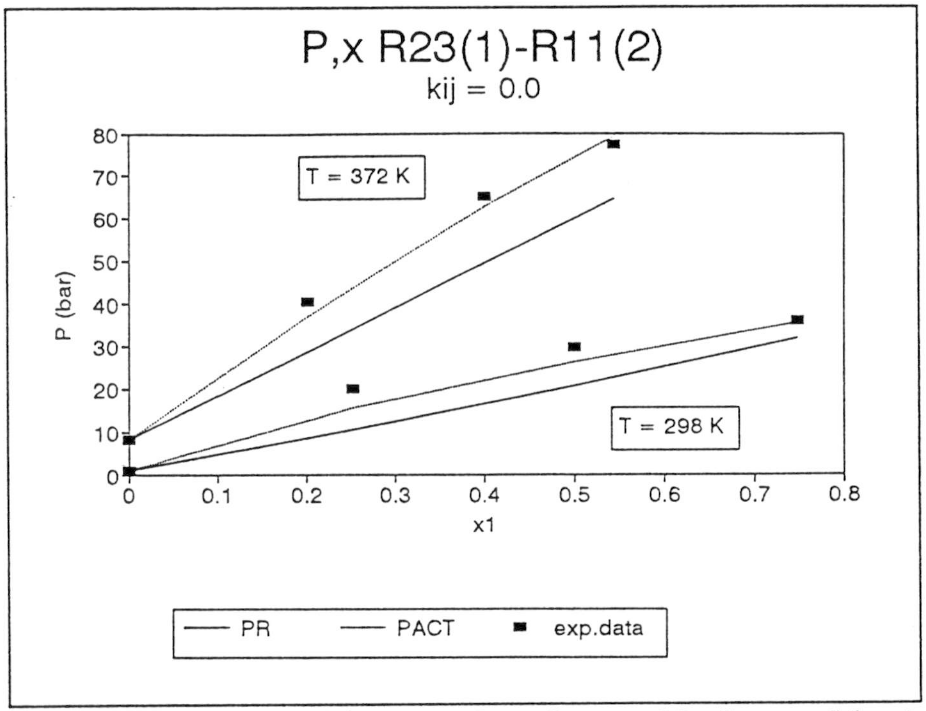

Figure 4.19 P,x diagram for freon 23-freon 11 at T=372 K and T=298 K calculated with the PACT and with the PR equation of state without a binary interaction parameter

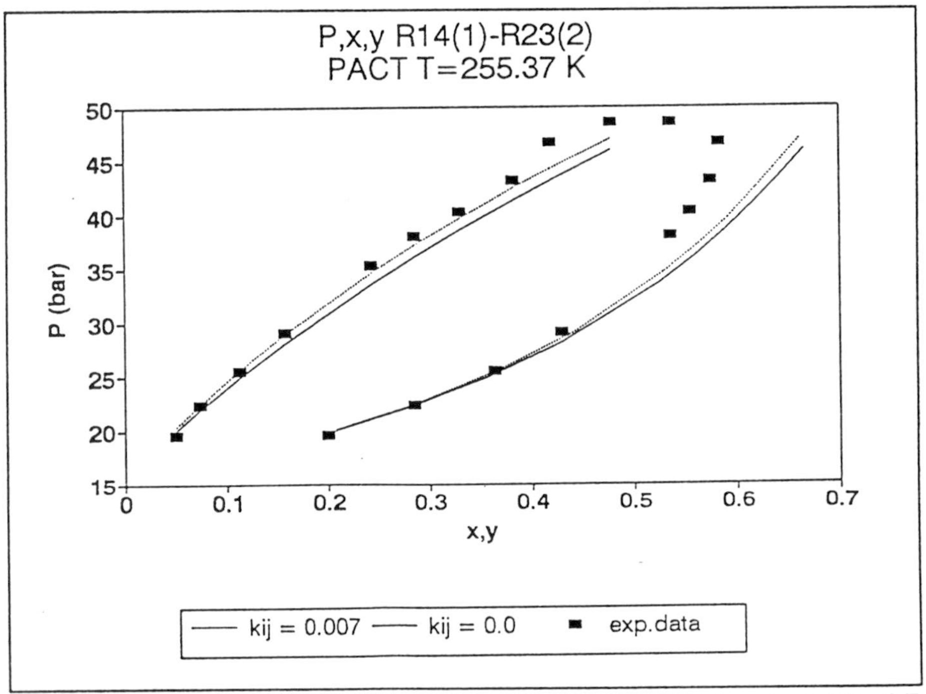

Figure 4.20 P,x,y diagram for R14-R23 at 255.37 K calculated with the PACT equation of state and with the PR equation of state without a binary interaction parameter

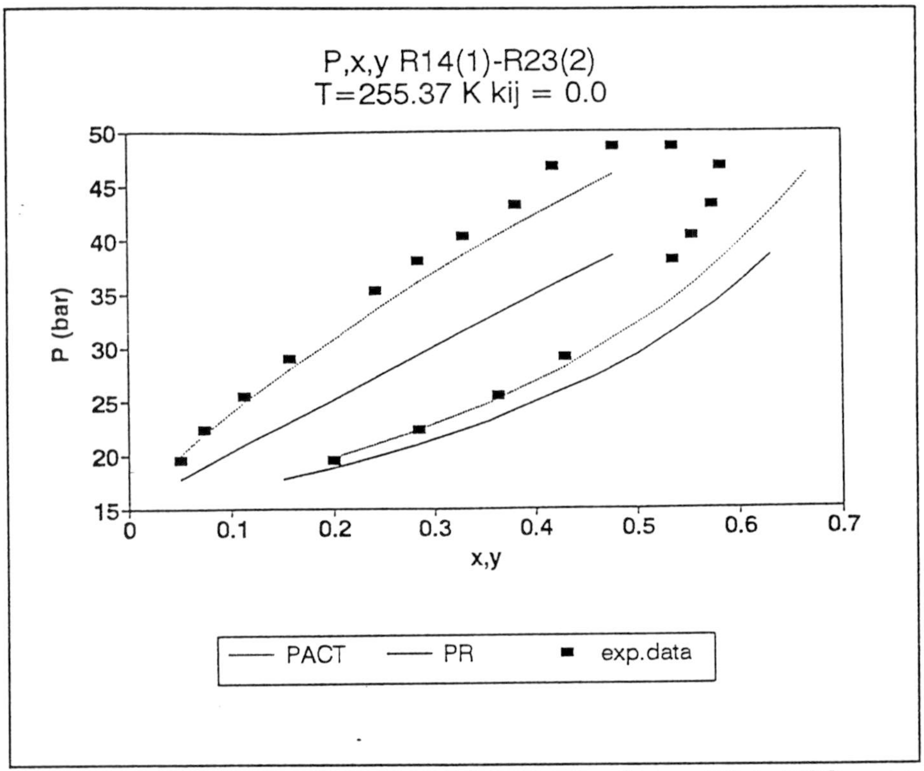

Figure 4.21 P,x,y diagram for R14-R23 at T=255.37 K calculated with the PACT equation of state

reason why the PR equation of state and the SRK equation of state are still describing these system within an error of ten percent. The general conclusion from all these binary freon mixture calculations is that although the systems are not very non-ideal, the PACT equation of state describes the systems much better without the introduction of a binary interaction parameter.

For two binaries the phase behavior is plotted (figures 4.17-4.21). In figure 4.17 a P,x diagram is given for the mixture R23-R11, calculated with the PACT equation of state. The dashed line is the VLE of the system with a correlated k_{ij} and the solid line is the prediction without a binary interaction parameter. It can be seen that the PACT equation of state is able to predict the VLE quite accurate and that the PACT equation of state is also able to correlate the experimental data. For the PR equation of state a similar figure is prepared (figure 4.18). This figure shows that the predicted VLE are not in quantitative agreement with the experimental data, but that it is possible to correlate these experimental data. In figure 4.19 the predicted VLE for the PR equation of state and for the PACT equation of state are shown. The conclusion is that for prediction purposes, the PACT equation of state should be used.

From the results for another binary, R14-R23, the same conclusion can be drawn (figure 4.20). In figure 4.20 the phase behavior of the system R14-R23 calculated with the PACT and with the PR equation of state is plotted. The results are again compared with experimental data and the general conclusion is that the PACT equation of state describes the system much better. In figure 4.21 the phase behavior of the same system is plotted, but this time the correlated binary interaction parameter is introduced. This binary interaction parameter is correlated over the entire temperature range. It does not describe the experimental data exactly at one particular temperature. Correlating the binary interaction parameter to only this temperature, will result in a better description of the experimental data points.

4.3.3 Binary freon-hydrocarbon mixtures

The phase behavior of a few binary freon-hydrocarbon mixtures has been calculated with the PACT equation of state and with the PR equation of state. The results are given in table 4.5.

Table 4.5 Binary freon-hydrocarbon mixtures, comparison between PACT, PR and SRK

System	PACT			PR			SRK[42]	
	%AAD in Pressure		k_{ij}	%AAD in Pressure		k_{ij}	%AAD in Pressure	
	Pred.	Opt. k_{ij}		Pred.	Opt. k_{ij}		Pred	Opt. k_{ij}
R113-Benzene*	7.45	0.69	-0.008	6.99	0.65	0.019		
R20-nHeptane	3.62	0.65	0.005	0.74	0.74	0.0		
R20-nHexane	3.67	0.63	0.006	1.44	0.44	0.005		
R13-iButane	3.71	1.37	0.024	7.92	0.45	0.065	7.67	0.47
R22-nPentane	14.79	1.82	0.032	19.56	1.02	0.092	18.80	1.32
R13-nButane	5.89	1.73	0.030	9.99	0.73	0.071	10.27	0.62

* calculations are based on two different experimental data sets

The first three systems of table 4.5 are calculated at pressures below 1 bar whereas the last three systems are calculated at pressures above 1 bar (see table 4.2). The SRK equation of state describes the phase behavior as good as the PR equation of state and in the cases where no results are reported for the SRK equation of state similar results are expected as for the PR equation of state. From the first three systems it is clear that the PACT equation of state is not describing the phase behavior better than the PR equation of state at pressures below one bar. At these low pressures the vapor phase is nearly ideal. Cubic equations of state are designed to describe such near-ideal systems, so much improvement could not be expected. When calculating more non-ideal situations as in the last three systems, the PACT equation of state becomes superior to the cubic equations of state. Correlating the binary interaction parameter to the experimental data, similar good results are obtained for all the equations of state.

4.3.4 Ternary freon mixtures

For three ternary freon mixtures the %AAD between the experimental data and the PACT equation of state and the PR equation of state has been calculated. The results are given in table 4.6.

Table 4.6 Ternary freon-mixtures, comparison between PACT and PR

system	PACT % AAD in Pressure		PR % AAD in Pressure	
	Pred. with $k_{ij}= 0$	Pred. with opt. k_{ij} from the bin.	Pred. with $k_{ij}= 0$	Pred. with opt. k_{ij} from the bin.
R11-R22-R23	2.50	2.17	8.63	4.79
R22-R23-R114	3.83	2.46	15.48	9.67
R13-R14-R23	10.85	2.86	15.53	2.46

The third and the fifth column are the %AAD calculated with the optimal binary interaction parameters from the binary mixtures. The improvement between the predicted %AAD in pressure without k_{ij} and the predicted %AAD with k_{ij} from the binaries depends on the number of binary interaction parameters that were known. For the third system all binary interaction parameters were known whereas for the other two systems only one or two were known. For the case where the optimal binary interaction parameter for a binary mixture is not known, it is taken equal to zero. Again the PACT equation of state is describing the mixtures much better than the PR equation of state.

4.3.5 Conclusion

All the results from the previous paragraphs are averaged and given in table 4.7 and table 4.8.

Table 4.7 Comparison between PACT, PR and SRK with $k_{ij} = 0.0$.

Group	% AAD in Pressure		
	PACT	PR	SRK[42]
Overall - prediction			
19 binaries + 3 ternaries	5.55	10.72	
15 binaries	5.73	11.37	11.56
Freon mixtures - prediction			
13 binaries + 3 ternaries (P>1 atm.)	5.19	11.82	
12 binaries (P>1 bar)	5.13	11.08	11.39
3 ternaries (P>1 bar)	5.73	16.55	
Freon-hydrocarbon mixtures - prediction			
6 binaries	6.52	7.77	
3 binaries (P>1 bar)	8.13	12.49	12.25
3 binaries (P<1 bar)	4.91	3.06	

Table 4.8 Comparison between PACT, PR and SRK with a correlated k_{ij}.

group	% AAD in Pressure		
	PACT	PR	SRK[42]
Overall - correlation			
19 binaries	1.93	1.70	
Freon mixtures - correlation			
12 binaries	2.42	2.28	1.73
Freon-hydrocarbon mixtures - correlation			
6 binaries	1.15	0.67	
3 binaries ($P > 1$ bar)	1.64	0.73	0.80
3 binaries ($P < 1$ bar)	0.66	0.61	

These tables confirm the idea that the PACT equation of state is about two times better than the PR equation of state and the SRK equation of state for these mixtures, when using the equations of state for pure predictions without a binary interaction parameter. Only for the freon-hydrocarbon mixtures at pressures below 1 bar, the PR equation of state is better. This is due to the fact that the PR equation of state (like many other cubic equations of state) is designed to describe these nearly ideal mixtures. When the systems are becoming more non-ideal the PACT equation of state is much better than these cubic equations of state. Introducing a binary interaction parameter results in the same results for all three equations of state. So when a correlated binary interaction parameter is demanded, any equation of state can be used. In this case the PR equation of state or the SRK equation of state would be preferred, since cubic equations of state are simple. However, for extrapolation and prediction purposes the PACT equation of state should be used.

5. CONCLUSION

Pure component molecular parameters for the APACT and the PACT equations of state have been calculated for a variety of components. The parameters were fitted to experimental vapor pressures and liquid densities. Most of the components examined in this work were freons. The PACT equation of state is able to describe the pure component properties with less than one percent error. Further, from comparing the results for different groups of freons, it is clear that the molecular parameters for the APACT (or PACT) equation of state are related to the size, dispersion energy and shape of the molecules. The fitting procedure is described and can now be used easily and quickly.

The system ethanol-hexane can be described accurately with the APACT equation of state without the introduction of a binary interaction parameter. This is in contrast with the PR equation of state, which is not able to describe the phase behavior of this system, even with a binary interaction parameter. The APACT equation of state is able to describe the entire phase behavior and furthermore it predicts the azeotrope accurately.

The APACT equation of state requires, for the system water-carbon dioxide, a binary interaction parameter. Two versions of the APACT have been tested for this system. It became clear that the three-sites version, i.e. the equation of state which assumes that a water molecule can hydrogen bond at three different sites per molecule, works better than the two-sites version. When the critical point is approached, a relative large binary interaction parameter is needed. LLE can be calculated with APACT in addition to VLE. However, it was impossible to correlate accurately with the same binary interaction parameter the solubility of water in CO_2 and the solubility of CO_2 in water.

Finally, the phase behavior for a number of freon mixtures has been calculated with the PACT and the predictions are compared with the PR equation of state. The PACT was able to describe all the binaries and ternaries mixtures approximately two times better than the PR equation of state and the SRK equation of state. Only for the freon-hydrocarbon mixtures at pressures below one bar, the PR equation of state was slightly better. This is due to the fact that the PR equation of state is designed to describe these nearly ideal mixtures. For a more non-ideal system, the PACT should be used. Introduction of a binary interaction parameter results in the accurate results for all the equations of state.

It is clear that for systems that exhibit hydrogen bonding and polar interactions, the APACT equation of state works better than the cubic equations of state and that for extrapolation or prediction purposes, the APACT (or PACT) equation of state should be used.

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APPENDIX A

Expressions for the terms in the APACT.

The APACT is given by :

$$Z = 1 + Z^{assoc} + Z^{rep} + Z^{attr} \tag{A.1}$$

For the association term the following expression is used :

$$Z^{assoc} = \frac{n_t}{n_0} - 1 \tag{A.2}$$

where n_0 is the "superficial" number of moles of associating species (i.e. the number of moles that would exist if there where no associating) and n_t is the sum of the "true" number of moles of associating species (i.e. moles of monomers, dimers etc.). When using the infinite equilibrium model as association model, the expression for n_t/n_0 is given by :

$$\frac{n_t}{n_0} = \frac{2}{1 + \sqrt{1 + 4KRT\rho}} \tag{A.3}$$

where ρ is the density and K is the equilibrium constant (which is assumed to be independent of the degree of association) and is given by :

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{A.4}$$

Where ΔH^0 is the enthalpy of association and ΔS^0 is the entropy of association.

For the repulsive term, the Carnahan-Starling[16] expression is used :

$$Z^{rep} = c\frac{4\left(\frac{\tau v_d^*}{v}\right) - 2\left(\frac{\tau v_d^*}{v}\right)^2}{\left(1 - \frac{\tau v_d^*}{v}\right)^3} \tag{A.5}$$

where c is one-third of total number of external degrees of freedom, $\tau = 0.7405$, v_d^* is the characteristic (soft-core) volume per molecule and v is the molar volume.

The attractive term contains three terms, accounting for the Lennard-Jones interactions, for the isotropic dipole-induced dipole interactions and for the anisotropic interactions :

$$Z^{attr} = Z_{att}^{LJ} + Z^{\mu ind\mu} + Z^{ani} \tag{A.6}$$

The Lennard-Jones interactions are given by :

$$Z_{att}^{LJ} = \frac{Z_1^{LJ} + Z_2^{LJ} - 2\,Z_1^{LJ}\frac{A_2^{LJ}}{A_1^{LJ}}}{\left[1 - \frac{A_2^{LJ}}{A_1^{LJ}}\right]^2} \tag{A.7}$$

$$Z_1^{LJ} = c\frac{T^*}{T}\sum_m^6 mA_{1m}\left(\frac{v_d^*}{v}\right)^m \tag{A.8}$$

$$Z_2^{LJ} = c\left(\frac{T^*}{T}\right)^2 \sum_m^4 \left[\frac{m}{2} C_{1m}\left(\frac{v_d^*}{v}\right)^m + (m+1)\, C_{2m}\left(\frac{v_d^*}{v}\right)^{m+1} + \frac{(m+2)}{2} C_{3m}\left(\frac{v_d^*}{v}\right)^{m+2}\right] \tag{A.9}$$

$$\frac{A_1^{LJ}}{nkT} = c\frac{T^*}{T}\sum_m^6 A_{1m}\left(\frac{v_d^*}{v}\right)^m \tag{A.10}$$

$$\frac{A_2^{LJ}}{nkT} = c\left(\frac{T^*}{T}\right)^2 \sum_m^4 \left[\frac{C_{1m}}{2}\left(\frac{v_d^*}{v}\right)^m + C_{2m}\left(\frac{v_d^*}{v}\right)^{m+1} + \frac{C_{3m}}{2}\left(\frac{v_d^*}{v}\right)^{m+2}\right] \tag{A.11}$$

where T^* is a pure component parameter determined by fitting liquid density and vapor pressure experimental data. The universal constants A_{1m} and C_{nm} are given in appendix B.

The isotropic dipole-induced dipole interactions are given by:

$$Z^{\mu ind\mu} = -2\sqrt{2\pi}\,\frac{c\alpha T_\mu^* v^*}{Tv} J^{(6)}\left[1 + \tilde{\rho}\frac{\partial J^{(6)}}{\partial\tilde{\rho}}\right] \tag{A.12}$$

$$\tilde{\rho} = \frac{v^*}{v} \tag{A.13}$$

$$\ln|J^{(n)}| = A_n(\sqrt{2}\tilde{\rho})^2 \ln\tilde{T} + B_n(\sqrt{2}\tilde{\rho})^2 + C_n(\sqrt{2}\tilde{\rho})\ln\tilde{T} + D_n(\sqrt{2}\tilde{\rho}) + E_n\ln\tilde{T} + F_n \tag{A.14}$$

$$\tilde{T} = \frac{T}{T^*} \qquad \textbf{(A.15)}$$

$$T_\mu^* = 3.048 \frac{\mu^2}{c v^*} \qquad \textbf{(A.16)}$$

where α is the average polarizability, μ is the dipole moment in debye and v^* is a fitted molecular parameter (representing the volume or size of the molecule). The constants A_n to F_n are given by Gubbins and Twu[43].

The anisotropic interactions are given by :

$$Z^{ani} = \frac{Z_2^{ani} + Z_3^{ani} - 2 Z_2^{ani} \dfrac{A_3^{ani}}{Z_2^{ani}}}{[1 - \dfrac{A_3^{ani}}{A_2^{ani}}]^2} \qquad \textbf{(A.17)}$$

$$Z_2^{ani} = Z_2^{\mu\mu} + Z_2^{QQ} \qquad \textbf{(A.18)}$$

$$Z_3^{ani} = Z_{3b}^{\mu\mu\mu} + Z_{3a}^{QQ} + Z_{3b}^{QQQ} \qquad \textbf{(A.19)}$$

$$Z_2^{\mu\mu} = -2.962 \frac{c (T_\mu^*)^2 v^*}{T^2 v} J^{(6)} [1 + \tilde{\rho} \frac{\partial \ln J^{(6)}}{\partial \tilde{\rho}}] \qquad \textbf{(A.20)}$$

$$Z_2^{QQ} = -12.44 \frac{c (T_Q^*)^* v^*}{T^2 v} J^{(10)} [1 + \tilde{\rho} \frac{\partial \ln J^{(10)}}{\partial \tilde{\rho}}] \qquad \textbf{(A.21)}$$

$$T_Q^* = 0.017464 \frac{Q^2}{c(v^*)^{5/3}} \tag{A.22}$$

$$Z_{3b}^{\mu\mu\mu} = 45.596 \frac{c(T_\mu^*)^3 (v^*)^2}{T^3 v^2} K_{\mu\mu\mu} [2 + \tilde{\rho} \frac{\partial \ln K_{\mu\mu\mu}}{\partial \tilde{\rho}}] \tag{A.23}$$

$$Z_{3a}^{QQ} = 2.611 \frac{c(T_Q^*)^3 v^*}{T^3 v} J^{(15)} [1 + \tilde{\rho} \frac{\partial \ln J^{(15)}}{\partial \tilde{\rho}}] \tag{A.24}$$

$$Z_{3b}^{QQQ} = 77.716 \frac{c(T_Q^*)^3 (v^*)^2}{T^3 v^2} K_{QQQ} [1 + \tilde{\rho} \frac{\partial \ln K_{QQQ}}{\partial \tilde{\rho}}] \tag{A.25}$$

$$A_2^{ani} = A_2^{\mu\mu} + A_2^{QQ} \tag{A.26}$$

$$A_3^{ani} = A_{3b}^{\mu\mu\mu} + A_{3a}^{QQ} + A_{3b}^{QQQ} \tag{A.27}$$

$$\frac{A_2^{\mu\mu}}{nkT} = -2.962 \frac{c(T_\mu^*)^2 v^*}{T^2 v} J^{(6)} \tag{A.28}$$

$$\frac{A_2^{qq}}{nkT} = -12.44 \frac{c(T_q^*)^2 v^*}{T^2 v} J^{(10)} \tag{A.29}$$

$$\frac{A_{3b}^{\mu\mu\mu}}{nkT} = 43.596 \frac{c(T_\mu^*)^3 (v^*)^2}{T^3 v^2} K_{\mu\mu\mu} \tag{A.30}$$

$$\frac{A_{3a}^{QQ}}{nkT} = 2.611\frac{c(T_q^*)^3 v^*}{T^3 v} J^{(15)} \tag{A.31}$$

$$\frac{A_{3b}^{QQQ}}{nkT} = 77.716\frac{c(T_q^*)^3 (v^*)^2}{T^3 v^2} K_{QQQ} \tag{A.32}$$

where Q is the quadrupole moment which should be expressed in esu$*10^{26}$.

For mixtures, equation A.1 is used again. All the other expressions are used, but some terms have to be expressed as mixture properties. This results in the introduction of mixing rules. Different mixing rules have been used for each group of parameters in order to eliminate the mean-field approximation. The mixing rules are given by Donohue and Prausnitz[8] and Vimalchand and Donohue[20]. One adjustable parameter has been introduced, which is a binary interaction parameter (k_{ij}) for the dispersion term :

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}\,(1 - k_{ij}) \tag{A.33}$$

where ϵ_{ij} is the segmental dispersion energy between molecule i and j.

APPENDIX B

Tabel B.1 Universal constants for the APACT equation of state.

A_{11}	-8.5380
A_{12}	-5.2761
A_{13}	3.7304
A_{14}	-7.5398
A_{15}	23.3070
A_{16}	-11.1971
C_{11}	-3.9382
C_{12}	-3.1927
C_{13}	-4.9300
C_{14}	10.0296
C_{21}	11.7026
C_{22}	-3.0915
C_{23}	4.0091
C_{24}	-20.0254
C_{31}	-37.0190
C_{32}	26.9271
C_{33}	26.6728
C_{34}	0.00

APPENDIX C

INPUT file for pure component fitting

TITLE
THEORY CALC IASS MDSR
QUD OCT
DIP DIN
TITLE
LL ITMAX IXMAX IPRT IPRINT
TITLE
TS1 VS1 C1 QS1 DIS EPS1 SRS
DELHO DSR VPL VPR[1]
XDELHO XDSR DELDSR[1]
TITLE
NPVT
DATA LIQUID DENSITY
TITLE
NVP
DATA VAPOR PRESSURE

Parameter	Function	Format
TITLE	can be anything	A20
THEORY	theory used	A7
	(PHCT, PSCT, PACT, APSCT, APACT, SPHCT or COMPACT)	
CALC	calculation	A6
IASS	association model	I3
MDSR	number of times $\Delta S/R$ is changed	I3
QUD	quadrupole moment	F10.0
OCT	octapole moment	F10.0
DIP	dipole moment	F10.0
DIN	polarizability	F10.0
LL	number of parameters that can be changed	I3
ITMAX	maximum number of iterations	I3

IXMAX	parameter that allow greater flexibility for the fitted parameters	I3
IPRT	determines the amount of output	I3
IPRINT	determines the amount of output	I3
TS1	initial estimation of T^*	F10.0
VS1	initial estimation of v^*	F10.0
C1	initial estimation of c	F10.0
QS1[2]	characteristic temperature for quadrupole-quadrupole interactions	F10.0
DIS[2]	characteristic temperature for dipole-dipole interactions	F10.0
EPS1[3]	dispersion energie	F10.0
SRS	non-zero parameter for hydrogen and zero-parameter for all other components	F10.0
DELHO	ΔH	F10.0
DSR	ΔS/R	F10.0
VPL[3]	left criterium for the calculation of the volume for the vapor pressure calculation of associating components	F10.0
VPR[3]	right criterium for the calculation of the volume for the vapor pressure calculation of associating components	F10.0
XDELHO	Δ(ΔH), used when one tries to fit ΔH	F10.0
XDSR	Δ(ΔS/R), used when one tries to fit ΔS/R	F10.0
DELDSR	Δ(ΔS/R), used when one tries to fit ΔS/R	F10.0
NPVT	number of PVT data	I3
NVP	number of VP data	I3

[1] if no association included, these lines should be skipped

[2] if not given, the program will calculate it

[3] program has a default value