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Complex Fluid Phase Equilibrium Modeling and Calculations

Gholamreza Vakili-Nezhaad

*Department of Petroleum & Chemical Engineering, College of Engineering, Sultan Qaboos University, Muscat
Oman &*

*Department of Chemical Engineering, Faculty of Engineering, University of Kashan,
Kashan
Iran*

1. Introduction

Thermodynamic modeling and calculations of different complex fluid mixtures are presented in this chapter. This study includes four parts. In the first part phase equilibrium calculations of the system polystyrene-methylcyclohexane with the Sanchez-Lacombe equation of state is presented using continuous thermodynamics. In this part the Sanchez-Lacombe equation of state is used to model the stability and cloud-point curves of polystyrene (PS) in methylcyclohexane (MCH) systems. An algorithm based on the work of Browarzik and Kowalewski is applied. Three different polymers are studied. Two of them are monodisperse, and the third is polydisperse. To describe the polydispersity of polystyrene, Schulz-Flory distribution function is considered. One of the monodisperse systems shows lower critical point (LCP) and upper critical point (UCP) curves at a certain temperature region, which turn into hour-glass shaped cloud-point curves by lowering the temperature. Excellent agreement with the experimental data is observed. Polymer parameters are fitted to the experimental data. These parameters are used in modeling the other systems and the results are compared with experimental data. The second part of this work presents the application of continuous thermodynamics to investigate the limited miscibility of methanol-gasoline blends. To predict the liquid-liquid equilibrium of these systems, the Gaussian distribution function was used to represent the composition of paraffins in the gasoline. The naphthenes and aromatics were represented by model compounds. A model has been developed using three different continuous versions of the UNIFAC model. Methanol is an associating component, and association affects phase equilibria. Therefore, the CONTAS (continuous thermodynamics of associating systems) model based on the Flory-Huggins equation, for multicomponent methanol-gasoline blends has also been investigated. The predicted results including the cloud point curve, shadow curve and phase separation data have been compared with experimental data and good agreement was found for the two UNIFAC and CONTAS models. In part three a method based on continuous thermodynamics has been presented for calculating the vapor pressure of undefined composition mixtures. In order to verify the proposed method the

experimental data of two real samples have been used. In this work by using the combination of the Trouton's rule and the Clausius–Clapeyron equation in the well-known equation of Antonie, the continuous version of the Raoult's law has been developed and the results of the modeling and calculations have been compared with the experimental data and good agreement was found. Moreover, for improving the results of the ideal continuous mixture, modeling of non-ideal behavior of such mixtures has been carried out by introducing the continuous version of the UNIFAC activity coefficient in the formulation and a better result has been obtained. In the last section a new approach based on the genetic algorithm has been proposed for solving three phase flash calculations containing two liquid phases and one vapor phase. Based on this approach choosing the initial guesses for the compositions of the involved phases is not an important step, which in the ordinary three phase algorithms affects directly the convergence of the calculations. A real problem has been solved with this approach and very good results have been obtained in comparison with the experimental data. φ - φ approach has been adopted for vapor-liquid-liquid equilibrium (VLLE) calculations based on the Peng-Robinson equation of state.

2. Phase equilibrium calculations of polymer solution systems using continuous thermodynamics

The Sanchez-Lacombe equation of state is used to model the stability and cloud-point curves of polystyrene (PS) in methylcyclohexane (MCH) systems. An algorithm based on the work of Browarzik and Kowalewski (2002) is applied. Three different polymers are studied. Two monodisperse systems and one polydisperse system have been studied in this section. To describe the polydispersity of polystyrene, Schulz-Flory distribution function is considered. One of the monodisperse systems shows lower critical point (LCP) and upper critical point (UCP) curves at a certain temperature region, which turn into hour-glass shaped cloud-point curves by lowering the temperature. Excellent agreement with the experimental data is observed. Polymer parameters are fitted to the experimental data. These parameters are used in modeling the other systems and the results are compared with experimental data (Behnam, 2008).

2.1 Introduction

The system polystyrene (PS) in methylcyclohexane (MCH) has been studied by some researchers (Xiong & Kiran, 2000; Wachnic & Van Hook, 2004) and a lot of experimental data exist for this system. Narita et al. (2003) determined a semiempirical equation of Gibbs free energy of mixing (ΔG) for the system based on the Flory-Huggins equation. The equation of ΔG was used in preparation of controlled size distribution microcapsules. Vanhee et al. (1994) used a nearly monodisperse PS. They applied a pressure-pulse -induced scattering (PPIS) technique and obtained spinodal and cloud-point curves. They observed the pressure-concentration diagram shows upper critical point (UCP) and lower critical point (LCP) behavior for some temperatures. These curves come closer and turn into hour-glass shaped curves by lowering the temperature. Browarzik and Kowalewski (2004) studied the mentioned system by using SWP (Sako-Wu-Prausnitz) equation of state which is able to predict polymer solutions. They also discussed the transition of the UCP/LCP behavior into the hour-glass diagrams for polydisperse polymer and studied the polydispersity effect on stability and phase equilibria. Koak et al. (1998) measured phase

equilibria for PS-MCH systems in the vicinity of the upper critical solution temperature (UCST) in the glass tube Cailletet apparatus for two samples of polystyrene. One was nearly monodisperse and the other was polydisperse. Here, the Sanchez-Lacombe equation of state has been chosen. Three different PS solutions based on the measurements of Vanhee et al. (1994) and Koak et al. (1998) were studied (Behnam, 2008). The method developed by Browarzik and Kowalewski (2002, 2004) was applied to obtain the stability and phase equilibria equations. To describe the molecular weight polydispersity of the polymer, Schulz-Flory distribution function which is appropriate to characterize PS samples (Browarzik & Kowalewski, 2002; Enders & de Loos, 1997) were considered and the results were compared with experimental findings.

2.2 Spinodal, cloud-point and critical conditions

Continuous thermodynamics is an appropriate method in treatment of multi-component mixtures such as polydisperse polymer solutions. A continuous distribution function is used to represent the polymer (B). The solvent is denoted as A. Considering the polymer described by the distribution function $W_s(r)$, where r shows the segment numbers of the molecules of the polymer species, $W_s(r) dr$ is the segment fraction of all polymer species with segment numbers between r and $r + dr$. So the integral of $W_s(r) dr$ over the entire range of r is 1. The limits of the integral are usually 0 and ∞ . Browarzik and Kowalewski (1999) developed a method based on an EOS to calculate spinodal curves and critical points of a system containing a polydisperse polymer, a solvent and a gas. In 2002, they studied a system containing a polymer and a solvent and determined the segment-molar Helmholtz energy of a mixture whose non-linear parts with respect to segment mole fractions can be presented as follows (Browarzik & Kowalewski, 2002) :

$$\Delta A_s = RT \left\{ \int \frac{\psi}{r} W_s(r) \ln[\psi W_s(r)] dr + \frac{1-\psi}{r_A} \ln(1-\psi) \right\} - \frac{RT}{\bar{r}^M} \ln V_s + J_s \quad (1)$$

The linear parts do not influence the stability. The first term on the right-hand side of Eq. (1) is the Flory-Huggins contribution. R is the universal gas constant and T is the temperature. $W_s(r)$ is the segment -molar distribution function of the polymer. r_A is the segment number of the solvent. ψ is the total segment-mole fraction of the polymer. Since it was assumed the segment number is proportional to the molecular weight, ψ is the total weight fraction of the polymer as well. \bar{r}^M is the number-averaged segment number of the mixture which reads:

$$\frac{1}{\bar{r}_M} = \frac{1-\psi}{r_A} + \frac{\psi}{\bar{r}_B}; \quad \frac{1}{\bar{r}_B} = \int \frac{W_s(r)}{r} dr \quad (2)$$

\bar{r}_B is the number-averaged segment number of the polymer B and is proportional to number average molar mass of the polymer (\bar{M}_n). By division of molar volume through \bar{r}^M the segment-molar volume, V_s , is obtained. The last term on the right hand side of Eq. (1), J_s , is related to the equation of state and is obtained by:

$$J_s = \int_{V_s}^{\infty} \left(p - \frac{RT}{\bar{r}_M V_s} \right) dV_s \quad (3)$$

In order to find spinodal points, the following equation should be solved:

$$K_0 = \alpha_{VV} \alpha_{\psi\psi} - (\alpha_{V\psi})^2 = 0 \quad (4)$$

$$\alpha_{VV} = J_{VV} + \frac{RT}{(V_s)^2} \left\{ \frac{1-\psi}{r_A} + \frac{\psi}{\bar{r}_B(1+U)} \right\} \quad (4a)$$

$$\alpha_{\psi\psi} = J_{\psi\psi} + RT \left\{ \frac{1}{r_A(1-\psi)} + \frac{1}{\bar{r}_B(1+U)\psi} \right\} \quad (4b)$$

$$\alpha_{V\psi} = J_{V\psi} + \frac{RT}{V_s} \left\{ \frac{1}{r_A} - \frac{1}{\bar{r}_B(1+U)} \right\} \quad (4c)$$

The parameters J_{VV} , $J_{V\psi}$ and $J_{\psi\psi}$ are the second derivatives of J_s with respect to V_s and ψ . U is non-uniformity and shows polydispersity of the polymer and is defined by:

$$U = \frac{\bar{r}_B^{(1)}}{\bar{r}_B} - 1 = \frac{\bar{M}_w}{\bar{M}_n} - 1 ; \quad \bar{r}_B^{(1)} = \int r W_s(r) dr ; \quad \bar{r}_B^{(2)} = \int r^2 W_s(r) dr \quad (5)$$

\bar{M}_w and \bar{M}_n are mass average molar mass and number average molar mass of the polymer respectively. Browarzik and Kowalewski (2004) developed two equations for critical points. The first is from Eq. (4) and the second is obtained by solving Eq. (6).

$$K_1 = L_V \alpha_{\psi\psi} - L_\psi \alpha_{V\psi} + L_r \bar{r}_B^{(1)} \left\{ \frac{\psi}{V_s} \left[1 - \frac{\bar{r}_B^{(2)}}{(\bar{r}_B^{(1)})^2} \right] \alpha_{\psi\psi} - \frac{\bar{r}_B^{(2)}}{(\bar{r}_B^{(1)})^2} \alpha_{V\psi} \right\} = 0 \quad (6)$$

$$L_V = \alpha_{\psi\psi} \left\{ J_{VVV} - \frac{2RT}{(V_s)^3} \left[\frac{1-\psi}{r_A} + \frac{\psi}{\bar{r}_B^{(1)}} \right] \right\} + \alpha_{VV} J_{\psi\psi V} - 2\alpha_{V\psi} \left\{ J_{V\psi V} - \frac{RT}{(V_s)^2} \left[\frac{1}{r_A} - \frac{1}{\bar{r}_B^{(1)}} \right] \right\} \quad (6a)$$

$$L_\psi = \alpha_{\psi\psi} \left\{ J_{VV\psi} + \frac{RT}{(V_s)^2} \left[-\frac{1}{r_A} + \frac{2}{\bar{r}_B^{(1)}} \right] \right\} + \alpha_{VV} \left\{ J_{\psi\psi\psi} + \frac{RT}{r_A(1-\psi)^2} \right\} - 2\alpha_{V\psi} \left\{ J_{V\psi\psi} - \frac{RT}{V_s} \frac{1}{\psi \bar{r}_B^{(1)}} \right\} \quad (6b)$$

$$L_r = -\frac{RT}{[\bar{r}_B^{(1)}]^2} \left\{ \frac{\alpha_{\psi\psi}}{(V_s)^2} + \frac{\alpha_{VV}}{\psi^2} + \frac{2\alpha_{V\psi}}{\psi V_s} \right\} \quad (6c)$$

To calculate phase equilibria, the fugacity coefficients are used. The equilibrium condition for the phases I and II reads (Browarzik & Kowalewski, 2002):

$$X_i^I \phi_i^I = X_i^{II} \phi_i^{II} \quad (7)$$

$$\psi_i = X_i \frac{r_i}{\bar{r}^M} \quad (8)$$

X_i is the mole fraction of the component i , ψ_i is the segment-mole fraction of i and r_i shows the segment-number of i . Combining Eq. (7) with Eq. (8) for solvent and the polymer species yields :

$$(1 - \psi^I) \phi_A^I \bar{r}^{MI} = (1 - \psi^{II}) \phi_A^{II} \bar{r}^{MII} \quad (9)$$

of the component i , ϕ_i , may be obtained by:

$$\ln \phi_i = \frac{1}{RT} \int_{\bar{V}}^{\infty} \left(\frac{\partial p}{\partial n_i} - \frac{RT}{\bar{V}} \right) d\bar{V} - \ln \left(\frac{p\bar{V}}{nRT} \right) \quad (10)$$

\bar{V} is the total volume ($\bar{V} = nV$) and V is the molar volume.

The fugacity coefficients of the solvent A and the species of the polymer B may be expressed by (Browarzik & Kowalewski, 2002):

$$\ln \phi_A = r_A B_A - \ln \bar{r}^M - \ln \left(\frac{pV_s}{RT} \right) \quad (11)$$

$$\ln \phi_B(r) = r B_B - \ln \bar{r}^M - \ln \left(\frac{pV_s}{RT} \right) \quad (11a)$$

B_A and B_B depend on the equation of state which is used for modeling. Combining Eq. (9) with Eq. (11) yields:

$$\frac{1}{r_A} \ln \left(\frac{(1 - \psi^I) V_s^{II}}{(1 - \psi^{II}) V_s^I} \right) + B_A^I - B_A^{II} = 0 \quad (12)$$

To represent the polymer, Schulz-Flory distribution function is chosen:

$$W_s^I(r) = \frac{k^k}{\Gamma(k) \bar{r}_B^I} \left(\frac{r}{\bar{r}_B^I} \right)^k \exp \left[-k \frac{r}{\bar{r}_B^I} \right] \quad (13)$$

Γ is the Γ -function and $k=1/U$. The distribution function of the phase II is also a Schulz-Flory function with the parameter \bar{r}_B^{II} and the same value of k . Introducing distribution functions of both phases into Eq. (9a) and combining with Eq. (11a) considering the resultant equation is valid for all amounts of r between 0 and ∞ , following equations are obtained :

$$\bar{r}_B^{\text{II}} = \bar{r}_B^{\text{I}} \left(\frac{\psi^{\text{II}} V_s^{\text{I}}}{\psi^{\text{I}} V_s^{\text{II}}} \right)^{U/U+1} \quad (14)$$

$$\left(\frac{\psi^{\text{I}} V_s^{\text{II}}}{\psi^{\text{II}} V_s^{\text{I}}} \right)^{U/U+1} - 1 + \bar{r}_B^{\text{I}} U (B_B^{\text{I}} - B_B^{\text{II}}) = 0 \quad (15)$$

For given temperature, the parameters of pressure p , the mass fraction of the polymer in phase II ψ^{II} , V_s^{I} and V_s^{II} are unknown. For given p and ψ^{II} , the values of V_s^{I} and V_s^{II} can be calculated by using the EOS. To find p and ψ^{II} , Eqs. (12) and (15) are solved simultaneously.

2.3 Sanchez-Lacombe equation of state

The Sanchez-Lacombe EOS (Sanchez & Lacombe, 1978; Sanchez & Lacombe, 1976) is used for calculation of stability and phase equilibria of the system PS-MCH. Gauter and Heidemann (2001) used this EOS for modeling polyethylene-solvent mixtures. The Sanchez-Lacombe equation has proven to be suitable for polymer systems. This EOS is used in the form reported by Koak and Heidemann (1996):

$$\frac{p}{RT} = \frac{1-d}{V} - \frac{d^2}{b} \ln \left(\frac{V-b/d}{V} \right) - \frac{a}{V^2} \quad (16)$$

$$b = \sum_{i=1}^{n_C} \sum_{j=1}^{n_C} X_i X_j b_{ij} ; \quad b_{ij} = d_i d_j v_{ij} = d_i d_j (v_{ii} + v_{jj}) / 2 \quad (16a)$$

$$a = \sum_{i=1}^{n_C} \sum_{j=1}^{n_C} X_i X_j a_{ij} ; \quad a_{ij} = d_i d_j \varepsilon_{ij} v_{ij} \quad \varepsilon_{ij} = \left(1 - k_{ij} \right) \sqrt{\varepsilon_{ii} \varepsilon_{jj}} \quad (16b)$$

$$d = \sum_{i=1}^{n_C} X_i d_i \quad (16c)$$

In order to apply continuous thermodynamics method, the Sanchez-Lacombe EOS is expressed in segment-molar notation. The segment-molar parameters a_s and b_s are obtained by division of a and b through $(\bar{r}^M)^2$ and the parameter d_s is obtained by division of d through \bar{r}^M . Mole fractions change into weight fractions through Eq. (8). The parameters d_A and d_B are:

$$d_A = d_{s,A} r_A ; \quad d_B = d_{s,B} \bar{r}^B \quad (17)$$

The Sanchez-Lacombe EOS in segment-molar notation is obtained by:

$$p = \frac{RT}{\bar{r}^M V_s} - \frac{RT d_s}{V_s} - \frac{RT d_s^2}{b_s} \ln \left(\frac{V_s - b_s / d_s}{V_s} \right) - \frac{a_s}{V_s^2} \quad (18)$$

$$a_s = \psi_A^2 d_{s,A}^2 \varepsilon_{AA} v_{AA} + \psi_B^2 d_{s,B}^2 \varepsilon_{BB} v_{BB} + 2 \psi_A \psi_B d_{s,A} d_{s,B} \varepsilon_{AB} v_{AB} \quad (18a)$$

$$b_s = \psi_A^2 d_{s,A}^2 v_{AA} + \psi_B^2 d_{s,B}^2 v_{BB} + 2 \psi_A \psi_B d_{s,A} d_{s,B} v_{AB} \quad (18b)$$

$$d_s = \psi_A d_{s,A} + \psi_B d_{s,B} \quad (18c)$$

By introducing the EOS into Eq. (3) J_s is found:

$$J_s = RTd_s \left[1 + \ln \left(\frac{V_s - b_s / d_s}{V_s} \right) \left(\frac{V_s d_s}{b_s} - 1 \right) \right] - \frac{a_s}{V_s} \quad (19)$$

J_{vv} , $J_{\psi\psi}$ and $J_{V\psi}$ are needed for calculation of spinodal curves. To calculate the cloud-point curves, Eqs. (10) and (11-11a) are used to find B_i ($i=A, B$).

$$B_i = d_{s,i} \left[F_i \frac{b_s}{d_s} + \ln \left(\frac{V_s - b_s / d_s}{V_s} \right) (F_i V_s - 1) - \frac{H_i}{RTV_s} \right] \quad (20)$$

$$F_A = \frac{2d_s}{b_s} \left(1 - \frac{d_s \tilde{b}_A}{b_s} \right); \quad \tilde{b}_A = \psi_A d_{s,A} \nu_{AA} + \psi_B d_{s,B} \nu_{AB} \quad (20a)$$

$$F_B = \frac{2d_s}{b_s} \left(1 - \frac{d_s \tilde{b}_B}{b_s} \right); \quad \tilde{b}_B = \psi_B d_{s,B} \nu_{BB} + \psi_A d_{s,A} \nu_{AB} \quad (20b)$$

$$H_A = 2 \tilde{a}_A; \quad \tilde{a}_A = \psi_A d_{s,A} \varepsilon_{AA} \nu_{AA} + \psi_B d_{s,B} \varepsilon_{AB} \nu_{AB} \quad (20c)$$

$$H_B = 2 \tilde{a}_B; \quad \tilde{a}_B = \psi_B d_{s,B} \varepsilon_{BB} \nu_{BB} + \psi_A d_{s,A} \varepsilon_{AB} \nu_{AB} \quad (20d)$$

2.4 Pure-component parameters

To calculate the segment numbers of the solvent and the polymer, the MCH molecules are chosen as reference segment with $r_A=1$. Since it was assumed the segment number is proportional to the molecular weight M , the segment number r of the polymer species is (Browarzik & Kowalewski, 2002):

$$r = 10.1852 \frac{M}{1000} \quad (21)$$

Three pure-component parameters are needed for both the solvent and the polymer. Koak (1997) determined these parameters of Sanchez-Lacombe EOS for MCH. Gauter and Heidemann (2001) determined equations to calculate three pure-component parameters of Sanchez-Lacombe EOS from critical temperature, critical pressure and acentric factor:

$$d = 5.1178 + 13.5698w + 5.9404w^2 - 1.2952w^3 \quad (22)$$

$$\varepsilon = \frac{RT_c}{2} \frac{(1 + \sqrt{d})^2}{d} \quad (23)$$

$$v = \frac{RT_C}{P_C} \left[\ln \left(\frac{1 + \sqrt{d}}{\sqrt{d}} \right) - \frac{\sqrt{d} - 1}{2d} \right] \quad (24)$$

For MCH, the resultant parameters and those of Koak (1997) are as follows:

$$v_{AA} = 0.01443 \frac{m^3}{kgmol}; \quad \varepsilon_{AA} = 4.2734 \frac{Mpa. m^3}{kgmol}; \quad d_{S,A} = 8.6222; \quad (25)$$

three polystyrene samples are used for modeling. They differ in their average molar mass and polydispersity. The first sample (PS1) used by Vanhee et al. (1994) had weight-average molar mass $\bar{M}_w = 17500$ (g/mol) and the ratio $\frac{\bar{M}_w}{\bar{M}_n} = 1.06$. To find three pure-component

parameters $d_{S,B}$, v_{BB} , ε_{BB} , and the interaction parameter k_{AB} , experimental data of PS1 is used. Since the interaction parameter has an important role and the results are extremely sensitive to this parameter, a temperature dependence is necessary to get good results. So, at the first step, the parameters were fitted to the experimental spinodal pressures at 20.8 °C. Two extreme points on both UCP/LCP curves and an arbitrary point on the UCP curve are used. The parameter v_{BB} was fixed and the remaining parameters were obtained. The best set of these parameters is:

$$v_{BB} = 0.007 \frac{m^3}{kgmol}; \quad \varepsilon_{BB} = 4.5742379 \frac{Mpa. m^3}{kgmol}; \quad d_{S,B} = 7.93475659; \quad (26)$$

$$k_{AB} = 0.0014877 \quad (26a)$$

To find the temperature dependence of k_{AB} , a linear temperature function is assumed. For PS1, experimental spinodal points and cloud-points at 20.6 and 20.7 °C are used for fitting:

$$k_{AB} = 0.0014877 - 0.00035 (T - 293.95) \quad (27)$$

There are transitions of UCP/LCP curves into hour-glass shaped two phase region curves for PS1 at 21.2 °C. Lowering the temperature causes the two miscibility gaps to come closer together. They merge and form an hour-glass shaped two-phase region at 20.6 °C. After formation of the hour-glass shaped curves, at temperatures below the merging of LCP and UCP, the critical points disappear and spinodal curves are not tangent to cloud-point curves anymore. It was shown that the hour-glass shape for the spinodal curves and for the cloud-point curves are formed at same temperatures. These are not the case in polydisperse samples (Browarzik & Kowalewski, 2002). Koak et al. (1998) reported cloud-point data for two samples of PS in MCH. They measured phase equilibria in the glass tube Cailletet apparatus. Temperatures and compositions were in the region of UCST behavior and pressures ranged from 1 to 14 MPa. One sample (PS2) was nearly monodisperse with $\bar{M}_w = 31600$ and $\bar{M}_n = 29100$ (g/mol). Another PS3 had $\bar{M}_w = 250000$ and $\bar{M}_n = 64000$

(g/mol). Experimental temperatures ranged from 297-306 K for PS2 and 323-331 K for PS3. The mass fractions of the polymer ranged from 0.03 to 0.27 for PS2 and between 0.02 and 0.14 for PS3. To calculate cloud-point curves of PS2 and PS3 systems, pure-component parameters of MCH and PS of the PS1 are used. Since k_{AB} can depend on the molecular weight, we fitted it again to experimental cloud-point data. Given data, at $\psi_B=0.2634$ for PS2 and at $\psi_B=0.136$, for PS3 are used to fit the function $k_{AB}(T)$ given by Eqs. (28) and (29).

$$\text{For PS2: } k_{AB} = -0.00039749270543 T + 0.120703166 \quad (28)$$

$$\text{For PS3: } k_{AB} = -0.00039740070 T + 0.128231617 \quad (29)$$

Calculated cloud-point data for other concentrations for both PS2 and PS3 systems deviate from experimental data to some extent. The reason might be the effect of temperature on the function $k_{AB}(T)$.

2.5 Discussion

The Sanchez-Lacombe equation of state may be able to model the stability and cloud-point curves of polystyrene (PS) in methylcyclohexane (MCH) systems. Polydispersity of polystyrene is described by using continuous thermodynamics. PS/MCH systems may show lower critical point (LCP) and upper critical point (UCP) curves at a certain temperature region. These curves turn into hour-glass shaped curves by lowering the temperature. Sanchez-Lacombe equation of state can predict this transition. By formation of hour-glass shaped curves, the critical points no longer exist, and spinodal curves are not tangent to cloud-point curves anymore. The hour-glass shape temperatures for the spinodal curves and for the cloud-point curves are the same. However, for polydisperse case the transition temperatures for spinodal and cloud-point curve may be different. The treatment may be able to predict other monodisperse and polydisperse systems if the temperature is not in a wide range.

3. Liquid-liquid equilibrium calculations for methanol-gasoline blends using continuous thermodynamics

In this section we present the application of continuous thermodynamics to investigate the limited miscibility of methanol-gasoline blends (Nasrollahi et al., 2009). To predict the liquid-liquid equilibrium of these systems, the Gaussian distribution function was used to represent the composition of paraffins in the gasoline. The naphthenes and aromatics were represented by model compounds. A model has been developed using three different continuous versions of the UNIFAC model. Methanol is an associating component, and association affects phase equilibria. Therefore, the CONTAS (continuous thermodynamics of associating systems) model based on the Flory-Huggins equation, for multicomponent methanol-gasoline blends has also been investigated. The predicted results including the cloud-point curve, shadow curve and phase separation data have been compared with experimental data and good agreement was found for the two UNIFAC and CONTAS models (Nasrollahi et al., 2009).

3.1 Introduction

Ethanol, methanol and their blends with gasoline are known as important alternative fuels for motor engines (Agarwal, 2007; Yuksel & Yuksel, 2004). A serious problem encountered in using gasoline-alcohol blends as motor fuel at low temperatures is the separation of the mixture into two liquid phases (French & Malone, 2005; Cox, 1979). Therefore, it is important to investigate the limited miscibility of alcohol-gasoline blends. In alcohol-gasoline systems phase separation is strongly influenced by the water content, temperature and composition of aromatic components in the gasoline. Gasoline is a multicomponent mixture of paraffins, naphthenes and aromatics. In order to apply conventional thermodynamics to phase equilibrium calculations of a complex mixture, a complete chemical analysis of the mixture is required. Even if such analysis were available, inclusion of all components would lead to massive calculations. The pseudo-component (Chorn & Mansoori, 1989; Neau et al., 1993) and continuous thermodynamics (Cotterman et al., 1985; Du & Mansoori, 1986) methods are the main approaches presented in the literature for phase equilibrium calculations of complex mixtures. In the pseudo-component approach the multicomponent mixture is represented by key components or model compounds. Whereas, in the continuous thermodynamics approach the composition of these complex mixtures is described by a continuous distribution function of a measurable variable like molecular weight, carbon number or boiling point temperature. This model is suitable for phase equilibrium calculation of systems containing many similar components like petroleum fluids, natural gases, vegetable oils and polymer solutions. In a majority of the published works, gasoline has been considered as a mixture of naphthenic, aromatic and paraffinic representative components and the pseudo-component approach has been applied to predict liquid-liquid equilibrium of gasoline-methanol blends (Leeper & Wankat, 1982). Ruzicka et al. (1983) developed a method based on the group-contribution concept to describe the fossil fuels in terms of model compounds. They generated LLE data over the temperature range of - 20 °C to 20 °C and subsequently developed LLE models to predict their experimental results (Ruzicka et al., 1986). They characterized gasoline by a set of naphthenic, aromatic and paraffinic model compounds to predict limited miscibility of methanol-gasoline blends applying the UNIFAC model. It was concluded that gasoline can be characterized as a mixture of three arbitrary model compounds. Kehlen et al. (1988) studied liquid-liquid equilibrium of systems containing petroleum fractions like gasoline-methanol blends applying the continuous thermodynamics method and a continuous version of the modified UNIFAC model. Strong H-bonds in methanol molecules lead to the formation of methanol chain associates in the gasoline mixture which strongly affects phase equilibria. Different methods for phase equilibria calculations of associating systems are proposed in the literature. Recently the highly accurate statistical association fluid theory (SAFT) based on physical theory has been applied extensively ([Huang & Radosz, 1991). Since the SAFT equation of state requires a high numerical expense, a simpler G^E -model which is called the CONTAS (continuous thermodynamics of associating systems) model has recently been introduced by Browarzik (2004). The model, which is suitable in the moderate pressure regions, is based on the Flory-Huggins theory and continuous thermodynamics approach. In this model the composition of chains of associates in the mixture is described by a continuous distribution function derived from the mass action law. Browarzik applied the CONTAS model to different binary associating systems (Browarzik, 2005), and presented the equations to calculate excess properties like the excess Gibbs energy and the excess enthalpy (Browarzik, 2007).

In this section both the pseudo component and the continuous thermodynamics approaches have been employed. The naphthenic and aromatic components in the gasoline were represented by two model compounds. The structure of these model compounds for the gasoline mixture is presented by Ruzicka et al. (1983). The compositions of paraffinic components were described by the Gaussian distribution function. The CONTAS model is applied to the multicomponent gasoline-methanol blends and the results obtained from the CONTAS model and a continuous version of the UNIFAC model, the Dortmund and Lyngby modified UNIFAC models were compared with experimental data (Ruzicka et al., 1986).

3.2 Theoretical background

A mixture of continuous paraffinic components (p), methanol (B) and two discrete naphthenic (n) and aromatic (a) model compounds were considered. The TBP distillation curve and properties of the investigated gasoline are presented by Ruzicka et al. (1986). The following PNA analysis is given: 64.6% paraffins, 27.6% naphthenes and 7.8% aromatics. They determined the structures of naphthenic and aromatic model compounds of this gasoline mixture. The symmetrical Gaussian distribution function which is suitable for petroleum fluids is employed to show the distribution of paraffinic components.

$$F_p(N) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left\{-\frac{(N - \bar{N})^2}{2\sigma^2}\right\} \quad (30)$$

The independent variable N is the carbon number of paraffins. The Gaussian distribution function is characterized by mean carbon number \bar{N} and standard deviation σ . For paraffinic components in the gasoline $\bar{N} = 7.8$ and $\sigma^2 = 0.5$.

3.2.1 The CONTAS model

The distribution function of associates is a function of association degree or the number of methanol monomers forming the associates. It indicates the mole fraction of chain associates consisting of r monomers. This function is normalized such that:

$$\int_1^{\infty} W(r) dr = 1 \quad (31)$$

The average number of the association degree is given by:

$$\bar{r}_B = \int_1^{\infty} rW(r) dr \quad (32)$$

Assuming methanol monomer as the standard segment, the segment number of naphthenes, aromatics and paraffins is defined as follows (Browarzik, 2004b):

$$r_i = V_{Wi} / V_{WB}, \quad i = n, a \quad (33)$$

$$r_p(N) = V_{Wp}(N) / V_{WB} \quad (34)$$

Where V_{Wi} is the Van der Waals volume of component i . For the discrete components, the segment number takes constant values while the segment number of continuous paraffinic components is a function of carbon number. V_{Wp} in Eq. (34) is calculated by:

$$V_{Wp}(N) = \sum_m v_{p,m}(N) V_{Wm} \quad (35)$$

Here, V_{Wm} denotes the Van der Waals volume of the group of type m and $v_{p,m}$ is the number of functional groups of type m in a paraffinic component consisting of N carbon atoms. The number of different functional groups in the paraffinic, naphthenic and aromatic components of a petroleum fraction has been approximated by a second order polynomial function of carbon number (Kehlen et al., 1988). The average segment number of paraffins and the mixture are defined by:

$$\bar{r}_p = \int_{N_0}^{N_t} r_p(N) F_p(N) dN \quad (36)$$

$$\bar{r}^{-M} = (1 - x_B)(x_p^g \bar{r}_p + x_n^g \bar{r}_n + x_a^g \bar{r}_a) + x_B \bar{r}_B \quad (37)$$

The quantity x_B is the mole fraction of associates in the gasoline-methanol mixture and x_i^g is the mole fraction of component i in the gasoline. The following equation can be written for the association equilibrium:



By applying the mass action law to the association equilibrium, the association constant is obtained (Browarzik, 2004).

$$K^L = \frac{x_B W(r) \gamma_B(r)}{x_B W(r-r') \gamma_B(r-r') x_B W(r') \gamma_B(r')} \quad (39)$$

Due to the similarity of associating systems and polymer solutions, the activity coefficient in this equation is calculated by using the Flory-Huggins equation of polymer solutions:

$$\ln \gamma_B(r) = \ln(r / \bar{r}^{-M}) + 1 - r / \bar{r}^{-M} + r \ln \gamma_{s,B} \quad (40)$$

The activity coefficients of naphthenes, aromatics and paraffins as well as the methanol activity coefficient are obtained by applying the Flory-Huggins theory. The activity coefficients of discrete naphthenic and aromatic components are:

$$\ln \gamma_i = \ln(r_i / \bar{r}^{-M}) + 1 - r_i / \bar{r}^{-M} + r_i \ln \gamma_{s,i}, \quad i = n, a \quad (41)$$

The activity coefficient of each paraffinic component as a function of carbon number is:

$$\ln \gamma_p(N) = \ln(r_p(N) / \bar{r}^{-M}) + 1 - r_p(N) / \bar{r}^{-M} + r_p(N) \ln \gamma_{s,p} \quad (42)$$

In the Flory-Huggins equation the intermolecular interactions are described by the quantity $\gamma_{s,i}$ which is called the segment molar activity coefficient.

$$\ln \gamma_{s,i} = \frac{1}{T} (\chi_i - \sum_i \psi_i \chi_i)^2 \quad (43)$$

In this equation the χ_i -parameter is related to the solubility parameter of i -th component as follows:

$$\chi_i = \left(\frac{V_s}{R} \right)^{0.5} \sigma_i \quad (44)$$

Where V_s is the molar volume of standard segment and σ_i is the solubility parameter of i -th component. The values of χ_i -parameters for the paraffins, naphthenes, aromatics and methanol should be fitted to experimental data. The parameter χ_i for the paraffinic components and methanol is assumed to be independent of carbon number and association degree. The summation is written over the paraffinic, naphthenic, aromatic and methanol components. ψ_i is the segment mole fraction of component i and it is given by:

$$\psi_i = x_i \bar{r}_i / \bar{r}^M \quad (45)$$

The quantity x_i is a function of true mole fraction of methanol and average number of association degree (Browarzik, 2004). Using this expression and Eqs. (37) and (45), the following equation for the segment mole fraction of methanol is derived:

$$\psi_B = \frac{x_B^t}{x_B^t + (1 - x_B^t)(x_p^s \bar{r}_p + x_n^s \bar{r}_n + x_a^s \bar{r}_a)} \quad (46)$$

Combining Eqs. (39) and (40) and after some rearrangement, the molar distribution function of associates is expressed by the following equation:

$$W(r) = -\lambda \exp[\lambda(r-1)] \bar{r}_B / r \quad (47)$$

Where λ takes negative values and it can be obtained by solving the following equation and with the aid of the expression for the temperature dependence of K^L (Browarzik, 2004).

$$\exp(\lambda) + K^L e^{\psi_B} \lambda = 0, \quad \lambda < 0 \quad (48)$$

Substitution of Eq. (47) into Eq. (32) and integration of this equation with respect to r results in:

$$1 / \bar{r}_B = \lambda \exp(-\lambda) \times \{0.57721567 + \ln|\lambda| + \frac{\lambda}{1 \times 1!} + \frac{\lambda^2}{2 \times 2!} + \frac{\lambda^3}{3 \times 3!} + \dots + \frac{\lambda^n}{n \times n!}\} \quad (49)$$

In order to perform phase equilibrium calculations, phase I is assumed to be at equilibrium with phase II and the quantity K_i is defined by the following equation:

$$K_i = \gamma_i^I / \gamma_i^{II} \quad (50)$$

With the aid of Eq. (50) K_i is obtained for the paraffinic, naphthenic, aromatic and methanol components.

$$K_i = \exp(r_i \rho_i) \bar{r}_m^{-II} / \bar{r}_m^{-I} \quad i = n, a \quad (51)$$

$$K_p(N) = \exp(r_p(N) \rho_p) \bar{r}_m^{-II} / \bar{r}_m^{-I} \quad (52)$$

$$K_B(r) = \exp(r \rho_B) \bar{r}_m^{-II} / \bar{r}_m^{-I} \quad (53)$$

Where

$$\rho_i = 1 / \bar{r}_m^{-II} - 1 / \bar{r}_m^{-I} + \ln \gamma_{s,i}^I - \ln \gamma_{s,i}^{II} \quad (54)$$

3.2.2 The semi-continuous UNIFAC models

In the UNIFAC model the methanol component is considered as a discrete component like naphthenes and aromatics. This is in contrast with the CONTAS model where methanol is considered as a continuous mixture of chain associates with a different association degree. The UNIFAC model is a suitable model for the prediction of activity coefficients of a mixture including different principal types of hydrocarbons. Using the UNIFAC model, the quantity K_i can be separated into two combinatorial and residual parts.

$$\ln K_i = \ln K_i^C + \ln K_i^R \quad (55)$$

To estimate the activity coefficient of paraffins, the continuous version of the UNIFAC model is employed (Kehlen et al., 1988). The $K_p^C(N)$ and $K_p^R(N)$ are calculated according to Eq. (50).

$$\ln K_p^R(N) = \sum_k v_{p,k}(N) Q_k \xi_k \quad (56)$$

$$\xi_k = \ln \sum_m \frac{Q_m \bar{v}_m^{-II} \psi_{mk}}{\sum_n Q_n \bar{v}_n^{-II}} - \ln \sum_m \frac{Q_m \bar{v}_m^{-I} \psi_{mk}}{\sum_n Q_n \bar{v}_n^{-I}} + \sum_m \frac{Q_m \bar{v}_m^{-II} \psi_{km}}{\sum_n Q_n \bar{v}_n^{-II} \psi_{nm}} - \sum_m \frac{Q_m \bar{v}_m^{-I} \psi_{km}}{\sum_n Q_n \bar{v}_n^{-I} \psi_{nm}} \quad (57)$$

$$\bar{v}_m = v_{B,m} x_B + (1 - x_B) [v_{n,m} x_n^g + v_{a,m} x_a^g + x_p^g \int_{N0}^{Nt} F_p(N) v_{p,m}(N) dN] \quad (58)$$

$$\psi_{nm} = \exp(-a_{nm} / T) \quad (59)$$

$$\ln K_p^C(N) = \ln \frac{\bar{r}}{\bar{r}^I} + r_p(N) \left(\frac{1}{\bar{r}} - \frac{1}{\bar{r}^I} \right) + \frac{z}{2} q_p(N) \left[\left(\frac{r_p(N)}{q_p(N)} \left(\frac{\bar{q}}{\bar{r}} - \frac{\bar{q}^I}{\bar{r}^I} \right) \right) + \ln \left(\frac{\bar{r}}{\bar{r}^I} \times \frac{\bar{q}}{\bar{q}^I} \right) \right] \quad (60)$$

$$\bar{r} = r_B x_B + (1 - x_B) \left[r_n x_n^g + r_a x_a^g + x_p^g \int_{N0}^{Nt} F_p(N) r_p(N) dN \right] \quad (61)$$

$$\bar{q} = q_B x_B + (1 - x_B) \left[q_n x_n^g + q_a x_a^g + x_p^g \int_{N0}^{Nt} F_p(N) q_p(N) dN \right] \quad (62)$$

$$r_p(N) = \sum_k v_k^p(N) R_k \quad (63)$$

$$q_p(N) = \sum_k v_k^p(N) Q_k \quad (64)$$

Here, the parameters R_k and Q_k are the volume and surface area parameters for group k , respectively, and z is the coordination number ($z = 10$). a_{nm} is the group interaction parameter between groups n and m . The UNIFAC group interaction parameter table, group volume and group surface parameters at temperatures between 10°C and 40°C have been presented by Magnussen et al. (1981). The average number of groups of type k in the mixture and the average volume and surface parameters are given by Eqs. (58), (61) and (62). In these equations the summations are written over the discrete naphthenic, aromatic and methanol components and the continuous paraffinic components. The activity coefficients are also calculated by employing the two continuous versions of modified Lyngby and Dortmund UNIFAC models. In contrast to the UNIFAC model, in the Lyngby and Dortmund modified UNIFAC models the group interaction parameters are described as function of temperature and the combinatorial terms are slightly modified. The group interaction parameters, group volume and group surface area parameters in the UNIFAC models are extracted from literatures (Magnussen et al., 1981; Larsen et al., 1987; Gmehling & Li, 1993). In the modified UNIFAC models the residual parts are the same as in the UNIFAC model. Inserting the expression for the combinatorial part of the activity coefficient of the continuous Lyngby modified UNIFAC model into Eq. (50) leads to the following equations (Kehlen et al., 1988).

$$\ln K_p^C(N) = \ln \frac{\tilde{r}^I}{\tilde{r}^I} + r_p^{2/3}(N) \left(\frac{1}{\tilde{r}^I} - \frac{1}{\tilde{r}^I} \right) \quad (65)$$

$$\tilde{r} = r_B^{2/3} x_B + (1 - x_B) \left[r_n^{2/3} x_n^A + r_a^{2/3} x_a^A + x_p^A \int_{N0}^{Nt} F_p(N) r_p^{2/3}(N) dN \right] \quad (66)$$

Using the Dortmund modified UNIFAC model, the quantity K_i^C may be calculated according to:

$$\ln K_p^C(N) = \ln \frac{\hat{r}^{II}}{\hat{r}^I} + r_p^{\frac{3}{4}}(N) \left(\frac{1}{\hat{r}^{II}} - \frac{1}{\hat{r}^I} \right) + \frac{z}{2} q_p(N) \left[\left(\frac{r_p(N)}{q_p(N)} \left(\frac{\bar{q}^{-I}}{r} - \frac{\bar{q}^{-II}}{r} \right) \right) + \ln \left(\frac{\bar{r}^{-I} \bar{q}^{-II}}{\bar{r}^{-II} \bar{q}^{-I}} \right) \right] \quad (67)$$

$$\hat{r} = r_B^{3/4} x_B + (1 - x_B) \left[r_n^{3/4} x_n^A + r_a^{3/4} x_a^A + x_p^A \int_{N0}^{Nt} F_p(N) r_p^{3/4}(N) dN \right] \quad (68)$$

Eqs. (55) to (68) can also be applied to the discrete naphthenic, aromatic and methanol components. For these components the quantities which are functions of carbon number are the constant quantities and they are not related to carbon number.

3.2.3 Liquid-liquid equilibrium

By applying the equality of chemical potentials in the UNIFAC models and equality of segment-molar chemical potentials in the CONTAS model, the following phase equilibrium equations can be derived for continuous and discrete components of the mixture.

$$x_i^{II} = x_i^I K_i \quad (69)$$

$$x_p^{II} F_p^{II}(N) = x_p^I F_p^I(N) K_p(N) \quad (70)$$

Where:

$$x_i = (1 - x_B) x_i^g \quad i = n, a, p \quad (71)$$

To predict the quantities K_i and $K_p(N)$, the activity coefficients are calculated by using the CONTAS and three UNIFAC models. The x_B quantity in the CONTAS model is the mole fraction of methanol chain associates and in the UNIFAC models it is the true mole fraction of methanol component.

The integration of Eq. (70) with respect to N results in:

$$x_p^{II} - x_p^I \int_{N0}^{Nt} F_p^I(N) K_p(N) dN = 0 \quad (72)$$

Multiplying Eq. (70) by N and integrating this expression, leads to the following equation for the mean carbon number of paraffinic components in phase II.

$$\bar{N}^{II} = \frac{\int_{N0}^{Nt} N F_p^I(N) K_p(N) dN}{\int_{N0}^{Nt} F_p^I(N) K_p(N) dN} \quad (73)$$

In the CONTAS model the phase equilibrium equation for the methanol component can be written as follows:

$$x_B^{II} W^{II}(r) = x_B^I W^I(r) K_B(r) \quad (74)$$

Using Eqs. (45) and (53), Eq (74) may be written as:

$$\psi_B^{\text{II}} W^{\text{II}}(r) / \bar{r}_B^{\text{II}} = \psi_B^{\text{I}} W^{\text{I}}(r) \exp(r \rho_B) / \bar{r}_B^{\text{I}} \quad (75)$$

Inserting the distribution function of associates from Eq (47) into Eq. (75) and integrating this equation leads to the final equilibrium equation for methanol component.

$$\lambda^{\text{I}} - \lambda^{\text{II}} + \rho_B = 0 \quad (76)$$

To investigate the phase split calculations a set of mass balance and equilibrium equations are needed. In this process the gasoline-methanol mixture in the feed phase is separated into two liquid equilibrium phases. The mass balance equation for naphthenes, aromatics, paraffins and methanol is given by

$$x_i^f = x_i^{\text{I}} + \phi(x_i^{\text{II}} - x_i^{\text{I}}) \quad (77)$$

Where parameter ϕ is the number of moles of phase II based on 1 mole feed. The mass balance equation for the paraffinic components consisting of N carbon atoms can be written as:

$$x_p^f F_p^f(N) = (1 - \phi)x_p^{\text{I}} F_p^{\text{I}}(N) + \phi x_p^{\text{II}} F_p^{\text{II}}(N) \quad (78)$$

The relation between the mean carbon number of the feed and the equilibrium phases may be obtained by multiplying Eq. (78) by N and integrating this equation.

$$\bar{N}^{\text{I}} = \frac{\bar{N}^f x_p^f - \phi \bar{N}^{\text{II}} x_p^{\text{II}}}{(1 - \phi)x_p^{\text{I}}} \quad (79)$$

In Eqs. (77) to (79), the quantities $x_i^f, x_i^{\text{I}}, x_i^{\text{II}}$ are the true mole fractions of i -th component in the feed, phase I and phase II respectively. Therefore, to use these equations in the CONTAS model, x_i quantities should be replaced by x_i^f . For the cloud-point and shadow curves calculations all quantities of the first phase including the distribution function of paraffins and composition of paraffins, naphthenes, aromatics and methanol are known. Numerical solution of four equilibrium equations leads to the estimation of equilibrium temperature and mole fraction of components in the second phase. Equilibrium equations in the UNIFAC models are Eq. (70) for paraffins and three other equations which are written based on Eq. (69) for the discrete naphthenic, aromatic and methanol components. However, in the CONTAS model for the associating methanol component, Eq. (76) is used instead of Eq. (69). In the first step the calculations are made based on the guessed values of unknown quantities. By using equilibrium equations and the Newton-Raphson method the new quantities are calculated and compared with the previous ones. To estimate these quantities, It is necessary to know the distribution function of paraffins in the second phase which is related to the mean carbon number of paraffins in the second phase. \bar{N}^{II} may be obtained with the aid of Eq. (73). This iterative procedure is repeated to obtain the final results. To apply the UNIFAC models, quantities $K_p(N), K_n, K_a$ and K_B has to be determined from Eqs.

(55) to (68). In the CONTAS model, the Eqs. (51) to (53) for the K_i quantities are related to the \bar{r}_m and ψ_i . To calculate \bar{r}_m and ψ_i from Eqs. (37) and (45), we need to know \bar{r}_B and mole fraction of associates. Mole fraction of associates can be obtained from the true mole fraction of methanol (Browarzik, 2004a). Based on Eq. (49) \bar{r}_B is a function of λ which is determined using Eqs. (46) and (48). For the phase separation calculations, the feed quantities like feed mole fraction of methanol and temperature are known and the quantities of the two equilibrium phases are determined by solving the equilibrium and mass balance equations. The guessed quantities in the first step of calculations are true mole fraction of paraffins, naphthenes and methanol in the first phase and true mole fraction of methanol in the second phase. True mole fraction of paraffins, naphthenes and aromatics in the second phase are obtained from Eq. 48. Additionally, according to Eq. (79) \bar{N}^I is calculated from the mean carbon number of paraffins in the second and feed phase.

3.3 Results and discussion

The LLE results of the gasoline-methanol blends based on the four different models UNIFAC, Lyngby modified UNIFAC, Dortmund modified UNIFAC and CONTAS at temperatures between -20 °C to 20 °C (Ruzicka et al., 1986) were obtained and compared with experimental data. The results of the CONTAS model are obtained using four adjustable parameters in Eq. (43) which are fitted to the LLE experimental data. The adjusted parameters are $\chi_p = 15.7 \text{ K}^{0.5}$, $\chi_n = 12.0179 \text{ K}^{0.5}$, $\chi_a = 3.5819 \text{ K}^{0.5}$, $\chi_B = 23.8539 \text{ K}^{0.5}$.

Unlike in binary systems, in polydisperse systems the solubility diagrams consist of a cloud-point curve and a shadow curve. The cloud-point curve indicates the composition of the first phase as a function of temperature at the onset of the second phase formation. The composition of the nearly formed phase is given by the shadow curve. The intersection point of the cloud-point curve and shadow curve is the critical point. The solubility diagrams indicate the phase separation boundaries. The methanol mole fraction in the methanol-lean part of the cloud-point curve gives the maximum amount of methanol that can be added to gasoline to avoid phase separation. The mutual miscibility of methanol and gasoline is related to temperature so that decreasing the temperature leads to a decrease in miscibility. The effect of the aromatics concentration on the liquid-liquid equilibrium of the methanol-gasoline blend was studied and showed that the two-liquid phase regions will be larger for the gasoline-methanol mixtures with lower amounts of aromatics. Furthermore we have a decrease in the upper critical solution temperature with increasing the concentration of aromatic components of gasoline. Thus the solubility of methanol and gasoline improves by increasing the aromatic content of the mixture. This effect can be explained based on the solubility of aromatics, naphthenes and paraffins with methanol. In contrast to paraffins and naphthenes which show a limited miscibility with methanol, aromatics are completely miscible with methanol. Therefore, adding aromatics to a system containing paraffins and naphthenes results in lowering of the critical solution temperature. Moreover, the effect of polydispersity or the variance of the paraffinic components on the solubility diagrams was studied. This study shows that by increasing the variance of the distribution function of paraffins (σ^2), the critical solution temperature and the distance between cloud-point curve and shadow curve increases. As mentioned above methanol and gasoline are partially miscible and a limited amount of methanol can be blended with gasoline. Adding more methanol leads to the separation of the mixture into two equilibrium

liquid phases. To predict the composition of paraffins, naphthenes, aromatics and methanol in the two formed liquid phases, phase separation calculations which are based on the mass balance and phase equilibrium equations, are necessary. The results of the phase separation calculations in comparison with experimental data based on the four different models CONTAS, UNIFAC, Lyngby and Dortmund modified UNIFAC were obtained. These results include the mole fraction of methanol and different hydrocarbon families in the lean and rich methanol phases at five temperatures over the range of -20 °C to 20 °C. It was found that in comparison with the experimental data, the results obtained from the CONTAS and UNIFAC models are more accurate than the results of the Dortmund and Lyngby modified UNIFAC models. The calculated compositions using the UNIFAC and CONTAS models are in reasonable agreement with the experimental ones. It was shown that the Dortmund and Lyngby modified UNIFAC models have not properly predicted experimental data. The results of the phase separation of methanol-gasoline blends predicted by the UNIFAC and CONTAS models, at temperatures 20 °C and -20 °C, for different feed compositions of methanol were obtained. These calculations show that the UNIFAC model, especially at temperatures between 0 °C to 20 °C, gives better agreement with the experimental data than the CONTAS model. This fact can be explained by the group interaction parameters of the UNIFAC model which have been developed for LLE calculations at temperatures between 10 °C to 40 °C (Magnussen et al., 1981). The upper critical solution temperature of the systems containing paraffins, naphthenes and methanol is about 300 K to 360 K (Kehlen et al., 1988). By adding aromatics to this system, the critical temperature decreases so that the critical temperature for the gasoline-methanol mixture cannot be higher than 360 K. However, the critical temperature predicted by the UNIFAC model is about 405 K and this temperature for the CONTAS model is about 329 K. Therefore, the CONTAS model predicts the critical solution temperature better than the UNIFAC model and it is an appropriate model for the liquid-liquid equilibrium prediction at high temperatures (Nasrollahi et al., 2009).

3.4 Conclusions

To predict the cloud-point curve, shadow curve and phase separation results of methanol-gasoline blends, the continuous thermodynamics procedure was applied and the four different models CONTAS, UNIFAC, Lyngby and Dortmund modified UNIFAC were examined. The CONTAS model includes four fitting parameters which are related to the solubility parameters of paraffins, naphthenes, aromatics and methanol. The common group interaction parameters were applied to predict limited miscibility of methanol-gasoline blends using the UNIFAC and modified UNIFAC models. The highest possible composition of methanol that can be added to gasoline decreases by decreasing the temperature and its value is estimated at the lean-methanol part of the cloud-point curve. The influence of the aromatics content and polydispersity of paraffins on the liquid-liquid equilibrium results were investigated. Due to the complete miscibility of aromatics and methanol, a larger amount of aromatics in the mixture leads to a lowering of the critical solution temperature. Furthermore by increasing the variance of the distribution function of paraffins, the critical temperature increases and the cloud-point and shadow curves get closer. The results calculated using the UNIFAC and CONTAS models are in good agreement with the experimental data. The prediction of the UNIFAC model in the temperature range of -20 °C to 20 °C is more accurate than the CONTAS model. However, the CONTAS model is more suitable for liquid-liquid equilibrium calculations at high temperatures.

4. Continuous thermodynamics of petroleum fluids fractions

A method based on continuous thermodynamics is introduced here for calculating the vapor pressure of undefined composition mixtures (Vakili-Nezhaad et al., 2001). In order to verify the proposed method the experimental data of an Indonesian petroleum fluid as well as a detailed true boiling point data on the lube-oil cut SAE 10 of Tehran Refinery have been used. In this work by using the combination of the Trouton's rule and the Clausius–Clapeyron equation in the well-known equation of Antonie, the continuous version of the Raoult's law has been developed and the results of the modeling and calculations have been compared with the experimental data and good agreement was found. Moreover, for improving the results of the ideal continuous mixture, modeling of non-ideal behaviour of such mixtures has been carried out by introducing the continuous version of the UNIFAC activity coefficient in the formulation and a better result has been obtained.

4.1 Modeling and calculations

Here we have carried out the boiling point calculations for two cases (i) ideal mixtures; and (ii) non-ideal mixtures. In the first case the continuous version of the Raoult's law has been presented and in the second case the continuous version of the UNIFAC model was used for developing the results of the ideal mixtures to the non-ideal mixtures.

4.1.1 Case one: ideal mixture

In general, the equilibrium vapor pressure of a multicomponent mixture with N distinct species can be calculated by the following equation (Smith et al., 2005):

$$P = \sum_{i=1}^N x_i p_i^{\text{sat}} \gamma_i \quad (80)$$

where, P is the total pressure, x_i is the mole fraction of the i^{th} component, P_i^{sat} is the saturation pressure and γ_i is the activity coefficient of the i^{th} component in the mixture. For the ideal mixtures because of the unity of all activity coefficients, this equation can be reduced to the following simple form:

$$P = \sum_{i=1}^N x_i p_i^{\text{sat}} \quad (81)$$

This equation is known as the Raoult's law and indicates that the partial pressure of the i^{th} component in the mixture is equal to the product of its mole fraction by the saturated vapor pressure (at the mixture temperature). If the number of components in the mixture goes to a very large number, in such a way that the composition of the mixture cannot be presented in usual forms of mole or mass fractions, a continuous distribution function can be applied for defining the composition of the mixture. In such cases the continuous version of the Eq. (81) may be written as follows:

$$P = \int F(I) P^{\text{sat}}(I) dI \quad (82)$$

where, $F(I)$ is a suitable distribution function of a proper characterization index ' I ' such as the molecular weight or boiling point. In application of Eq. (82), an equation for expressing P^{sat} is required. In this work the well-known equation of Antonie has been applied (Smith et al., 2005),

$$\log_{10} P^{sat} = A_A - \frac{B_A}{t + C_A} \quad (83)$$

where, P^{sat} is the vapor pressure of a pure component at temperature t and A , B and C are the special constants for each component. It is obvious that for the application of Eq. (82) the continuous form of the Antonie's equation is needed. If we combine the Trouton's rule with the Clapeyron- Clausius equation, the following equation can be obtained:

$$P^{sat}(T) = P_{atm} \exp \left[10.58 \left(1 - \frac{T}{T_s} \right) \right] \quad (84)$$

where T is the boiling point in distribution functions (in Kelvin) and T_s is the temperature at which distillation occurs. Therefore, by combining Eq. (82) and Eq. (84) we have,

$$P = \int_{IBP}^{FBP} P_{atm} \exp \left[10.58 \left(1 - \frac{T}{T_s} \right) \right] F(t) dT \quad (85)$$

The lower and upper limits of the integral (IBP and FBP) are the initial and final boiling points of the petroleum fluids fractions, respectively. Therefore, if we have the distribution function of the mixture, we will be able to calculate the equilibrium vapor pressures of such complex mixtures. To verify the proposed method we have examined various distribution functions. These equations were used in the Eq. (85) for calculating the normal boiling point of the lube-oil cut SAE 10 of the Tehran Refinery. The error analysis based on these distribution functions showed that Eq. (86) has the minimum absolute average deviation (AAD) compared with the other distribution functions. The probability density function which has been used for our calculations can be expressed in the following form (Riazi, 1997):

$$F(T) = \frac{1}{T_0} \frac{B^2}{A} \left(\frac{T - T_0}{T_0} \right)^{B-1} \exp \left[-\frac{B}{A} \left(\frac{T - T_0}{T_0} \right)^B \right] \quad (86)$$

All the parameters of this equation which have been calculated by the regression analysis method can be given as:

$$A=0.01862 \quad (87)$$

$$B=3.5298 \quad (88)$$

$$T_0=554.45 \text{ K} \quad (89)$$

$F(T)$ from Eq. (86) was introduced in Eq. (85) and the integral was calculated by numerical methods. The results of the calculations are:

$$T=674.45 \text{ K} \quad (90)$$

$$P=1.014 \times 10^5 \text{ Pa} \quad (91)$$

4.1.2 Case two: non-ideal mixtures

It is evident that the proposed formulation for ideal mixture could not handle the related calculations for the non-ideal mixtures, therefore, we have to generalize the results of the non-ideal mixtures. In this case the equilibrium vapor pressure of the continuous mixture M can be written as:

$$P = \int F(I)P^{sat}(I)\gamma(I,T)dI \quad (92)$$

where $\gamma(I,T)$ is the continuous version of the activity coefficient of the mixture components. The composition of the complex mixtures such as petroleum fractions are not well defined therefore, in this work we have used the predictive model of UNIFAC. For applying this model for the petroleum fluids fractions its continuous version is required, but when using the continuous form of the UNIFAC model for phase equilibrium calculations, it is necessary to know the analytical expressions for the number of the various functional groups in the mixture. A polynomial of order 2 has been used by some researchers (Kehlen et al., 1988) for calculating the number of different functional groups in the light petroleum fractions but these equations are not suitable for heavier petroleum fractions such as lube-oil cut which is our interest in the present work. Therefore, we have proposed higher order polynomials (up to 8) for this purpose (Vakili-Nezhaad, 1999). The coefficients of these equations have been obtained using the detailed experimental data on lube-oil cut SAE 10 of Tehran Refinery and an Indonesian oil (Jaubert et al., 1995) by using the powerful numerical software of TABLE CURVE (TC). Since a petroleum fraction have been made mainly from three different homologue series as paraffinic, naphthenic and aromatic hydrocarbons, we have divided these hydrocarbon homologues to two parts, i.e. aromatic hydrocarbons and paraffinic+naphthenic hydrocarbons. Therefore, by using this approach the continuous version of UNIFAC model for each continuous parts of the mixture including aromatic or paraffinic+naphthenic parts were obtained. In the UNIFAC model the activity coefficient comprises of two parts, i.e. combinatorial and residual, therefore, the activity coefficient of the continuous ensembles of aromatic or naphthenic+paraffinic parts were obtained. For the ideal mixtures it has been demonstrated that the best distribution function for the examined mixture was Eq. (86), therefore for the non-ideal mixture too we used this function and the following results were obtained (Vakili-Nezhaad et al., 2001):

$$T=390.94 \text{ K} \quad (93)$$

$$P=1.502 \times 10^7 \text{ Pa} \quad (94)$$

In order to verify the accuracy of the proposed method, these theoretical results were compared with the experimental data of an Indonesian petroleum fluid (Jaubert et al., 1995). This comparison indicated a good agreement between theoretical results and experimental data. Thus it can be said that the proposed formulation based on the application of the continuous form of the activity coefficient model can improve the accuracy of the calculations (Vakili-Nezhaad et al., 2001).

4.2 Conclusion

Based on the concepts of continuous thermodynamics a method has been proposed for the vapor pressure calculation of the complex petroleum fluids fractions. At first the continuous

version of the Raoult's law has been developed for applying in those mixtures that comprise of similar species and their behaviour can be considered as ideal mixtures. Comparison between modeling and experimental data on the lube-oil cut SAE 10 of the Tehran Refinery showed that for these types of petroleum fractions the proposed modeling and calculations give the best results with the Riazi distribution function. The above mentioned method has been developed to the case of non-ideal mixtures using the continuous version of the UNIFAC-model and the results have been compared with the experimental data of an Indonesian oil, and better accuracy has been obtained (Vakili-Nezhaad et al., 2001).

5. Three phase flash calculations using genetic algorithm approach

In this section a new approach based on the genetic algorithm is introduced for solving three phase flash calculations containing two liquid phases and one vapor phase (Vakili-Nezhaad et al., 2010). Based on this approach choosing the initial guesses for the compositions of the involved phases is not an important step, which in the ordinary three phase algorithms affects directly the convergence of the calculations. A real problem has been solved with this approach and very good results have been obtained in comparison with the experimental data. Phi-Phi approach has been adopted for vapor-liquid-liquid equilibrium (VLLE) calculations based on the Peng-Robinson equation of state (Vakili-Nezhaad et al., 2010).

5.1 Introduction

Information about vapor-liquid-liquid equilibrium (VLLE) is essential for many chemical processes and the separation operations (Christov & Dohrn, 2002). Among these industrial processes the recovery of organic acids from dilute solution resulting from fermentation processes and the extraction of aromatic compounds from petroleum fluid fraction are only two examples of the potential of VLLE operations in the chemical and petrochemical industries (Taghikhani et al., 2001; Vakili-Nezhaad et al., 2001; Vakili-Nezhaad et al., 2002; Vakili-Nezhaad et al., 2004). For designing and optimization of the liquid extraction processes as well as various separation equipments one has to know the equilibrium conditions due to complex nature of the VLLE calculations it can be said that for obtaining reliable results one has to examine every specific case to check its convergence. To confirm this point one may refer to the works of Fang-Zhi et al (1993) and Yokozeki (2004). Therefore as an important result it may be mentioned that presentation of a unique algorithm for VLLE calculation is a crucial step in the subject. In this work a simple and efficient approach based on the genetic algorithm has been proposed for VLLE calculations and good results have been obtained for a ternary system (Vakili-Nezhaad et al., 2010).

5.2 Problem statement

The compositions of the liquids and vapor phases are given by the following equations:

$$X1(I) = \frac{s(I)}{x(1) * (1 - R1(I)) + x(2) * (R1(I) / R2(I)) + R1(I)} \quad (95)$$

$$X2(I) = \frac{(s(I) * R1(I) / R2(I))}{x(1) * (1 - R1(I)) + x(2) * (R1(I) / R2(I) - R1(I)) + R1(I)} \quad (96)$$

$$Y(I) = \frac{(s(I) * R1(I))}{x(1) * (1 - R1(I)) + x(2) * (R1(I) / R2(I)) + R1(I)} \quad (97)$$

$x(1)$ and $x(2)$, equals to the number of moles of the liquid phases No. 1 and No. 2 respectively. Considering the above relations, it is obvious that in a three-phase system the value of $x(1)$ and $x(2)$ must be known. These values will be the answers of a nonlinear system of equations which will be obtained from the following equations:

$$\sum_{i=1}^3 X2(i) = 1 \quad (98)$$

$$\sum_{i=1}^3 (X1(i) - Y(i)) = 0 \quad (99)$$

Using these two relations, the system of equation will be obtained:

$$f_1 = \sum_{k=1}^3 \frac{s(k) * R1(k) / R2(k)}{x(1) * (1 - R1(k)) + x(2) * (R1(k) / R2(k) - R1(k)) + R1(k)} - 1 = 0 \quad (100)$$

$$f_2 = \sum_{k=1}^3 \frac{s(k) * (1 - R1(k))}{x(1) * (1 - R1(k)) + x(2) * (R1(k) / R2(k) - R1(k)) + R1(k)} = 0 \quad (101)$$

where,

$$R1(I) = [1.4529 \quad 0.2103 \quad 0.0001] \quad (102)$$

$$R2(I) = [0.1518 \quad 0.2876 \quad 0.0009] \quad (103)$$

$R1$ and $R2$ are the K -values of different components in the mixture. These values have been calculated by the Peng-Robinson equation of state. Now by considering the above equations we can carry out the VLE calculations for ternary system. The feed consists of Methane (1) - Ethane(2) - n-Octane (3). In this work, we have chosen the composition of feed as $s(1)=0.8054$, $s(2)=0.1385$, $s(3)=0.0560$.

5.3 Genetic algorithm

The genetic algorithm (GA) is a stochastic search technique based on the mechanism of natural selection and natural genetics to imitate living beings for solving difficult optimization problems with high complexity and an undesirable structure. The GA approach represents a powerful, general-purpose optimization paradigm in which the computational process mimics the theory of biological evolution (Holland, 1992; Storn & Price, 1997). It has been successfully used in job-shop scheduling, production planning, line balancing and process optimization. Goldberg (1989) proposed the most common and useful form of GA. Different from traditional point-to-point descending and ascending search techniques, a GA starts from one set of random solutions called a population. Each individual solution in the population is called a chromosome. At each generation, the GA performs genetic operations such as crossover and mutation on the selected chromosomes to yield offspring to produce the next generation. During each generation, these chromosomes evolve into better fitness by applying an evolution operation, called the selection. From

generation to generation, eventually, the chromosomes in the population will converge. In this case, the best chromosome is found. Generally, the basic steps of a GA approach in solving an optimization problem can be summarized in Table 1.

1.	Represent the problem variable as a chromosome of a fixed length, and choose the size of a chromosome population, the crossover probability, and the mutation probability.
2.	Define a fitness function to measure the fitness of an individual chromosome in the problem domain.
3.	Randomly generate an initial population of chromosomes.
4.	Calculate the fitness of each individual chromosome.
5.	Select a pair of chromosomes for mating from the current population. Parent chromosomes are selected with a probability related to their fitness. Highly fit chromosomes have a higher probability of being selected formatting. The roulette wheel method is usually applied in chromosome selection.
6.	Create a pair of offspring chromosomes by applying the genetic operators: crossover and mutation.
7.	Place the created offspring chromosomes in the new population.
8.	Repeat step 5 until the size of the new chromosome population is equal to the size of the initial population.
9.	Replace the initial (parent) chromosome population with the new (offspring) population.
10.	Repeat steps 4–9 until the termination criterion is satisfied.

Table 1. The Genetic Algorithm Steps

5.4 Discussion

In this work, The Genetic toolbox in MATLAB® has been used (Chipperfield, 2007). Equations (100) and (101) are the objective functions (f_1 and f_2) which have been combined to form a unique objective function or fitness function. This function may be read as:

$$F = \frac{w_1 f_1 + w_2 f_2}{w_1 + w_2}$$

(104)

As X_1 , X_2 and Y are mole fractions they must be in the interval $[0, 1]$ the nonlinear constraints have been considered. The genetic algorithm toolbox uses the Augmented Lagrangian Genetic Algorithm (ALGA) to solve nonlinear constraint problems. The Genetic Algorithm in MATLAB was run with the parameters reported in Table 2. The best solution in last generation is $x(1)=0.4132$ and $x(2)=0.2095$ which by these value the composition of two liquid phases and one vapor phase are as follows:

$$X_1 = [0.657123 \ 0.214483 \ 0.128288]$$

(105)

$$X_2 = [0.828907 \ 0.156835 \ 0.014254]$$

(106)

$$Y = [0.954734 \ 0.045106 \ 0.000013]$$

(107)

The experimental data on the liquid phases are as follows:

$$X1 = [0.682 \ 0.187 \ 0.131]$$
(108)

$$X2 = [0.806 \ 0.158 \ 0.036]$$
(109)

In comparison with these data we find that the method handled the relevant calculations very well.

Population size	20
Parameters	2 $0 \leq x(1) \leq 1, 0 \leq x(2) \leq 1$
Generation	30
Nonlinear constraints	$X_2(i)-1 \leq 0$ $X_1(i) -1 \leq 0$ $Y_1(i)-1 \leq 0, \text{ for } i=1:3$
Hybrid with Local Optimization	Pattern search
Encoding	Real value

Table 2. Parameters Used in Genetic Algorithm Calculation

6. Concluding remarks

Thermodynamic modeling and calculations of different complex fluid mixtures were presented in this chapter. Phase equilibrium calculations for some complex fluid systems were presented. Continuous thermodynamics was applied for modeling and phase equilibrium calculations of polymer solutions and petroleum fluids. This approach (continuous thermodynamics) was shown as a powerful tool for these kinds of complex phase equilibrium calculations. In the last part of the present work a new approach of genetic algorithm (GA) for doing phase equilibrium calculations was introduced, and it was shown that GA can be applied for some complex vapor-liquid-liquid equilibrium systems. Application of GA in fluid phase equilibria is going to be increased and developed as a reliable tool.

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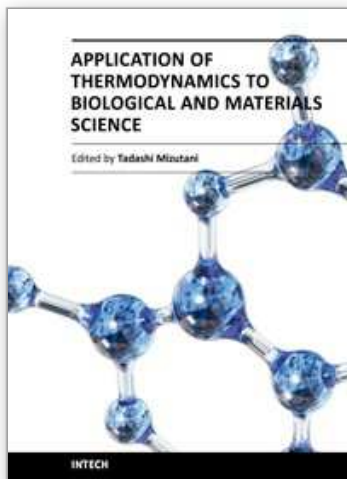
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University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
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Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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