LBL-35431

UC-401

**A New Association-Model for Binary VLE
of Alcohol/Hydrocarbon and Amine/
Hydrocarbon Mixtures**

J. v. Schnitzler and J. M. Prausnitz

**Department of Chemical Engineering
University of California
and
Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720, U.S.A.**

March 1994

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Molecular Thermodynamics:

A New Association-Model for Binary VLE of Alcohol / Hydrocarbon and Amine / Hydrocarbon Mixtures

J. v. Schnitzler and J.M. Prausnitz

March 1994

Department of Chemical Engineering
University of California
Berkeley

Contents:

Abstract

1. Introduction

2. Derivation of the Poisson-Association Model

2.1 Activity Coefficient in an Associating Solution

3. Calculations and Comparison with Experimental Data

4. Discussion and Conclusion

5. Tables

6. Figures

Appendix 1: The Poisson Distribution Function

Appendix 2: Computer Program

Notation

Literature

Abstract

An association model for binary vapor-liquid equilibria (VLE) has been developed using the Poisson distribution function to describe the relation between consecutive association reactions and their equilibrium constants. This model considers the probability of consecutive association reaction and the effect of that probability on the entropy of association.

The Poisson-distribution model is compared with a classical linear-association model with the same number of adjustable parameters (two equilibrium constants and one physical parameter). Both models are able to represent the properties of alcohol-hydrocarbon and amine-hydrocarbon mixtures. The Poisson-distribution model, however, appears to be superior for those mixtures where the molecules of the associating component form rings rather than chains. Analysis of the VLE data provides some trends about the behavior of the model parameters with respect to temperature and molecular size of the associating component.

1. Introduction

The process industries have recognized for many years the importance of thermodynamic and physical properties of solutions in design calculations. Environmental problems in the form of excessively high carbon monoxide levels are attributed mostly to automotive emissions. One of the methods used to reduce CO emissions is the use of oxygenates such as ethanol or methanol in gasoline blends. As these blends are now of more commercial importance, it becomes necessary to understand their behavior and equilibrium characteristics to optimize the processes used for their production and handling. Therefore, thermodynamic informations in the form of vapor-liquid equilibria (VLE) are of particular interest.

Alcohol-hydrocarbon blends, for example, form associated solutions due to hydrogen bonding between the alcohol molecules. The behavior of this type of solutions has been studied by several investigators [1,7]. The most common model is the linear-association model (LAM) where the consecutive association reactions are assumed to be 'repeatable steps': All consecutive association reactions are assumed to have the same equilibrium constant ($K_{12}=K_{23}=K_{34}=....etc.$).

In contrast to this simplification, some studies have been reported [4 and 7] where the equilibrium constants depend on the degree of association. A

good example is given by Wolff and Höpfner [4] who studied the system n-Hexane/Methylamine at several temperatures. Although this work is only concerned with the first three equilibrium constants of the association reaction (1), it shows that they are not the same; they increase in the order $K_{12} < K_{23} < K_{34}$. With regard to the heat of formation of dimers, trimers and tetramers, the same value (about 1800cal/mol) was found. Considering the equation $-\ln K = \Delta h/RT - \Delta s/R$, the increase of the equilibrium constants is mainly caused by a change in the entropy term.

Usually those models where the equilibrium constant is allowed to depend on the degree of association, require a large number of adjustable parameters. The algebraic complexity is much larger than that for a LAM, unless some effort is made to find a relation between the different association constants.

2. Derivation of the Poisson-Association Model

We have a general association reaction

We give attention to the relation between an equilibrium constant of the association reaction (2.1) and its association number j . In general, the equilibrium constant can be expressed as

$$K_{j+1} = f(j) K \quad (2.2)$$

where $f(j)$ is a distribution function that depends on the nature of the associating compound and K is a constant. We use the Poisson distribution function as discussed by Anderko and Prausnitz [8]. If constant K is chosen to be the equilibrium constant of the dimerization reaction (dimerization constant), then $f(j)$ must be normalized to $f(1) = 1$.

As shown in Appendix 1, $\Pi(j)$, the probability that j molecules form an associate A_j , can be expressed by a Poisson distribution function

$$\Pi(j) = \frac{\kappa^j}{j!} e^{-\kappa} \quad (2.3)$$

where κ is a constant. From Eq. (2.3) we obtain an expression for $f(j)$

$$f(j) = \frac{\kappa^{j-1}}{j!} \quad (2.4)$$

Equilibrium constant $K_{j,j+1}$ is then given by

$$K_{j,j+1} = K_{1,2} \cdot \frac{\kappa^{j-1}}{j!} \quad (2.5)$$

Figure 1 shows the distribution function $f(j)$ for different values of κ .

2.1 Activity Coefficients in an Associating Solution

We consider a component i in a binary solution ($i = A, B$) at constant temperature. In this solution component A can self-associate according to Equation (2.1). The second component B is a solvent which does not self-associate and does not solvate with component A. The equation of phase equilibrium is

$$f_i^V = f_i^L \quad (2.6)$$

The fugacity in the vapor phase is

$$f_i^V = \phi_i \cdot y_i \cdot P \quad (2.7)$$

where ϕ is the fugacity coefficient, y is the mole fraction in the gas phase and P is the total pressure. At low pressure, the fugacity coefficient goes to unity. In this work we set $\phi_i = 1$.

For the liquid phase, the fugacity of component A can be written

$$f_A^L = \gamma_A^{\text{chem}} \cdot \gamma_A^{\text{phys}} \cdot X_A \cdot f_{\text{pure A}}^L \quad (2.8)$$

where γ^{chem} is the activity coefficient caused by the self-association of component A, γ^{phys} is the physical contribution to the activity coefficient,

x_A is the mole fraction of component A in the liquid phase and $f_{\text{pure A}}$ is the fugacity of pure component A, all at system temperature.

We now use the general theorem (Appendix VII of [9]) that the fugacity of an associating component A is equal to the fugacity of its monomer. Equation (2.8) then becomes

$$\gamma_A^{\text{chem}} \cdot \gamma_A^{\text{phys}} \cdot x_A \cdot f_{\text{pure A}}^L = z_{A1} \cdot f_{\text{pure A1}}^L \quad (2.9)$$

where z_{A1} is the 'true' mole fraction of monomer A1. The ratio of the two fugacities $f_{\text{pure A}}/f_{\text{pure A1}}$ can be expressed as

$$\frac{f_{\text{pure A}}^L}{f_{\text{pure A1}}^L} = \lim_{x_A \rightarrow 1} z_{A1} = z_{A1}^0 \quad (2.10)$$

With Eqs. (2.9) and (2.10) we obtain an expression for γ_A^{chem} . Provided that we also adopt an expression for γ^{phys} , to consider the physical interactions, caused by the different size and shape of the two molecules, we assume that

$$\ln \gamma_A^{\text{phys}} = \frac{\beta}{RT} \cdot v_A \cdot \Phi_B^2 \quad \text{and} \quad \ln \gamma_B^{\text{phys}} = \frac{\beta}{RT} \cdot v_B \cdot \Phi_A^2 \quad (2.11)$$

where v_i is the molar volume of component i and the volume fractions Φ are

$$\Phi_A = \frac{(v_A / v_B) x_A}{(v_A / v_B) x_A + x_B} \quad \text{and} \quad \Phi_B = \frac{x_B}{(v_A / v_B) x_A + x_B} \quad (2.12)$$

Binary parameter β reflects physical interactions between components A and B. Equations (2.9)-(2.12) give the final expression for activity coefficients

$$\gamma_A = \frac{z_{A1}}{x_A \cdot z_{A1}^0} \cdot \exp \left[\frac{\beta}{RT} v_A \left(\frac{x_B}{(v_A / v_B) x_A + x_B} \right)^2 \right] \quad (2.13)$$

$$\gamma_B = \frac{z_B}{x_B} \cdot \exp \left[\frac{\beta}{RT} v_B \left(\frac{(v_A / v_B) x_A}{(v_A / v_B) x_A + x_B} \right)^2 \right] \quad (2.14)$$

According to Equations (2.13) and (2.14) we need an expression for z_{A1} , z_{A1}^0 and z_B , which can be obtained from stoichiometry and from chemical-equilibrium relations as discussed in the next section.

3. Calculations and Comparison with Experimental Data

The true mole fractions of monomer A_1 , either in pure A or in the mixture, are obtained from stoichiometric relations

$$z_{Aj} = \frac{n_{Aj}}{n_t} \quad (3.1)$$

where n_{Aj} is the number of moles of the j -mer of component A and n_t is the total number of moles of component A and B. From chemical equilibrium

$$z_{Aj} = K_{j-1,j} \cdot z_{Aj-1} \cdot z_{A1} \quad j=2,3,\dots,m \quad (3.2)$$

For calculating the chemical contribution to the total nonideality of the mixture, we assume that the solution of 'true' species forms an ideal solution. From mass balances

$$n_A = \sum_{j=1}^m j \cdot n_{Aj} \quad \text{and} \quad n_t = \sum_{j=1}^m n_{Aj} + n_B \quad (3.3)$$

where m is the highest degree of association; each further contribution is assumed to be negligibly small. In this work, m is 12. Table 1 shows that the difference between calculations with $m=12$ and $m=14$, for the three (important) true mole fractions z_{A1}^0 , z_{A1} and z_B , is always less than 10^{-5} ; in most cases it is less than 10^{-8} .

To calculate z_{A1} and z_{A1}^0 , we use a computer program which solves the set of Equations (3.1) - (3.3) simultaneously and also fits the three parameters $K_{1,2}$, κ and β to experimental data. A short description and the listing of the computer program are given in Appendix 2.

To fit the three parameter to a specific system, we minimize the deviation of the calculated total pressure, using the relative root-mean-squared errors (rms).

Comparison with Experimental Data

The Poisson-association model is applied to alcohol / hydrocarbon and amine / hydrocarbon mixtures. All the experimental data used here satisfy the two thermodynamic consistency tests (Point test of Van Ness and Integral test of Redlich-Kister), as discussed in the guide of the tables of the data collection of Gmehling and Onken [10].

Results from the Poisson-association model are compared with those from a three-parameter linear-association model (LAM) that requires a dimerization constant ($K_{1,2}$), a polymerization constant ($K_{2,3}$) and physical parameter β . For this three-parameter LAM, Equations (3.2) must be written:

$$z_{A2} = K_{1,2} \cdot z_{A1}^2 \quad (3.4)$$

and

$$z_{Aj} = K_{2,3} \cdot z_{Aj-1} \cdot z_{A1} \quad j=3,4,\dots,12 \quad (3.5)$$

The activity coefficients are again obtained from Equations (2.13) and (2.14).

Table 2 shows results of both models with the optimized three adjustable parameters and the root-mean-squared errors (rms P and rms y). Some illustrative examples are shown in Figures 2 to 6.

4. Discussion and Conclusion

The advantage of the calculation procedure presented here is based on a computer program which solves several algebraic equations simultaneously.

Table 2 shows some trends concerning the model parameters. Poisson-parameter κ depends strongly on the system. It seems that κ increases with decreasing temperature. Dimerization constant K_{12} increases slightly with decreasing temperature, as indicated by results for the system Methylamine/n-Hexane at 20, -10 and -40 deg.C, where $\kappa=3.6$ and $K_{12}=1.1$ (20 'C), $\kappa=4.5$ and $K_{12}=1.4$ (-10 'C) and $\kappa=5.3$ and $K_{12}=1.8$ (-40 'C). This trend is apparent for most of the other systems. The system 1-Propanol/Hexane (50 'C and 25 'C), for example, shows the same trend: with decreasing temperature, we again find an increase of κ and K_{12} .

Concerning the different alcohols, κ seems to decrease with a rise in the size of the molecules, as shown by results for Ethanol/Benzene (50 'C), 2-Propanol/Benzene (50 'C) and Butanol/Benzene (45 'C).

In addition to the temperature and the size of the alcohol molecules, parameters $K_{1,2}$, κ and β also depend on the type of solvent.

These are only rough trends. Unfortunately, the results also depend strongly on the quality of the experimental data. Although all of the systems studied here satisfy the criteria of the two thermodynamic consistency tests, calculated parameters for some systems depend strongly on the initial parameters of the fitting-process; for different sets of initial guesses, we get different sets of 'optimized' parameters. These systems are not listed in Table 2.

An example of 'high quality' experimental data are those from Wolff and Höpfner [4] for the system Methylamine/n-Hexane, for several temperatures. In this case, high quality means that, for almost any combination of initial guessed parameters, we converge upon the same final result for $K_{1,2}$, κ and β .

5. Tables

κ	K_{12}	diff z_{A1}^0	diff z_{A1}	diff z_B
6.0	6.0	2.18E-06	6.7E-07	8.68E-06
6.0	5.0	2.29E-06	6.9E-07	7.74E-06
5.0	10.0	< 1E-08	1E-08	2E-08
5.0	5.0	1E-08	< 1E-08	1E-08
5.0	3.0	< 1E-08	< 1E-08	< 1E-08
4.0	10.0	< 1E-08	< 1E-08	1E-08
4.0	6.0	< 1E-08	< 1E-08	< 1E-08
4.0	4.0	< 1E-08	< 1E-08	< 1E-08
4.0	2.0	< 1E-08	< 1E-08	< 1E-08
3.0	3.0	< 1E-08	< 1E-08	< 1E-08

Table 1: Differences of the true mole fractions z_{A1}^0 , z_{A1} and z_B for calculations with $m=12$ and $m=14$

	κ	K_{12}	β	$rms P$	$rms y$	K_{12}	K_{23}	β	$rms P$	$rms y$
System (temperature, deg C)	/	/	[cal/mol]	(10 ⁻³)	(10 ⁻³)	/	/	[cal/mol]	(10 ⁻³)	(10 ⁻³)
Methanol/Benzene (45)	6.0	6.5	170.9	2.24	6.71	6.1	14.5	102.6	3.25	7.32
Ethanol/Trimethylpentane (50)	5.5	5.3	119.0	2.81	3.45	6.0	16.4	106.9	2.88	3.26
Ethanol/Hexane (40)	5.7	5.5	191.2	2.06	4.54	6.7	20.9	115.0	4.03	5.79
Ethanol/Cyclohexane (25)	6.0	6.9	130.5	2.36	8.90	3.5	24.7	111.0	4.55	10.30
Ethanol/Benzene (50)	4.6	5.6	155.0	2.53	7.53	4.2	5.4	133.5	3.29	9.39
Ethanol/Toluene (35)	4.6	6.8	110.3	2.77	4.37	4.6	5.8	161.8	3.37	10.20
1-Propanol/Hexane (25)	5.3	8.2	122.5	0.91	0.51	14.1	13.6	103.5	5.63	1.07
1-Propanol/Hexane (50)	4.3	6.6	169.7	5.96	3.65	6.1	7.1	184.6	9.85	6.39
1-Propanol/Benzene (60)	2.8	6.4	151.1	2.61	5.24	9.4	5.0	112.3	5.88	9.37
1-Propanol/Benzene (25)	3.3	7.2	178.5	3.20	1.50	14.6	6.1	178.8	1.92	0.90
2-Propanol/Benzene (50)	3.0	7.1	143.3	1.77	2.70	12.6	4.9	152.5	3.61	5.39
1-Butanol/Benzene (45)	3.0	6.0	107.1	7.80	1.61	14.9	3.8	170.9	8.88	1.82
1-Butanol/Toluene (100)	2.2	4.7	107.6	1.63	6.00	9.2	1.4	154.5	1.66	5.99
2-Butanol/Toluene (60)	2.4	5.1	106.1	2.11	3.23	4.5	2.0	139.4	5.00	9.62
2-Butanol/Heptane (65)	2.9	5.1	110.2	2.61	7.58	4.2	4.1	131.1	7.37	10.20
Methylamine/n-Hexane (-40)	5.3	1.8	199.8	1.65	0.19	3.8	7.6	196.4	4.83	0.56
Methylamine/n-Hexane (-10)	4.5	1.4	203.6	1.26	1.09	2.0	3.5	209.3	4.01	2.37
Methylamine/n-Hexane (20)	3.6	1.1	230.0	2.30	1.68	1.6	1.9	178.1	4.08	1.35
			Poisson					3-parameter LAM		

Table 2: Parameters for the Poisson model and for the LAM model, including the relative root-mean-squared errors (rms)

6. Figures

Figure 1: Distribution function $f(j)$ as a function of j and parameter κ .

Figure 2: n-Hexane (1) / Methylamine (2), 20 °C

Parameter: Poisson $\kappa = 3.6$, $K_{12}=1.1$, $\beta=230.0$ cal/mol
 LAM $K_{12}=1.6$, $K_{23}=1.9$, $\beta=178.1$ cal/mol

Figure 3: n-Hexane (1) / Methylamine (2), -10°C

Parameter: Poisson $\kappa = 4.5$, $K_{12}=1.4$, $\beta=203.6$ cal/mol
 LAM $K_{12}=2.0$, $K_{23}=3.5$, $\beta=209.3$ cal/mol

Figure 4: n-Hexane (1) / Methylamine (2), $-40\text{ }^{\circ}\text{C}$

Parameter: Poisson $\kappa = 5.3$, $K_{12}=1.8$, $\beta=199.8\text{ cal/mol}$
 LAM $K_{12}=3.8$, $K_{23}=7.6$, $\beta=196.4\text{ cal/mol}$

Figure 5: Hexane (1) / 1-Propanol (2), 25 °C

Parameter: Poisson $\kappa = 5.3$, $K_{12}=8.2$, $\beta=122.5$ cal/mol
 LAM $K_{12}=14.1$, $K_{23}=13.6$, $\beta=103.5$ cal/mol

Figure 6: Hexane (1) / 1-Propanol (2), 50 °C

Parameter: Poisson $\kappa = 4.3$, $K_{12}=6.6$, $\beta=169.7$ cal/mol
 LAM $K_{12}=6.1$, $K_{23}=7.1$, $\beta=184.6$ cal/mol

Appendix 1

The Poisson Distribution Function

Following Anderko [8], we assume that a central molecule is surrounded by n molecules and p is the probability that another molecule will join the central one to form an associate. We assume further that this probability is the same for all n molecules and they are independent from each other. Therefore, $\Pi(j)$, the probability that j molecules will join the central one to form an associate A_j , is given by the binomial distribution:

$$\Pi(j) = \binom{n}{j} p^j (1-p)^{n-j} \quad (\text{A1.1})$$

We assume that n is a large but finite number and p is necessarily between zero and unity. Thus, the conditions that are necessary to apply the Poisson distribution are satisfied and eq. (A1.1) can be simplified to

$$\Pi(j) = \frac{(np)^j}{j!} e^{-np} = \frac{\kappa^j}{j!} e^{-\kappa} \quad (\text{A1.2})$$

where κ is the product (np) .

The entropy change for the association reaction (2.1) can be written as

$$\Delta s_{j,j+1} = \Delta s^+ + R \ln \left[\frac{\kappa^j}{j!} \right] \quad (\text{A1.3})$$

where Δs^+ is the component of the association entropy that is not related to the size of the multimer. Therefore, the Gibbs energy of change of reaction (2.1) is

$$\begin{aligned} \Delta g_{j,j+1} &= \Delta h_{j,j+1} - T \Delta s^+ = \Delta h^+ - T \Delta s^+ - RT \ln \left[\frac{\kappa^j}{j!} \right] \\ &= \Delta g^+ - RT \ln \left[\frac{\kappa^j}{j!} \right] \end{aligned} \quad (\text{A1.4})$$

And $\Delta g_{j,j+1} = -RT \ln K_{j,j+1}$ (A1.5)

The consecutive association constant $K_{j,j+1}$ then becomes

$$K_{j,j+1} = \exp\left[-\frac{\Delta g^+}{RT}\right] \cdot \frac{\kappa^j}{j!} \quad (\text{A1.6})$$

For normalization it is convenient to introduce the dimerization constant $K_{1,2} = K$

$$K_{1,2} = \exp\left[-\frac{\Delta g^+}{RT}\right] \cdot \kappa \quad (\text{A1.7})$$

The distribution function $f(j)$ then becomes

$$f(j) = \frac{\kappa^{j-1}}{j!} \quad (\text{A1.8})$$

and Equation (A1.6) can be written

$$K_{j,j+1} = K_{1,2} \cdot \frac{\kappa^{j-1}}{j!} \quad (\text{A1.9})$$

Appendix 2:

Computer Program

The computer program is written in Fortran 77. It contains the main-program **ACTIVITY COEFFICIENT** and four subroutines. It also uses some 'canned' equation-solver programs from the MINPACK-1 package. This is a package of Fortran subprograms for numerical solution of systems of nonlinear equations and nonlinear least-squares problems.

The main program **ACTIVITY COEFFICIENT** reads the initial guesses for the model parameter, the system constants (v_A , v_B , P_A^0 , P_B^0 and the number of experimental data l) and the experimental data (P , x and y). Further, the main program calls the subprogram **LMDIF**. This MINPACK-1 subprogram **LMDIF** varies the three model parameter and minimizes an 'user-defined' function, which is, in our case, the deviation of the calculated pressure.

This user-defined function is placed in the first subroutine **FUNC**. Further, **FUNC** contains the model equations for the calculation of the equilibrium constants $K_{j,j+1}$ and it calls the subroutine **FCNAL**, for calculating the true mole fraction of the pure associating component (x_{b1al}), and the subroutine **FCN**, for calculating the true mole fraction of the mixture (x_{A1} and x_{B1}).

Finally, **FUNC** calculates the output data, the activity coefficients (γ_{A1} and γ_{B1}), the pressure (P_{cal}) and the mole fraction of the vapor phase (y_{cal}); (the mole fractions of the liquid phase are given from the experimental data).

The subroutine **FCNAL** contains the equations (3.1) to (3.3) for the case of the pure association component. The equation solver for these equations is **HYBRD1**, from the MINPACK-1 package.

The subroutine **FCN**, together with its subroutine **REGFAL** is an equation solver, especially written to solve equations (3.1) to (3.3) for the mixture. It is so designed, that it starts at $X_B=1$ (pure associating component); it uses the solution of **HYBRD1** (**FCNAL**) x_{b1al} as initial guess. From this point ($X_B=1$), the subroutine **FCN** searches stepwise to the next solutions for the next given mole fraction from the input file (going from $X_B=1$ to $X_B=0$ (pure solvent A)).

An example of the input file, the control files and an output file is attached.

Notation:

A	associating component
B	solvent
f	fugacity
f(j)	distribution function
h	enthalpy
j	degree of association
K_{jj+1}	equilibrium constant of the consecutive association reactions
m	highest degree of association
n	number of moles
p	probability
P	total pressure
R	general gas constant
S	entropy
T	absolute temperature
U	internal energy
v	molar volume
x	mole fraction in liquid phase
y	mole fraction in gas phase
z	true mole fraction in liquid phase

Greek letters:

β	physical parameter of the Poisson model
Φ	volume fraction
ϕ	fugacity coefficient
γ	activity coefficient
κ	Poisson distribution parameter

Literature:

- [1] P.J. Flory, *Thermodynamics of Heterogeneous Polymers and Their Solutions*, *J. Chem. Phys.*, Vol. 12, No. 11, 425 (1944)
- [2] O. Redlich, A.T. Kister, *On the Thermodynamics of Nonelectrolyte Solutions and Its Technical Applications*, *J. Chem. Phys.*, Vol. 15, No. 12, 849 (1947)
- [3] C.B. Kretschmer, R. Wiebe, *Thermodynamics of Alcohol-Hydrocarbon Mixtures*, *J. Chem. Phys.*, Vol.22, No. 10, 1697 (1954)
- [4] H. Wolff, A. Höpfner, *Die Wasserstoffbrückenassoziation von Methylamin in n-Hexan*, *Z. Elektrochem.*, 66, 149 (1962)
- [5] H.C. Van Ness, J. Van Winkle, H.B. Hollinger, *Infrared Spectra and the Thermodynamics of Alcohol-Hydrocarbon Systems*, *J. Phys. Chem.*, Vol. 71, No. 5, 1483 (1967)
- [6] H. Renon, J.M. Prausnitz, *On the Thermodynamics of Alcohol-Hydrocarbon Solutions*, *Chem. Eng. Sci.*, Vol. 22, 229 (1967); Errata, 1891 (1967)
- [7] E. Tucker, and E.Lippert, *The Hydrogen Bond: Recent Developments in Theory and Experiment*, Chapter 17., Amsterdam: North-Holland Publishing Company (1976)
- [8] A.Anderko, J.M. Prausnitz, *On the Relationship Between the Equilibrium Constants of Consecutive Association Reactions*, LBL-Report-34023, UC Berkeley(1993). Fluid Phase Equilibria (in press,1994)
- [9] J.M. Prausnitz, R.N. Lichtenthaler, E.G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall (1986)
- [10] J. Gmehling, U. Onken, *Vapor-Liquid Equilibrium Data Collection*, DECHEMA Chemistry Data Series, Vol. 1, Part 2a (1977)

PROGRAM ACTIVITY COEFFICIENT

```

c*****c
c  this program fits the three parameter of the Poisson model      c
c  to observed data, by minimizing the root-mean-squared          c
c  error of the calculated vapor pressure                          c
c*****c
c  k1 = kappa (the Poisson parameter)
c  K2 = equilibrium constant of dimerization
c  beta = physical parameter of the Poisson model
c  x2,y2 = observed mole fraction of the association component B
c  pp = observed vapor pressure
c  T = absolute temperature [K]
c  PA0,PB0 = pure component vapor pressures
c  vA,vB = pure component molar volumes
c  ycal,pcal = calculated mole fraction, vapor pressure
c  gamaA,gamaB = activity coefficients of component A and B
c
c  maxfev,mode,nprint,nfev,ldfjac,ipvt = LMDIF parameters
c  ftol,xtol,gtol,epsfcn,factor,dmpar = LMDIF parameters
c  x(nn),f(nn),diag(nn),fjac(nn,mm),qtf(nn) = LMDIF variables
c  wa1(nn),wa2(nn),wa3(nn),wa4(mm),diag(nn) = LMDIF variables
c
c  ml=number of exp data points, mm=ml=1
c  nn=number of parameters

parameter(nn=3,mm=100,ml=100)
implicit double precision(a-h,o-z)
integer maxfev,mode,nprint,nfev,ldfjac,
1      ipvt(nn)
double precision ftol,xtol,gtol,epsfcn,factor
double precision x(nn),f(mm),diag(nn),fjac(mm,nn),qtf(nn),
1      wa1(nn),wa2(nn),wa3(nn),wa4(mm),diag(nn),
2      pp(ml),x2(ml),y2(ml),y3(ml),pcal(ml),y2cal(ml),
3      gamaA(ml),gamaB(ml),x3(ml),
4      PA0,PB0,k1,K2,beta,vA,vB,T
double precision dmpar

character*100 infile,infile2,outfile,infofile
character*75 name
external func

common/block1/pp,x2,y2
common/block2/pcal,y2cal,gamaA,gamaB
common/block3/T,pa0,pb0
common/block4/k1,K2,vA,vB,beta
common/block7/infile2

open(unit=9,file='run.ctl',status='unknown')
  read(9,*)infile
  read(9,*)infile2
  read(9,*)outfile
  read(9,*)infofile
close (9)

c  input: read in the model parameters (initial guesses) and
c  system constants

open(unit=10,file=infile,status='unknown')
read(10,'(A)')name
read(10,*)beta      ! physical parameter
read(10,*)vA,vB     ! molar volume of A and B
read(10,*)k1,K2     ! two parameters from the Poisson model
read(10,*)T         ! constant system temperature
read(10,*)PA0       ! vapor pressure of pure A
read(10,*)PB0       ! vapor pressure of pure B
read(10,*)l         ! number of exp data points

```

```

c      input: experimental data

      do i=1,1
        read(10,*)pp(i),x2(i),y2(i)
      enddo

      close (10)

      open(unit=11,file=outfile,status='unknown')

c
c ** solve the system of m nonlinear equations and minimize the error **
c *****

c      number of parameters to be optimized
      n=nn
c      total nuber of functions to be minimized
c      m=1
c      convergenz and toleranz parameters of LMDIF

      ftol=dsqrt(dpmpar(1))
      xtol=dsqrt(dpmpar(1))
      gtol=0.0d0
      ldfjac=100

      maxfev=600
      epsfcn=1.0d-5
      factor=1.0d+1
      mode=1
      nprint=1

      x(1)=k1
      x(2)=K2
      x(3)=beta

      call lmdif(func,1,n,x,f,ftol,xtol,gtol,maxfev,epsfcn,diag,mode,
1          factor,nprint,infof,nfev,fjac,ldfjac,ipvt,qtf,wal,
2          wa2,wa3,wa4)

c ==> output

      k1 =x(1)
      K2 =x(2)
      beta=x(3)*1.99*T

      write(6,*)'infof = ',infof
      write(11,*)name
      write(11,*)
      write(11,*)'      POISSON-DISTRIBUTION MODEL'
      write(11,*)
      write(11,120)k1
120  format('k1      = ',f7.3,' (Poisson distribution const.)')
      write(11,121)K2
121  format('K2      = ',f7.3,' (dimerization const.)')
      write(11,122)beta
122  format('beta = ',f7.3,' [cal/mol]')
      write(11,123)vA,vB
123  format('v1      = ',f5.2,',      v2 = ',f5.2,' (molar volumes)')
      write(11,150)T
150  format('Temperature = ',f5.1,' [K]')
      write(11,*)
      write(11,170)
170  format('P [mmHg]',5x,'x2',8x,' y2',8x,'P calc',5x,'y2 calc')
      write(11,*)

```



```

do i=1,1
  y3(i)=1-y2(i)
  x3(i)=1-x2(i)
  write(11,200)pp(i),x3(i),y3(i),pcal(i),y2cal(i)
enddo
200 format(f7.2,5x,f6.4,5x,f6.4,4x,f7.2,5x,f6.4)

c calculate root mean squared error of pcal and ycal

ssqp=0.0d0
ssqy=0.0d0
do i=1,1
  ssqp = ssqp+((pp(i)-pcal(i))/PP(i))**2
enddo

do i=1,1
  ssqy=ssqy+((y2(i)-y2cal(i))/y2(i))**2
enddo

rmsp = dsqrt((ssqp)/float(1))
rmsy = dsqrt((ssqy)/float(1))

write(11,*)'_____ '
write(11,*)
write(11,*)'relative rms error vap pressure = ',real(rmsp)
write(11,*)'relative rms error mole fract. = ',real(rmsy)

close(11)

end

```

```

SUBROUTINE func(l,n,x,f,iflag)
c*****
c    This subroutine calculates the residuals of the function
c    to be minimized
c*****
c    XA,XB = mole fractions of components A (1) and B (2)
c    xal,xbl = true mole fractions of the monomers of A and B
c    xblal = true mole fraction of associating component B
c
c    f(i) = function to be minimized
c    w(i) = variables for the true mole fractions
c    nal,infocc,tol,lwa = HYBRID1 parameters
c    wa,fvecal = HYBRID1 variables

parameter(nn=3,nk=12,mm=100,ml=100)
implicit double precision(a-h,o-z)
integer nal,infocc,lwa
double precision x(nn),f(mm),pp(ml),x2(ml),y2(ml),w(2),
1          pcal(ml),y2cal(ml),gamaA(ml),gamaB(ml),
2          wa(500),fvecal(1),K(nk),
3          k1,K2,XA,XB,vA,vB,beta

character*100 infile2

external fcna1,fcna

common/block1/pp,x2,y2
common/block2/pcal,y2cal,gamaA,gamaB
common/block3/T,pa0,pb0
common/block4/k1,K2,vA,vB,beta
common/block5/K
common/block6/XA,XB
common/block7/infile2

c    initial guesses for the parameters

k1 =x(1)
K2 =x(2)
beta=x(3)

do i=1,nn
  if(x(i).le.0.0d0) then
    do j=1,1
      f(j)=10000
    enddo
    goto 99
  endif
enddo

write(6,*)'k1 = ',x(1)
write(6,*)'K2 = ',x(2)
write(6,*)'beta=',x(3)

c    calculation of the equilibrium constants of the n-mers
K(2)=K2
K(3)=k1**2/6.*K2
K(4)=k1**3/24.*K2
K(5)=k1**4/120.*K2
K(6)=k1**5/720.*K2
K(7)=k1**6/5040.*K2
K(8)=k1**7/40320.*K2
K(9)=k1**8/362880.*K2
K(10)=k1**9/3628800.*K2
K(11)=k1**10/39916800.*K2
K(12)=k1**11/479001600.*K2
c    K(13)=k1**12/6227020800.*K2

```

```

c      K(14)=k1**13/87178291200.*K2
c      setting convergence criterium

      tol=dsqrt(dpmpar(1))
      lwa=500

      open(unit=10,file='infile2',status='unknown')

      do i=1,2
        read(10,*)w(i)
      enddo

      close(10)

c      calculation of the mole frac. of monomer B in pure alcohol(B)

      nal=1
      XB=1
      XA=0

      call hybrdl(fcnal,nal,w,fvecal,tol,infocc,wa,lwa)

      xblal=w(1)

c      calculation of the mole fractions in the mixture
c      ==>important: start with x2=1(pure comp. B), or close to it!!
c      otherwise change XA=x2 and XB=(1-x2)

      do j=1,1
        XB=x2(j)
        XA=1-x2(j)

c      ==> Iteration process

        call FCN(w)

c      ==> calculation of output data

        xal=w(2)
        xbl=w(1)

        gamaA(j)=xal/XA*dexp(beta*vA*(vB/vA*XB/(XA+vB/vA*XB))**2)
        gamaB(j)=xbl/(XB*xblal)*dexp(beta*vB*(XA/(XA+vB/vA*XB))**2)
        Pcal(j)=gamaA(j)*(1-XB)*PA0+gamaB(j)*XB*PB0
        y2cal(j)=gamaB(j)*XB*PB0/Pcal(j)

c      write(6,*)'gamaA(j) = ',gamaA(j)
c      write(6,*)'gamaB(j) = ',gamaB(j)
c      write(6,*)'pcal(j) = ',Pcal(j)
c      write(6,*)'yBcal = ',y2cal(j)

        f(j)=((pp(j)-pcal(j))/pp(j))**2

c      f(j)=((y2(j)-y2cal(j))/y2(j))**2

      enddo

99      return
      end

```

```

      SUBROUTINE FCNAL(n,w,fvec,iflag)
c*****
c   this subroutine contains the system of n nonlinear
c   equations to calculate the true mole fraction of the
c   i-mers in pure alcohol B
c*****
c   w(i)= true mole fraction of i-mer B,i=1,12
c   P(i) = product of chem. equilibrium equations (P(i) = w(i))
c   n = number of equations to be solved (n=1)

      parameter(ml=100,nk=12)
      implicit double precision(a-h,o-z)
      integer n,iflag
      double precision K(nk),w(n),fvec(n),P(nk),
1      XA,XB
      real sumwi

      common/block5/K
      common/block6/XA,XB

      if((w(1).lt.0).or.(w(1).gt.1)) then
         fvec(1)=10000
         goto 99
      endif

      P(2)=K(2)*w(1)**2
      P(3)=K(3)*P(2)*w(1)
      P(4)=K(4)*P(3)*w(1)
      P(5)=K(5)*P(4)*w(1)
      P(6)=K(6)*P(5)*w(1)
      P(7)=K(7)*P(6)*w(1)
      P(8)=K(8)*P(7)*w(1)
      P(9)=K(9)*P(8)*w(1)
      P(10)=K(10)*P(9)*w(1)
      P(11)=K(11)*P(10)*w(1)
      P(12)=K(12)*P(11)*w(1)
c   P(13)=K(13)*P(12)*w(1)
c   P(14)=K(14)*P(13)*w(1)

      sumwi=w(1)
      do I=2,nk
         sumwi=sumwi+P(I)
      enddo

      fvec(1)=XB-sumwi

99   return
      end

```

```

SUBROUTINE FCN(w)
C*****
C  this subroutine contains the system of nonlinear
C  equations to calculate the true mole fraction of the
C  n-mers B and the mole fraction of A, by starting at XB=1
C  with the value of w(1) of pure alcohol B and
C  searching for the next result for w(1), by reducing
C  the value of w(1) in very small steps.
C*****
C  w(1)= true mole fraction of monomer B
C  w(2)= true mole fraction of monomer A
C  sump = sum of P(i), (sum of the true mole fractions)
C  sumwi = sum of i*P(i)
C  K(i) = equilibrium constants of the association reaction
C
C  maxit = maximum iteration cycles
C  S = sign

parameter(ml=100,nk=12)
implicit double precision(a-h,o-z)
integer maxit
double precision K(nk),w(2),P(nk),XA,XB
real sumwi,sump,sump2

common/block5/K
common/block6/XA,XB

p(1)=w(1)
P(2)=K(2)*w(1)**2
P(3)=K(3)*P(2)*w(1)
P(4)=K(4)*P(3)*w(1)
P(5)=K(5)*P(4)*w(1)
P(6)=K(6)*P(5)*w(1)
P(7)=K(7)*P(6)*w(1)
P(8)=K(8)*P(7)*w(1)
P(9)=K(9)*P(8)*w(1)
P(10)=K(10)*P(9)*w(1)
P(11)=K(11)*P(10)*w(1)
P(12)=K(12)*P(11)*w(1)
C  P(13)=K(13)*P(12)*w(1)
C  P(14)=K(14)*P(13)*w(1)

sump=0
do i=1,nk
    sump=sump+P(i)
enddo

sumwi=0
do I=1,nk
    sumwi=sumwi+I*P(I)
enddo

w(2)=1-sump

fvec=XB-(sumwi/(sumwi+w(2)))

step=1.0d-5
100 S=dsign(1,fvec)
w(1)=w(1)-step

P(1)=w(1)
P(2)=K(2)*w(1)**2
P(3)=K(3)*P(2)*w(1)
P(4)=K(4)*P(3)*w(1)
P(5)=K(5)*P(4)*w(1)
P(6)=K(6)*P(5)*w(1)

```

```

P(7)=K(7)*P(6)*w(1)
P(8)=K(8)*P(7)*w(1)
P(9)=K(9)*P(8)*w(1)
P(10)=K(10)*P(9)*w(1)
P(11)=K(11)*P(10)*w(1)
P(12)=K(12)*P(11)*w(1)
c   P(13)=K(13)*P(12)*w(1)
c   P(14)=K(14)*P(13)*w(1)

sump=0
do i=1,nk
    sump=sump+P(i)
enddo

sumwi=0
do i=1,nk
    sumwi=sumwi+I*P(I)
enddo

w(2)=1-sump

fvec=XB-(sumwi/(sumwi+w(2)))

if (dsign(1,fvec).eq.S) goto 100

A=w(1)
B=w(1)+step

c  set convergence parameters for REGFAL
    maxit=200

    Assign=dsign(1,fvec)

    call REGFAL(A,B,Assign,maxit,sump2)

    w(2)=1-sump2
    w(1)=(A+B)/2

200 return
end

```

```

      SUBROUTINE REGFAL(A,B,Asign,maxit,sump)
c*****c
c      this subroutine calculates the zero of the function in the small c
c      interval x=A and x=A+B. The iteration method is based on a c
c      regula-falsi-method c
c*****c
      parameter(nk=12)
      implicit double precision(a-h,o-z) /
      integer maxit
      double precision K(nk),P(nk),A,B,L,x2,XA,XB
      real tol,Asign,sump,sumwi

      common/block5/K
      common/block6/XA,XB

      tol=1.0d-8

101  do j=1,maxit
      L=(B-A)/2
      A=A+L

c      write(6,*)'L,A,tol = ',L,A,tol

      if(i.eq.maxit) then
        write(6,*)'number of loops reached maxit'
        goto 201
      endif

      if(L.lt.tol) then
        goto 201
      endif

      P(1)=A
      P(2)=K(2)*A**2
      P(3)=K(3)*P(2)*A
      P(4)=K(4)*P(3)*A
      P(5)=K(5)*P(4)*A
      P(6)=K(6)*P(5)*A
      P(7)=K(7)*P(6)*A
      P(8)=K(8)*P(7)*A
      P(9)=K(9)*P(8)*A
      P(10)=K(10)*P(9)*A
      P(11)=K(11)*P(10)*A
      P(12)=K(12)*P(11)*A
c      P(13)=K(13)*P(12)*A
c      P(14)=K(14)*P(13)*A

      sump=0
      do i=1,nk
        sump=sump+P(i)
      enddo

      sumwi=0
      do i=1,nk
        sumwi=sumwi+i*P(i)
      enddo

c      x2 is the true mole fraction of A (non-associating comp.)
      x2=1-sump

      fvec=XB-sumwi/(sumwi+x2)

      if(dsign(1,fvec).ne.Asign) then
        B=A
        A=A-L
        Asign=dsign(1,fvec)

```

X

```
        goto 101
    else
        goto 101
    endif
enddo
201  return
    end
```


c System: n-Hexane(1)/Methylamin(2), -40'C, Wolff and Hoepfner (1961)

POISSON-DISTRIBUTION MODEL

k1 = 5.320 (Poisson distribution const.)

K2 = 1.767 (dimerization const.)

beta = 199.864 [cal/mol]

v1 = 2.79, v2 = 1.00 (molar volumes)

Temperature = 233.0 [K]

P [mmHg]	x2	y2	P calc	y2 calc
126.00	0.9999	0.9999	126.29	0.9999
125.30	0.9690	0.9900	124.44	0.9888
122.60	0.9250	0.9810	122.35	0.9815
121.60	0.8770	0.9780	120.87	0.9783
120.10	0.8270	0.9760	119.98	0.9770
119.20	0.7830	0.9760	119.56	0.9765
118.90	0.7350	0.9750	119.31	0.9763
117.70	0.6620	0.9750	119.05	0.9761
117.90	0.6290	0.9750	118.90	0.9760
116.70	0.5430	0.9750	118.18	0.9756
115.20	0.4490	0.9740	116.49	0.9749
113.60	0.3600	0.9730	113.44	0.9738
109.10	0.2820	0.9720	108.97	0.9721
103.90	0.2150	0.9700	102.90	0.9699
99.20	0.1750	0.9680	97.60	0.9679
89.50	0.1290	0.9640	88.79	0.9640
74.80	0.0860	0.9560	75.43	0.9568
63.70	0.0626	0.9470	64.02	0.9484
48.70	0.0415	0.9310	49.29	0.9320
36.10	0.0274	0.9060	36.28	0.9065
23.20	0.0154	0.8510	23.06	0.8514
12.60	0.0068	0.7220	12.47	0.7229
3.60	0.0001	0.0370	3.61	0.0371

relative rms error vap pressure = 1.64835E-03

relative rms error mole fract. = 1.92827E-04

c System: n-Hexane(1)/Methylamin(2), -40'C, Wolff and Hoepfner (1961)

0.3			! beta
2.785	1.0		! v1 v2
6.0	1.0		! k1 K2
233			! Temperature in [K]
3.48			! P10
126.3			! P20
23			! number of data points
126.0	0.9999	0.9999	! P2 x2 y2
125.3	0.969	0.990	
122.6	0.925	0.981	
121.6	0.877	0.978	
120.1	0.827	0.976	
119.2	0.783	0.976	
118.9	0.735	0.975	
117.7	0.662	0.975	
117.9	0.629	0.975	
116.7	0.543	0.975	
115.2	0.449	0.974	
113.6	0.360	0.973	
109.1	0.282	0.972	
103.9	0.215	0.970	
99.2	0.175	0.968	
89.5	0.129	0.964	
74.8	0.086	0.956	
63.7	0.0626	0.947	
48.7	0.0415	0.931	
36.1	0.0274	0.906	
23.2	0.0154	0.851	
12.6	0.0068	0.722	
3.6	0.0001	0.037	

OBJECTS=activ1.o activ2.o activ3.o activ4.o activ5.o\

./home_b/MINPACK/LMDIF/enorm.o \
./home_b/MINPACK/LMDIF/qrfac.o \
./home_b/MINPACK/LMDIF/dpmpar.o \
./home_b/MINPACK/LMDIF/fdjac2.o \
./home_b/MINPACK/LMDIF/lmdif.o \
./home_b/MINPACK/LMDIF/lmpar.o \
./home_b/MINPACK/LMDIF/qrsolv.o \
./home_b/MINPACK/HYBRD/dogleg.o \
./home_b/MINPACK/HYBRD/fdjac1.o \
./home_b/MINPACK/HYBRD/qform.o \
./home_b/MINPACK/HYBRD/r1mpyq.o \
./home_b/MINPACK/HYBRD/r1updt.o \
./home_b/MINPACK/HYBRD/hybrd.o \
hybrd1.o

activ: \$(OBJECTS)
f77 -O -o act.exe \$(OBJECTS)

makefile

amin2.f
test1.in2
out
test1.info

run.ctl

DATE

FILMED

6 / 2 / 94

END