Program for Calculating Phase Equilibria and Thermodynamic Properties of High-Temperature Electrolyte Systems

OLI Systems Inc.
240 Cedar Knolls Road, Cedar Knolls, New Jersey 07927, United States

Introduction

The program PROPERTC.EXE contains the model for simulating the properties of high-temperature systems containing water, electrolytes and nonelectrolytes as described in the paper "Equation of state for high-temperature aqueous electrolyte and nonelectrolyte systems" by J.J. Kosinski and A. Anderko. This paper is included in this document.

PROPERTC.EXE is a DOS program. Sample input and output files are included in the files PROPERTY.INP and PROPERTY.OUT, respectively. The input file can be modified with any text editor. For each of the conditions specified in the input file, the program performs phase equilibrium (solid-calculations and computes the properties of individual phases.

A list of components that are supported by the program is included below. Each component is followed by its molecular weight, critical temperature, critical pressure and acentric factor. For salts, the critical parameters and acentric factor are not included because they are not accessible and are not used by the program.

In addition to the components listed below, the program can also work with "generic" components, which are characterized by their critical temperature, pressure and acentric factor. To define the additional components, the file APEOSDAT.INP is used. If desired, the APEOSDAT.INP file can also be used to specify the ideal-gas heat capacity. The attached APEOSDAT.INP file shows examples how "generic" components can be defined.

List of Compounds Supported in the Program

		MW	Tc/K	Pc/kPa	omega
1	H2O	18.0153	647.070	22120.	0.00000
2	NaCl	58.4428	0.000	0.	0.00000
3	KCl	74.5550	0.000	0.	0.00000
4	CO2	44.0100	0.000	0.	0.00000
5	CH3OH	32.0424	512.640	8097.	0.56399
6	O2	31.9988	154.580	5043.	0.02218
7	Na2SO4	142.0430	0.000	0.	0.00000
8	K2SO4	174.2674	0.000	0.	0.00000
9	Na2CO3	105.9890	0.000	0.	0.00000
10	NaF	41.9882	0.000	0.	0.00000
11	NaOH	39.9971	0.000	0.	0.00000
12	Na3PO4	163.9410	0.000	0.	0.00000
13	CaCl2	110.9830	0.000	0.	0.00000
14	KCl	74.5550	0.000	0.	0.00000
15	LiCl	42.3900	0.000	0.	0.00000
16	CH4	16.0428	190.530	4598.	0.01000
17	C2H6	30.0696	305.340	4871.	0.10000
18	C3H8	44.0965	369.850	4248.	0.15200
19	C4H10	58.1234	425.160	3796.	0.20000
20	C5H12	72.1503	469.690	3364.	0.25200
21	C6H14	86.1772	507.850	3058.	0.30300
22	C7H16	100.2040	540.150	2736.	0.35000
23	C8H18	114.2310	568.760	2487.	0.39800
24	C9H20	128.2580	595.650	2306.	0.43771
25	C10H22	142.2850	617.700	2120.	0.48900
26	C12H26	170.3380	658.200	1820.	0.57500
27	C16H34	226.4460	722.000	1410.	0.74200
28	n-C5H12	72.1503	433.750	3196.	0.19700
29	N2	28.0135	126.200	3400.	0.03700
30	Ar	39.9480	150.860	4898.	-0.00400
31	Kr	83.8000	209.390	5496.	-0.00200
32	Xe	131.2900	289.740	5821.	0.00200
33	C2H5OH	46.0690	513.920	6148.	0.64524
34	C3H7OH	60.0959	536.780	5175.	0.62175
35	C4H9OH	74.1228	563.050	4423.	0.59349
36	C5H11OH	88.1497	586.150	3880.	0.59376
37	C6H13OH	102.1770	611.350	3510.	0.57911
38	C7H15OH	116.2030	631.900	3150.	0.58739
39	C8H17OH	130.2300	652.500	2860.	0.59412
40	C9H19OH	144.2570	668.900	2600.	0.62667
41	C10H21OH	158.2840	684.400	2370.	0.66122
42	C11H23OH	172.3110	704.000	2080.	0.58724
43	C12H25OH	186.3380	719.400	1994.	0.66635
44	C16H33OH	242.4450	761.000	1510.	0.74801

List of Files

PROPERTC.EXE   executable
PROPERTY.INP   sample input file
PROPERTY.OUT   sample output file
APEOSDAT.INP   sample data file for specifying nonelectrolyte components on the basis
                of the corresponding-states principle

Equation of State for High-Temperature Aqueous Electrolyte and Nonelectrolyte Systems

Jerzy J. Kosinski and Andrzej Anderko[1]

OLI Systems, Inc.
240 Cedar Knolls Road, Cedar Knolls, New Jersey 07927, United States

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[1] Author to whom correspondence should be addressed. E-mail: aanderko@olisystems.com.

ABSTRACT

An equation of state has been developed for the representation of the phase behavior of high-temperature and supercritical aqueous systems containing salts and nonelectrolytes. The equation includes a reference part that is based on a model for hard-sphere ion pairs and dipolar solvent molecules. In addition to the reference part, the equation contains a perturbation part, which is expressed by a truncated virial-type expansion. To enhance the predictive capability of the EOS for normal fluids such as hydrocarbons, the equation has been reformulated using the three-parameter corresponding-states principle. For salt-water systems for which little experimental information is available, a predictive procedure has been developed that relies on similarities in the fluid phase behavior of various salt-water systems. This procedure utilizes the equation of state for $NaCl+H_2O$ as a prototype system and introduces a transformation of parameters for the salt of interest. The equation accurately represents vapor-liquid equilibria, solid-liquid equilibria and densities for systems containing water, salts and hydrocarbons.

1. INTRODUCTION

Phase behavior of high-temperature and supercritical aqueous systems is important for a variety of applications, including the study of geological systems, power plant engineering and supercritical reaction technology. In particular, the knowledge of phase equilibria and thermodynamic properties of multicomponent systems containing water, salts and nonelectrolytes is needed for the development of supercritical waste oxidation technologies [1]. In view of the complexity of the phase behavior of such systems, it is desirable to develop a comprehensive thermodynamic model that could reproduce the available experimental data and provide reasonable predictions at conditions for which experimental data are unavailable or fragmentary.

In a previous study [2], a comprehensive equation of state was developed for the NaCl-H_2O system at temperatures ranging from 573 to ca 1200 K. This equation was later extended to other systems [3-6]. In the present work, we use it as a starting point for the development of a model that is applicable to aqueous systems containing various salts and nonelectrolytes. In particular, the objective of this study is to:

(1) Extend the applicability of the EOS to systems containing hydrocarbons and other normal fluids in addition to water and salts and

(2) Extend the model to reproduce or estimate the properties of water-salt systems for which only fragmentary experimental information is available.

2. EQUATION OF STATE

The equation of state used in this study consists of a reference part and a perturbation contribution. The reference part represents the properties of a mixture of hard-sphere, dipolar or quadrupolar ion pairs and solvent molecules. This reference model is appropriate in view of the fact that salts tend to form ion pairs in high-temperature systems (above ca. 300 °C). The perturbation part arises from all other interactions and is expressed by a truncated virial term. Thus, the fundamental expression for the residual Helmholtz energy is written as

$$a^{res}(T,v,x) = a^{rep}(v,x) + a^{dip}(T,v,x) + a^{per}(T,v,x) \tag{1}$$

where a^{rep}, a^{dip} and a^{per} are the repulsive, electrostatic and perturbation contributions, respectively. Expressions for these terms, together with associated mixing rules, are given by Anderko and Pitzer [2] and, therefore, they will not be repeated here.

In this study, we extend the equation of state to normal fluids in addition to water and salts. To enhance the predictive capability of the EOS, it is worthwhile to generalize it using the three-parameter corresponding-states principle. For this purpose, we use the approach developed by Anderko and Pitzer [7] in conjunction with a different equation of state.

The original equation is written in terms of dimensionless density η defined as

$$\eta = \frac{b\rho}{4} \tag{2}$$

This quantity can be rewritten in terms of reduced density ρ_r, i.e.,

$$\eta = \frac{b}{4v_c^*}\rho_r = \frac{b^*}{4}\rho_r \tag{3}$$

where v_c^* is a standardized critical volume, calculated from the critical temperature, pressure and acentric factor as [7].

$$v_c^* = \frac{z_c^* RT_c}{P_c} \tag{4}$$

where z_c^* is calculated from a correlation with the acentric factor, i.e.,

$$z_c^* = 0.2905 - 0.0787\omega \tag{5}$$

This reduces the inherent variations in z_c because the uncertainty of ω is small. The

parameter b^* is further expressed as a linear function of the acentric factor, i.e.,

$$b^* = b_0^* + b_1^*(\omega - \omega_{CH_4}) \tag{6}$$

where methane is used as a reference fluid. With the redefined density, the repulsive term of the EOS can be computed using the corresponding-states principle. For the perturbation term, i.e.,

$$\frac{a^{per}}{RT} = -\frac{4a}{RTb}\eta\left(1 + c\eta + d\eta^2 + e\eta^3\right) = -\frac{a^*}{T_r}\rho_r\left(1 + c\eta + d\eta^2 + e\eta^3\right), \tag{7}$$

the attractive parameter a is redefined as a reduced quantity a^*. The parameter a^* can be expressed using the reduced temperature:

$$a^* = a_0 + \frac{a_1}{T_r} + \frac{a_2}{T_r^2} + \frac{a_3}{T_r^3} + \frac{a_4}{T_r^4} \tag{8}$$

with an additional dependence on the acentric factor:

$$a_i = a_{0i} + a_{1i}(\omega - \omega_{CH_4}) \qquad i = 0,..., 4 \tag{9}$$

The parameters c and d in the perturbation term are given by expressions that are analogous to eq. (4) and the parameter e is assigned a common value for all normal fluids. Thus, the equation of state can be used now for any normal fluid that can be characterized by the critical temperature, critical pressure and acentric factor.

3. DETERMINATION OF PARAMETERS

For pure substances, the equation of state requires the co-volume b, dipole moment μ, and the perturbation parameters a, c, d and e. For mixtures, there are additional parameters α_{ij}, γ_{ijk}, δ_{ijkl} and ε_{ijklm}. Although these parameters formally pertain to binary, ternary and higher-order interactions, they have been reduced to binary parameters by introducing suitable combining rules [2, 3]. As described in a previous paper [3], the mixture parameters for multicomponent systems are defined once the parameters are obtained for the constituent binary subsystems. The default values of the binary parameters are 1. The number and temperature dependence of binary parameters depend, in general, on the particular system. For water, the pure component parameters have been fitted to PVT and vapor pressure data generated from the equation of Hill [8]. The obtained parameters are listed in Appendix A. With these parameters, the equation of state reproduces the properties of water from 283 to 1473 K. For normal fluids, the EOS parameters have been evaluated by simultaneously regressing PVT and vapor pressure data for 20 compounds previously selected by Anderko and Pitzer [7]. These parameters are also listed in Appendix A.

The binary parameters can be evaluated if sufficient experimental data are available for the mixture of interest. In the case of salt-water systems, a comprehensive experimental database exists only for NaCl. Fragmentary VLE, PVT and solubility data are available for KCl, CaCl$_2$ and Na$_2$SO$_4$. For other salts, experimental data are limited to solid solubilities or are lacking altogether. Therefore, a two-level approach to parameter evaluation has been adopted in this study, i.e.,

(1) Parameters for the NaCl+H$_2$O system have been regressed using all available VLE, density and SLE data to create a comprehensive equation of state and

(2) The resulting equation of state for NaCl-H$_2$O has been used as a "master EOS" for other salt-water systems. As described in the next section, only selected parameters have been adjusted to match the behavior of other systems.

It should be noted that the equation of state represents only the properties of fluid phases. However, it can also be used to calculate solid-fluid equilibria by utilizing a relationship between the fugacities of the solid (f_s) and fluid (f_f) phases. By using the pure subcooled liquid solute as a standard state, the following general relationship between f_s and f_f can be derived from standard thermodynamics:

$$\ln f_f - \ln f_s = \frac{\Delta H_m}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right) + \frac{\Delta C_{pm}}{R}\left(1 - \frac{T_m}{T} + \ln\left(\frac{T_m}{T}\right)\right) - \frac{\Delta C_{pT}}{2RT}(T - T_m)^2 +$$
$$-2\frac{\Delta C_{p\sqrt{T}}}{R\sqrt{T_m}}\left(\sqrt{\frac{T_m}{T}} - 1\right)^2 - \frac{\Delta C_{pT^2}}{2R}\left(\frac{1}{T} - \frac{1}{T_m}\right)^2 + \frac{(p - p°)}{RT}\left(\Delta V_m + \frac{(p - p°)}{2}\Delta V_1\right)$$

(10)

where T$_m$ is the melting temperature, ΔH$_m$, ΔC$_{pm}$ and ΔV$_m$ are the changes in enthalpy, heat capacity and volume on melting and the remaining parameters represent the dependence of ΔC$_{pm}$ and ΔV$_m$ on temperature and pressure, respectively. These parameters are separate from the EOS parameters and have been obtained from tabulated thermochemical data [9].

To obtain the "master EOS" for the NaCl-H$_2$O system, the database previously selected by Anderko and Pitzer [2] has been used for temperatures above 573 K.

Additionally, the equation has been constrained to reproduce phase equilibrium and volumetric property data [10] for temperatures between 373 and 573 K. It should be noted that the theoretical basis of the EOS used in this study is valid only at conditions at which salts exist predominantly as ion pairs, i.e., above ca. 573 K. However, the equation can be empirically extended to lower temperatures. This is useful if the equation is to be used as a thermodynamic model for supercritical oxidation processes, in which temperatures may significantly vary in different parts of the process. The parameters for the NaCl-H_2O system are given in Appendix B.

4. ESTIMATION FOR SYSTEMS WITH LIMITED EXPERIMENTAL DATA

As discussed above, it is not practical to regress all EOS parameters for numerous salt-water systems of practical importance. Therefore, it is necessary to develop a procedure for estimating the parameters for systems for which experimental data are scarce.

In the case of pure ionic fluids, corresponding-states methods [11-13] have been proven useful for estimating the properties of salts at high temperatures. However, no rigorous corresponding-states treatment is available for salt-water mixtures. At the same time, analysis of the phase behavior of several electrolyte systems at high temperature reveals significant regularities [14, 3], which may be regarded as a manifestation of a corresponding-states behavior. For example, the shape of vapor-liquid coexistence curves is similar for aqueous NaCl, KCl and NaOH solutions. This indicates that a mapping transformation can be found that would map the properties of several salts onto the properties of the well-known NaCl+H_2O system. In this study, we utilize the properties of the equation of state for salt-water systems to propose such a transformation.

The equation of state for pure ion pairs is characterized by three parameters, i.e., a, b and μ. If the behavior of the ion-pair fluid obeys the corresponding-states principle, a generalized equation of state can be written in terms of three reduced variables $\tilde{a}$, $\tilde{b}$ and $\tilde{\mu}$, i.e.,

$$\tilde{a} = \frac{a}{a^*}; \quad \tilde{b} = \frac{b}{b^*}; \quad \tilde{\mu} = \frac{\mu}{\mu^*} \tag{11}$$

where the asterisk denotes a reducing parameter, which is substance-specific, but generally unknown. Since the behavior of ion-pair fluids should be the same under the same reduced conditions, the equation of state for an MeX fluid can be mapped onto the equation of state for NaCl by applying a transformation of parameters, i.e.,

$$a_{MeX} = \frac{a^*_{MeX}}{a^*_{NaCl}} a_{NaCl} = k_{MeX,NaCl} a_{NaCl} \tag{12}$$

$$b_{MeX} = \frac{b^*_{MeX}}{b^*_{NaCl}} b_{NaCl} = l_{MeX,NaCl} b_{NaCl} \tag{13}$$

$$\mu_{MeX} = \frac{\mu^*_{MeX}}{\mu^*_{NaCl}} \mu_{NaCl} = m_{MeX,NaCl} \mu_{NaCl} \tag{14}$$

where the factors $k_{MeX,NaCl}$, $l_{MeX,NaCl}$ and $m_{MeX,NaCl}$ are temperature-independent proportionality constants. Further, it can be assumed that the MeX-H_2O binary interaction parameters can be approximated by those for NaCl-H_2O. Thus, the equation of state for the MeX-H_2O fluid can be mapped onto the equation for NaCl-H_2O by adjusting the three factors $k_{MeX,NaCl}$, $l_{MeX,NaCl}$ and $m_{MeX,NaCl}$.

5. RESULTS

When applied to the prototype NaCl+H_2O system, the equation of state accurately reproduces VLE, SLE and PVT data. This is illustrated in Figures 1 and 2 for VLE and saturated volumes, respectively. The quality of the representation of the data is similar to that obtained in the previous study [2]. However, the validity range of the model has been extended.

The equation of state is also applicable to water-nonelectrolyte systems. Figures 3 and 4 show the representation of phase equilibria for water-methane and water-decane systems. A particularly interesting phase behavior is observed for the water-decane system, which shows two distinct two-phase regions, which originate from the vapor pressure points of both pure components. At 563.15 K, these two regions merge and show a three-phase

VLLE locus. At higher temperatures, they are separate. The equation of state accurately reproduces this behavior.

After verifying the performance of the EOS for both salt and nonelectrolyte systems, the transformation of parameters (eq. 12-14) has been applied to extend the model to salt-water systems for which little experimental information is available. A good test system is provided for by the $KCl-H_2O$ mixture, for which fragmentary phase equilibrium data are available. In this case, the "master" EOS for $NaCl-H_2O$ has been applied with the transformation parameters $k_{MeX,NaCl}$, $l_{MeX,NaCl}$ and $m_{MeX,NaCl}$ equal to 1.363, 1.339 and 1.214, respectively. As shown in Figure 5, vapor-liquid equilibrium data are reproduced for this system with good accuracy. It should be noted that an EOS for $KCl-H_2O$ was previously established by determining system-specific binary parameters [3]. However, the present treatment is much preferred because it ensures correct predictions at temperatures above 773 K, for which no data are available for KCl. For many other salts the amount of experimental information is so small that the use of a "master" EOS with transformed parameters is the only reasonable option.

The transformation of parameters based on corresponding-states considerations applies only to fluid properties. The solid-phase properties remain entirely substance-specific. Thus, when applying the "master" EOS with transformed parameters, it is necessary to adjust some of the parameters for computing the solid-phase fugacities (cf. eq. 10). Once these parameters are adjusted, solid-fluid equilibria can be accurately computed. This is illustrated in Figures 6 and 7 for the systems $KCl-H_2O$ and $Na_3PO_4-H_2O$, respectively. It is noteworthy that the $Na_3PO_4-H_2O$ mixture is a system of the second kind [14], in which the solubility decreases with temperature and the critical curve is intersected by a solid solubility locus. With appropriate melting parameters (cf. eq. 10) and the "master" EOS derived from NaCl properties, this behavior can be reasonably approximated.

6. CONCLUSIONS

An equation of state has been developed for the representation of the phase behavior of high-temperature and supercritical aqueous systems containing salts and nonelectrolytes. For normal fluids such as hydrocarbons, the equation has been reformulated using the three-parameter corresponding-states principle. For salt-water systems for which little experimental information is available, a predictive procedure has been developed that utilizes the equation of state for $NaCl+H_2O$ with suitably transformed parameters. The equation has been shown to accurately represent vapor-liquid equilibria, solid-liquid equilibria and densities.

7. ACKNOWLEDGEMENT

8. REFERENCES

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APPENDIX A: PURE COMPONENT PARAMETERS

For water, the parameters *a, c* and *d* are expressed as functions of temperature as:

$$par = par_0 + \frac{par_1}{T_r} + \frac{par_2}{T_r^2} + \frac{par_3}{T_r^4}; \quad par = a, c, d \tag{A-1}$$

and the parameters *e* and *b* are independent of temperature. The values of these parameters

are collected in Table 1. The values of the dipole moment and critical temperature are 1.85 D

and 647.067 K, respectively.

For normal fluids, the values of the EOS parameters in the corresponding-states framework (cf. eqs. 4-9) are given in Table 2. These parameters have been adjusted by using the values $R=8.31451$ and $\omega_{CH_4}=0.01$ for the gas constant and the acentric factor of methane, respectively.

APPENDIX B: PARAMETERS FOR THE NaCl-H₂O BINARY

The parameters for pure subcooled NaCl and the binary parameters for NaCl-H₂O were

regressed simultaneously. The parameter *a* for NaCl is given by

$$a = a_0 + a_1 e^{a_{11}(\theta + a_{12})^2} + a_2 e^{a_{21}(\theta + a_{22})^{a_{23}}} \qquad \text{for } T > 573.15 \text{ K} \tag{B-1}$$

$$a = a_{L0} + \frac{a_{L1}}{\theta} \qquad \text{for } T < 573.15 \text{ K} \tag{B-2}$$

where $\theta = T/100$ and the values of the coefficients are listed in Table 3. The dipole moment of the solvated NaCl ion pair is assumed to be equal to 6.4 D [2]. The binary parameters are:

$$\tau = \left(1 + t_1 q + t_2 q^2 + t_3 q^3 + t_4 q^4\right)\left(t_0 + t_{10} e^{t_{11}(q - 0.57315)^{12}}\right) + t_{20} e^{t_{21}(\theta - t_{22})^2} \tag{B-3}$$

$$\alpha_{12} = \left(a_0 + a_1\theta + a_2\theta^2 + a_3\theta^3 + a_{10} e^{a_{11}(\theta + a_{12})^2}\right)\tau \tag{B-4}$$

$$\gamma_{112} = \left(g_{00} + g_{01}\theta + g_{010} e^{g_{011}(\theta - 0.57315)^8}\right)\tau \tag{B-5}$$

$$\gamma_{122} = \left(g_{10} + g_{11}\theta + g_{110} e^{g_{111}(\theta + g_{112})^2}\right)\tau \tag{B-6}$$

$$\delta_{1222} = \left(d_1 + d_{10} e^{d_{11}(\theta - 5.7315)^2}\right)\tau \tag{B-7}$$

$$\delta_{1122} = d_2 \tau \qquad \text{(B-8)}$$

$$\delta_{1112} = d_3 \tau \qquad \text{(B-9)}$$

$$\varepsilon = \tau \qquad \text{(B-10)}$$

where $q=(T-573.15)/1000$ and the values of the coefficients are listed in Table 4.

Table 1. EOS parameters for pure water

i	a_i (Pa m^6 mol^{-1})	b_i (cm^3 mol^{-1})	c_i	d_i	e_i
0	0.273299606	28.4959143	1.97137125	2.067608326	-9
1	0.029222588		-6.280811855	8.338243831	
2	0.164605437		1.553507149	-2.113207391	
3	0.038208843		-0.039555271	0.06103284	

Table 2. EOS parameters for normal fluids in the corresponding-states framework

j	0	1
a_{j0}	18.83663863	-26.84106104
a_{j1}	-4.220283177	54.74073074
a_{j2}	5.477649244	-37.2449596
a_{j3}	-1.853225265	16.31930205
a_{j4}	0.195132049	-2.919639772
b_j	511.1845534	28.39567768
c_j	-0.666796544	-0.666796544
d_j	6.062040977	1.774573288
e_j	-9	

Table 3. EOS parameters for subcooled NaCl.

a_0	a_1	a_{11}	a_{12}	a_2	a_{21}	a_{22}
1.2982440	0.24577564	-0.4817	-8.959	-.52826704	-0.6154	-5.403
a_{23}	a_{L0}	a_{L1}	c_0	d_0	e_0	b_0
3.26	1.46948756	5.91450097	-2.7501	8.0969	-9	59.7968948

Table 4. Binary parameters for NaCl-H$_2$O.

t_0	t_1	t_2	t_3	t_4	t_{10}	t_{11}
0.00238929	5.90197690	-34.636854	134.850732	-110.4615	8.72760971	-6.37899119
t_{12}	t_{20}	t_{21}	t_{22}	a_0	a_1	a_2
0.7891385	0.32166894	-0.43188550	7.81729112	-4.37934044	1.55751866	-0.15275184
a_3	a_{10}	a_{11}	a_{12}	g_{00}	g_{01}	g_{010}
0.00574625	0.58269932	-0.66227352	-5.22300719	0.32701322	0.18184612	0.3334116
g_{011}	g_{10}	g_{11}	g_{110}	g_{111}	g_{112}	d_1
-7.7981E-7	1.02059581	0.10921746	0.18843553	-0.73818752	-5.37534469	1.30703424
d_{10}	d_{11}	d_2	d_3			
0.00104018	-1.10945871	1.357186949	1.216764357			

FIGURE CAPTIONS

Figure 1. Vapor-liquid equilibria in the system NaCl-H$_2$O. The lines have been calculated from the EOS and the symbols denote the data of Bischoff and Pitzer [15] and Bodnar et al. [16], as recalculated by Chou [17]. The lowest pressure for each isotherm corresponds to the three-phase solid-liquid-vapor locus.

Figure 2. Molar volumes along the vapor-liquid saturation line for the system NaCl+H$_2$O. The lines have been obtained from the EOS and the symbols denote the values reported by Bischoff [18].

Figure 3. Vapor-liquid equilibria in the system CH$_4$-H$_2$O. The lines have been calculated from the EOS and the symbols denote the data of Sultanov et al. [19] and Shmonov et al. [20].

Figure 4. Phase equilibria in the system C$_{10}$H$_{22}$-H$_2$O. The lines have been obtained from the EOS and the symbols denote the data of Wang and Chao [21] and Skripka [22].

Figure 5. Vapor-liquid equilibria in the system KCl+H$_2$O. The lines have been obtained from the EOS for NaCl+H$_2$O after applying a transformation of parameters (eqs. 12-14). The symbols represent the data of Khaibullin and Borisov [23] and Hovey et al. [24]. The lowest pressure for each isotherm corresponds to the three-phase solid-liquid-vapor locus.

Figure 6. Solid-fluid equilibria for the system KCl-H$_2$O. The lines have been obtained from the model and the symbols represent the data of Chou et al. [25].

Figure 7. Solid-fluid equilibria for the system Na$_3$PO$_4$-H$_2$O. Unlike in the previous figures, the calculated results are shown as a line along the SLV locus and as hollow circles at the conditions of experimental data (not necessarily at SLV). The remaining symbols denote the experimental data of Borovaya and Ravich [26], Panson et al. [27] and Linke and Seidell [28].
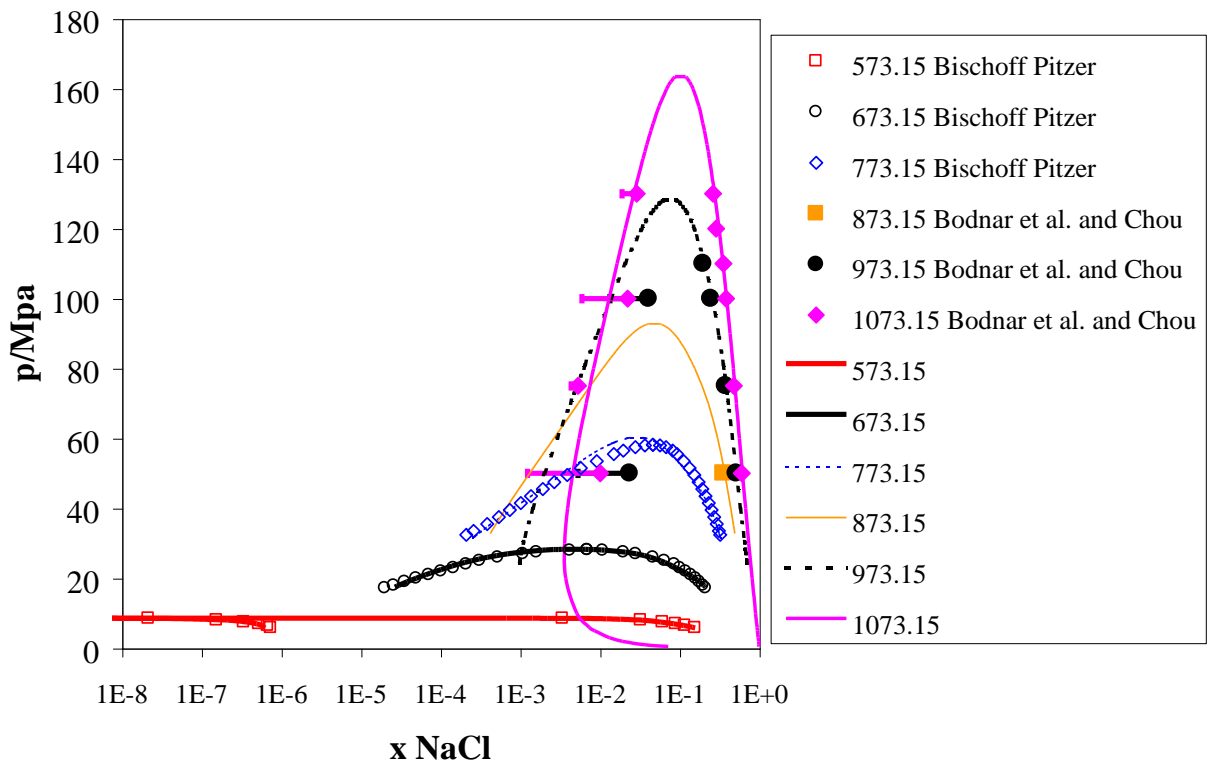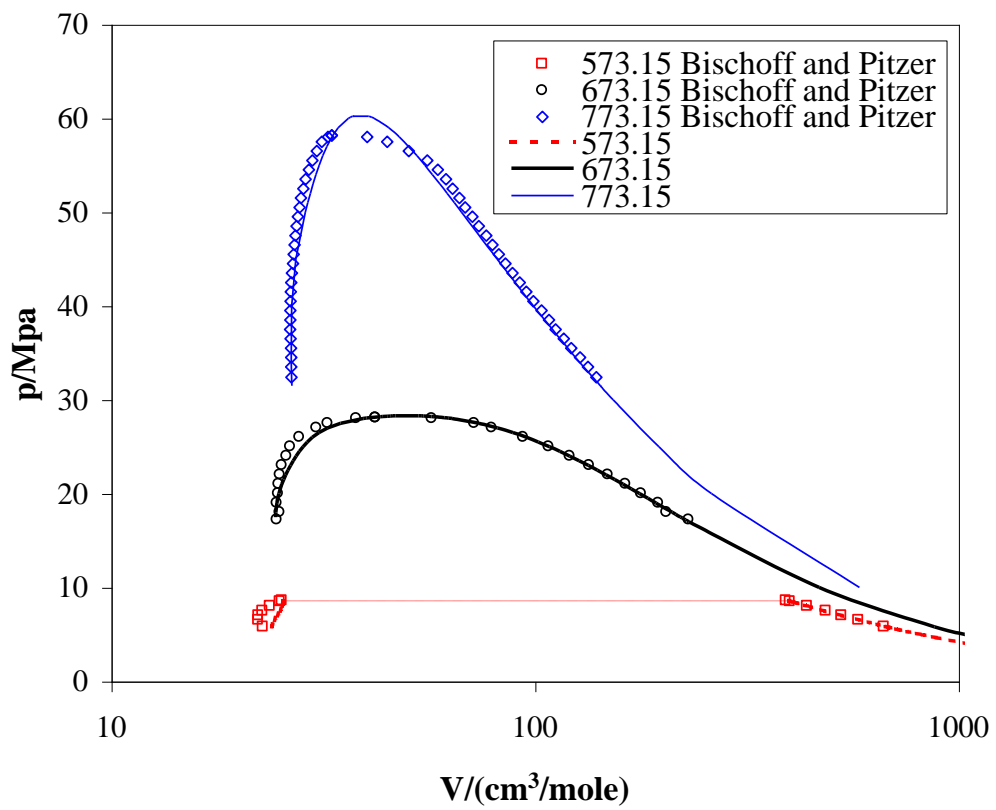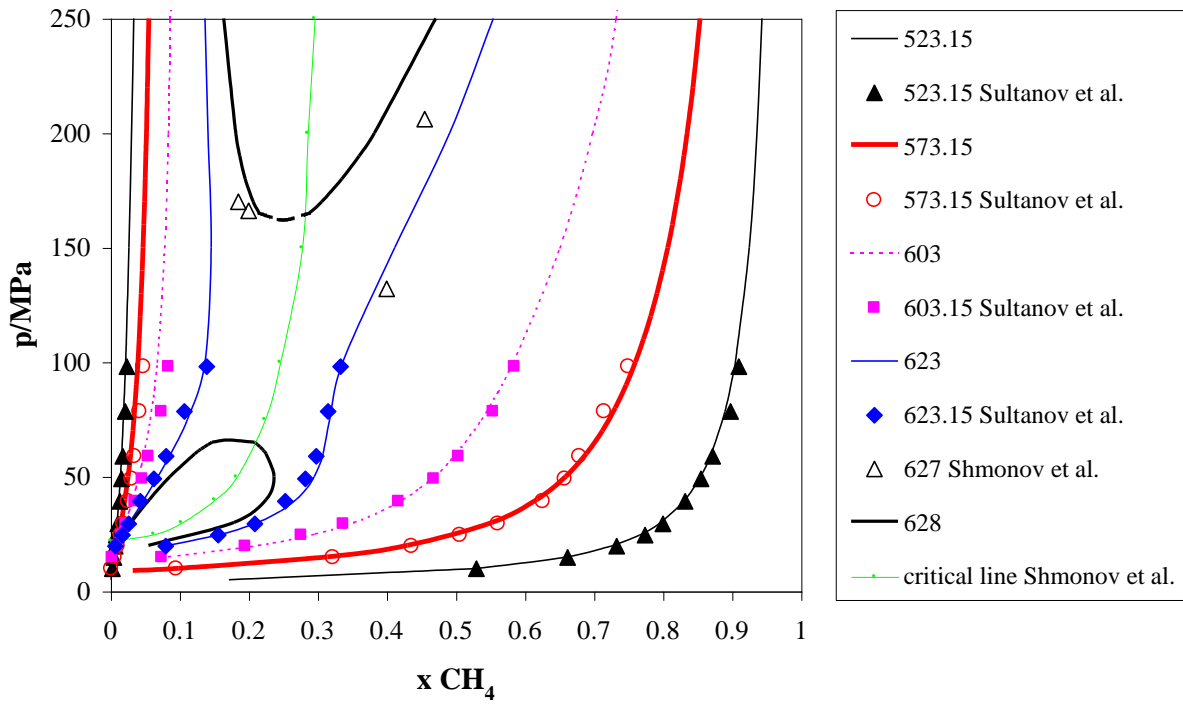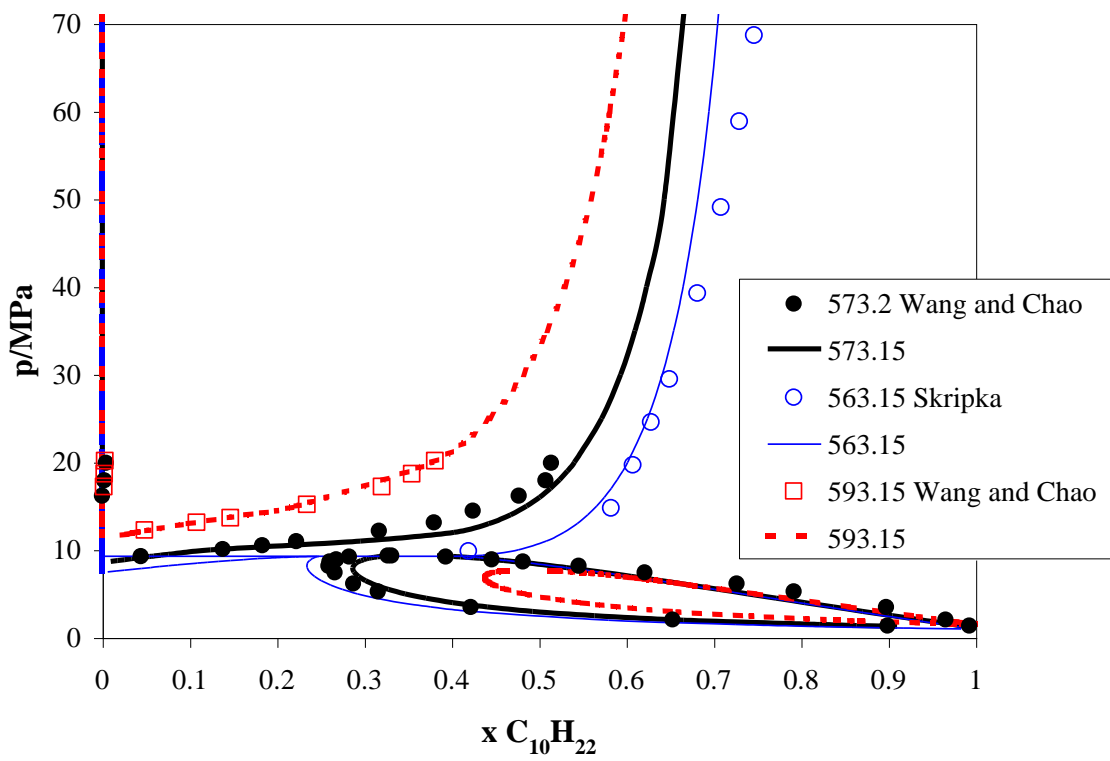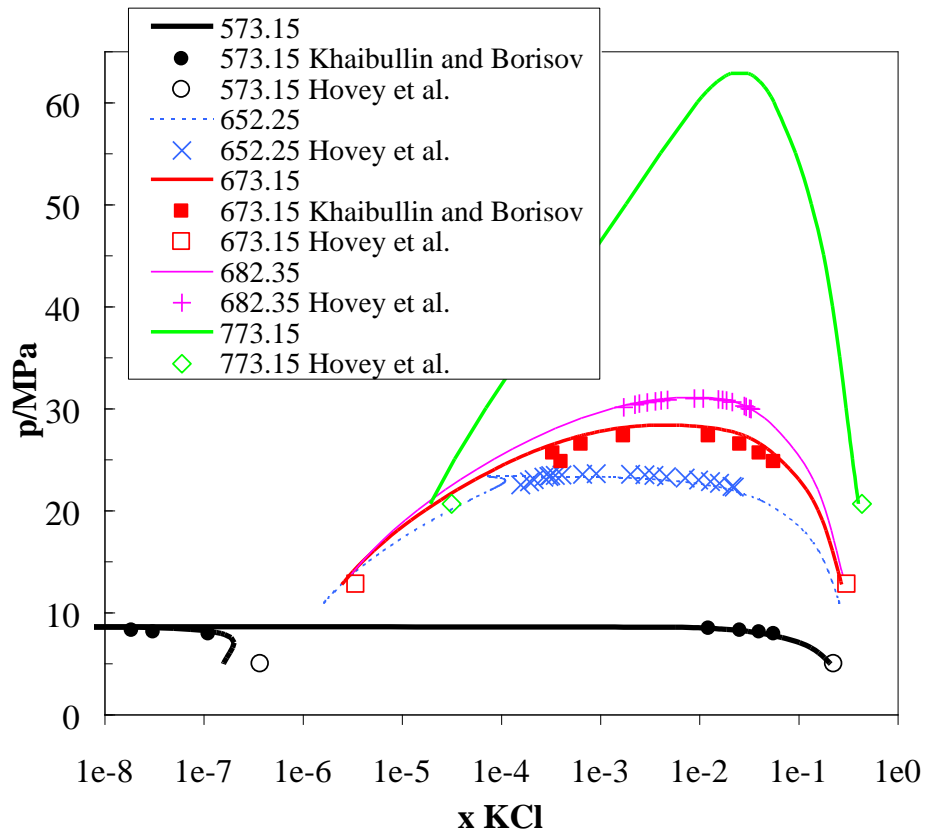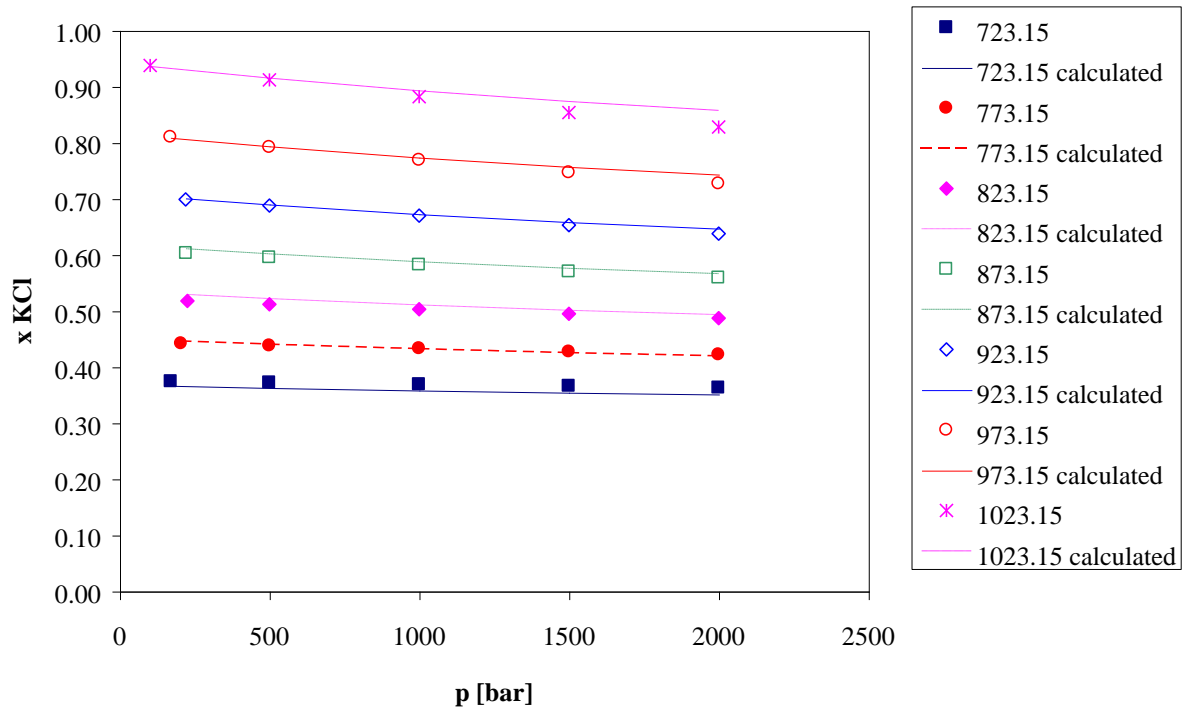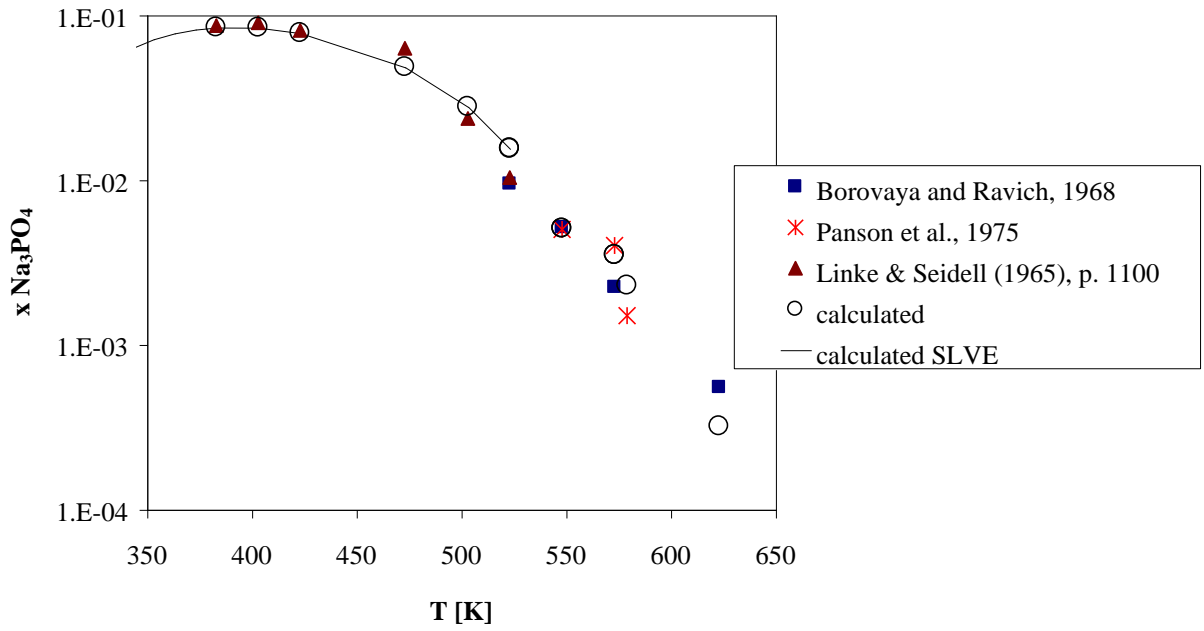
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7