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Measurements and Models for Hazardous Chemical and Mixed Wastes

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Executive Summary

Mixed solvent aqueous waste of various chemical compositions constitutes a significant fraction of the total waste produced by industry in the United States. Not only does the chemical process industry create large quantities of aqueous waste, but the majority of the waste inventory at the Department of Energy (DoE) sites previously used for nuclear weapons production is mixed solvent aqueous waste. In addition, large quantities of waste are expected to be generated in the clean-up of those sites. In order to effectively treat, safely handle, and properly dispose of these wastes, accurate and comprehensive knowledge of basic thermophysical properties is essential.

The goal of this work is to develop a phase equilibrium model for mixed solvent aqueous solutions containing salts. An equation of state was sought for these mixtures that a) would require a minimum of adjustable parameters and b) could be obtained from available data or data that were easily measured. A model was developed to predict vapor composition and pressure given the liquid composition and temperature. It is based on the Peng-Robinson equation of state, adapted to include non-volatile and salt components. The model itself is capable of predicting the vapor-liquid equilibria of a wide variety of systems composed of water, organic solvents, salts, nonvolitile solutes, and acids or bases. The representative system of water + acetone + 2-propanol + $NaNO_3$ was selected to test and verify the model. Vapor-liquid equilibrium and phase density measurements were performed for this system and its constituent binaries.

Model

The Peng-Robinson-Stryjek-Vera (PRSV, 1986a, 1986b) equation of state with the Wong-Sandler (1992) mixing rules is used to predict the vapor-liquid equilibrium of mixed solvent electrolyte solutions. The Wong-Sandler mixing rules require the excess Gibbs free energy and the liquid phase activity coefficients. These activity coefficients are the sum of a short-range local composition contribution and a long-range contribution from ions that are present. The activity coefficient model of Chen *et. al.* (1986) is used for the local composition part of the excess Gibbs free energy and activity coefficients, and the model of Pitzer and Simonson (1986) is used for the long-range contributions to the excess Gibbs free energy and activity coefficients. The dielectric constant of the aqueous solvent mixture is calculated for the long-range contribution. In addition, the liquid volume is corrected using an empirical formula. The vapor pressure of the solution and the vapor composition are predicted when given the liquid composition and temperature of the solution.

There are two pure-fluid adjustable parameters, one for the equation of state, and the other is a liquid density correction factor. The model contains one solvent-solvent equation of state adjustable parameter, one solvent-solvent dielectric constant parameter, two local composition parameters for each binary, and two adjustable parameters for each solvent-salt

binary. The model uses no higher-order adjustable parameters to cover a broad range of temperature, pressure and composition. The model is applied to the system water + acetone + 2-propanol + sodium nitrate using data obtained as outlined below, and values from the literature. The system has also been extended to include the solvents ethanol and methanol using literature measurements. Details concerning the model can be found in Watts (in preparation).

Measurements

A dynamic phase equilibrium apparatus (Watts and Louie, 2000) was used to measure the vapor pressure, vapor composition and density, and liquid density of the system water + acetone + 2-propanol + $NaNO_3$, and the constituent binaries. This apparatus is constructed of corrosion resistant materials for all of the wetted parts. Measurements can be performed from 300 to 425 K (to 700 K without density measurements) and to 35 MPa. The apparatus consists of an equilibrium cell with a sapphire viewing window, vapor and liquid pumps for recirculation, and two vibrating-tube densimeters. The equilibrium cell and densimeters are housed in an aluminum block to minimize the temperature gradients. The temperature is measured with a standard reference grade 25 Ω PRT in the equilibrium cell wall, and a 100 Ω PRT for each of the densimeters. The temperature was maintained using a convection oven. Measurements for the vapor pressure of water + $NaNO_3$ were performed on a similar apparatus without density measurement capabilities. Measurements were performed from 300 K to 370 K for salt concentrations up to 5.6 molal. A detailed analysis of these results are presented in Watts and Outcalt (in preparation).

Results

In summary, the equation of state developed in this project works very well for predicting the vapor pressure and phase composition of mixtures of water and other solvents, and the description of salts is very promising.

Future work for this research may include developing a better density correlation for the liquid phase, and investigating other local composition models for the Gibbs free energy calculation. Extension of the model to include salt solubility prediction and ionic speciation present in the liquid phase would also be possible. The model could be extended to other fluids and salts of interest. This would involve measuring the VLE and infinite dilution activity coefficient of additional water + organic solvent + salts over a wider range of salt composition.

Research Objectives

Mixed solvent aqueous waste of various chemical compositions constitutes a significant fraction of the total waste produced by industry in the United States. Not only does the chemical process industry create large quantities of aqueous waste, but the majority of the waste inventory at the Department of Energy (DoE) sites previously used for nuclear weapons production is mixed solvent aqueous waste. In addition, large quantities of waste are expected to be generated in the clean-up of those sites. In order to effectively treat, safely handle, and properly dispose of these wastes, accurate and comprehensive knowledge of basic thermophysical properties is essential.

The goal of this work is to develop a phase equilibrium model for mixed solvent aqueous solutions containing salts. An equation of state was sought for these mixtures that a) would require a minimum of adjustable parameters and b) could be obtained from available data or data that were easily measured. A model was developed to predict vapor composition and pressure given the liquid composition and temperature. It is based on the Peng-Robinson equation of state, adapted to include non-volatile and salt components. The model itself is capable of predicting the vapor-liquid equilibria of a wide variety of systems composed of water, organic solvents, salts, nonvolitile solutes, and acids or bases. The representative system of water + acetone + 2-propanol + $NaNO_3$ was selected to test and verify the model. Vapor-liquid equilibrium and phase-density measurements were performed for this system and its constituent binaries.

The specific goals of this project were to:

- develop and validate models that accurately predict the phase equilibria and thermodynamic properties of hazardous aqueous systems necessary for the safe handling and successful design of separation and treatment processes for hazardous chemical and mixed wastes;
- accurately measure the phase equilibria and thermodynamic properties of a representative system (water + acetone+ 2-propanol + sodium nitrate) over the applicable ranges of temperature, pressure, and composition to provide the experimental data required for model development and testing.

Methods and Results

Peng-Robinson-Stryjek-Vera Model

The Stryjek and Vera (1986a, 1986b) modification to the Peng-Robinson (1976) cubic equation of state was used as the basis for this work. The Peng-Robinson-Stryjek-Vera (PRSV) cubic equation of state relates the pressure (P) to the molar volume (v) and temperature (T):

$$P=\frac{RT}{v-b_m}-\frac{a_m}{v^2+2vb_m-b_m^2}$$

with the pure fluid energy parameter a

$$a_i=(0.457235R^2T_{ci}^2/P_{ci})\alpha_i$$

and the pure fluid excluded volume parameter b_i

$$b=0.077796RT_{ci}/P_{ci}$$

where α_i is

$$\alpha_i=[1+\kappa_i(1-T_{Ri}^{0.5})].$$

In the PRSV equation, the κ_i term is determined by

$$\kappa_i=\kappa_{oi}+\kappa_{1i}(1+T_{Ri}^{0.5})(0.7-T_{Ri})$$

where

$$\kappa_{oi}=0.378893+1.4897153\omega_i-0.17131848\omega_i^2+0.0196554\omega_i^3$$

and κ_{1i} is a empirical pure fluid parameter, ω_i is the Pitzer acentric factor, and T_{Ri} is the reduced temperature, defined as $T_{Ri} = T/T_{ci}$.

The excluded volume parameter (b_i) for ionic species is obtained from the Carnahan-Starling type equation of Zuo and Guo (1991):

$$b_i=(2/3)\pi N_A\sigma_i^3.$$

where N_A is Avogadro's number, and σ_i is the ionic diameter of the cation or anion. The energy parameter for ionic species is obtained from the development of Zhao and Lu (1998):

$$a_i=Z_{Mi}V_{0i}RT[\exp(\varepsilon_i/2kT)-1]$$

where k is Boltzmann's constant, Z_{Mi} is the lattice coordination number (18 for the ionic species of interest here), and V_{0i} is the ionic excluded volume, defined as:

$$V_{0i}=N_A\sigma_i^3/\sqrt{2}$$

ε_i/k is the Lennard-Jones energy parameter (Harvey and Prausnitz, 1989):

$$\varepsilon_i/k=2.2789\times10^{-11}Z_i^{1/2}\alpha p_i^{3/2}\sigma_i^{-6}.$$

The units on ε_i/k are $K\cdot m^{3/2}$, Z_i is the absolute value of the ionic charge, and αp_i is the ionic polarizability.

In this model, an accurate liquid density is needed for the proper determination of the phase equilibria. The simple empirical correction of Mathias *et.al.* (1989) is applied. The corrected molar volume is given by

$$v^{corr}=v^{PRSV}+s+f_c\left(\frac{0.41}{0.41+\delta}\right)$$

where δ is the bulk modulus of the fluid and is defined as

$$\delta=-\frac{v^2}{RT}\left(\frac{\partial P}{\partial v}\right)_T.$$

The function f_c is selected to obtain the true critical volume

$$f_c=v_c-(v_c^{PRSV}+s)$$
$$v_c^{PRSV}=3.946b$$

The adjustable parameter s is fit to pure fluid density data, and may be temperature dependent with the form

$$s=c_0+c_1/T$$

where c_0 and c_1 are empirical constants.

Mixing Rules

Mixing rules are used in cubic equations of state to provide a method of obtaining the *a*, *b* and *s* parameters for the overall mixture. The mixing rules of Wong and Sandler (1992) are used for both the neutral and ionic species. The Wong-Sandler mixing rules for the PRSV equation of state are given by

$$b_m = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij}}{\left(1 - \sum_i x_i \frac{a_i}{b_i RT} + \frac{A_\infty^E}{CRT} \right)}$$

and

$$\frac{a_m}{RT} = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \left(\sum_k x_k \frac{a_k}{b_k RT} + \frac{A_\infty^E}{CRT} \right)}{\left(1 - \sum_i x_i \frac{a_i}{b_i RT} + \frac{A_\infty^E}{CRT} \right)}$$

with

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{\left(b_i - \frac{a_i}{RT} \right) + \left(b_j - \frac{a_j}{RT} \right)}{2} (1 - k_{ij}),$$

where k_{ij} is a mixing parameter.

The Wong-Sandler mixing rules use the relationship:

$$G^E = A^E + PV^E$$

relating the excess Helmholtz free energy to the excess Gibbs free energy, and the approximation that for low pressure the V^E term is small. This allows the direct application of excess Gibbs free energy formulations to the mixing rules. When ions are present in solution, the excess Gibbs free energy is often divided into long- and short-range contributions. The long-range contributions are usually modeled using a Debye-Huckel formulation as modified by Pitzer (PDH, Pitzer and Simonson, 1986). The short-range contributions are modeled using local composition equations. The excess Gibbs free energy then takes on the form of a sum:

$$\frac{g^E}{RT} = \frac{g^{E,PDH}}{RT} + \frac{g^{E,LC}}{RT}.$$

The mixing rule for the volume correction terms s and v_c are given by the simple rules:

$$s_m = \sum_i x_i s_i \text{ and } v_{cm} = \sum_i x_i v_{ci}.$$

Long-Range Force Model

The long-range force contribution to the excess Gibbs free energy is the Debye-Huckel term of Pitzer and Simonson (1986), and is

$$\frac{g^{PDH}}{RT} = -\left(\sum_i x_i\right)(1/M_s)^{1/2}(4A_\varphi I_x/\rho)\ln(1+\rho I_x^{1/2})$$

where M_s is the solvent average molecular weight, and ρ is related to the solvent hard-core diameter, and is taken as a constant equal to 14.9 nm. I_x is the mole fraction based ionic strength, and is defined as:

$$I_x = \frac{1}{2}\sum_i x_i z_i^2$$

where z_i is the ionic charge. The Debye-Huckel parameter A_φ is

$$A_\varphi = (1/3)(2\pi N_A d_s)^{1/2}(e^2/4\pi\varepsilon_0 D_s kT)^{3/2}$$

where d_s and D_s are the solvent density and dielectric constant, respectively. The term $4\pi\varepsilon_0$ is the permitivity of free space, and e is the charge on an electron.

The long-range part of the activity coefficients for the solvent components and the ions are:

$$\ln\gamma_s^{DH} = 2A_\varphi(1/M_s)^{1/2}I_x^{3/2}/(1+\rho I_x^{1/2})$$
$$\ln\gamma_i^{DH} = -z_i^2 A_\varphi(1/M_s)^{1/2}[(2/\rho)\ln(1+\rho I_x^{1/2}) + I_x^{1/2}(1-2I_x/z_i^2)/(1+\rho I_x^{1/2})]$$

The solvent density is obtained from the equation of state, and is used here to calculate the solvent mixture dielectric constant using the method of Harvey and Prausnitz (1987). This adds one binary interaction coefficient, δ_{ij}.

Local Composition Model

The short-range forces for the excess Gibbs free energy are modeled with the non-random two-liquid model (NRTL) of Renon and Prausnitz (1968). This model was extended to electrolyte

solutions by Chen and Evans (1986) and developed for phase equilibria for mixed solvent electrolytes by Mock *et al*. (1986).

The excess Gibbs free energy is given by:

$$\frac{g^{E,LC}}{RT}=\sum_m X_m \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_k X_k G_{km}}+\sum_c X_c \sum_{a'} \frac{X_{a'}\sum_j X_j G_{jc,a'c}\tau_{jc,a'c}}{\sum_{a''} X_{a''}\sum_k X_k G_{kca'c}}$$
$$+\sum_a X_a \sum_{c'} \frac{X_{c'}\sum_j X_j G_{ja,c'a}\tau_{ja,c'a}}{\sum_{c''} X_{c''}\sum_k X_k G_{ka,c'a}}$$

In the above equation, the subscript *m* is molecular (uncharged) species, *j* and *k* are any species, and *c* and *a* are cations and anions respectively. The local composition mole fraction (X_j) is charge-adjusted for ionic species, and is defined as:

$$X_j = x_j C_j$$

where C_j is the absolute value of the charge for the ionic species, and unity for uncharged species. The NRTL parameters G_{ij} and τ_{ij} are temperature-dependent binary parameters related through the equation:

$$G_{ij}=\exp(\alpha_{ij}\tau_{ij})$$

The non-randomness factor, α_{ij} is set equal to 0.3 for this work. Two methods of modeling the temperature dependence of τ_{ij} were tested. The first is the method outlined in Chen and Evans (1986):

$$\tau_{i,j}=a_1+a_2\left(\frac{1}{T}-\frac{1}{\theta}\right)+a_3\left[\left(\frac{\theta-T}{T}\right)+\ln\left(\frac{T}{\theta}\right)\right]$$

where a_1, a_2 and a_3 are empirical constants, and θ is the reference temperature, 298.15 K, for this work. An alternative is to fit the NRTL energy parameter (g_{ij} - g_{jj}) directly and obtain τ_{ij} from the relationship:

$$\tau_{ij}=\frac{g_{ij}-g_{jj}}{RT}.$$

The activity coefficients are obtained by taking the appropriate derivative of the excess Gibbs free energy.

Model Parameters

The pure-fluid parameters for the equation of state are the critical constants (T_c, P_c and v_c), the molecular weight, the acentric factor (ω_i), an empirical pure-fluid parameter (κ_i), the dipole moment, the polarizability, and the pure fluid density correction parameters (c_0 and c_1). κ_i is fit to each fluid using vapor pressure data over the range of temperature of interest. The density parameters are obtained by fitting to liquid density data over the pressure range of interest. The ionic species require the molecular weight, charge, ionic diameter (σ_i) and polarizability (α_i). All of these parameters are obtained from basic properties of the ions and are not fit to the model.

The binary interaction parameters include the k_{ij} introduced in the Wong-Sandler mixing rules, δ_{ij} from the dielectric constant calculation, and the NRTL parameters for τ_{ij}. The δ_{ij} values obtained by Harvey and Prausnitz (1987) are used. The other parameters are obtained by optimizing the liquid phase activity or osmotic coefficients obtained from vapor pressure and vapor composition measurements from the literature, or measured at NIST and presented in the following section. Orthogonal distance regression methods are used to obtain these parameters for this model using verified data. The parameters for the system water + acetone + 2-propanol + $NaNO_3$ are included below, along with the parameters for methanol and ethanol. The pure fluid κ_i parameter and the density parameters are presented in Table I. The binary interaction parameters for the PRSV solvent-solvent interactions are presented in Table II, and the NRTL energy parameters are presented in Table III. The binary interaction parameters for the dielectric constant are presented in Table IV.

Table I. Optimized pure solvent PRSV and density parameters.

Solvent	κ_i	c_0 (density)	c_1 (density)
water	-0.06635	-4.884×10^{-6}	5.518×10^{-4}
acetone	-0.00888	-6.874×10^{-6}	-2.405×10^{-3}
2-propanol	0.23264	-1.538×10^{-6}	-1.653×10^{-4}
methanol	-0.16816	-6.5×10^{-6}	0.0
ethanol	-0.03374	-3.117×10^{-6}	0.0

Table II. Optimized PRSV binary interaction parameters k_{ij} for solvent-solvent interactions.

Solvent	water	acetone	2-propanol	methanol	ethanol
water	0	0.2454	0.3333	0.1088	0.2548
acetone	0.2454	0	0.0625	0.1139	0.0310
2-propanol	0.3333	0.0625	0	0.0239	-0.0033
methanol	0.1088	0.1139	0.0239	0	0.0245
ethanol	0.2548	0.0310	-0.0033	0.0245	0

Table III. Optimized NRTL binary interaction parameters $(g_{ij}-g_{jj})/1000$.

i \ j	water	acetone	2-propanol	methanol	ethanol	NaNO3
water	0	4.648	6.768	3.200	4.682	-1.7085
acetone	2.095	0	1.756	1.427	-0.264	-0.325
2-propanol	0.0464	-0.0866	0	2.066	0.200	0.173
methanol	-0.8049	0.2977	-1.970	0	-1.010	na
ethanol	-0.2050	2.051	-0.300	1.093	0	8.76
$NaNO_3$	2.060	2.38	-0.016	na	15.5	0

Table IV. Optimized dielectric binary interaction parameter δ_{ij} for solvent-solvent interactions.

Solvent	water	acetone	2-propanol	methanol	ethanol
water	0.000	0.042	-0.151	0.046	-0.038
acetone	0.042	0.000	0.000	-0.041	0.000
2-propanol	-0.151	0.000	0.000	0.000	0.000
methanol	0.046	-0.041	0.000	0.000	-0.014
ethanol	-0.038	0.000	0.000	-0.014	0.000

Additional details concerning the model and determination of the parameters can be found in Watts (in preparation).

NIST Measurements for Water + Acetone + 2-Propanol + $NaNO_3$

A dynamic phase equilibrium apparatus (Watts and Louie, 2000) was used to measure the vapor pressure, vapor composition and density, and liquid density of the system water + acetone + 2-propanol + $NaNO_3$, and the constituent binaries. This apparatus is constructed of corrosion-resistant materials for all of the wetted parts. Measurements can be performed from 300 to 425 K (to 700 K without density measurements) and to 35 MPa. The apparatus consists of an equilibrium cell with a sapphire viewing window, vapor and liquid pumps for recirculation, and two vibrating-tube densimeters. The equilibrium cell and densimeters are housed in an aluminum block to minimize the temperature gradients. The temperature is measured with a standard reference grade 25 Ω PRT in the equilibrium cell wall, and a 100 Ω PRT for each of the densimeters. The temperature was maintained using a convection oven. Measurements for the vapor pressure of water + $NaNO_3$ were performed on a similar apparatus without density measurement capabilities. Measurements were performed from 300 K to 370 K for salt concentrations up to 5.6 molal. The full description of the VLE apparatus is presented in Watts and Louie (2000). The measurement results are presented in Table V.

The first set of measurements are the vapor pressures (bubble points) of mixtures of water + $NaNO_3$. These measurements were made in a small-volume VLE apparatus. The main components of the apparatus are an equilibrium cell and a vapor recirculation pump. This apparatus has an equilibrium cell of approximately 30 cm^3 volume, which is roughly one-tenth of the volume of the cells in the high-accuracy vapor-liquid equilibrium apparatus used for the remaining experiments. The components are immersed in a bath of heat-transfer fluid contained within a strip-silvered Dewar vessel. The bath temperature is measured with a standard platinum resistance thermometer, and pressure measurements are made with a commercially available pressure transducer. The temperature range of the apparatus is 260 - 400 K, with pressures to approximately 6 MPa. The accuracy of the temperature measurement is ± 0.03 K, and the pressure measurements are accurate to ± 0.1% of the pressure. An automated data acquisition system is used to record temperature and pressure at equilibrium.

The remaining data were collected on the azeotropic VLE apparatus. The second set of data are for the water + acetone system at three compositions over the temperature range of 308 K to 368 K. The next set of data complements this set by adding $NaNO_3$ to the solutions. The fourth and fifth sets of data are for the water + 2-propanol and water + 2-propanol + $NaNO_3$ systems, at only one composition. The final sets of data are for the full system water + acetone + 2-propanol, and water + acetone + 2-propanol + $NaNO_3$. These data, along with published data, are used to evaluate the model, and the results are presented in the following section. A more detailed analysis of these results are presented in Watts and Outcalt (in preparation).

Table V. VLE and phase densities for the system water + acetone + 2-propanol + $NaNO_3$: T, temperature (ITS-90); P, bubble point pressure; ρ_v, vapor density; ρ_l, liquid density; x, salt-free liquid mole fraction; m, salt molality; y, salt-free vapor mole fraction.

T (K)	P (MPa)	ρ_v ($kg \cdot m^{-3}$)	ρ_l ($kg \cdot m^{-3}$)	x Water	x Acetone	x 2-Propanol	m $NaNO_3$	y Water	y Acetone	y 2-Propanol
299.905	0.00326	na	na	1.000			0.100	1.000		
320.066	0.00972	na	na	1.000			0.100	1.000		
339.952	0.02569	na	na	1.000			0.100	1.000		
359.934	0.06051	na	na	1.000			0.100	1.000		
300.012	0.00343	na	na	1.000			1.001	1.000		
319.957	0.00943	na	na	1.000			1.001	1.000		
339.993	0.02451	na	na	1.000			1.001	1.000		
359.937	0.05799	na	na	1.000			1.001	1.000		
299.977	0.00300	na	na	1.000			5.647	1.000		
319.967	0.00818	na	na	1.000			5.647	1.000		
339.938	0.02152	na	na	1.000			5.647	1.000		
359.917	0.05000	na	na	1.000			5.647	1.000		
308.229	0.04656	1.177	785.087	0.123	0.877			0.050	0.950	
323.228	0.08136	1.991	767.478	0.123	0.877			0.081	0.919	
339.103	0.13942	3.199	748.032	0.123	0.877			0.100	0.900	
353.291	0.21644	4.655	729.718	0.123	0.877			0.141	0.859	
367.975	0.32786	6.969	710.445	0.123	0.877			0.153	0.847	
308.260	0.04177	1.108	836.537	0.473	0.527			0.119	0.881	
323.316	0.07326	1.690	819.835	0.473	0.527			0.196	0.804	
338.332	0.12186	2.572	802.244	0.473	0.527			0.203	0.797	
353.471	0.19692	3.784	784.289	0.473	0.527			0.213	0.787	
368.727	0.30738	5.635	766.612	0.473	0.527			0.315	0.685	
308.286	0.02809	0.531	954.358	0.902	0.098			0.096	0.904	

T (K)	P (MPa)	ρ_v (kg·m^{-3})	ρ_l (kg·m^{-3})	x Water	x Acetone	x 2-Propanol	m $NaNO_3$	y Water	y Acetone	y 2-Propanol
323.191	0.05187	0.959	943.690	0.902	0.098			0.244	0.756	
338.078	0.08990	1.629	931.957	0.902	0.098			0.253	0.747	
352.559	0.14661	2.572	919.705	0.902	0.098			0.287	0.713	
367.379	0.23120	4.000	906.785	0.902	0.098			0.317	0.683	
307.984	0.04459	1.488	784.952	0.124	0.876		0.005	0.081	0.920	
323.182	0.07963	2.271	766.687	0.124	0.876		0.005	0.101	0.899	
339.398	0.13982	3.710	747.265	0.124	0.876		0.005	0.136	0.864	
353.182	0.21478	5.512	730.255	0.124	0.876		0.005	0.146	0.854	
368.328	0.32908	7.644	709.994	0.124	0.876		0.005	0.139	0.861	
308.194	0.04303	0.958	867.498	0.496	0.504		0.525	0.100	0.900	
323.800	0.07480	1.552	850.357	0.496	0.504		0.525	0.126	0.874	
338.604	0.12603	2.437	833.445	0.496	0.504		0.525	0.160	0.840	
353.506	0.20197	3.688	818.862	0.496	0.504		0.525	0.214	0.786	
308.252	0.02905	0.580	1002.944	0.899	0.102		1.013	0.114	0.886	
323.115	0.05354	1.384	991.764	0.899	0.102		1.013	na	na	
337.848	0.09351	1.896	979.661	0.899	0.102		1.013	na	na	
352.360	0.15337	2.758	960.548	0.899	0.102		1.013	na	na	
367.289	0.24298	4.163	956.563	0.899	0.102		1.013	na	na	
308.027	0.01038	0.677	780.648	0.100		0.900		0.120		0.880
318.141	0.01924	0.905	771.051	0.100		0.900		0.114		0.886
328.056	0.03189	1.219	761.312	0.100		0.900		0.123		0.877
338.209	0.05161	1.392	750.946	0.100		0.900		0.133		0.867
348.254	0.07962	1.941	740.152	0.100		0.900		0.138		0.862
307.924	0.01099	0.612	781.703	0.100		0.900	0.032	0.109		0.891
317.962	0.01895	0.851	772.498	0.100		0.900	0.032	0.092		0.908

T (K)	P (MPa)	ρ_v (kg·m^{-3})	ρ_l (kg·m^{-3})	x Water	x Acetone	x 2-Propanol	m $NaNO_3$	y Water	y Acetone	y 2-Propanol
328.044	0.03203	1.174	762.751	0.100		0.900	0.032	0.095		0.905
338.076	0.05095	1.538	752.406	0.100		0.900	0.032	0.098		0.902
348.171	0.07940	2.116	741.742	0.100		0.900	0.032	0.098		0.902
307.944	0.03099	0.730	793.284	0.216	0.397	0.388	0.000	0.090	0.737	0.177
318.015	0.04701	1.091	782.484	0.216	0.397	0.388	0.000	0.115	0.709	0.177
328.169	0.06964	1.510	771.328	0.216	0.397	0.388	0.000	0.128	0.672	0.200
338.242	0.10034	2.357	760.015	0.216	0.397	0.388	0.000	0.132	0.643	0.226
348.254	0.14134	2.870	748.379	0.216	0.397	0.388	0.000	0.148	0.615	0.238
307.987	0.03086	0.688	800.481	0.230	0.390	0.380	0.099	0.102	0.741	0.157
318.113	0.04698	1.042	790.032	0.230	0.390	0.380	0.099	0.126	0.698	0.176
328.165	0.06927	1.441	778.905	0.230	0.390	0.380	0.099	0.131	0.671	0.197
338.289	0.10010	2.049	767.526	0.230	0.390	0.380	0.099	0.139	0.642	0.219
348.101	0.14009	3.016	756.189	0.230	0.390	0.380	0.099	0.156	0.614	0.230

na: not available.

Results

The results of the modeling are presented in Table VI and Figures 1 through 25 on the pages that follow, and are discussed here for the ability of the model to predict the vapor pressure, phase composition and phase density of the pure solvents, solvent mixtures, and solvent mixtures with salt added. Figures 1 through 11 present the results of modeling the pure fluids (water, acetone, 2-propanol, methanol and ethanol) for the density and the saturated vapor pressure calculations compared to literature data. One of the drawbacks of cubic equations of state is the poor performance in predicting the liquid phase density. In this model, an empirical correction was used to overcome this, as the density is needed to calculate the dielectric constant of the mixture. In most cases the saturated liquid density is reproduced to within ± 2% except in the critical region, which is adequate for the dielectric constant calculation. The equation of state also is acceptable for predicting the compressed liquid density, with a maximum error of -5% at 150 MPa for 2-propanol (Figure 11). The model for the vapor pressures of the pure solvents is adequate for present purposes, with a maximum absolute deviation over the range of data less than 2%, and less than 1% in our region of interest, from 300 to 400 K. Methanol and ethanol exhibited systematic deviations, but it is not clear if the error is in the literature data or the model.

The liquid density calculation of water + acetone is given in Figure 12, and presents both the corrected and uncorrected values predicted by the model. It can be seen that the density correction acts only to offset the density calculated by the equation of state. The density correction factor was developed for a different version of the Peng-Robinson equation of state with traditional mixing rules that do not allow salts to be included in the model. Our model has a maximum in density introduced by the new mixing rules. This causes errors in liquid density of over 20 % even after the correction is applied, and renders this method of obtaining the mixture density of little use. An empirical correlation based on critical properties of the pure fluid is used in the model to obtain the density for the dielectric constant. This is a problem that needs to be solved with future work on the model.

Figures 13 through 18 present the results of modeling the binary solvent mixtures for the saturated vapor pressure and the vapor composition given the liquid composition and temperature. The percent absolute error in the pressure and the average absolute error in the vapor composition are given in Table VI. The bubble point vapor pressure for the mixtures is predicted to within 1.5 to 3.5 % for all of the binary mixtures. The error in the vapor composition ranged from 0.015 to 0.022 mole fraction.

Figure 19 presents the modeling results of the vapor pressure of water + $NaNO_3$ solutions to 27 molal in salt to 400 K. The maximum absolute pressure deviation given in Table VI is 2.8%, and indicates that modeling of a salt solution with an equation of state is usable. The error is largest at high temperature and high salt concentration.

Figures 20 through 23 present the results for modeling binary solvent mixtures with and without $NaNO_3$ present, and the full system of water + acetone + 2-propanol with and without salt are presented in Figures 24 and 25. The error in the bubble point vapor pressure is usually within the range for the binary mixtures, but does show more error at high temperature and high salt concentration. The model predicts that the salt has a stronger effect on the vapor composition than the measured result. The vapor composition is twice the range measured for

the binary combinations. In this case, the model underpredicts the effect of the salt on the vapor composition compared to the measured result. With low salt composition, the full system was well predicted. When the measurements were made, it was assumed that the high solvent side would be more difficult to predict, but more data that are high in salt and contain small concentrations of solvent would be a more significant test of the model.

Table VI. Correlation of VLE data for mixtures with the model and parameters of this work.

System	Number of data points*	Absolute pressure deviation, %	Average absolute error of y
Water + acetone	145	3.5	0.017
Water + 2-propanol	229	3.0	0.015
Acetone + 2-Propanol	18	1.5	0.022
Water + $NaNO_3$	108	2.8	na
Water + acetone + $NaNO_3$	15	7.4	0.039
Water + 2-propanol + $NaNO_3$	5	2.5	0.031
Water + acetone + 2-propanol + $NaNO_3$	5	0.5	0.031

* Includes selected literature data as well as results of measurements performed at NIST.

In summary, the equation of state developed in this project works very well for predicting the vapor pressure and phase composition of mixtures of water and other solvents, and the predictions for systems containing salts is very promising.

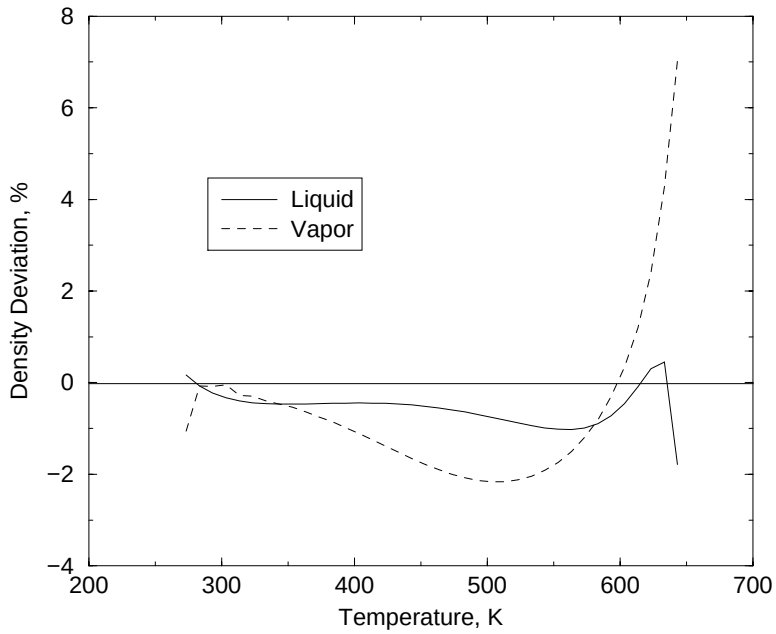


Figure 1. Density deviation of water for the saturated vapor and liquid phases compared to the Saul and Wagner (1989) equation of state.

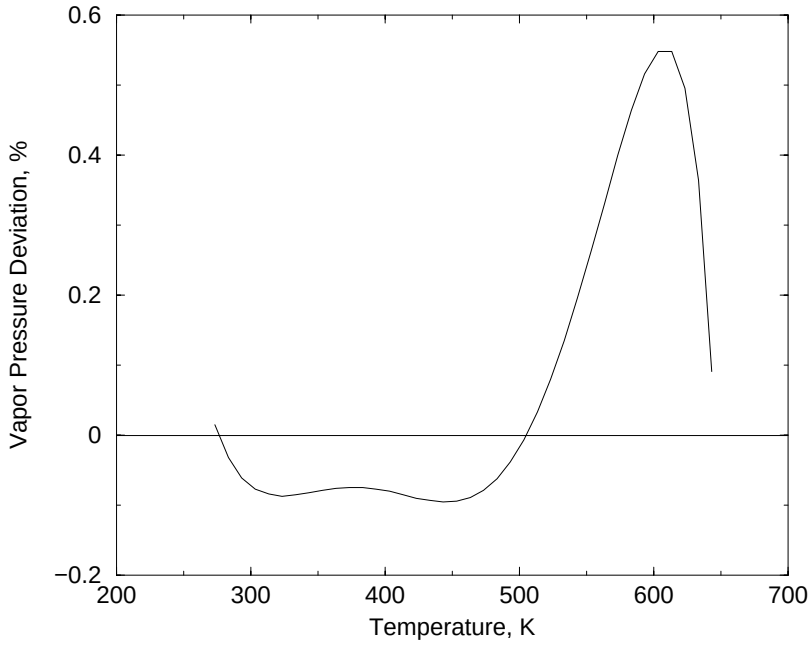


Figure 2. Saturated vapor pressure deviation of water compared to the Saul and Wagner (1989) equation of state.

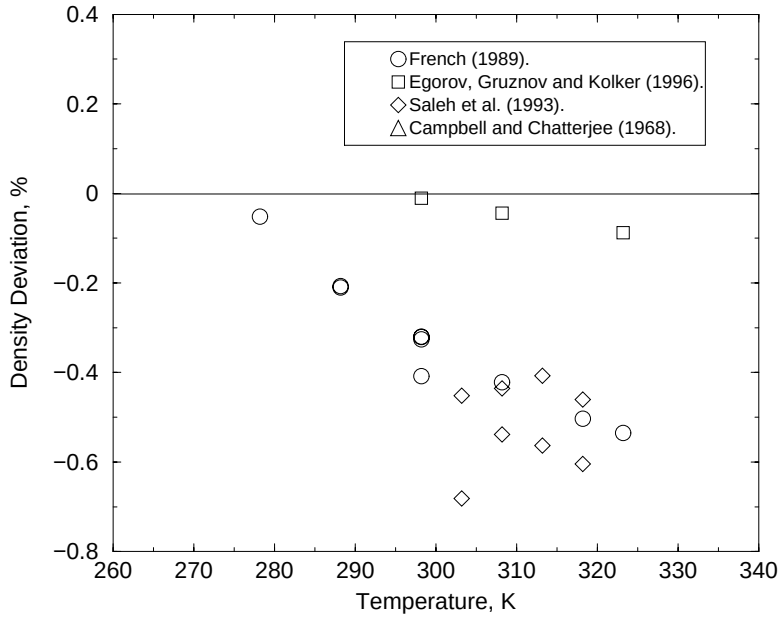


Figure 3. Saturated liquid density deviation of acetone.

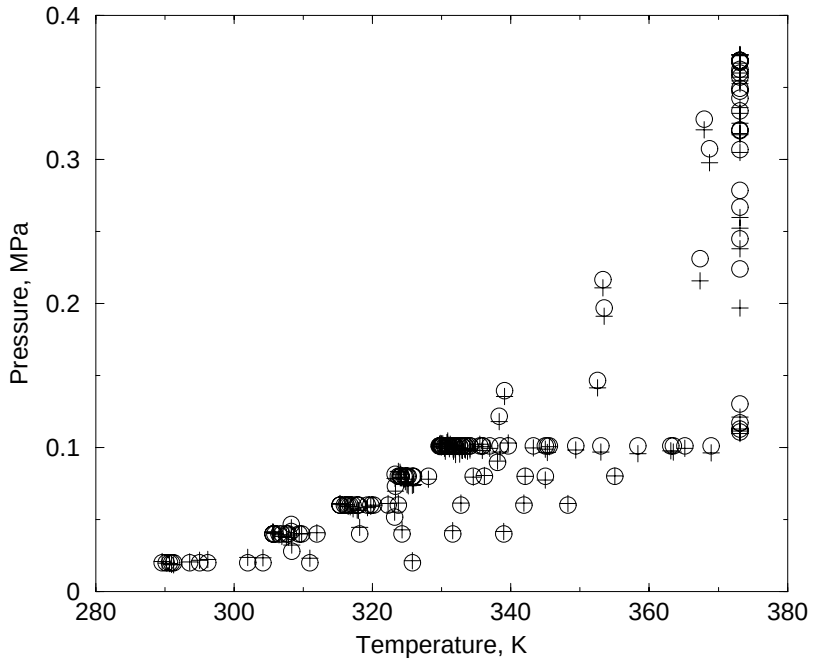


Figure 4. Measured (open symbol) and predicted (+) saturated vapor pressure deviation of acetone.

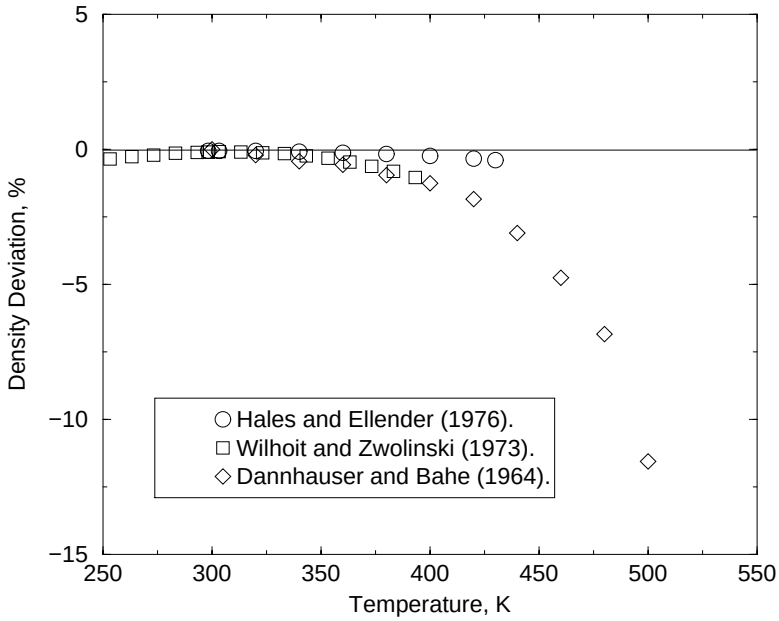


Figure 5. Saturated liquid phase density deviation of 2-propanol.

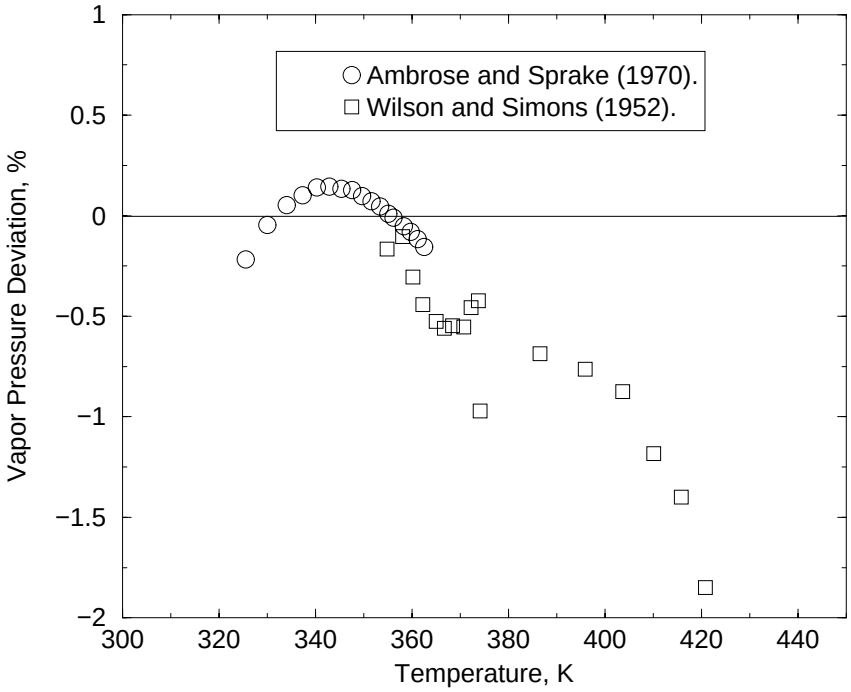


Figure 6. Saturated vapor pressure deviation of 2-propanol.

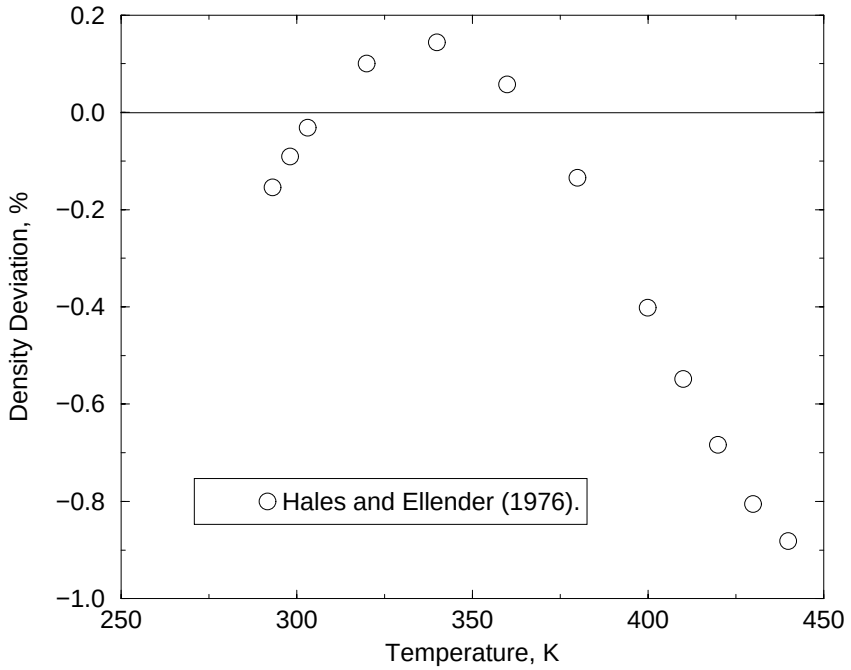


Figure 7. Saturated liquid density deviation of methanol.

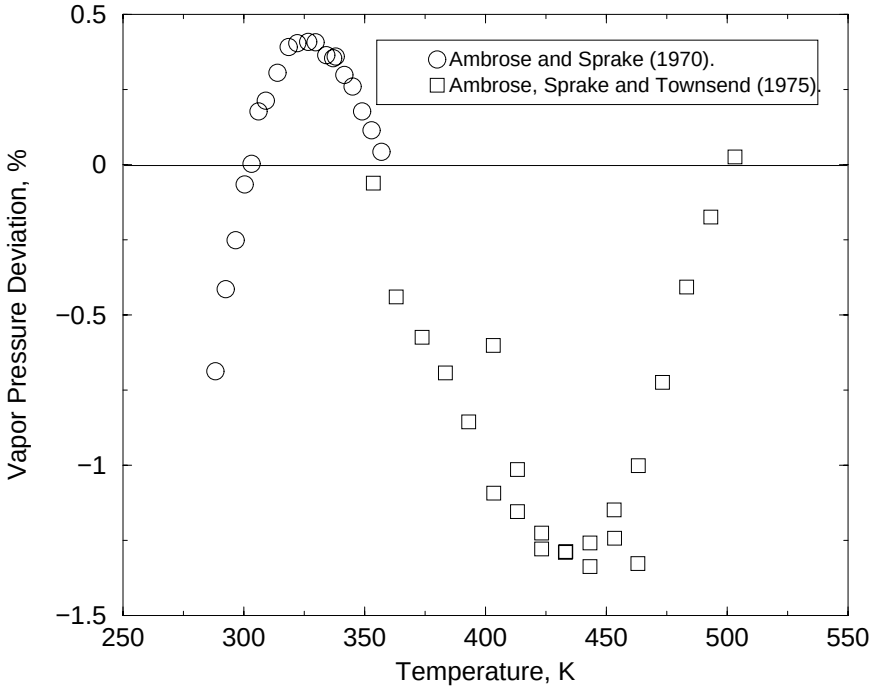


Figure 8. Saturated vapor pressure deviation of methanol.

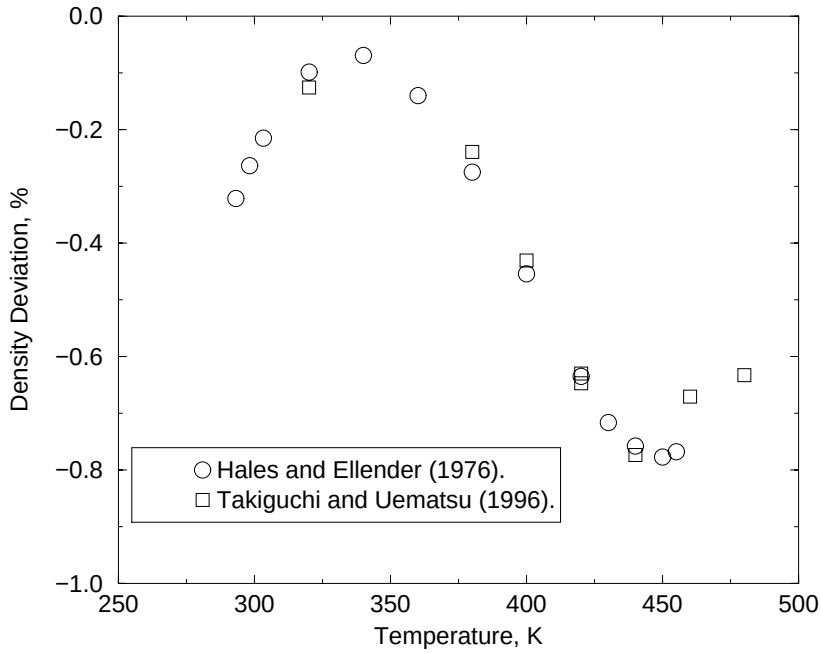


Figure 9. Saturated liquid density deviation of ethanol.

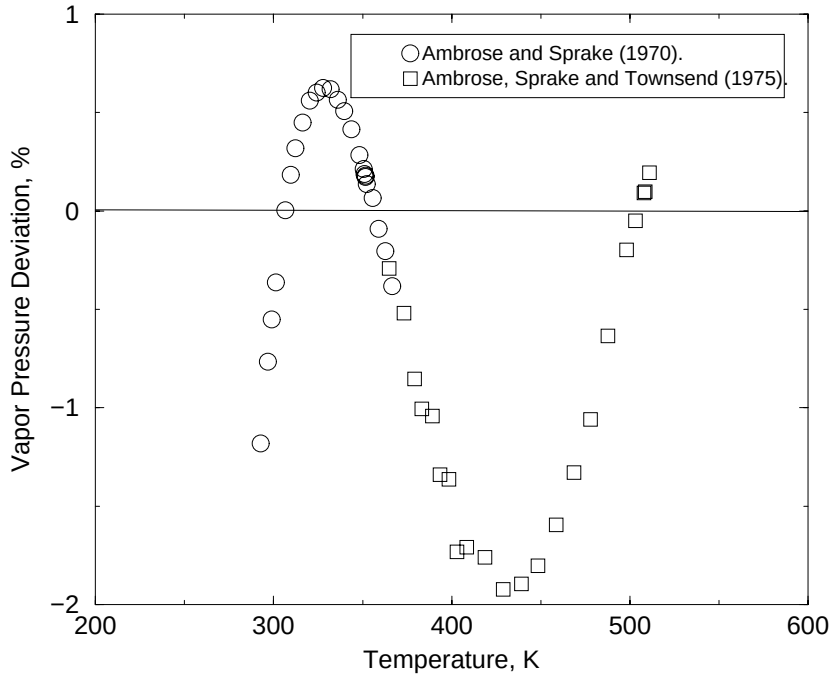


Figure 10. Saturated vapor pressure of ethanol.

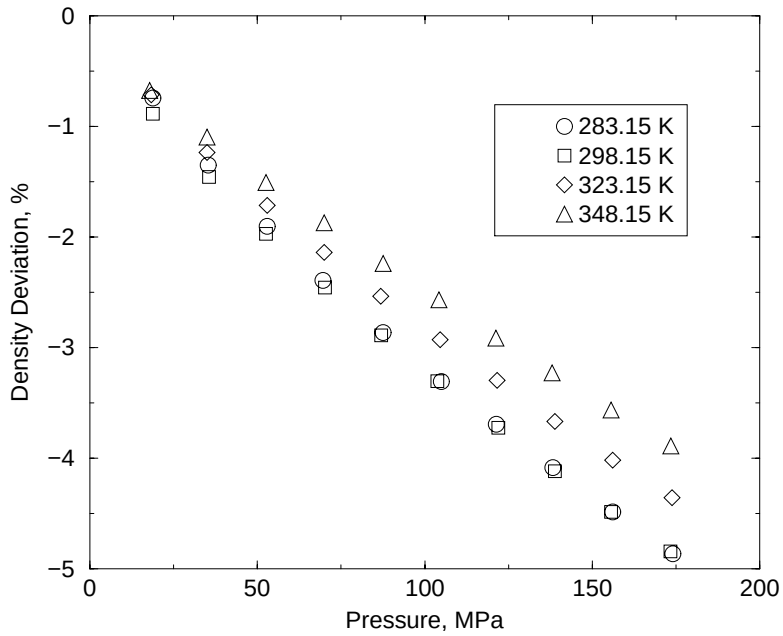


Figure 11. High pressure liquid density of 2-propanol over a range of temperature. Data from Kubotu, Tanaku and Makita (1987).

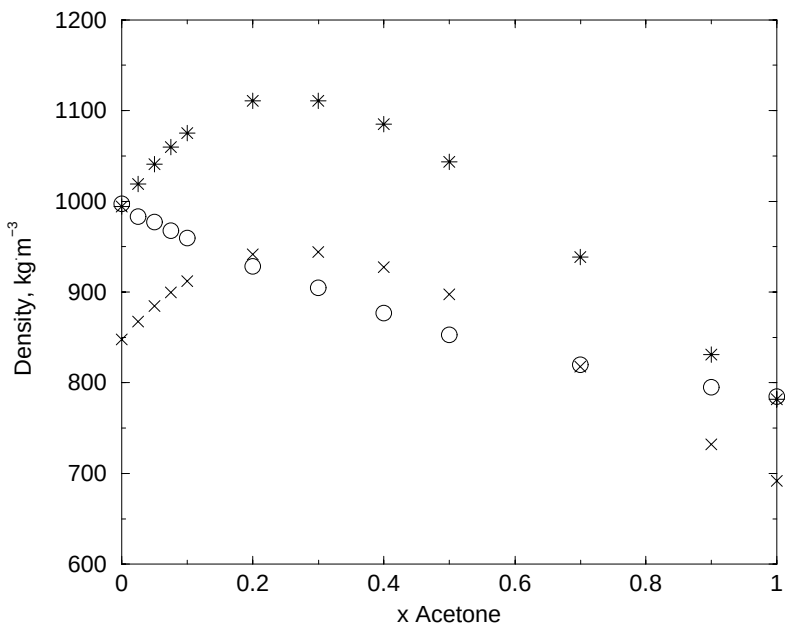


Figure 12. Measured saturated liquid density (open symbol) and predicted results (× uncorrected, ✳ corrected) of mixtures of water + acetone. Data from Kubotu, Tanaku and Makita (1987).

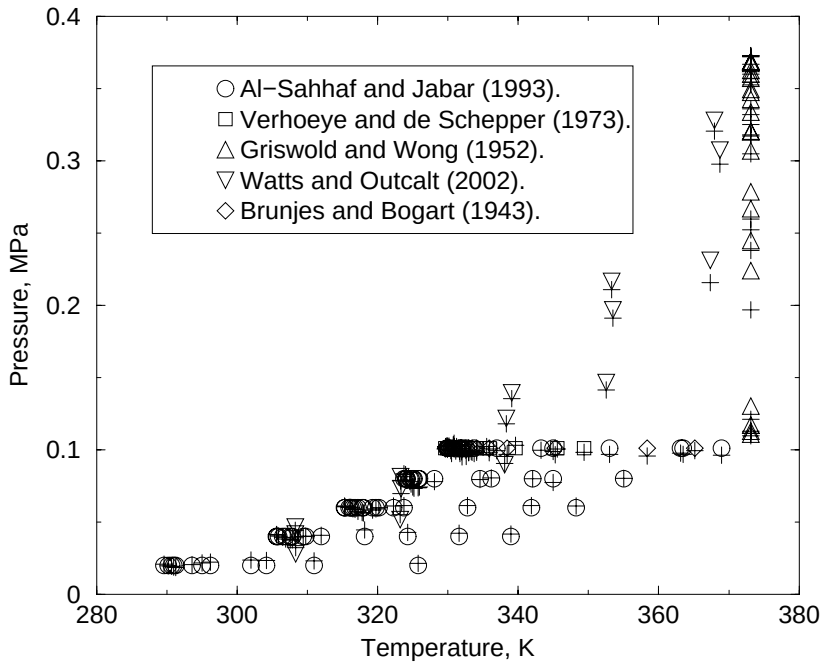


Figure 13. Measured (open symbols) and predicted (+) saturated vapor pressures of water + acetone mixtures over a range of composition and temperature.

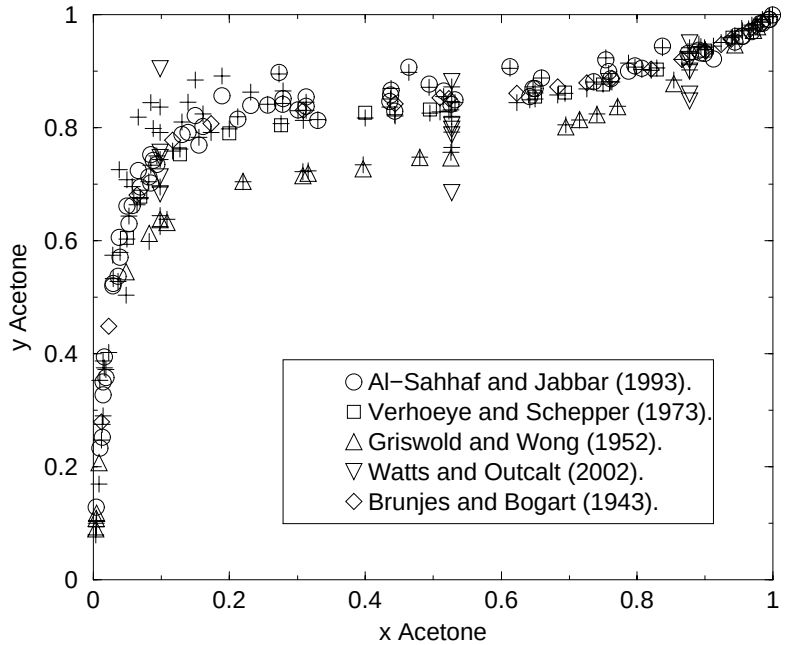


Figure 14. Measured (open symbols) and predicted (+) saturated vapor compositions of mixtures of water + acetone over a range of liquid composition and temperature.

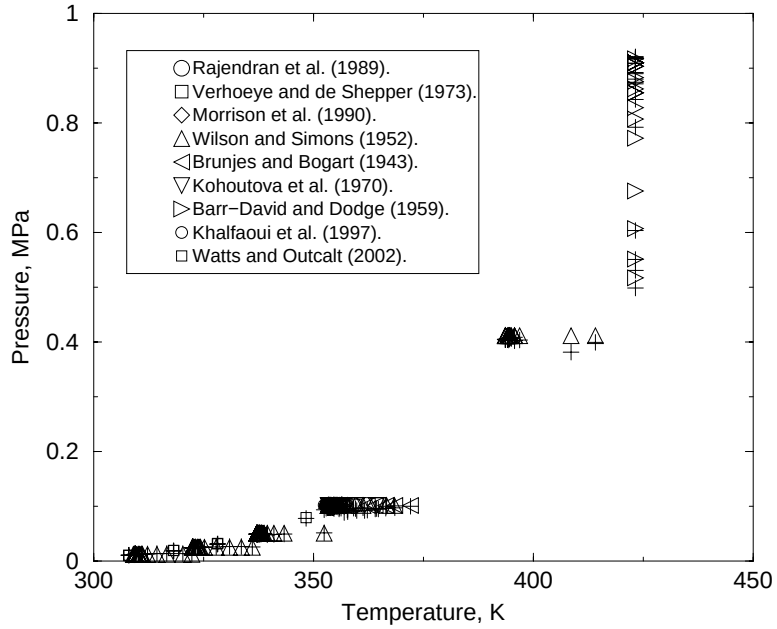


Figure 15. Measured (open symbols) and predicted (+) saturated vapor pressures for mixtures of water + 2-propanol over a range of composition and temperature.

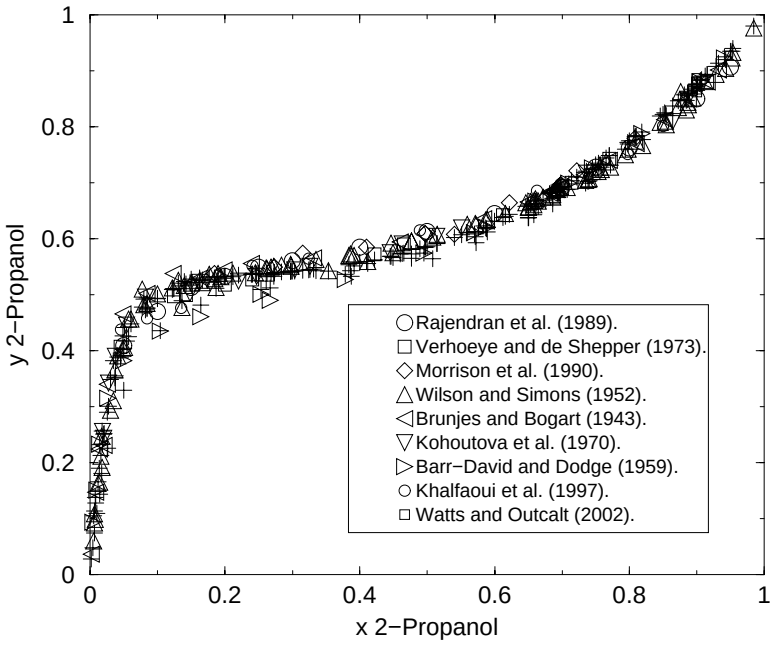


Figure 16. Measured (open symbols) and predicted (+) saturated vapor composition for mixtures of water + 2-propanol over a wide range of liquid composition and temperature.

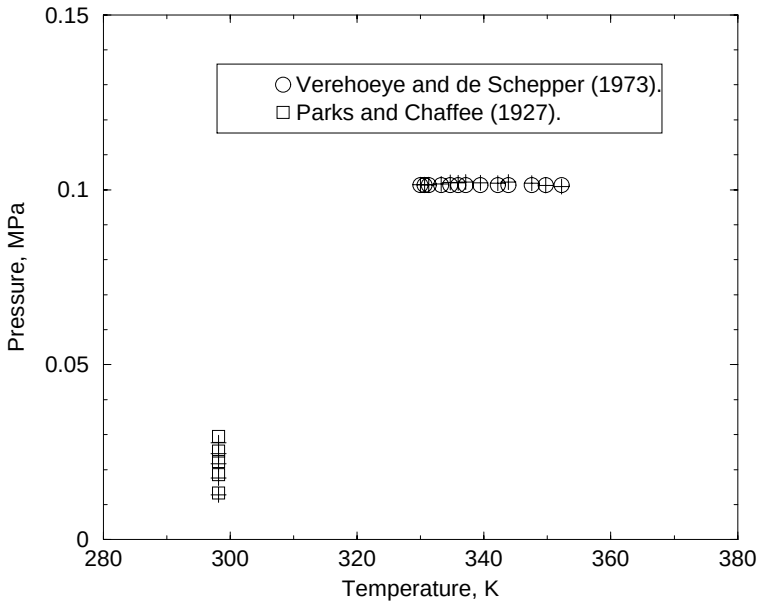


Figure 17. Measured (open symbols) and predicted (+) saturated vapor pressure of acetone + 2-propanol mixtures over an range of composition and temperature.

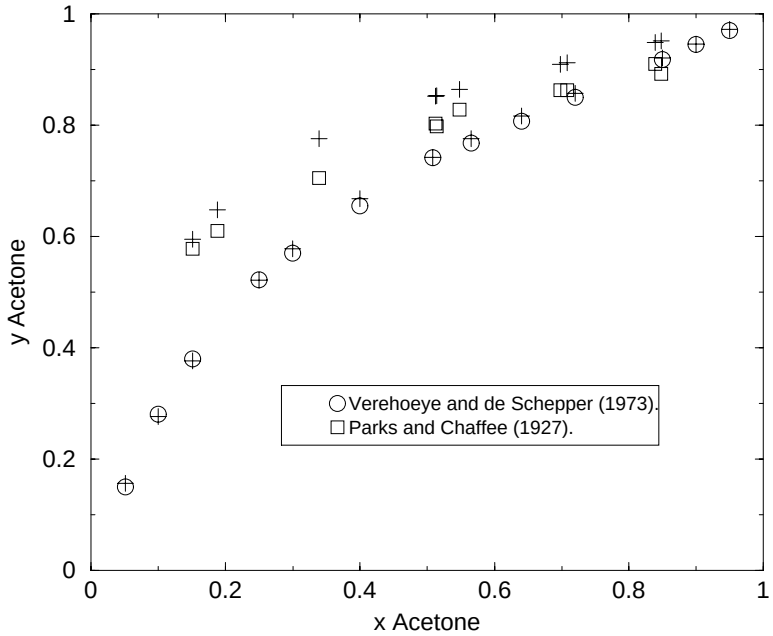


Figure 18. Measured (open symbols) and predicted (+) saturated vapor compositions of mixtures of acetone + 2-propanol over a range of composition and temperature.

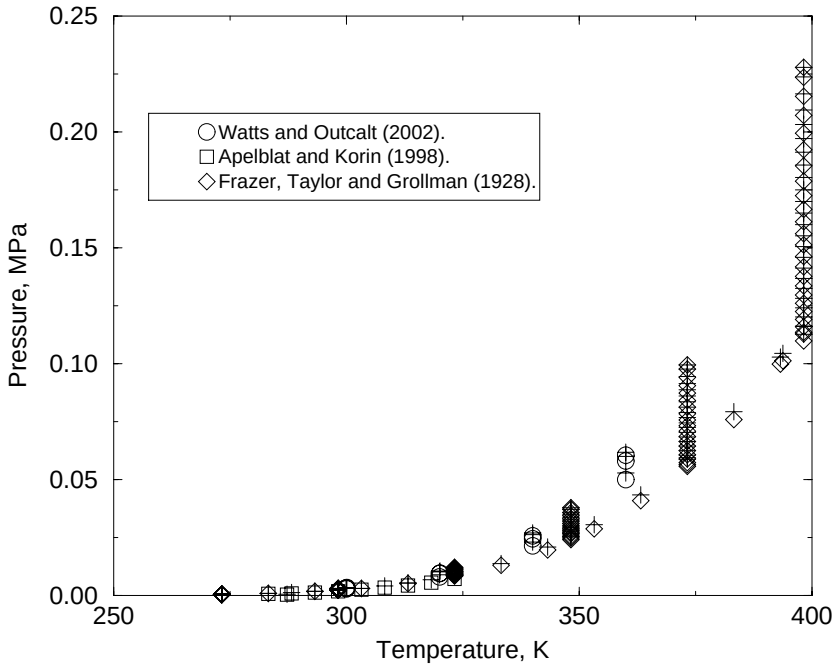


Figure 19. Measured (open symbols) and predicted (+) saturated vapor pressure for mixtures of water + $NaNO_3$ to 27 molal in salt over a wide range of temperature.

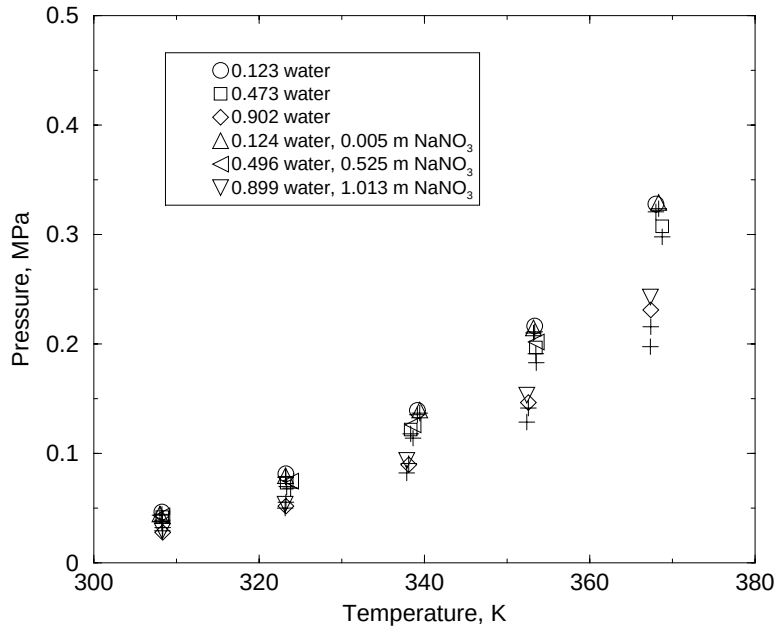


Figure 20. Measured (open symbols, Watts and Outcalt, 2002) and predicted (+) saturated vapor pressures for mixtures of water + acetone + $NaNO_3$ over a range of composition and temperature. Water composition is in salt-free mole fraction.

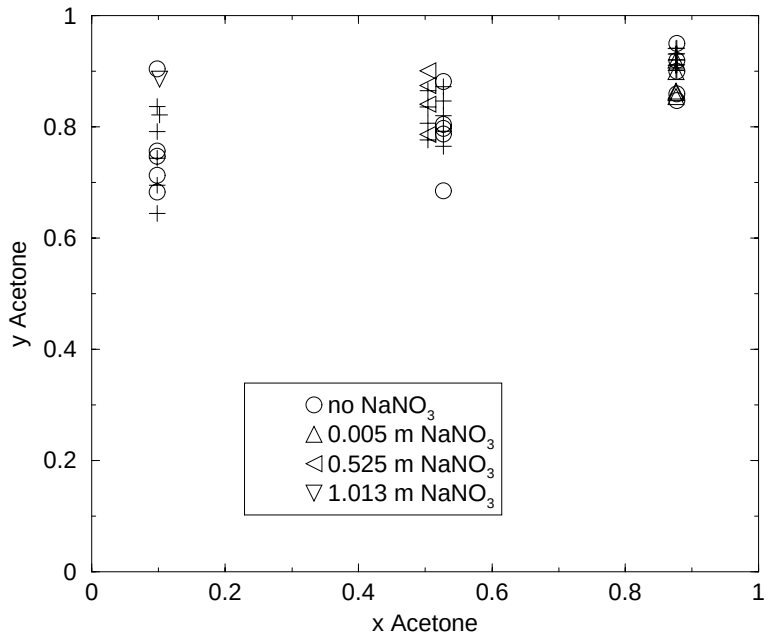
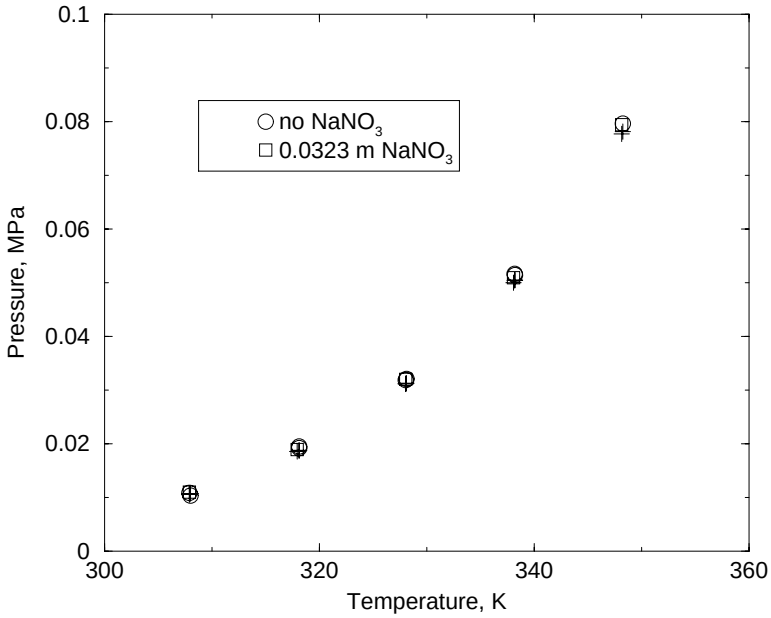


Figure 21. Measured (open symbols, Watts and Outcalt, 2002) and predicted (+) saturated vapor compositions for mixtures of water + acetone + $NaNO_3$ over a range of composition and temperature. Salt-free mole fractions are used.

Figure 22. Measured (open symbols, Watts and Outcalt, 2002) and predicted (+) saturated vapor



pressures for a mixture of water + 2-propanol with and without $NaNO_3$ over a range of temperature. Salt-free mole fractions are used.

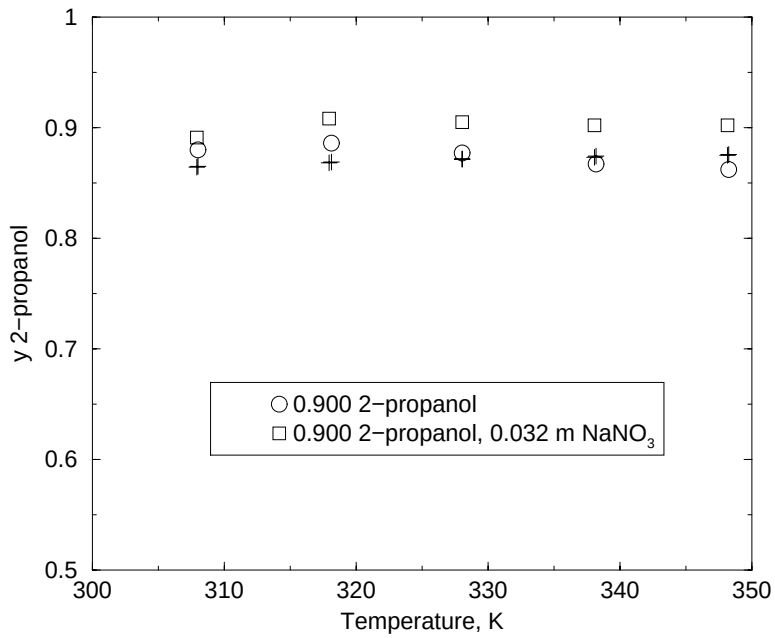


Figure 23. Measured (open symbols, Watts and Outcalt, 2002) and predicted (+) vapor compositions for mixtures of water + 2-propanol with and without $NaNO_3$ added over a range of temperature.

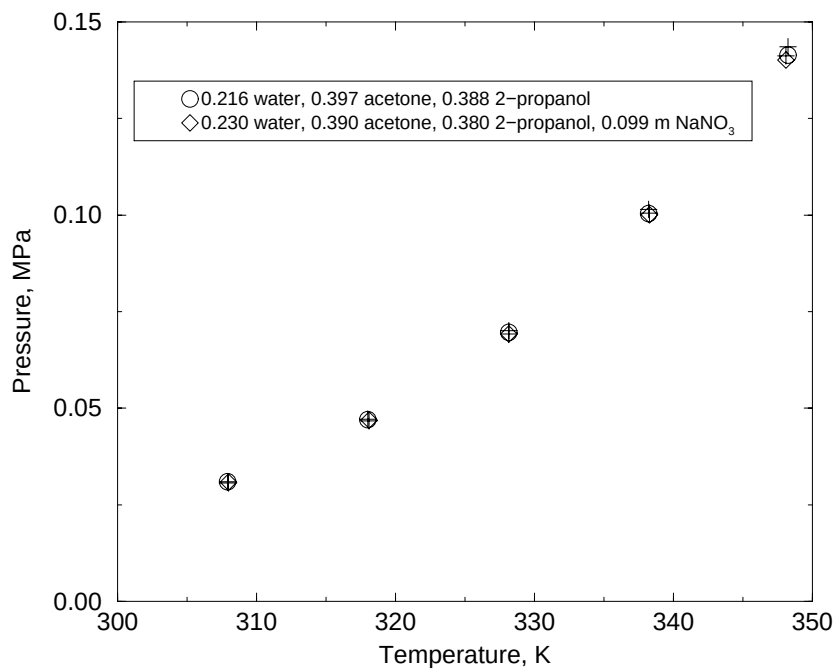


Figure 24. Measured (open symbols, Watts and Outcalt, 2002) and predicted (+) saturated vapor pressures for a mixture of water + acetone + 2-propanol with and without $NaNO_3$ added over a range of temperature. Salt-free mole fractions are used.

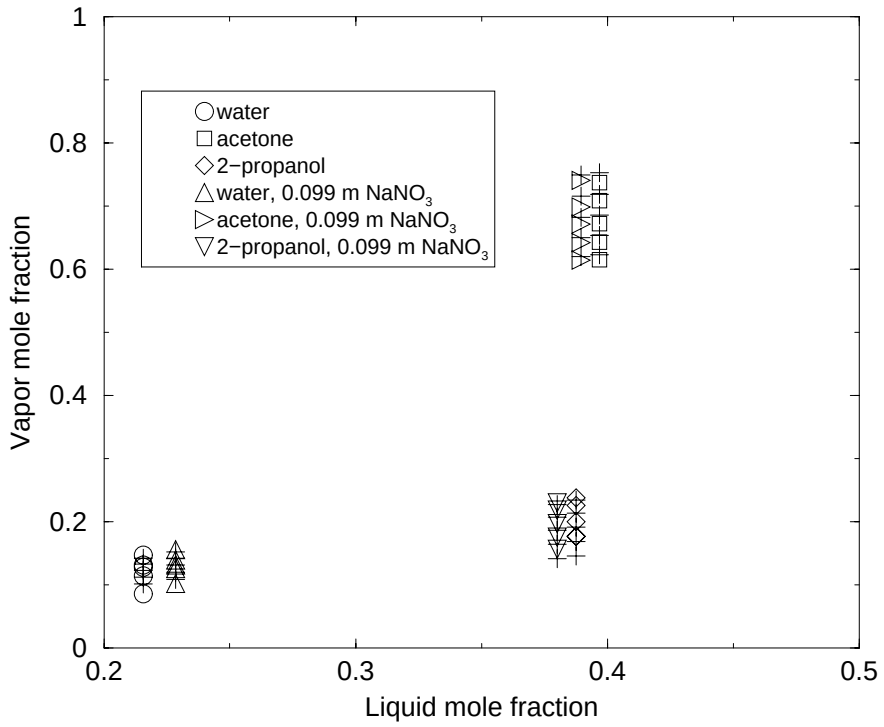


Figure 25. Measured (open symbols, Watts and Outcalt, 2002) and predicted (+) saturated vapor pressure of mixtures of water + acetone + 2-propanol with and without $NaNO_3$ at five temperatures. Mole fractions are on a salt free basis.

Relevance, Impact, and Technology Transfer

Publications and Presentations

L. A. Watts, Vapor-Liquid Equilibrium Prediction of Mixed Solvent Electrolyte Solutions with the Peng-Robinson-Stryjek-Vera Equation of State, in preparation.

L. A. Watts and S. Outcalt, VLE and Phase Density Measurements for the System Water + Acetone + 2-Propanol + $NaNO_3$, in preparation.

L. A. Watts, Vapor-liquid Equilibrium of Mixed Solvent Electrolyte Solutions: Measurements and Models, *9th Biennial International Spectrum Conference*, American Nuclear Society, Reno, Nevada, Aug. 4-8, 2002.

C. D. Holcomb, L. A. Watts, S. L. Outcalt, B. Louie, M. E. Mullins, and T. N. Rogers, Measurements and Models for Hazardous Chemical and Mixed Wastes, *EMSP National Workshop*, Atlanta, Georgia, April 24-28, 2000.

Watts, L. A. and B. Louie, Apparatus for Measuring Vapor-Liquid Equilibria and Phase Densities of Complex Aqueous Solutions. *Int. J. Thermophysics* 21(5): 1139-1151, 2000.

L. A. Watts, C. D. Holcomb, S. L. Outcalt, and B. Louie, Measurements and Models for Hazardous Chemical and Mixed Wastes, *Fourteenth Symposium on Thermophysical Properties*, Boulder, Colorado, June 25-30, 2000.

C. D. Holcomb, L. A. Watts, S. L. Outcalt, B. Louie, M. E. Mullins, and T. N. Rogers, Measurements and Models for Hazardous Chemical and Mixed Wastes, *EMSP Workshop*, Chicago, Illinois, July 27-30, 1998.

L. A. Watts, Modeling Mixed Solvent Electrolyte Solutions using a Cubic Equation of State, *Thirteenth Symposium on Thermophysical Properties*, Boulder, Colorado, June 22-27, 1997.

L. A. Watts and B. Louie, A New Apparatus for Measuring VLE and Phase Density of Aqueous-Organic-Salt Solutions, *Thirteenth Symposium on Thermophysical Properties*, Boulder, Colorado, June 22-27, 1997.

Collaborations Information

This project has been conducted in formal collaboration with Dr. Michael Mullins and Dr. Tony Rogers from Michigan Technological University (MTU). This arrangement was devised to obtain complementary measurements, with NIST performing VLE and density measurements, and

MTU performing ebouliometric measurements to obtain infinite dilution activity coefficients. Pariyachat Chatkun Na Ayuttaya, a Ph.D. student from MTU, came to NIST in Boulder to make measurements on a small-volume VLE apparatus, and Dr. Watts from NIST visited MTU to consult on modeling progress and measurements. We also held informal meetings at scientific gatherings where we were in attendance.

The project has also been contacted by various DoE researchers with problems directly related to the work, and those of a similar nature concerning VLE and density measurements and prediction. Modeling mixed solvent electrolyte systems is an area of interest to many, and we have been contacted by such diverse groups as researchers in Azerbaijan designing heat pumps to energy producers trying to predict methane solubility in process streams containing salts and other dissolved solids. AIChE's Design Institute for Physical Properties (DIPPR) will assist in dissemination of this information through the 911 project at MTU.

Personnel Supported:

The NIST portion of the funding for this project supported the following personnel:

Dr. Laurel A. Watts, NIST
Dr. Cynthia D. Holcomb, NIST
Stephanie L. Outcalt, NIST
Dr. Beverly Louie, NIST
Pariyachat Chatkun Na Ayuttaya, a PhD graduate student from MTU performed experiments during her stay at NIST.
Brianna McFarlane, a BS student at Colorado School of Mines, Golden, CO.

Future Work

Future work for this research may include developing a better density correlation for the liquid phase, and investigating other local composition models for the Gibbs free energy calculation. Extension of the model to include salt solubility prediction and ionic speciation present in the liquid phase would also be possible. The model could be extended to other fluids and salts of interest. This would involve measuring the VLE and infinite dilution activity coefficient of additional water + organic solvent + salts over a wider range of salt composition.

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