Comparative work about UNIFAC based models for hydroalcoholic systems with electrolytes

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ABSTRACT – An alternative technology for anhydrous ethanol production is extractive distillation with salts such as potassium acetate and calcium chloride. Salting out effects in hydroalcoholic systems may be modeled using group contribution methods such as UNIFAC. This work presents a comparison between these models in the background of anhydrous ethanol production. The evaluated system is a ternary one (water, ethanol and salt – potassium acetate or calcium chloride) whose experimental data were taken from the literature. Although the results depend on reparametrizations carried out for each piece of work, it was observed that the best models (with lower deviations) were the simplest ones, without accounting for medium range interactions or solvation.

1. INTRODUCTION

In the literature, many researchers have analyzed several ethanol dehydration processes (FROLKOVA and RAEVA, 2010; HUANG *et al.*, 2010; KUMAR *et al*, 2010). Saline extractive distillation has the advantage of providing a purer top product, using small quantities of salt to promote the salting out effect for ethanol. There is a large application of potassium acetate (KAc) and calcium chloride ($CaCl_2$) in saline extractive distillation because of their low toxicity and capacity to increase the relativity volatility between ethanol and water.

The accuracy in phase equilibrium predictions is essential for a correct analysis of distillation behavior. The activity coefficient describes non-idealities of the liquid phase such as the presence of azeotropy (in hydroalcoholic mixtures, for example). Several studies (PINTO and WOLF-MACIEL, 2000; LIGERO and RAVAGNANI, 2003; LLANO-RESTREPO and AGUIAR-ARIAS, 2003; HASHEMI, 2011) have used activity coefficients based on Non Random Two Liquids (NRTL) (RENON and PRAUSNITZ, 1968) and UNIversalQUAsi-Chemical (UNIQUAC) models (ABRAMS and PRAUSNITZ, 1975). However, parametrization of NRTL and UNIQUAC models needs a large amount of experimental data.

For organic and electrolyte systems such as hydroalcoholic + congener + salt systems, there are not enough available data. The solution for this problem is to apply semi-predictive methods such as the group contribution UNIQUAC Functional-group Activity Coefficient (UNIFAC) (FREDENSLUND *et al.*, 1977) approach. The UNIFAC method assumes that a system can be described by functional groups. The advantage of this method is that there are much fewer functional groups than

possible molecules.

This paper presents a comparative work between four models (KIKIC *et al.*, 1991; ACHARD *et al.*, 1994; YAN *et al.*, 1999; AZNAR and TELLES, 2001) based on the UNIFAC model to calculate activity coefficient. The assessment was carried out concerning deviations between calculated and experimental data (CIPARIS, 1966; BURNS and FURTER, 1979; MERANDA and FURTER, 1966; SCHMITT, 1975; NISHI, 1975; HASHITANI *et al.*, 1968) of water + ethanol + salt (KAc and CaCl2) systems.

2. THEORY

Due to the complex nature of thermodynamic equilibrium behavior of electrolyte systems, the required effort would be massive to solve the problem if all the equilibriums were considered.

Matugi (2013) assessed the sensitivity of vapor-liquid equilibrium (VLE) calculations with respect to the non-ideal behavior of the vapor phase, for hydroalcoholic systems at room pressures: results based on the ideal gas assumption and using the fugacity coefficient estimated by Redlich-Kwong (REDLICH and KWONG, 1949) and Hayden-O'Connell (HAYDEN and O'CONNELL, 1975) equations were essentially the same.

Therefore, in this work the vapor phase was assumed ideal gas, both for the mixture and for the pure components, giving the modified Raoult Law:

$$y_i.P = x_i.\gamma_i.P_i^{sat} \tag{1}$$

where y_i is the mole fraction of component i in the vapor phase, P is the system pressure, x_i is the mole fraction of component i in liquid phase, γ_i is the activity coefficient of component i, and P_i^{sat} is the saturation pressure of component I, which was calculated by the Korean Data Bank (www.cheric.org/research/kdb) correlation.

It must be emphasized that equation 1 was calculated just for the non-electrolytic compounds of the mixture (salts exist only in liquid phase). However, molar fractions of non-electrolyte substances should take into account the salt fraction. In fact, in saline distillation must employ salt concentrations below saturation. The activity coefficient models assume that salts are totally dissociated/ionized, and the salt molar fraction is represented by the ions molar fractions of the salt itself.

In applicable models of activity coefficient for electrolyte systems, the partial molar Gibbs free energy of excess is a sum of contributions. They take into consideration van der Waals (or short range, SR) interactions and electrostatic (or long range, LR) interactions. The latter are described by Debye-Hückel theory (DEBYE and HÜCKEL, 1923). Moreover, there are models that take into account charge (or medium range, MR) interactions.

Lei and coworkers (2008) reported three approaches for predictive molecular thermodynamic models (KIKIC *et al.*, 1991; ACHARD *et al.*, 1994; YAN *et al.*, 1999) for electrolyte systems, in a

classical thermodynamic context (see Table 1). Furthermore, there is AZNAR and TELLES, 2001 used another approach, which considered only the SR term. This assumption was based on the studies accomplished by Dahl and Macedo (1992), Mock *et al*. (1986) and Cardoso and O'Connell (1987).

Table 1 shows a summary of the UNIFAC based models for electrolyte systems used in this study.

Table 1 – Overview of studied models in this work.

	Kikic *et al.*(1991) – KFR	Achard *et al.*(1994) – ADG	Yan *et al.*(1999) – YAN	Aznar and Telles (2001)– AT
Terms	SR = UNIFAC LR = DH	SR = UNIFAC LR = DH	SR = UNIFAC MR = VIRIAL LR = DH	SR = UNIFAC -Dortmund
Reference state	$\gamma_{ion} \to 1$ as $x_n \to 1$ and $I \to 0$ $\gamma_n \to 1$ as $x_n \to 1$	$\gamma_{ion} \to 1$ as $x_n \to 1$ and $I \to 0$ $\gamma_n \to 1$ as $x_n \to 1$	$\gamma_{ion} \to 1$ as $x_n \to 1$ and $I \to 0$ $\gamma_n \to 1$ as $x_n \to 1$	$\gamma_n \to 1$ as $x_n \to 1$
Features	Group interaction parameters independent of concentration.	Solvation of ions in water only. KAc is not considered.	MR parameters dependence of concentration.	Same equation as the original one.
Limitations for this model	Salt saturation. Systems used for parameter fit not reported.	Molality range between 5 and 10mol per kg of water. Water-ethanol-CaCl$_2$ system used for parameter fit.	Salt saturation. Water-ethanol-KAc system used for parameter fit.	Salt saturation.

*DH: Debye-Hückel

3.METHODS: LITERATURE EXPERIMENTAL DATA AND PREDICTION OF VLE

In papers of simulation of saline extractive distillation for anhydrous ethanol production (PINTO and WOLF-MACIEL, 2000; LIGERO and RAVAGNANI, 2003; LLANO-RESTREPO and AGUIAR-ARIAS, 2003), the input stream of the distillation column was a hydroalcoholic wine and the concentration of salt used was lower than the saturation for both salts. In our data selection, these assumptions were considered, choosing the appropriated concentration ranges for ethanol and salts.

Table 2 presents an outline of the selected data. There were 138 experimental points for water + ethanol + KAc and 87 points for water + ethanol + CaCl$_2$ system in published research (CIPARIS, 1966; BURNS and FURTER, 1979; MERANDA and FURTER, 1966; SCHMITT, 1975; NISHI, 1975; HASHITANI *et al.*, 1968).

Table 2 – Data characteristics.

System	Water + ethanol + KAc	Water + ethanol + CaCl2
Reference	Ciparis (1966); Burns and Furter (1979); Meranda and Furter (1966); Schimitt (1975)	Ciparis (1966); Nishi (1975); Hashitani*et al.* (1968)
Number of points	138	87
Range of pressure/kPa	100.41 – 101.33	101.33
Range of temperature/K	351.45 – 368.25	351.55 – 369.15
Range of ethanol molar fraction in liquid phase	0.018 – 0.983	0.019 – 0.980
Percentage of experimental points whose ethanol molar fraction in liquid phase is between:		
Lower fraction– 0.05	4.07	8.47
0.05 – 0.1	3.25	8.47
0.1 – 0.5	43.09	20.34
0.5 – 0.894	36.59	38.98
0.894 – upper fraction	13.00	23.74
Range of salt molar fraction	$4.0 \times 10^{-3} – 0.276$	$2.1 \times 10^{-4} – 0.061$
Percentage of experimental points whose ethanol molar fraction in liquid phase is between:		
Lower fraction – 0.005	11.38	37.29
0.005 – 0.01	12.20	5.08
0.01 – 0.05	29.27	47.46
0.05 – 0.1	24.39	10.17
0.1 –upper fraction	22.76	zero

Data were disregarded when the molar fraction of solvents in free salt basis was equal to zero. Bubble point temperatures were calculated using Solver® from Excel®. Nonlinear Generalized Reduced Gradient (GRG) was the chosen numeric method. Experimental data were used for the startup of the calculations.

4. RESULTS

Figure 1 illustrates an example of predicted VLE data for a particular molar concentration of KAc and molality of $CaCl_2$, at 100.41 kPa and 101.33 kPa, respectively. There were similar results for KAc data (figure 1.a), while for $CaCl_2$ data (figure 1.b), there were large deviations in YAN model (up to one order of magnitude higher than the others), and ADG model had an unfeasible behavior (the saturated liquid line crosses the saturated vapor line).
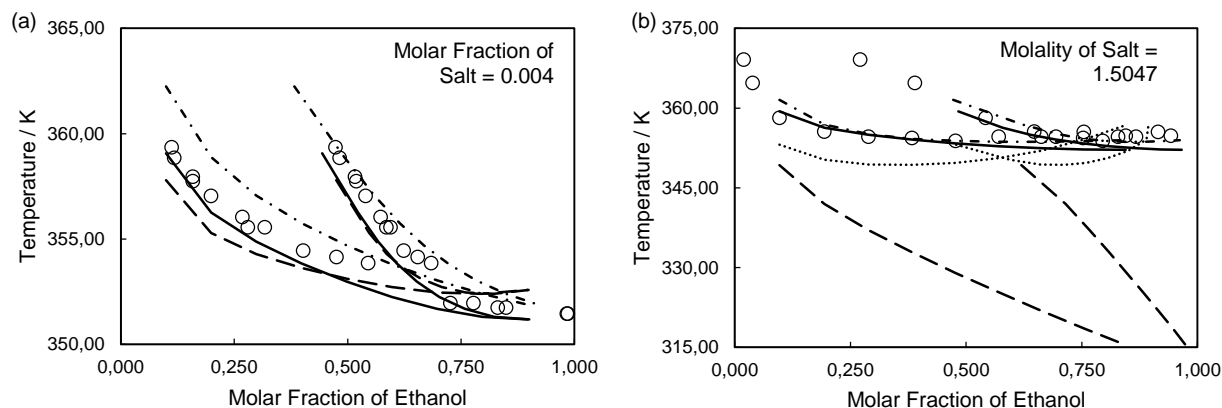
Figure 1 – Example of VLE predictions for (a) water + ethanol + KAc system (molar fraction of salt equal to 0.004) at 100.41 kPa and (b) water + ethanol + CaCl$_2$ system (molality of salt equal to 1.5047 mol. kg^{-1}) at 101.33 kPa. The circles (○) represent experimental points, the lines were estimated by the KFR model (——), ADG model (⋯⋯), YAN model (‒ ‒ ‒), and AT model (‒ ⋅ ‒ ⋅). The experimental data for KAc are from Schimitt (1975) and for CaCl$_2$ from Nishi (1975).

Figure 2 evaluates the influence of ethanol molar fraction in liquid phase on deviations of temperature and ethanol molar fraction in vapor phase. Figure 2.a and figure 2.c indicate that the concentration of ethanol in liquid phase has low effect on temperature deviations, except for YAN model in CaCl$_2$ systems. Diluted concentration range has larger deviations (funnel shape in figure 2.b and figure 2.d), despite the salt solubility decrease by ethanol addition. This behavior may have been caused by symmetric convention in activity coefficient calculation adopted for all models.

Figure 3 assesses the impact of salt molar fraction on deviations. The temperature deviation tendency (figure 3.a and figure 3.c) was similar for both salts despite the fact that figure 3.c does not show it, as its ordinate axis is compressed. Molar fraction of salt had not as much influence on deviations as molar fraction of ethanol in vapor phase (figure 3.b and figure 3.d). KFR and YAN models presented a higher correlation between molar fraction of salt and deviations.
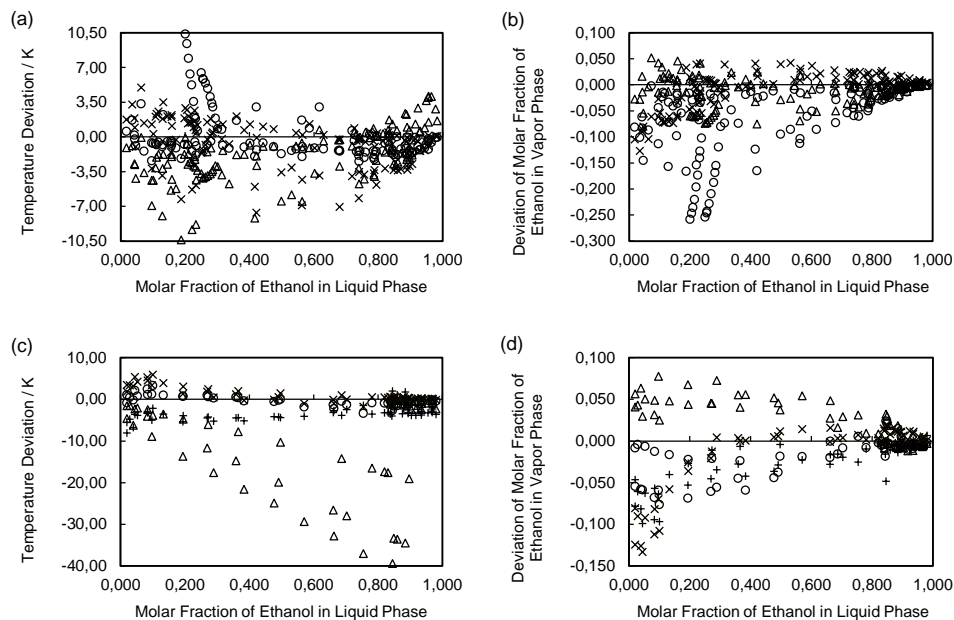
Figure2 – Deviation of temperature and molar fraction of ethanol in vapor phase versus molar fraction of ethanol in liquid phase for (a and b) water + ethanol + KAc system and (c and d) water + ethanol + CaCl$_2$ system: KFR (○), ADG (+), YAN (Δ), and AT (×).
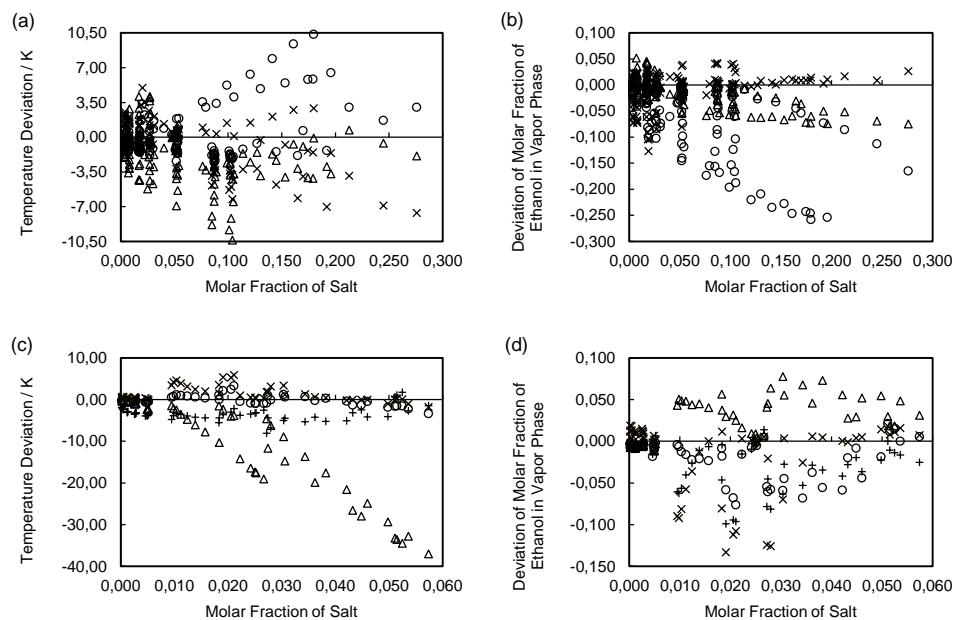

Figure3 – Deviation of temperature and molar fraction of salt in vapor phase versus molar fraction of ethanol in liquid phase for (a and b) water + ethanol + KAc system and (c and d) water + ethanol + CaCl$_2$ system: KFR model (○), ADG model (+), YAN model (Δ), and AT model (×).

The results of VLE data predictions were condensed using mean values of absolute deviations, in Table 3. Larger deviations were obtained by ADG and YAN models in spite of the fact that systems containing $CaCl_2$ and KAc, respectively, were considered for estimation of these models' parameters. These results may indicate that medium range interactions or solvation phenomena have a minimum effect of on the studied systems, thus enforcing a super-parametrization of ADG and YAN models.

Table 3 – Mean absolute deviations for electrolyte models.

Water + ethanol + KAc system	KFR	ADG	YAN	AT
Temperature (K)	1.71	na	2.57	1.83
Ethanol molar fraction in vapor phase	0.062	na	0.022	0.024
Water activity coefficient	0.358	na	0.269	0.135
Ethanol activity coefficient	0.302	na	0.198	0.264
Water + ethanol + CaCl2 system	KFR	ADG	YAN	AT
Temperature (K)	0.84	3.42	10.02	1.26
Ethanol molar fraction in vapor phase	0.020	0.024	0.026	0.026
Water activity coefficient	0.160	0.337	0.601	0.146
Ethanol activity coefficient	0.177	0.186	1.297	0.408

*na: not available

Furthermore, because AT values were similar to KFR's for $CaCl_2$ systems and AT has fewer parameters than KFR, the AT model would be more suitable for modeling of sailne distillation for production of anhydrous ethanol. However, important limitations need to be considered: KFR and AT models work on a narrow range of salt concentrations. Besides, and the parameters of AT model lack physical meaning.

5. CONCLUSIONS

Four UNIFAC-based models were investigated, aiming at calculating activity coefficient for hydroalcoholic systems with electrolytes. KFR and AT model are best fit for simulation of saline distillation for anhydrous ethanol production. Nonetheless, it is recommended that further statistical research be undertaken concerning parameter estimation and deviation analyses of each model.

6. ACKNOWLEDGEMENTS

access to experimental data banks and Professor Luiz Fernando de Moura for his invaluable collaboration.

7. REFERENCES

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