MODELING OF ALCOHOL THERMODYNAMIC PROPERTIES: PURE COMPONENTS AND MIXTURES WITH SUPERCRITICAL CARBON DIOXIDE.

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Introduction

Thermodynamic knowledge of the high-pressure phase behavior of alcohol-CO_2 mixtures, particularly in supercritical conditions, is essential for the design and implementation of numerous processes. Among the most important are: the supercritical fluid extraction (SFE) and the supercritical fluid chromatography (SFC). The short chained alcohols like methanol, ethanol and propanol are employed to control the polarity of supercritical fluid solvents in SFE and as carriers or modifiers for SFC. In the oil and natural gas industry, some low-molecular weight alcohols and glycols are injected in the pipe-lines to prevent formation of hydrates. Data of carbon dioxide-long chained alcohol systems are of great importance in the pharmaceutical, cosmetic, and surfactant industries.

In addition, data of systems of all sorts and sizes of alcohols with carbon dioxide are important in the development of predictive thermodynamic models. In order to improve understanding of these binary systems, the phase equilibria database of alcohol/CO_2 mixtures has been greatly expanded on in publications over the last few years. Currently, there is a lot of data available on primary linear alcohols (C_1-C_{20}) at a wide range of temperatures and pressures. Information on binary systems including supercritical CO_2 and secondary, unsaturated, tertiary alcohols and glycols is much more rare. In our previous work, we chose to carry out phase equilibrium measurements on binary systems involving CO_2 and the following alcohols: 2-undecanol, 6-undecanol, 10-undecen-1-ol and 2-methyl-2,4-pentanediol at 313, 323 and 333 K.

The purpose of this work is to correlate our data with the Peng-Robinson equation of state[1] (PR-EOS) and different mixing rules: Abdoul's model[2] which combines the PR-EOS and the Van Laar g^{Ex} model, or quadratic mixing rules for $a(T)$ and b parameters with temperature dependent k_{ij} and l_{ij}.

In a first step, it is essential to assess the critical parameters and the acentric factor of pure components which are required for the calculation of the PR-EOS parameters. The absence of experimental values (T_c, P_c, w) for alcohols studied, let us to use a group contribution method for estimation purposes. Once the properties of pure substances are well understood, it is possible to correlate our data with temperature dependant k_{ij} and l_{ij} , and with Abdoul's model[2].

Comparison of published methods for the prediction of critical parameters

The critical parameters used in the EOS cannot be found in literature for the following molecules: primary alcohols with a carbon number greater than twelve and secondary

alcohols with a carbon number greater than ten. Experimental data are often not available for tertiary, unsaturated alcohols and glycols.

For these reasons the following methods for the prediction of critical parameters have been tested and compared:

- The Constantinou and Gani method[3,4]

In this method (*Gani method*), the three properties T_c, P_c and w are estimated by a full group contribution technique. To improve the results, the authors added second-order group contributions. The role of them is to provide more information about the portions of the molecular structure of a compound where the description through the first-order group is insufficient (for example isomers). This method has the advantage of not requiring the normal boiling point (T_b) to calculate T_c.

- Joback's modification of Lydersen's method[5]

Joback modified a group contribution technique that was originally proposed by Lydersen. The properties of a compound (T_c, P_c and w) are estimated as a summation of the contributions of simple first-order groups. In this method the normal boiling point and the molecular weight are needed. One simple relation has been proposed by Joback to obtain a very approximate estimation of T_b when no experimental values are be available. We will note *Joback* (T_b^{exp}) the method using the experimental T_b value and *Joback* the full group contribution technique.

- Ambrose method[6, 7]

The Ambrose group contribution method is valid only for critical temperatures and pressures. In this method the normal boiling point and the molecular weight are required. For compounds whose normal boiling point is not available from experimental data it could be possible to calculate it using another group contribution method. However in this work we will only consider the *Ambrose* (T_b^{exp}) method based on the experimental value of T_b. The acentric factor has also to be calculated in an external manner; in this work we have chosen the Edminster method[8], which estimates it from the knowledge of the normal boiling point.

In order to test the efficacy of these three group contribution methods, we selected :

- 37 alcohol molecules (14 primary (C_4-C_{12}), 20 secondary (C_4-C_{12}) and 3 tertiary (C_5-C_6) alcohols) for which T_b and T_c are available from experimental data.
- 24 alcohol molecules (13 primary (C_4-C_{12}), 9 secondary (C_4-C_9) and 2 tertiary (C_5-C_6) alcohols) for which the experimental critical pressure P_c is known.

For critical temperatures, we considered: the methods of *Ambrose* (T_b^{exp}) and *Joback* (T_b^{exp}) using the experimental boiling point and the *Gani* and *Joback* full group contribution techniques.

For critical pressures, since T_b is not required, there are only three methods to consider: *Ambrose*, *Gani* and *Joback* group contributions.

Table1: *Critical temperatures: comparison between experimental and group contribution values.*

Compounds	N_c	Deviations on critical temperatures (ΔT_c %)			
		Ambrose (T_b^{exp})	Joback (T_b^{exp})	Gani	Joback
Linear primary alcohols	8	1.04	14.33	6.14	27.77
Substituted primary alcohols	6	3.31	5.91	4.56	13.39
Linear secondary alcohols	14	3.01	10.21	3.99	19.09
Substituted secondary alcohols	6	17.68	19.43	7.69	23.77
Tertiary alcohols	3	8.92	29.71	6.97	12.00
Mean deviations	**37**	**5.49**	**13.48**	**5.39**	**20.23**

Table2: *Critical pressures: comparison between experimental and group contribution values.*

Compounds	N_c	Deviations on critical pressures (ΔP_c %)		
		Ambrose	**Gani**	**Joback**
Linear primary alcohols	8	1.12	2.07	0.93
Substituted primary alcohols	5	1.87	2.09	1.55
Linear secondary alcohols	7	1.12	1.11	1.36
Substituted secondary alcohols	2	0.19	0.20	0.72
Tertiary alcohols	2	1.27	1.23	1.40
Mean deviations	**24**	**1.21**	**1.57**	**1.21**

The results are shown in Tables 1 and 2. Globally, for *critical temperatures*, the full group contribution method of *Gani* and the *Ambrose* method give similar results and the smallest errors. Concerning the *Joback* method, even when using experimental values of the normal boiling point, the accuracy remains very poor. For *critical pressures*, whatever the method considered, results are comparable and very satisfactory.

We will focus only on critical temperatures, considering the *Ambrose* (T_b^{exp}) and *Gani's* methods in order to verify which one is more adapted for each class of alcohols. For linear primary alcohols, the *Ambrose* (T_b^{exp}) method shows the best results and constant deviations, when the alcohol chain length is increasing, which is not the case for *Gani's* method. For substituted primary and linear secondary alcohols, *Ambrose* and *Gani* methods give almost the same deviations. However for substituted secondary and tertiary alcohols, the *Gani* group contribution gives the best results on T_c.

We have also checked the influence of the method used for estimating T_c, P_c and *w* on the prediction of the alcohol saturated vapor pressures. The saturation vapor pressures P_{sat} are estimated by means of the PR-EOS[1]:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \tag{1}$$

For pure components, parameters of the EOS (Eq.1) are calculated from the following expressions, using for *a(T)* the Soave type function[9]:

$$b = 0.0078 \, RT_c \, / \, P_c \tag{2}$$

$$a(T) = 0.4572 \frac{R^2 T_c^2}{P_c} \left\{ 1 + m\left[1 - \sqrt{\frac{T}{T_c}} \right] \right\}^2 \tag{3}$$

with:
$$m = 0.3746 + 1.5423w - 0.2699w^2 \tag{4}$$

Table 3 compares calculated and experimental values of P_{sat} by using the critical parameters obtained from the Ambrose method (*Ambrose* (T_b^{exp})) and the Constantinou and Gani full group contribution method (*Gani*). In this last case, we also give the results corresponding to the Gani's method (*Gani**) but using for the acentric factor the value deduced from the Edminster correlation with the experimental normal boiling point. For comparison, the deviations obtained with use of the experimental T_c, P_c, and ω values were also reported (*Lit*).

The database here is constituted of 24 alcohol molecules: 13 primary (C_4-C_{11}), 10 secondary (C_4-C_9) and 1 tertiary (C_6) for which experimental vapor pressures[10], T_b, T_c and P_c are available.

Table 3*: Deviations on saturated vapor pressures (**DP**$_{sat}$ %) with the Peng-Robinson EOS*

Compounds	N_c	N_p	Ambrose (T_b^{exp})	Gani	Gani*	Lit
Linear Primary Alcohols	8	291	24.09	25.68	24.95	23.40
Substituted Primary Alcohols	5	209	16.40	22.77	20.32	19.42
Linear Secondary Alcohols	7	221	15.62	27.54	14.89	18.05
Substituted Secondary Alcohols	3	85	18.66	25.96	19.67	27.54
Ternary Alcohols	1	17	8.22	40.11	11.78	12.66
Mean deviations	**24**	**823**	**18.98**	**25.77**	**20.25**	**21.16**

In the case of vapor pressure calculations, the Ambrose method using the experimental normal boiling point (*Ambrose (T_b^{exp})*) provides the best results whatever the class of alcohols considered ; indeed, even for the *Gani* method using the acentric factor estimated from the experimental normal boiling point (*Gani **), deviations always remain superior.

Conclusion

As a conclusion, for high molecular weight compounds where critical temperature and pressure are not measurable, a group contribution method should be used for their estimation. When the experimental normal boiling point is available, the Ambrose method (*Ambrose(T_b^{exp})*) should be used both for the estimation critical parameters and saturated pressures. When the experimental normal boiling point is not available, the *Gani* method should be considered.

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