THERMODYNAMIC PROPERTIES OF HOP EXTRACTS THROUGH PSEUDOCOMPONENTS

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Hop extraction goes back over 150 years to the early nineteenth century. By far the predominant extracts are "organic" solvent extracts (hexane) and carbon dioxide (CO_2) extracts (supercritical and liquid). Supercritical CO_2 is more selective than the organic solvents and extracts less of the tannins and waxes and less water and hence water-soluble components. The yield of alpha acids extracted with supercritical CO_2 (91 - 94%) is similar to that obtained with the organic solvents (93 - 96%). Following extraction there is the process of solvent removal which for organic solvents involves heating to cause volatilization. Despite this, trace amounts of solvents do remain in the extract. The removal of CO_2, however, simply involves a release of pressure to volatilize the CO_2. Solvent extracts are increasingly falling out of favor worldwide due to perceived problems with the residues. CO_2 extracts on the other hand are gaining favor as they are seen to be produced with a "natural" solvent.
In order to optimize the extraction and to verify the possibility to move towards a continuous process it is necessary to evaluate the thermodynamic properties of the mixtures constituting the hop extracts.
Due to the number of components a lumping procedure must be adopted. In this procedure a reduced number of “pseudocomponents” is defined and through these components the thermodynamic properties of the complex mixtures can be evaluated. Experimental results of fugacity coefficients at infinite dilution of carbon dioxide and other organic solvents are used in order to determine the numerical values of the binary interaction parameters of the Peng-Robinson equation of state. Using these parameters the performance of carbon dioxide as extractive agent in different temperature and pressure conditions is evaluated.

INTRODUCTION

Hop (*Humulus lupulus*) is a climbing herbaceous plant belonging to the family of the Cannabaceae in the order of Urticales. Because hops provide taste and flavour to beer, analysis of the composition of varieties of hops is a major issue in the brewing industry.
The lupulin glands in the female cones produce humulones and lupulones as a mixture of so called n-, co and ad-compounds. [1]
Compounds derived from hops have several effects on beer. The resinous compounds, alpha- and beta-acids, give a bitter taste to beer while essential oils are responsible for the hoppy aroma. [2]
Historically the management of hop additions to beer was, for most brewers, a relatively simple process. Whole hops were added to the boiling wort and the spent hops provided a filter bed for the wort as it was passed on to fermentation.
During brewing hops are boiled in the kettle with the wort. This process leads to isomerisation of the humulones to cis/trans pairs of isohumulones which impart their bitter taste to beer and stabilize the beer foam. [1]

Brewers could vary the amount of bitterness and the intensity and quality of hop aroma by varying the varieties and the amount of hops and the time of addition during the wort boiling process.
Many components of raw hops deteriorate during storage. Those substances are sensitive towards heat and oxygen. To overcome the quality loss and inconvenient handling of raw hops, hop products were developed in the past. Today, the brewer can use either raw hops or hop pellets or hop extract or chemically modified hop products. The estimated share of hops, which are extracted, is 1/3 of the global production.
Extraction is a process by which the hop resins and hop oils are extracted from the cone of the hop.
These resins can then be standardized to a particular alpha percentage with glucose. Hop resin extract will vary depending on the hop variety extracted, and usually contains from 40 to 60% alpha acids. Hop extracts are used primarily for bittering the beer. They typically add little aroma, and often a brewer using extracts will add aroma pellets later in the brewing cycle [3].
There are various types of solvent extracts. The use of hexane is an older technology; in Germany ethanol was used as a solvent to extract the hop resins. These solvents virtually extract all the lupulin components, they extract also plant pigments, cuticular waxes, water and water- soluble materials.
Solvent extracts are generally being phased out in favor of supercritical CO_2 extracts [3].
Supercritical CO_2 is more selective than the organic solvents and extracts less of the tannins and waxes and less water and hence water-soluble components. It does extract some of the plant pigments like chlorophyll but rather less than the organic solvents do.
All the essential hop constituents (alpha-acids, beta-acids, and hop oils) are captured and preserved in this extremely pure and consistent CO_2 hop extract.
This extract is typically a golden yellow color when produced. It is free flowing at elevated temperatures and is a semi-solid paste at room temperature and has excellent storage properties.
The resin's active ingredients remain intact over extended periods of time assuring brewing characteristics.
The resin has a pronounced hop aroma, and is a pure product with no other foreign substance.
The low temperatures and high pressure used during processing plus the inert nature of supercritical carbon dioxide combine to produce exceptional efficiency in extracting the alpha acids [3].
Undesirable hop constituents such as hard resins, deteriorated resins, tannins, polyphenols, nitrates, hop protection chemicals, fats and waxes are reduced. CO_2 hop extract will produce a beer similar to or better than traditional hopping methods [3].
Within the brewing process the major advantages of extracts relate to reduced bulkiness, improved storage, standardization, consistency, utilization and reduced wort losses.
The major disadvantage of extracts is the slightly higher cost per bitterness unit compared to whole hops or pellets. This varies from 8 - 10% higher with organic solvent extracts and perhaps as much as 15 - 20% for the CO_2 forms.
Aim of this work is the investigation of thermodynamic properties of the mixtures constituted by three different extract hops and CO_2.
The method is based on the choice and definition of pseudocomponents in order to represent each extract as a ternary mixture of an alpha acid, a beta acid and a hydrocarbon component and successively the determination for each extract of the fugacity coefficients at infinite dilution of carbon dioxide and other organic solvents.

I – EXPERIMENTAL MATERIALS AND METHOD

NATECO$_2$ GmbH & Co. KG provides the following hop extracts: an oil poor fraction (HHM), an oil rich fraction (HHE OF) and a total resin extract (HHE TR). These fractions were obtained by extraction with supercritical CO_2.

ATO provides a fourth extract (HHM ARF) achieved with the C-REX process operating at different experimental conditions.

CO_2 was obtained from SIAD with a purity of 99.98%. The solutes used were reagent-grade products obtained from Fluka and Sigma-Aldrich.

Hop fractions were characterized by inverse gas chromatography (IGC) technique at 323K and 333K.

From chromatographic experimental quantities the fugacity coefficient of CO_2 at infinite dilution (Φ^{∞}_{CO2}) in the different fractions is obtained.

Details on the experimental technique and calculations procedure are reported elsewhere [4].

The results have been utilized in order to characterize the extracts in terms of dipolarity / polarizability, hydrogen-bond basicity / acidity and lipophilicity by means of the equation of solvation proposed by Abraham.

II – EXPERIMENTAL RESULTS: ABRAHAM CHARACTERIZATION

Abraham method [5-7] proposed the solvation equation, which allows to obtaine a set of coefficients characteristics of the stationary phase from the chromatographic experimental data and from a set of characteristic parameters of the solutes injected.

The specific retention volume data, V_g^0, obtained from experimental measurements with IGC, can be considered as the result of partitioning equilibrium between solute molecules and the stationary phase, with the following solvation equation:

$$\log V_g^0 = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l\log L^{16} \qquad (1)$$

Each term of this equation refers to particular solute-solvent interaction. In particular there are five parameters which represent solute properties: R_2, π_2^H, α_2^H, β_2^H and L^{16}.

R_2 is a modified polarisability parameter that characterizes the ability of a solute to interact via π- or n-electron pairs;

π_2^H is the solute dipolarity;

α_2^H is the solute hydrogen-bond acidity;

β_2^H is the solute hydrogen-bond basicity;

$\log L^{16}$ where L^{16} is the solute Ostwald solubility coefficient on hexadecane at 25°C.

The constants c, r, s, a, b and l serve to characterize a solvent phase in terms of specific solute/solvent interactions; they are found by the method of multiple linear regression analysis (MLRA) from the experimental values of $\log V_g^0$.

c is a constant of the correlation;

r: reflects the ability of a solute to interact with a solvent through π and n electron pairs;

s: reflects the stationary phase polarizability;

a: reflects interactions between hydrogen bond solute acids and a hydrogen bond solvent base (it's a measure of the stationary phase basicity);

b: reflects interactions between hydrogen bond solute basics and a hydrogen bond solvent acid (it's a measure of the stationary phase acidity);
l: represents a combination of general dispersion interactions and cavity effects.
The parameters of solvation equation are reported in table 1 for all the hop extract examined. R^2 is the coefficient of determination.

Extract	T (K)	c	r	s	a	b	l	R^2
HHM	323	-2,474	-0,796	3,847	7,447	1,845	2,165	0,987
	333	-1,274	-0,436	2,957	5,797	1,328	1,720	0,991
HHE OF	323	-0,998	-0,566	2,381	5,036	0,726	1,853	0,997
	333	-1,273	-0,552	2,432	4,875	0,570	1,792	0,997
HHE TR	323	-0,583	-0,463	2,456	5,216	1,047	1,746	0,992
	333	-0,923	-0,407	2,448	5,022	0,917	1,701	0,992
HHM ARF	323	-1,204	-0,537	2,743	5,821	0,940	1,806	0,994
	333	-1,406	-0,504	2,721	5,568	0,809	1,737	0,994

Table 1: Abraham's constants characterizing hop extracts.

From a numerical point of view, a and s-constants are the predominant parameters for the extracts studied in this paper.
a-constant is greater than b for all the temperatures investigated denoting the basicity of all the examined extracts. The difference between a and b-constants is more relevant for HHM and HHM ARF.
The basicity, measured by a-constant, decreases increasing temperature for all extracts. It should be noticed that for both temperature a is greater for HHM.
s-constant value shows a high polarizability of the stationary phases investigated: it is bigger for HHM and HHM ARF. The tendency of stationary phase to interact with polarizable solutes, measured by the r-constant is similar for all the extracts studied and decreasing with temperature. Finally, l-constant, decreases with temperature for all the stationary phases.

III – EXPERIMENTAL RESULTS: FUGACITY COEFFICIENT CALCULATION

The extracts were considered on the basis of analytical data as a ternary mixture of alpha acids, beta acids and hydrocarbon (essential oils). The following pseudocomponents were chosen in order to represent the ternary mixture: cohumulon, colupulon and α-humulen for alpha acids, beta acids and hydrocarbon respectively.
The composition of each extract fraction is presented in table 2.
The Peng Robinson equation of state was used for the interpretation of the experimental data from a thermodynamic point of view.
With this particular characterization, is possible to consider the mixture constituted by each hop extract and CO_2, from which the extract was obtained, as a quaternary mixture.

Extract	α (Cohumulon) (%)	β (Colupulon) (%)	HC (α-humulen) (%)
HHM	49.2	29.2	21.7
HHE OF	10.7	38.8	50.5
HHE TR	16.0	50.5	33.5
HHM ARF	25.7	25.2	49.1

Table 2: Hop extracts composition (Data are expressed as mass fraction percentage).

Pure components parameters needed for the calculations (critical temperature, critical pressure, and acentric factor) were previously calculated with group contribution methods. [8].

In each mixture, the fugacity coefficient at infinite dilution of CO_2 obtained with the Peng Robinson equation of state will depends not only from pure components properties but also from relative binary interaction parameters k_{ij}.

Due to the limited available set of experimental data, only cohumulon – CO_2, colupulon - CO_2 and α-humulen – CO_2 interactions were considered as predominant if compared to those cohumulon - colupulon, cohumulon - α-humulen, and colupulon - α-humulen, for which k_{ij} was set equal to zero.

Extract	ln Φ^{∞}_{CO2} exp	ln Φ^{∞}_{CO2} calc	Error (%)
HHM	3.77	4.32	55
HHE OF	4.73	4.73	0
HHE TR	4.07	4.68	62
HHM ARF	4.79	4.56	23

Table 3: Experimental and calculated values of Φ^{∞}_{CO2} at 323K.

Numerical values of these binary parameters are obtained with the fitting of experimental data of Φ^{∞}_{CO2} in HHM, HHE OF and HHE TR fractions at 323 and 333 K.

With these values is therefore possible to predict the value of Φ^{∞}_{CO2} in the fourth fraction extract considered, HHM ARF.

Calculations results are reported in table 3 and table 4 at 323 and 333 K respectively with the absolute percentage error. For each extract considered a comparison between experimental and calculated value is presented. From these results it can be noticed that for both temperature the best results are obtained for the extract HHE OF leading to a percentage error of the 0%.

Globally, the calculation gives better results at the higher temperature considered.

Finally, referring to the last part of this work it appears evident that the prediction of Φ^{∞}_{CO2} in the fraction HHM ARF is good, especially at 323K; at this temperature the error is quite the half of those obtained at 333K.

Extract	ln Φ^{∞}_{CO2} (exp)	ln Φ^{∞}_{CO2} (calc)	Error (%)
HHM	4.47	4.43	4
HHE OF	4.75	4.75	0
HHE TR	5.22	4.80	42
HHM ARF	4.13	4.54	41

Table 4: Experimental and calculated values of Φ^{∞}_{CO2} at 333K.

CONCLUSIONS

A lumping procedure was adopted in order to characterize from a thermodynamic point of view four hop extract obtained with supercritical CO_2 extraction. The method is based on the definition of pseudocomponents in order to consider each extract as a ternary mixture.

The procedure globally gives good results in the thermodynamic characterization of hop extracts.

In particular, it allows predicting Φ^{∞}_{CO2} of the extract HHM ARF with a good agreement between experimental and predicted data, once known the thermodynamic description of the other three extracts.

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