Methodology for Process Modelling of Supercritical Fractionation with Application to Separation of Detergent Range Alkanes and Alcohols

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ABSTRACT

Due to the complexities associated with the thermodynamics of supercritical processes, process modelling is no easy task. This paper presents and applies a methodology for the development of a process model applicable to supercritical fluid fractionation in a commercial process simulator. The methodology consists of fitting the interaction parameters of a relatively simple equation of state to binary solvent/solute data followed by testing of the fit against multicomponent bubble- and dew-point data. The fitted thermodynamic model can then be used in a process simulator. The methodology was applied to the separation of detergent range alkanes and alcohols using supercritical CO_2. The results show that the thermodynamic model is able to predict the phase equilibria quite well, especially in the important high solvent concentration range, and that the process model is able to reproduce pilot plant data within an error of 25 %. The methodology can therefore be used to develop a process model for a supercritical fluid fractionation process.

INTRODUCTION

Supercritical fluid fractionation (SCF) processes utilize high pressure gases to achieve separations in a similar manner to a liquid solvent in liquid-liquid extraction. Typically such SCF processes are operated near the critical temperature of the solvent. At the operating conditions the supercritical (SC) solvent has a density of the same magnitude as the solutes, and as such significant molecular interactions occur between the solvent and the solute. Furthermore, in the vicinity of the critical point the density is highly dependent on both the temperature and pressure. SCF processes are also more often than not applied to difficult separations where the components to be separated have a high molecular mass. As a result of the proximity of the critical point of the solvent and the high molecular mass of the solutes, process modelling of SCF processes is not as straight forward as for low pressure separations, predominantly due to the complicated thermodynamics. Additionally, SCF process modelling is also hampered by limited phase behaviour data, especially for multicomponent mixtures, and the lack of pilot plant data.

The aim of this paper is to present a methodology for process modelling of SCF processes. In particular, the methodology has been developed for the fractionation of detergent range alkanes and alcohols (C10 to C16) using Aspen Plus® as process simulator. Firstly, the developed methodology is presented. Thereafter the validity of the methodology is proven for the separation of n-decane from a mixture containing n-decane, 1-decanol, 3,7-dimethyl-1-octanol and 2,6-dimethyl-2-octanol. Finally, using the proposed methodology, process

modelling is used to predict the separation that can be achieved for a mixture of n-dodecane, 1-decanol and 3,7-dimethyl-1-octanol.

METHODOLOGY

General approach

The aim of this work is to present a methodology that can be used to model a SCF process. The process model should require a minimal amount of phase equilibrium data to obtain parameters for a thermodynamic model already present in the process simulator. In order to develop a process model a thermodynamic model and a selection of unit operations are required. The thermodynamic model provides information on the properties of the co-existing phases. In general, for separations involving two or more fluid phases, rigorous unit operation models based on the number of equilibrium stages have been developed. Fundamentally these models can be applied to SCF processes provided that the thermodynamics can be fully characterised. This work thus envisions to use an already available thermodynamic model together with standard unit operations to develop a process model. In order to do so, the following steps are thus required:

1. Select a suitable thermodynamic model based on the inherent structure of the model and the ability of the model to predict the phase equilibria.

2. Using experimental solvent/solute phase equilibrium and pure component vapour pressure data, model parameters and binary interaction parameters (BIPs) are determined. In some cases this step may be combined with step 1 above, especially when the choice of model is not clear.

3. The suitability of the thermodynamic model is tested by comparing the predicted bubble and dew-point measurements of a multicomponent mixture to experimental data, should such data be available.

4. A process model using standard unit operations is developed in a process simulator.

To illustrate the methodology, Aspen Plus$^{®}$ was used in this work. However, the methodology presented is not limited to Aspen Plus$^{®}$ and could be applied to other process simulators.

Problem specific methodology

In this work the methodology is applied to two separations involving detergent range alkanes and alcohols. Firstly, the separation of n-decane from a mixture of n-decane, 1-decanol, 3,7-dimethyl-1-octanol and 2,6-dimethyl-2-octanol. The results from the process model are then validated by comparison with experimental measurements. Secondly, the methodology is applied to the separation that can be achieved for a mixture of n-dodecane, 1-decanol and 3,7-dimethyl-1-octanol. Referring to the four steps mentioned above, the following approach was followed for each application:

1. Selection of a thermodynamic model: The RK-Aspen thermodynamic model was selected based on previous work indicating the suitability of the said model [1] to model the binary solvent/solute data of CO_2 with detergent range alkanes and alcohols. The model employs the framework of the Soave modification of the Redlich-Kwong equation of state (EoS) [2] but uses the Mathias alpha function [3] for subcritical components (i.e. the solutes) and the Boston-Mathias alpha function [4] for SC components. For subcritical components the RK Aspen model thus requires an additional pure component parameter, the polar parameter η_i, which can be regressed from pure component vapour pressure data. The RK-Aspen model is extended to mixtures using a slight adaptation of the van der Waals mixing rules (a double summation for the b-parameter) [5] and two temperature independent BIPs ($k_{a,ij}$, $k_{b,ij}$).

2. Fitting of pure component parameters and BIPs: Pure component critical properties were used as given in Aspen Plus$^®$. The polar parameters were fitted to vapour pressure data present in Aspen Plus$^®$ [5] in combination with that presented in the NIST database [6]. The BIPs were fitted to experimental solvent/solute data using the Aspen Plus$^®$ regression function through implementation of the Britt-Luetke algorithm to obtain the maximum likelihood estimation of the minimization of error.

3. For both separation problems experimental bubble/dew point data are available for a multicomponent mixture containing all the components present [1],[7]. This data were used to verify the thermodynamic model.

4. A process model was developed using a liquid-liquid extraction column unit operation to model the fractionation column and a flash drum unit operation to model the separator. It should be noted that total separation was not achieved in the separator and as such the solvent exiting the separator still contained a significant amount of solute. The solute present in the solvent was taken into account by modifying the composition of the feed to the extraction column. A schematic representation of the process model developed is shown in Figure 1.
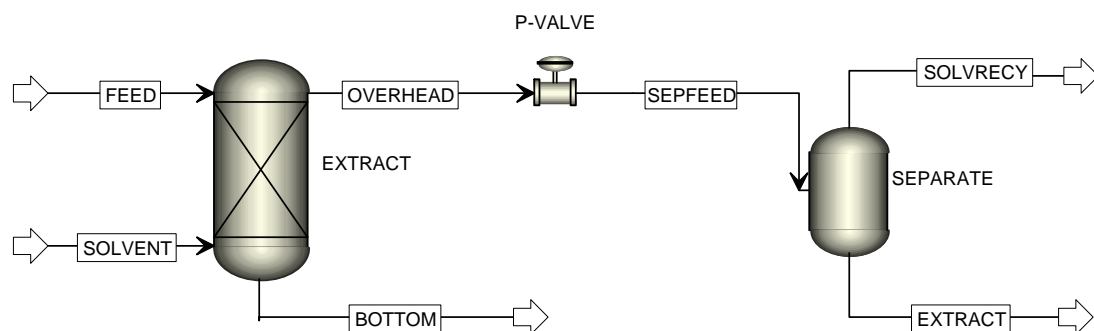
Figure 1: Schematic representation of process model for SCF of detergent range alkanes and alcohols

PROOF OF CONCEPT: SEPARATION OF N-DECANE FROM A N-DECANE/1-DECANOL/3,7-DIMETHYL-1-OCTANOL/2,6-DIMETHYL-2-OCTANOL MIXTURE

Previously published phase equilibrium data of the solutes in SC CO_2 [8] was used to determine the polar parameters and the BIPs for the solute/solvent interactions. These values are given in Table 1 and the prediction and fit of the model to the data is seen in Figure 2.

Table 1 : RK Aspen Model parameters and BIPs

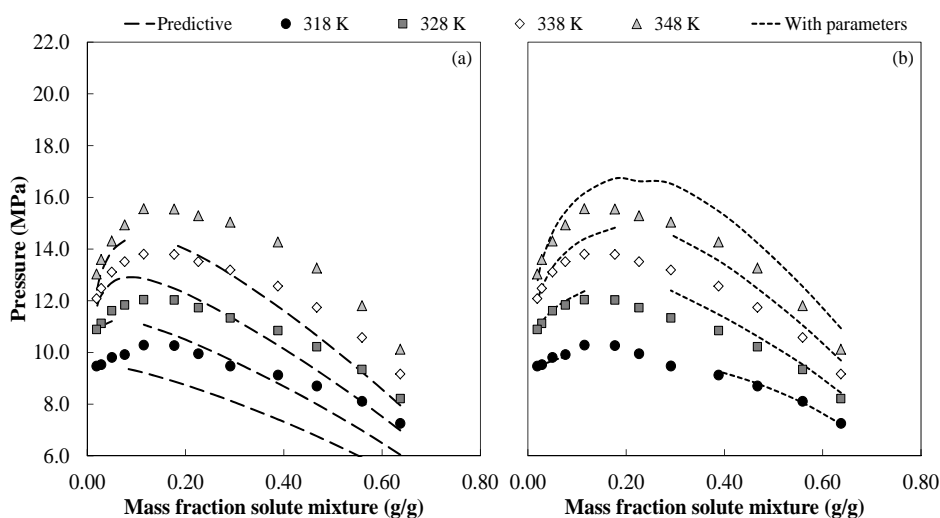|	Polar parameter	Binary solute/solvent interaction parameter with CO_2	
	η_i	$k_{a,ij}$	$k_{b,ij}$
***n*-decane**	0.0253	0.0957	0.0286
***1*-decanol**	-0.4196	0.0850	-0.0305
***3,7*-dimethyl-*1*-octanol**	0.0924	0.0774	-0.0140
***2,6*-dimethyl-*2*-octanol**	0.0214	0.0655	-0.0034

Figure 2: RK Aspen (a) prediction and (b) fit of the CO_2/(25 % by mass of each n-decane/1-decanol/3,7-dimethyl-1-octanol/2,6-dimethyl-1octanol) system at 308 K to 348 K.

Figure 2 shows that a significant improvement is obtained upon inclusion of the BIPs. While the data is not predicted with high accuracy in the mixture critical region, the fitted model (part b) does provide a good representation in the low solute mass fraction region, a region that is important in fractionation processes.

Using the developed thermodynamic model and the parameters given in Table 1, process simulation runs were conducted at conditions similar to experimental pilot plant data [7]. The process model configuration was similar to that illustrated in Figure 1 and also mimics the experimental setup. A comparison of the simulated results and experimental data is given in Table 2. The process model is thus able to provide a good rendition of the experimental results with a maximum error of no larger than 25 %, in most cases less than 15 %. These results are highly promising considering the accuracy of the experimental data. The model can thus be regarded as validated and can be used predictively provided the accuracy limit is noted.

Table 2: Comparison of Experimental and Simulated Results for the Fractionation of a feed containing 25 % by mass of each n-decane, 1-decanol, 3,7-dimethyl-1-octanol and 2.6-dimethyl-1-octanol

	Run 4		Run 5		Run 6	
	Measured	Simulated	Measured	Simulated	Measured	Simulated
Fractionation Conditions						
Number of Stages	Unknown	20	Unknown	20	Unknown	7
Temperature (K)	344.5	344.5	344.1	344.1	344.5	344.5
Pressure (MPa)	13.0	13.0	13.6	13.6	13.1	13.1
Feed Flow rate (kg/h)	0.808	0.851	0.772	0.826	0.499	0.534
Solvent flow rate (kg/h)	15.0	15.0	14.4	14.4	14.6	14.6
Bottoms						
Flow rate (kg/h)	0.372	0.403	0.236	0.240	0.142	0.122
Composition (mass%)						
***n*-decane**	7.0	8.2	5.3	5.0	5.8	5.7
***1*-decanol**	44.6	43.2	51.5	51.3	56.0	56.6
***3,7*-dimethyl-*1*-octanol**	31.2	31.8	38.4	37.5	32.7	32.8
***2,6*-dimethyl-*2*-octanol**	17.2	16.9	4.8	5.8	5.6	5.7
Extract						
Flow rate (kg/h)	0.479	0.447	0.590	0.585	0.392	0.411
Composition (mass%)						
***n*-decane**	42.0	43.8	38.8	37.3	34.8	34.3
***1*-decanol**	16.6	15.4	15.2	15.7	17.2	18.5
***3,7*-dimethyl-*1*-octanol**	16.8	15.7	17.4	16.9	19.2	20.0
***2,6*-dimethyl-*2*-octanol**	24.7	25.3	28.6	30.3	28.8	27.3

## APPLICATION TO SEPARATION OF N-DODECANE FROM A N-DODECANE/1-DECANOL/3,7-DIMETHYL-1-OCTANOL MIXTURE

The same methodology, as used for the first separation case, was applied to the n-dodecane/1-decanol/3,7-dimethyl-1-octanol separation. For the alcohols, the same polar parameters and solvent/solute BIPs were used (See Table 1). For the CO_2/n-dodecane system the parameters were determined in a similar manner and resulted in $\eta_i = 0.0096$, $k_{a,ij} = 0.0900$ and $k_{b,ij} = 0.0489$.

Using the parameters mentioned above, the fit of bubble- and dew-point data of a 20 mass % n-dodecane, 70 mass % 1-decanol and 10 mass % 3,7-dimethyl-1-octanol in CO_2 was determined. As seen in Figure 3, an acceptable prediction is obtained. Once again the fit over-predicts the mixture critical region but does provide a good representation of the low mass fraction region.

The developed thermodynamic model was then used in a process model to predict the SCF using SC CO_2 of a fed containing (by mass) 20 % n-dodecane, 70 % 1-decanol and 10 % 3,7-dimethyl-1-octanol. The composition of the feed was selected to represent a typical detergent range mixture that needs to be fractionated. The effect of temperature and pressure on the separation is shown in Figure 4. The results presented in Figure 4 show that it is definitively possible to fractionate detergent range alkanes and alcohols using SCF and that by manipulating the process operating parameters the desired separation can be achieved.
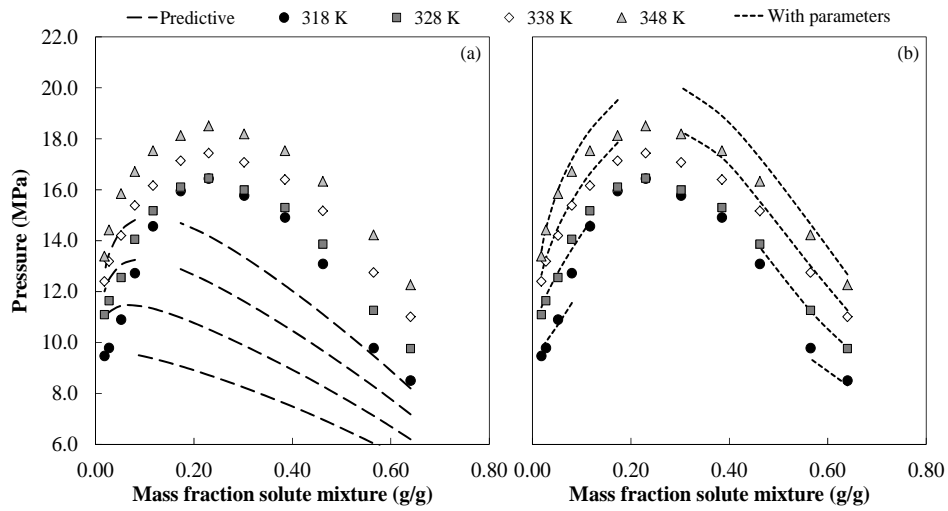
Figure 3: RK Aspen (a) prediction and (b) fit of the CO_2/(20 mass % n-dodecane; 70 mass % 1-decanol; 10 mass % 3,7-dimethyl-1-octanol) system at 308 K and 348 K.
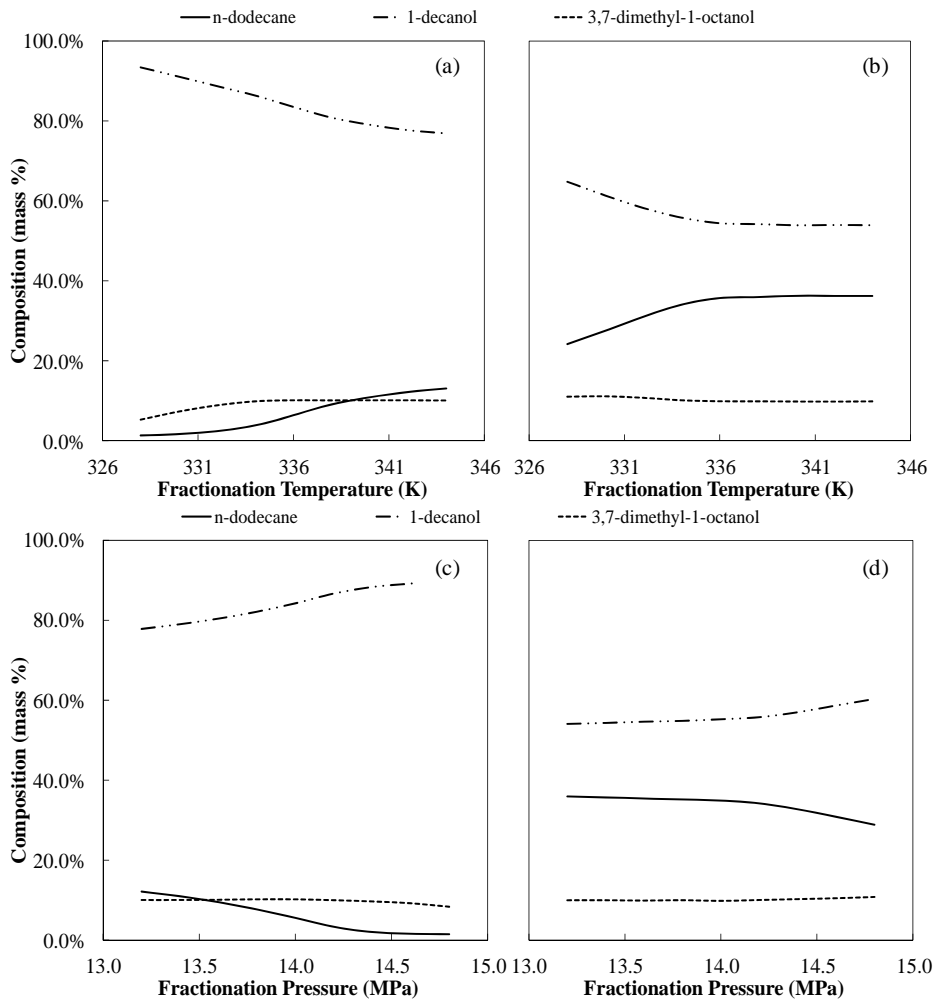
Figure 4: Effect of temperature (a and b) and pressure (c and d) on the composition of the bottoms (a and c) and extract (b and d) phases for the SC CO_2 fractionation at a solvent to feed ratio of 17.6

CONCLUSION

This paper has shown that it is possible to develop a process model for SCF. A reasonably simple thermodynamic model, with parameters fitted to a limited amount of experimental binary phase equilibrium and multicomponent bubble and dew-point data, can be used to describe the underlying thermodynamics of the system. Using standard unit operations (liquid-liquid extraction column) a process model can be built. This methodology was used to separate two different streams, both containing detergent range alkanes and alcohols, thus proving the method. A method of process modelling was thus proposed that can, in the future, be used not only to simulate a process, but to obtain an indication of the optimum operating conditions and provide a first estimation of the energy and operating costs of a SCF process.

ACKNOWLEDGEMENTS

NOMENCLATURE

BIP	Binary interaction parameter
EoS	Equation of State
$k_{a,ij}$	Binary interaction parameter
$k_{b,ij}$	Binary interaction parameter
SC	Supercritical
SCF	Supercritical fluid fractionation
η_i	Polar parameter in RK Aspen model

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