

THE DESIGN OF SUPERCRITICAL FLUID PROCESSES: AVAILABILITY AND SHORTCOMINGS OF THERMODYNAMIC AND TRANSPORT DATA

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Abstract

Supercritical fluids (SCFs) show promise in the separation of high molecular mass compounds as they are able to distinguish between the hydrocarbon backbone length and the type and position of the functional group present. In order to design such a separation process one needs to estimate the number of theoretical stages required and determine the column diameter and height, both of which require accurate models, which in turn needs to be validated against experimental data. The aim of this paper is to evaluate the availability of the phase behaviour as well as thermodynamic and transport data required for the design of a SCF separation process. Additionally, the extent to which these properties can be predicted will be investigated.

For binary systems containing CO₂ some phase behaviour data is available yet in many cases additional measurements may be required. For binary systems containing other SCFs and for ternary and multi-component systems data is considerably more scarce and additional measurements are required. Additionally, due to the complexity of the interaction present, accurate thermodynamic modelling relies on mathematically complex equations of state (EOSs) that, to date, are not widely implemented.

The thermodynamic data (enthalpy, heat of mixing, density etc.) are also required. In many cases, the density is measured together with the phase equilibria yet the other thermodynamic properties have only been measured for a few compounds highlighting a need for additional measurements. In theory, thermodynamic properties can be estimated using an EOS, yet, with possible exception of the density, EOSs generally provide an order of magnitude estimation rather than an accurate description of the thermodynamic properties.

Transport property data (viscosity, interfacial tension, diffusivity etc.) are used to determine the column height and diameter. Transport properties data is quite scarce, especially for mixtures and estimation techniques are not well developed.

Keywords

Phase equilibria, thermodynamics, transport properties, experimental, models

Introduction

In the petrochemical industry the separation of high molecular mass compounds are often difficult with traditional techniques due to their high boiling points, low vapour pressures and often very close physical properties. Supercritical fluid (SCF) separation processes is an attractive alternative method to separate high molecular mass petrochemicals. The SCF acts as a mass separation agent resulting in separation.

As in all processes that use an auxiliary medium, SCF separation processes constitute two main steps: In the first step the SCF is used to remove one, a selection or a group of compound(s) and in the second step the SCF is separated from the extracted compound(s). For high molecular mass compounds, such as those investigated in this work, the second step is usually straightforward: Separation is often achieved in a vessel through the reduction of pressure and/or a change in temperature. The focus of the technical viability, the initial design, as well as a large amount of the current questions of the later design process, is thus predominantly on the first step i.e. the extraction step.

SCF separations are analogous to liquid-liquid and other separation processes and hence the general method to design such a process is similar: A technique is required to determine the number of theoretical separation stages needed after which the hydrodynamics need to be characterised to determine the geometry of the equipment. In order to implement the above processes the following properties are required for the system to be investigate:

- Phase behaviour (for equilibrium relationships)
- Caloric thermodynamic properties (e.g. enthalpy and heat of vapourisation etc. for energy balance equations)
- Physical properties (e.g. viscosity, density, surface tension, diffusivity etc. for hydrodynamic calculations)

The aim of this paper is to evaluate the above groups of data, specifically the quantity of experimental data that has been measured and the availability and state of the art of prediction techniques. The focus will specifically be on the availability and quality of the data rather than trends observed in the data.

Traditionally carbon dioxide has been the main SCF used, however due to their improved solubility of high molecular mass compounds, low molecular mass alkanes such as ethane and propane are becoming more popular. The focus of the evaluation presented here will thus be on these three solvents with high molecular mass linear compounds containing various functional groups. However, comments made may be just as applicable to other solvents and solutes.

Phase behaviour data and its prediction

The function of phase behaviour data in the design process is threefold:

- Firstly, the phase behaviour is used to evaluate the difference in the solubility to determine if separation can be achieved at all. In addition, the phase behaviour also

provides information as to the size and location of the two phase region (i.e. the operating parameters) and will also indicate the presence, where applicable, of any three phase region.

- The phase behaviour can be used to compare the ability of various solvents to achieve the desired separation.
- The phase behaviour is used to develop and test thermodynamic models.

Of all the properties investigated in this paper, phase behaviour data is probably the most abundant. Phase behaviour is often the departure point in a feasibility study for a desired separation, hence its abundance compared to other properties. Over the years four review publications have summarised all high pressure (larger than 1 MPa) phase behaviour data in selected time frames [1-4]. n-Alkanes are by far the most studied homologous series and Table 1 summarises the available phase equilibrium data for alkanes in the various solvents.

Table 1: Number of sets of phase equilibrium data for n-alkanes (decane and larger) in selected SCFs according to publication years

	1978 – 1987 Fornari et al. [1]	1988 – 1993 Dohrn and Brunner [2]	1994 – 1999 Christov and Dohrn [3]	2000 – 2004 Dohrn et al. [4]
Binaries with carbon dioxide	17	34	33	26
Binaries with ethane	6	6	11	9
Binaries with propane	0	2	8	11
Binaries with other low molecular weight alkanes	2	14	26	2
All ternaries and multi-component systems with SC solvent and n-alkanes	9	10	13	6
TOTAL	34	56	91	54

From the data presented in Table 1 it is clear that the most data is available for carbon dioxide binaries with limited data available for ethane, propane, ternary and multi-component systems. At a first glance these numbers may indicate that a large amount of data has already been measured. However, upon careful perusal of the data itself it becomes clear that there is still a large amount of work that needs to be done. Many publications provide data only on either the liquid phase or the vapour phase and in most cases only a limited temperature and/or pressure range is investigated. In addition, for multi-component systems, the multitude of possible systems needs to be taken into account and as a result only the tip of the iceberg has been measured. Table 1 only considers n-alkanes yet long chain petrochemical often contain one or more functional end group. However, even less data exists for other functional group homologous series. Additional measurements, especially for non-carbon dioxide and for ternary and multi-component systems, and for non-alkanes, are thus required.

Theoretically phase equilibrium data can be replaced by calculated data should a thermodynamic model exist that is able to describe the system fully. Although an all-encompassing model is to date elusive, there are an abundance of equation of state (EOS) thermodynamic models that have been developed. These range from the widely known cubic EOSs, such as the Peng Robinson [5], Soave-Redlich Kwong [6] and Patel Teja [7]

EOS models to the current state of the art models such as the newest version of Cubic-Plus-Association (CPA) [8] and Crossover-Soft-SAFT [9] EOS. These models may not necessarily have been developed for petrochemical applications, but have often been developed with organic compounds in mind as they are often well characterised in terms of critical and physical properties making them ideal candidates as compounds for EOS development.

The phase behaviour of the systems required for SCF processing of high molecular mass petrochemicals are complicated by a number of issues: These systems are highly asymmetrical. One molecule is small while the other is large, more often than not an order of magnitude larger in molecular mass. In addition, accurate description of non-spherical molecules that are able to take up a number of conformations is not easy. Although not applicable to all systems, some systems contain polar groups and the interactions thereof are not easy to describe. Lastly, description of the phase behaviour near and at the (mixture) critical point is difficult due to the fact that small changes in pressure and/or temperature lead to large changes in density and fluctuation of other properties. EOSs are often not able to describe these changes accurately.

The first few generations of EOSs were cubic in volume and can thus easily be solved. Many of these cubic EOS and some of their later modifications have been incorporated into design packages such as ASPENPlus and Pro/II, and can be used in petrochemical applications. Additionally, even if these EOSs are not incorporated, due to their mathematical simplicity incorporation into commercial and even in house simulators is not such a tedious task. However, due to their intrinsic limitations, application of these models is often not very successful for SCF processing of high molecular mass compounds and mixtures often require large temperature dependent interaction parameters that can not easily be determined without fitting of experimental data.

Skjold-Jørgensen [10] developed a group contribution EOS based on four well known principles of thermodynamics: The van der Waals EOS, the NRTL activity coefficient equation, the Carnahan-Starling expression for the hard sphere term and the group contribution principle. This EOS has been widely used in the SCF separations involving natural products but application to SCF processing of high molecular weight petrochemicals as well as implementation in commercial simulators is to date elusive.

State of the art EOS, such as CPA [8] and Crossover-Soft-SAFT [9] have a much stronger fundamental basis and are thus able to predict the phase behaviour quite well, often being able to describe the system qualitatively without the use of any interaction parameters. For high molecular mass petrochemical compounds the pure component parameters can easily be regressed from the molecular structure and with the use of small, generally temperature independent, interaction parameters they are able to predict the binary phase behaviour quite well. These models do have a major disadvantage: Due to their mathematical complexity widespread application is difficult with only limited implementation in process simulators.

System specific practical models have also been developed. These models are not necessarily cubic but are accurate, mathematically more simple than state of the art models and can easily be implemented. For example, du Rand [11] developed a mathematically simple EOS based on the perturbed hard chain theory [12] that is accurate for non-polar

SCFs with heavy n alkane systems. However, these system specific models are limited in application to the systems they have been developed for and thus practical use beyond their reference systems is not recommended. Development of these models require accurate phase behaviour data and these models thus rather complement phase behaviour experiments than act totally predictively.

From the discussion above it is thus clear that a significant amount of work has been conducted on the phase behaviour in the supercritical region. However, the accurate models are rather complex and generally not implemented in process simulators. In the future there should thus be a move towards implementation of process models into these simulators and improving the general accessibility of the models to users beyond those working on thermodynamic modelling.

Caloric thermodynamic data

In order to solve the energy balances over every stage and to calculate the duties of any heat exchanger required, the relationships for the enthalpy as a function of temperature, pressure and composition is required.

The enthalpy or heat capacity (isobaric or isochoric) of supercritical systems are not studied as widely as the phase behaviour and specifically the critical region is not well documented. For SCF separations a large amount of derived thermodynamic data is available for the pure component SCF. However, for pure high molecular mass petrochemicals and for the mixtures data is scarce and often not available at all. With regard to mixtures containing a SCF and a petrochemical, a few systems have been measured. However, most of these systems contain a SCF and low molecular weight petrochemical compound. Examples include ethane – ethanol [13], ethane – acetone [13], water – iso butaric acid [14], water – methanol [15], carbon dioxide – water – ethanol [16] and carbon dioxide – n-decane [17]. Experimental measurements of binary and multi-component mixtures with high molecular mass petrochemicals are not readily available and alternative techniques need to be developed to determine these properties.

The lack of experimental data for the caloric thermodynamic properties required in the design process of SCF separation processes pose a severe challenge in the design process on both a technical as well as an economic level. Although techniques are available to estimate the required properties there is no way to verify that the data is correct. Additional measurements of these properties are thus desperately needed.

Thermodynamic caloric properties can either be estimated from empirical correlations or EOS.

Empirical correlations are usually very specific in application and require good experimental measurements for correlation of their parameters. However, predictive correlations have been developed and are usually based on the group contribution method. For example, Schwarz [18] used the group contribution technique of Ruzicka et al. [19,20] to estimate the heat capacity properties of a pure alcohol ethoxylate and then assumed ideal mixing to describe the mixture with supercritical propane. Such techniques, although useful and generally well developed at low pressures for petrochemicals, may introduce

large errors at higher pressures and are often more of an order of magnitude estimation than an accurate description. Widespread practical implementation is thus difficult, especially due to the lack of experimental data to verify the methods.

On the other hand, if a fundamental thermodynamic model is able to describe a system accurately, it can be used to determine the derived thermodynamic properties. However, the main focus of EOS models is usually to predict the correct phase behaviour while derived thermodynamic properties, such as heat capacity, are secondary. In many cases only pure component vapour pressure and liquid density data are used for the pure component parameter regression and phase equilibria data is used to fit the interaction parameter resulting in bias towards these properties. In addition, difficulties associated with the thermodynamic modelling with regard to the phase behaviour are just as relevant to the description of the derived thermodynamic properties. Generally, the more fundamental a model, the better its ability to predict the derived thermodynamic properties. The caloric properties require first and second order derivatives of the state function and thus errors in the state function are often magnified in the caloric properties. As a result of both the pure component and interaction parameter fitting procedure as well as inherent errors, many EOS models, especially those with more of an empirical background, are often not able to predict derived thermodynamic properties well.

With respect to petrochemical compounds, current state of the art EOS models are able to predict the derived thermodynamic properties qualitatively, yet some adjustment is still required with regard to quantitative prediction [21]. In addition, generally the higher the molecular mass, the larger the deviation between the qualitative prediction and the actual experimental values. A large amount of work is thus still required with regard to the estimation of derived thermodynamic properties required for the SCF processing of high molecular mass petrochemicals. The work is not limited to the high pressure region yet when improving thermodynamic model prediction of derived properties, the high pressure region should be taken into account.

Transport property data

In order to do the hydrodynamic design calculations for supercritical separation equipment a number of properties are required. Obviously, the specific properties required will be a function of the type of equipment and nature of the system. This paper focuses on petrochemical applications and therefore the required properties for SCFE (supercritical fluid extraction) in the fluid phase will be emphasized with less attention given to supercritical extraction from the solid state (which is often applied to natural products). Mixer-settler set-ups can be used, but this section will focus on packed and tray columns. Counter-current mixer-settler set-ups can be used especially when high viscosities present problems and by increasing the residence time one can ensure that equilibrium is reached in each stage – thus reducing the dependency on transport properties in the design stage. For more information on counter-current mixer-settler set-ups the reader is referred to the work of Chuang and Brunner [22]. For conventional counter-current extraction processes the measured thermodynamic phase equilibria (or the modelled) data can be used to determine the number of theoretical stages required.

The hydrodynamic design defines the column dimensions by considering especially the height equivalent to a theoretical stage (HETP), the column diameter and the efficiency. These parameters are a function of the thermodynamic properties, the transport properties and the flow conditions in the column. Schwarz and Knoetze [23] recently reviewed some of the methods and the available information for the hydrodynamic design of SCFE processes. The properties required include the mass transfer coefficient, the diffusion coefficients, the densities, viscosities and in some cases the interfacial tension. In addition where the mass transfer is limited by heat transfer consideration of the thermal conductivity is also required. The availability of accurate values for these properties is vital for the successful design of supercritical extraction processes. These properties can vary considerably and even small quantities of the dissolved solvent in the solute or solute in the solvent rich phase may influence the properties significantly.

Density

Density is the best documented transport property and the estimation of the density of co-existing phases is an integral part of the thermodynamic modelling of the co-existing phase behaviour and are usually calculated during the solution algorithm of the EOS. Densities of pure SC (supercritical) solvents are well documented and experimental density data of mixtures with SC solvents are often measured when measuring phase equilibria – but are usually a secondary result with relatively large errors. Schwarz and Knoetze [23] showed that on a composition-density plot for n-alkanes – SC solvent systems at the phase boundary the densities of the n-alkanes in low molecular mass SC alkane solvents are very similar at similar solvent reduced temperatures, while SC carbon dioxide shows a higher density. They also provide an estimation of the densities of co-existing phases: the vapour phase density is usually between 300 and 450 kg/m³ while the liquid phase density is usually between 600 and 750 kg/m³, depending on the composition and temperature. The molecular mass and the presence and position of functional groups do not influence the density of either the liquid or vapour phase significantly. Density predictions are complicated by the possibility of density inversions. For example, the carbon dioxide – n-alkane homologous series exhibits density inversions at very low n-alkane mass fractions and low temperatures [24], and one should ensure that the region of operation does not include density inversions.

Viscosity

Viscosity can be expressed as either the dynamic viscosity (kgm⁻¹s⁻¹) or the kinematic viscosity (m²s⁻¹). In the case of SC mixtures the viscosity can be significantly influenced by the addition of either a small quantity of the solvent to the solute or of the solute to the solvent. Abbott et al [21] found that as the mass fraction of solute is increased the dynamic viscosity first reduces going through a minimum and then increases. This means that a simple combinatorial rule does not suffice in describing the viscosity of mixtures in the supercritical regime. The viscosity of a number of systems with SC carbon dioxide have been measured [25, 26, 27], but experimental measurements with other SC solvents are scarce and application specific. Predictive models for viscosity are rather limited, but Kraska et al. [28] showed how an EOS could be used to estimate the viscosity if the EOS pressure prediction can be divided into an attractive and repulsive part. De Haan and de Graauw [29] used a group contribution method to estimate the viscosity.

The existing methods rely on the fitting of parameters on data, therefore no universally accepted fundamental method exists for the prediction of the viscosity of mixtures of SC fluids. Additional measurements and development of the fundamentals are required. Nwobi et al. [30] used a molecular dynamics technique to compute transfer coefficients for a number of reactive systems in the supercritical regime (mostly applicable to propulsion systems) by using Green-Kubo formulae in which a correlation function is integrated over time. These autocorrelation functions provide a powerful tool for describing the dynamics of fluids and give insight into the microscopic behaviour. They obtained realistic values for the shear viscosity (when compared to experimental results), but only tested it on systems applicable to propulsion and as such do not offer a direct solution to the prediction of the viscosity required for the design of SC separation systems.

Diffusion Coefficients

Diffusion coefficients are very important in obtaining mass transfer coefficients. Suárez et al. [31] reviewed the available diffusion coefficient data in SC fluids and diffusion coefficients have been measured for a large number of high molecular mass compounds. Subsequently diffusion coefficients have also been reported by Fu et al. [32], Yang et al. [33], Kong et al. [34] and Han et al. [35]. For systems with more than two compounds very little information is available and for these systems diffusion data will have to be measured. Škergat and Knez [36] estimated the binary diffusion coefficients with the Takahashi method (as presented by Reid et al [37]) and the external mass transfer coefficient with the Wakao and Kaquei correlation (presented by Brunner [38]). They found that the Takahashi method was not adequate at higher temperatures and emphasized the fact that data pertaining to mass transfer between SCF and solid phases are scarce.

The various methods used to predict binary diffusion coefficients were reviewed by Funazukuri et al. [39]. Methods reviewed included the Dymond free volume equation, the D/T- viscosity correlation, the polynomial Schmidt correlation and the Stokes-Einstein relationship. Apart from the Stokes-Einstein relation, they all require some kind of parameter fit, indicating that more experimental measurements are required.

Interfacial Tension

Very little information is available on the interfacial tension at supercritical conditions and reported investigations are limited to experimental measurements of selected systems with supercritical carbon dioxide as solvent. The results show that from atmospheric pressure to around the critical pressure of carbon dioxide, the interfacial tension decreases linearly after which it is independent or only slightly dependent on pressure [39-41]. The addition of the supercritical solvent at high pressure results in a dramatic decrease in interfacial tension. Low interfacial tensions are characteristic of SC processes and one of the main advantages of SCF processing. However, should values for the interfacial tension be required, experimental measurements are required.

General Comments on Transport Properties

Quite often processes are modelled with a number of equations with 4 or 5 unknown parameters and the parameters solved by simultaneous curve fitting. Although these

models resemble a fundamental model initially, the final model is more empirical in nature because of the curve-fitting. These fitted parameters are usually related to the transport properties. It is thus important to note that there is scope for additional work both with regard to the fundamental prediction of transport properties as well as experimental measurements.

Conclusions and future work

From the analysis above it is clear that in all facets there is still a large amount of work to be conducted with regard to both experimental measurements as well as development of models to predict the data. The foundation of a large amount of the work has already been conducted and as such the framework exists for future work. In addition to the measurement of the experimental data and the development of the models predicting the data, there needs to be a concerted drive towards implementation of the models into a process simulator, albeit a commercial package such as Aspen and Pro/II or into a specifically developed package.

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References

1. R.E. Fornari, P. Alessi, I. Kikic, *Fluid Phase Equilib.* 57 (1990) 1-33.
2. R. Dohrn, G. Brunner, *Fluid Phase Equilib.* 106 (1995) 213-282.
3. M. Christov, R. Dohrn, *Fluid Phase Equilib.* 202 (2002) 153-218.
4. R. Dohrn, S. Peper, J.M.S. Fonseca, *Fluid Phase Equilib.* 288 (2010) 1-54.
5. D.-Y. Peng, B.D. Robinson, *Ind. Eng. Chem. Fund.* 15 (1976) 59-64.
6. G. Soave, *Chem. Eng. Sci.* 27 (1972) 1197-1203.
7. N.C. Patel, A.S. Teja, *Chem. Eng. Sci.* 37 (1982) 463-473.
8. G.M. Kontegeorgis, M.L. Michelsen, G.K. Folas, S. Devari, N. von Solms, E.H. Stenby, *Ind. Eng. Chem. Res.* 45 (2006) 4855-4868.
9. F. Lovell, L.F. Vega, *J. Phys. Chem. B* 110 (2006) 1350-1362.
10. S. Skjold-Jørgensen, *Ind. Eng. Chem. Res.* 27 (1988) 110-118.
11. M. du Rand, *Practical Equation of State for Non-Spherical and Asymmetric Systems*, Doctoral dissertation in Chemical Engineering, University of Stellenbosch, South Africa (2004).
12. M.D. Donohue, J.M. Prausnitz, *AIChE Journal* 24 (1978) 849-861.
13. T. Mu, X. Zhang, B. Han, H. Li, J. Liu, W. Wu, J. Chen, J. Du, *Fluid Phase Equilib.* 214 (2003) 53-65.
14. N. Hadden, M. Bouanz, *J. Mol. Fluids* 130 (2007) 11-14.
15. N.G. Polihrondrini, I.M. Abdulagatov, G.V. Stepanov, R.G. Batyrova, *Fluid Phase Equilib.* 252 (2007) 33-46.

16. E. Pérez, Y. Sánchez-Vicente, A. Cabañas, C. Pando, J.A.R. Renuncio, *J. Supercrit. Fluids*, 36 (2005) 23-30.
17. N.G. Polihrondrini, R.G. Batyrova, I.M. Abdulagatov, J.W. Magee, G.V. Stephanov, *J. Supercrit. Fluids*, 33 (2005) 209-222.
18. C.E. Schwarz, *The processing of wax and wax additives with supercritical fluids*, Doctoral dissertation in Chemical Engineering, University of Stellenbosch, South Africa (2005).
19. V. Ruzicka, E.S. Domalski, *J. Phys. Chem. Ref. Data* 22 (1993) 597-618.
20. V. Ruzicka, E.S. Domalski, *J. Phys. Chem. Ref. Data* 22 (1993) 619-665.
21. A.P. Abbott, E.G. Hope, D.J. Palmer, *J. Phys. Chem. B* 111 (2007) 8114-8118.
22. M. Chuang, G. Brunner, *J. Supercrit. Fluids*, 37 (2006) 151-156.
23. C.E. Schwarz, J.H. Knoetze, In: Belinsky M.R. (Ed), *Supercritical Fluids*, Nova Science Publishers (2009), Ch 5.
24. T. Charoensombut-Amon, R.J. Martin, R. Kobayashi, *Fluid Phase Equilib.*, 31 (1986) 89-104.
25. R. Sih, F. Dehghani, N.R. Foster, *J. Supercrit. Fluids*, 41 (2007) 148-157.
26. K.D. Tilly, N.R. Foster, S.J. Macnaughton, D.L. Tomasko, *Ind. Eng. Chem. Res.*, 33 (1994) 681-688.
27. P. Kashulines, S.S.H. Rizvil, P. Harriott, J.A. Zollweg, *J. Am. Oil Chem. Soc.*, 68 (1991) 912-921.
28. T. Kraska, S.E. Quiñones-Cisneros, U.K. Deiters, *J. Supercrit. Fluids*, 42 (2007) 212-218.
29. A.B. de Haan, J. de Graauw, *Ind. Eng. Chem. Res.*, 30 (1991) 2463-2470.
30. O.C. Nwobi, L.N. Long, M.M. Micci, *AAIA Paper*, (1997), 97-0598.
31. J.J. Suárez, I. Medina, J.L. Bueno, *Fluid Phase Equilib.*, 153 (1998) 167-212.
32. H. Fu, L.A.F. Coelho, M.A. Matthews, *J. Supercrit. Fluids*, 18 (2000) 141-155.
33. X.N. Yang, L.A.F. Coelho, M.A. Matthews, *Ind. Eng. Chem. Res.*, 39 (2000) 3059-3068.
34. C.Y. Kong, S. Kagei, T. Funazukuri, Infinite-dilution binary diffusion coefficients for unsaturated fatty acids and their derivatives in supercritical carbon dioxide, 6th *International Symposium on Supercritical Fluids*, Versailles, France, 2003.
35. Y. Han, Y. Yang, P. Wu, *J. Chem. Eng. Data*, 52 (2007) 555-559.
36. M. Škergat, Z Knez, *Computers and Chemical Engineering* 25 (2001) 879-886.
37. R.C. Reid, J.M. Prausnitz, B.E. Poling, *The Properties of Gases and Liquids*, McGraw-Hill, New York. Fourth Edition (1987) 587.
38. G Brunner, *Ber Bunsergo. Phys Chemistry* 88 (1984) 887-891.
39. T. Funazukuri, C.Y. Kong, S. Kagei, *J. Supercrit. Fluids*, 38 (2006) 201-210.
40. B-SChun, G.T. Wilkinson, *Ind. Eng. Chem. Res.*, 34 (1995) 4371-4377.
41. O. Boutin, E. Badens, G. Charbit, *Measurement of interfacial tension and investigation of liquid dispersion in supercritical media* 6th *International Symposium on Supercritical Fluids*, Versailles, France, (2003).