

Phase equilibria with supercritical components

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Abstract - Supercritical fluid extraction as an attractive separation process requires the quantitative thermodynamic description for reliable design of extraction units. Both experimental data and prediction or description procedures are necessary. Recent developments in this field are surveyed. Generally, while experimental techniques are being continuously developed, no significant evolution takes place for "software" based usually on equations of state. Needs and subsequent outlooks are outlined. A survey of investigations conducted at the ICPF concerning supercritical fluid extraction is presented.

INTRODUCTION

Knowledge of phase equilibrium in systems containing supercritical fluids is prerequisite to practical application of separation process called supercritical fluid extraction. This kind of extraction is nothing more than regular extraction which is carried out at superambient conditions corresponding approximately to the upper critical region of the solvent, particularly at temperatures and pressures higher than its critical ones.

Classical separation processes based on fluid phase equilibria are supported by abundant theoretical and experimental background. There are data and computation models available as well as reliable prediction methods; there are no principal problems for almost any case. Similarly, the practical realization of supercritical fluid extraction requires the same support and tools. However, information resources are much more limited compared with the potentiality of those available for "traditional" phase equilibria.

There is a lot of space for new investigations of this separation procedure that emerged for practical use only recently. Therefore, in the global view all relevant studies seem to be chaotic and heterogeneous. Investigations are not aimed at any systematic research but often at a solution to a special problem, or at experiments that are easy. However, two main trends can be recognized: (i) solvent and conditions screening and (ii) thermodynamic description. The former concerns the rapid qualitative selection of solvent and subsequently the effectiveness of the process, while the latter provides quantitative relations required by designers. Both paths should converge to reliable prediction of phase equilibria.

Let us review unavoidable steps to any scientific advancement.

1. Collection of information
2. Creation of hypothesis and model
3. Experimental verification
4. Formulation of theory

A new quality will appear usually in connection with the last step and the cycle is restarted again.

In the case of supercritical fluid extraction, this scheme must be separately applied to both screening and thermodynamic description. As for the screening, the collection of information was initiated by the discovery that the solubility of liquid (or solid) compounds in compressed gases increases significantly in a certain high pressure region. Such a diverse behavior was obviously attributed to the distinct behavior of matter at its critical conditions. The experimental verification of this assumption was easily proved and exploited in the theory of critical behavior of (diluted) solutions. Some regularities could be found for observed "irregularities", which are affected by the nature of solvent, providing a direction for solvent choice at the end.

The quantitative thermodynamic description is based predominantly on equations of state. The development of equations of state up to the contemporary state-of-the-art clearly illustrates the four steps mentioned above: it can be traced from simple P-V-T measurements, formulation of basic principles, their verification on effectively selected systems, which finally lead to a definitive form of equation of state. Then, the cycle has started again dealing with the form of mixing rules, effect of interaction parameters, etc., in order to find the most general model. At present, these investigations still remain around step 2.

Summarizing all information applicable to supercritical fluid extraction, the following items are now available:

- data on solubility in compressed gases;
- data on phase (gas-liquid) equilibrium;
- data on applications; and
- methods of quantitative thermodynamic description.

The further needs can be listed as it follows:

- additional data on phase equilibria (particularly those aimed at filling the gaps in the data base) necessary for the development of prediction models (e.g. extrapolation to similar systems);
- development of better thermodynamic descriptions via equations of state;
- development of group contribution models as the easiest way to phase behavior estimation; and
- enlargement of validity ranges for the existing models.

AVAILABLE INFORMATION

Phase equilibria

The experimental determination of phase equilibria usually requires very complicated and often expensive equipment. In addition, the experiments are time consuming and are not easy, and skill of the operator is essential. Even though these attributes do not favor the struggle for experimental data, there are still enthusiasts doing such a job.

The systems investigated can be divided roughly according to the purpose of their utilization in two groups, namely (i) model systems, and (ii) practical (applied) systems.

A *model* system is usually a mixture consisting of not too many components which are usually simple and well defined compounds. The data on such a system can be applied both to justify a (new) thermodynamic model and to verify correct functioning of (new) experimental equipment. Moreover, since physicochemical properties of simple compounds are usually well known, no problems (e.g. resulting from missing pure component data) could be expected during calculation or during any quantitative thermodynamic processing. The experiment is designed so as to obtain the data supporting the proposed thermodynamic model.

A *practical* system is the system of special interest. Provided that supercritical fluid extraction was found as the most advantageous separation process for that particular case, and consequently having available initial composition and output required, then the best operating conditions must be determined. The experiment must be aimed at this purpose.

Comparing both systems, it can be concluded that model systems are selected to justify a given model, while practical systems are given and the model must be selected. In some cases it is difficult to distinguish which system is a model or an applied one. The statistics show that the ratio of model/practical system is equal to one, approximately.

Even though supercritical fluid extraction is a hot topic, almost complete information can be found in a few basic journals such as e.g. *Journal of Chemical & Engineering Data*, *Fluid Phase Equilibria*, and *Journal of Supercritical Fluids*. It is to be pointed out that the literature survey presented in this paper covers the last three years only in order to obtain a very fresh outline. The recent surveys can often be found in irregularly published articles and reviews (e.g. ref. 33). Due to this short period, the present survey does not incorporate the whole evolution. However, it may indicate the fields deserving attention.

As for the particular phase equilibrium, it is recommended to use any bibliographic compilation where the reference to direct experimental data can be found. From the practical point of view, as a supercritical solvent CO_2 is exploited almost solely. The reason for its use is the economical and environmental safety. Light hydrocarbons (ethane, ethylene, propane, neopentane) are used very scarcely as alternative extraction fluids. Nevertheless, some types of model systems are investigated repeatedly. Among them are water and/or alcohol, phenolic compounds, higher fatty acids, aromatics, and different hydrocarbons. The studies of practical systems are aimed at more special cases in order to obtain more precise data on systems of promising industrial utilization. They concern the natural-like compounds and also the not well defined continuous fractions of oil, bitumen, flavorings, and other specialties.

Applications

The main advantage of supercritical fluid extraction consists in separation of nonvolatile components that possibly decompose before reaching their boiling point. Therefore, the important area of use is directed to food and beverage industries including concentration of natural products or flavorings. Among others it concerns namely the oil refining processes, the recovery of carboxylic acids, the degreasing of various products, the concentrating of aqueous alcoholic solutions or separating of alcohols from fermentation. Besides the separation of pigments, alkaloids, fragrances, essential oils, and other specialties from natural raw materials (seeds, plants, algae), there is a continuously growing group of environmental applications such as detoxication of soil, removal of phenolic compounds from wastewater or elimination of dioxine from edible oil, etc.

Supercritical fluid extraction serves not only as a separation process but it is used also in many indirect applications. For instance, one can mention the production of aerogels, and of well defined particles, controlled aggregation, binder removal from ceramic materials, extraction of adsorbed component from solid carrier, thermolysis of polymer under supercritical conditions, preparation of mesophase pitch for carbon fibres production, etc. Special attention is paid to biocatalytic (enzymatic) reactions carried out in supercritical fluid environments.

Thermodynamic description of phase equilibria

In the vast majority of cases, equations of state (EOS) are used as the starting (empirical) information which must be set in (exact) thermodynamic relations. In the following paragraph the very recent achievements are summarized. It must be said beforehand that the summary takes into account only investigations directly related to supercritical fluid extraction. Besides, there are plenty of other studies concerning EOS themselves or related to other types of phase equilibria which cannot be discussed here.

A generalized procedure using the Peng - Robinson (PR) EOS was proposed by Trebble et al. (ref. 1) to predict two- and three-phase equilibria in systems containing dense CO_2 with either well-defined hydrocarbon or continuous oil component. However, the PR EOS with one adjustable parameter is not able to reproduce the phase behavior of systems with large differences in molecular size of components. In ref. 2 serious limitations were found for the system CO_2 - essential oils (vanillin, phenylacetic acid). Poor correlation was also obtained for solubility of penicillin in CO_2 perhaps due to unknown pure compound properties (ref. 3). In many cases the results are very good e.g. for CO_2 with naphthalene, quinolin, methylnaphthalene (ref. 4), or for CO_2 - ethylbenzene/styrene systems (ref. 5). Phase equilibrium in the decaline - decane - CO_2 system is described quantitatively and PR EOS provides good prediction of molar volumes. Nevertheless, scaling effects in the near critical region and inadequate mixing rules affect the result (ref. 6). Also for mixed solvents (CO_2 + ethane, CO_2 + propane) the solubility of naphthalene and description of three-phase behavior was reasonably good (ref. 7). Solubility of carotene in CO_2 -containing entrainer (such as ethanol, methanol or methyl chloride) is well predicted, too (ref. 8). The PR EOS in combination with UNIQUAC provides a better description compared to the truncated virial EOS (ref. 9). Augmented PR EOS (ref. 10) represents pure fluid state behavior around the critical point. Even though it was developed for pure compounds, special mixing "external" rules were proposed with promising results. Generally, the increased attention paid to the PR EOS is due to relatively good flexibility despite its simplicity.

The Redlich - Kwong (RK) EOS and many of its modifications are widely applied as very flexible correlations. For instance, by using the nonquadratic Panagiotopoulos - Reid mixing rules (two interaction

parameters) the systems CO₂ - fatty acids or esters can be well described (ref. 11). The Peneloux modification with properly adjusted parameters under reasonable assumptions describes very well solubility of solids in supercritical solvent (ref. 12). The RK-Soave EOS was successfully used for the bitumen - CO₂ system (ref. 13) or for the solubility of phenol and catechol in dense CO₂ (ref. 14).

The Patel - Teja EOS provides a good description of solubility of solids in supercritical fluids using the van der Waals type mixing rules with two interaction parameters. A comparison with the Huron - Vidal mixing rules (in combination with UNIFAC group contributions) favors the latter. The method was applied to complex natural and biological compounds with good results (ref. 16). Ikawa et al. (ref. 17) have used nonrandom mixing rules to describe the water - ethanol - CO₂ system. A slightly modified EOS by Martin, containing three interaction parameters in classical mixing rules was found reliable for expressing CO₂ solubility in heavy oils and bitumen (ref. 5).

The simplified perturbed hard chain theory (SPHCT) was applied to the CO₂ - hydrocarbon systems (with one interaction parameter evaluated and listed for 70 systems) with very satisfactory results (ref. 18). This was also confirmed by finding its superiority over the PR EOS for the tetratriacontane - propane system (ref. 19) and for CO₂ - bitumen solubility (ref. 20). The perturbed dipolar hard sphere EOS was used in ref. 21 for the description of the ethanol - water - CO₂ system.

Using simple mixing rules with one parameter the Carnahan - Starling - De Santis - RK (CSDRK) EOS is capable of modeling the phase behavior both qualitatively and quantitatively in systems containing very polar components such as phenol or water (ref. 28). The results are better than those obtained with use of the PR EOS. The lattice fluid EOS is successful for polymer - supercritical fluid systems in a wide range of conditions and chain lengths of the molecule (ref. 22). A similar model with one interaction parameter was used in ref. 23 to correlate the solubility of a number of various solids in supercritical solvent.

The validity of statistical associating fluid theory (SAFT) EOS was extended from simple molecules up to molar weights of 100,000. This is a physically sound EOS requiring three nonspecific parameters: segment number, segment volume, and segment-segment interaction energy. The segment parameters were originally listed only for pure compounds in ref. 25 and further were extended to mixtures (ref. 26) where two types of mixing rules are used: (i) Van der Waals one fluid approximation (conformal solution theory), and (ii) volume fraction approximation (similar to GC EOS). The second rules are better in the critical region. Since this EOS has been developed explicitly to account for molecular size, shape (chain length), and association parameter, it suits especially well the description of systems with polymers (ethylene - propylene copolymer in supercritical ethylene or propylene) (ref. 27). Prediction of phase equilibrium in the CO₂ - bitumen system is very accurate (ref. 24).

The modified Huron - Vidal 2nd order (MHV2) EOS belongs to the class of group-contribution (GC) EOS. It is the RKS EOS matched with the excess Gibbs free energy which, moreover, can be easily expressed using the UNIFAC method (ref. 29). It describes well the water systems with various entrainers such as alcohols, acetone or hydrocarbons. Since the GC EOS does not work well for systems containing water, Zabaloy et al. (ref. 30) have modified its association term according to the SAFT EOS to cover the association effects due to hydrogen bonds. This was applied successfully to model systems related to the process of alcohol dehydration.

The semiempirical methods are based mainly on equations in which concentration or enhancement factor is correlated with the density of supercritical solvent. These methods are frequently used to represent the solubility of solid compounds with complex molecule e.g. penicillin, flavorings, theobromine, caffeine, terpenes, etc. Among others the Chrastil equation (ref. 31) or Krichevsky - Kasarnovsky relation (ref. 32) should be mentioned.

In conclusion it must be pointed out that all cubic EOS give comparable results. However, they are not able to describe systems containing compounds with higher molecular weight. Besides this, problems arise from the lack of physical properties for such structurally complex and heavy components. From this point of view, equations having sound theoretical basis could significantly help to solve these difficulties.

ACTIVITIES AT THE INSTITUTE OF CHEMICAL PROCESS FUNDAMENTALS

The investigations of high pressure vapor-liquid equilibria at the ICPF have been carried out for more than twenty years. The long-term attention has been paid to the near critical region of the most volatile component which finally resulted in the studies of supercritical fluid extraction. These studies started with model systems containing CO₂ as a supercritical solvent with alkane and/or alkene, followed with systems with natural-like compounds such as pinene (ref. 34), p-cymene (ref. 35), etc. For the measurements, a static windowed cell is used which was designed for pressures up to 10 MPa and temperatures up to 370 K with a simple capillary sampling technique (ref. 36). The measured data are isothermal and complete: i.e. the phase compositions, pressure, and temperature are determined.

The research is also aimed towards more practical needs, but some basic physicochemical data are obtained, too. For this purpose the equipment has been designed suitable for supercritical fluid extraction of different raw materials. However, solubility of solids in compressed gas can be also determined. The equipment operates at pressures up to 30 MPa on the basis of a transpiration flow method. The solubilities of solid terpenes such as menthol or cis-verbenol in CO₂ were measured (ref. 37). The data are "incomplete" since the composition of liquid phase cannot be determined. The exact thermodynamic data obtained using both the above mentioned studies are immediately applicable to check prediction methods or to fill up gaps in phase equilibrium data bases.

In addition, theoretical thermodynamic studies are being carried out concerning the development of equations of state based on statistical thermodynamic principles. The computation and prediction methods lead finally to the preparation of very good software: a reliable general procedure using a maximum likelihood method for evaluation of mixing rule interaction parameters can be pointed out as an example.

Other investigations closely related to these thermodynamic activities also deserve mentioning. These studies deal with kinetics of extraction as a function of temperature, pressure and flow rate of dense CO₂ and furthermore on mechanical preparation of raw material for extraction (ref. 38). The supercritical fluid extractions of carvone and limonene from caraway seed, oil from grape seed, carotenoids and lipids from algae, and menthol from mint illustrate a range of activities. The determination of diffusion coefficients and subsequently of mass transfer and of the mechanism of extraction are chemical engineering problems. However, there are a lot of points of contact with the thermodynamics of phase equilibrium.

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