Ternary phase equilibrium data of caffeine-water-scCO2 and consequences for supercritical decaffeination processes

Arne Pietsch

Luebeck University of Applied Sciences, Luebeck, Germany; pietsch.arne@fh-luebeck.de

ABSTRACT

The ternary phase equilibrium caffeine-supercritical CO2-water is of importance in large scale industrial high-pressure processes. Equilibrium data of this system were determined with a static-analytic method for a wide range of caffeine concentrations. The results at 28MPa show, that the partition coefficient for the coexisting two phases is not constant for higher caffeine concentrations. Literature data are in the same order of magnitude but had not clarified the influence of the system temperature so far. Results at 28 MPa show, that the partition coefficient (supercritical/aqueous phases) declines in the temperature range 313–413K. The obtained phase equilibrium data is discussed in the context with related industrial processes.

INTRODUCTION

One of the established large-scale process with supercritical fluids in the food sector is the decaffeination of and tea and coffee [1-6]. In the case of coffee, unroasted green coffee beans are extracted with supercritical carbon dioxide (scCO2). One option to regenerate and recirculate the caffeine-loaded CO_2 either from tea or coffee extraction is a counter-current washtower with water [4]. Other high-pressure decaffeination process-concepts attempt to decaffeinate liquid coffee extracts with supercritical CO_2 [7,8,29]. All of these processes are significantly influenced by the ternary - or even quasi-ternary - phase equilibrium caffeine-water-CO2. Little consistent data has been published about this industrially relevant ternary system so far.

Caffeine is an active ingredient in coffee and black and green teas. Although caffeine is commonly appreciated for its stimulating and awakening effect there is a non-negligible percentage of consumers which wants to refrain from caffeine. The annual production of decaffeinated coffee in Europe amounted to 234,000 metric tons in 2016. Typical caffeine content in coffee (green unroasted beans) varies significantly from batch to batch. Mean values are around 1.1 wt% for the species Arabica and 2.2 wt% for Robusta. Caffeine content in tea varies also, typical values of black tea are 2.2-2.8 wt%. The maximum caffeine content for decaffeinated products is regulated in national laws. For coffee the European and US regulations restrict decaffeinated coffee beans to max 0.1wt%db and tea to max 0.4et%db. The chemical structure of this intensively researched chemical substance with the IUPAC name 1,3,7-trimethylpurine-2,6-dione is shown in Fig.1. Caffeine is a white powder at standard conditions and exhibits in pure state two different crystalline forms plus a hydrate in presence of water (Fig.1). Various processes for the decaffeination of tea and coffee have been proposed

and realized. The early industrial processes used a very wide variety of solvents. All of them require complex technical installations and therefore decaffeination is today performed on an industrial scale with high investment costs. There is a clear trend towards large-scale installations, several factories with annual capacities below 5000 t have been shut down in the last decade. Solvents in use today are water, ethyl acetate, dichloromethane and compressed carbon dioxide. Naturally all processes have their specific advantages and limitations from which especially product quality, yield and costs are crucial. A description of today's decaffeination processes with respect to coffee was published recently[9].

Figure 1. Chemical structure of caffeine (left) and caffeine crystals (middle). Coffee decaffeination plant with scCO2: water wash tower during construction; with courtesy NATEX Prozesstechnik GesmbH, Austria

High pressure CO_2 is used since the pioneering work of Zosel [1] in the 1980ies. Today two concepts with CO_2 are in use: either compressed liquid CO_2 [10] or supercritical CO_2 (scCO2). Typical extraction parameters are in the range of 20-30 MPa and 60-120°C. Process times are long [2]. The feed materials are natural products and therefore there is always some variation in process performance. A robust online monitoring technology is not realized so far and therefore proof of sufficient decaffeination is provided afterwards by chemical analysis of the product. Despite a current trend to consider significantly higher pressures for new CO2 extraction processes no data on decaffeination performance at higher pressures has been reported so far. Reasons are possibly on one hand that extraction performance is not only limited by equilibrium data but also significantly by kinetic effects (intra-bean diffusion) [10] and on the other that selectivity regarding aroma components or precursors has to be observed.

The binary phase equilibrium caffeine - scCO$_2$ has been investigated by several researchers in the past, Fig. 2 shows data from Johannsen[11]. Several other authors have published binary
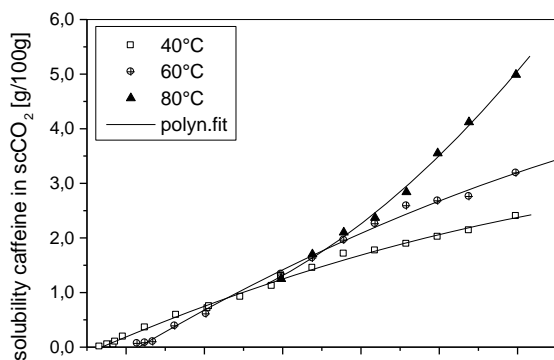

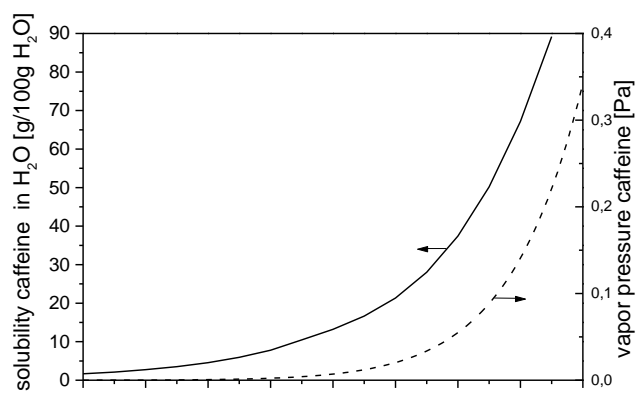**Figure 2.** Solubility of caffeine in scCO2, data from Johannsen & Brunner [11]

Figure 3. Solubility of caffeine in water and vapor pressure, data [12], app. pressure extrapolated for temp. below 80°C

solubility data, most of them with slightly lower values. For a compilation and discussion see the same [11]. Investigations with added liquid organic co-solvents like methanol or isopropanol show generally a significant increase of the caffeine solubility in the supercritical phase [11,13] but have not found industrial application so far. With increasing pressure the density of CO_2 increases and subsequently solvent power for caffeine. Consequently pressures above 20 MPa are applied in industrial processes. The temperature influence is pressure dependent: below the so-called cross-over pressure (range here 17-22 MPa) higher solvent density at lower temperature dominates solubility while above the cross over pressure the effect of increasing caffeine vapor-pressure (data see Fig. 3) overrides the impact of density decrease with rising temperature. Industrial processes are enhanced by humidification of the feed material and the solvent CO_2. Three factors are stated in the literature for the enhancing effect: first some authors measured, that caffeine solubility increases in wet CO_2 [14,15], second caffeine diffuses faster in a wet and therefore swollen feed material matrix[2] and lastly the caffeine needs to be freed from a caffeine-chlorogenic acid complex[4,24]. In this context it should also be mentioned, that experimental determination of caffeine solubility in scCO2 using coffee beans rather than neat caffeine have shown significantly reduced values compared to the pure binary systems[4]. The same effect was stated recently for tea leaves although the used dynamic method does not seem to be appropriate[16]. However, in both processes CO_2 extracts the caffeine from the feed material (tea or coffee) and needs to be regenerated before recycling to the extractor. Regeneration is possible either with pressure reduction, or with an isobaric process cycle using adsorption (usually activated carbon) or absorption (usually a water wash column). A comparison of these concepts with experimental lab-data is published[17]. Other concepts like high-pressure membrane separation[18], mixed bed of feed and adsorbent[19], use of co-solvents and de-eintrainment[20] and mixer-settler systems [21] have not found industrial realization so far. The main stated advantages of a water wash tower - a scrubber – are a better selectivity for caffeine, easier caffeine recovery and an energetic beneficial isobaric cycle process.

The basic flow sheet of a wash-tower process as proposed in an early patent from Zosel and realized in industrial tea and coffee decaffeination plants[2] is shown in Fig.4. The caffeine loaded CO_2 enters a high-pressure column at the bottom and is contacted with water in a counter-current mode. Packed columns are generally preferred for processes with compressed gases and at typical process parameters the existing density gradient between scCO2 and an aqueous phase is sufficient for an acceptable flow behavior. A further extension of this process to concentrate/recycle the aqueous caffeine solution is possible with reverse osmosis [27,28].
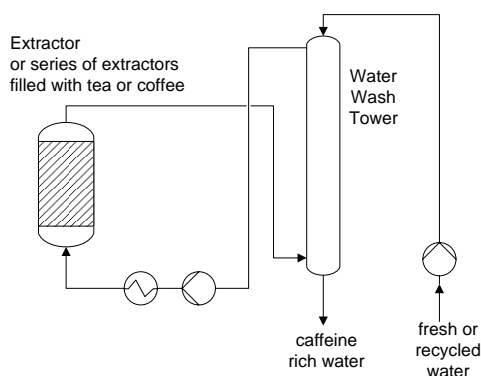
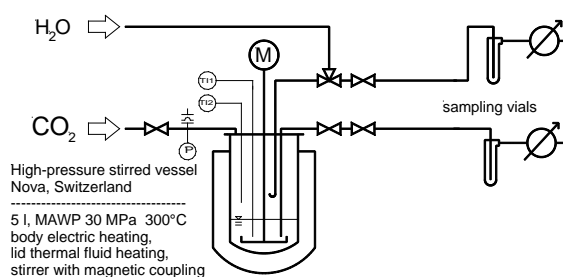

Figure 4. extraction process with wash column

Figure 5. flow sheet equilibrium apparatus

MATERIALS AND METHODS

Ternary phase equilibrium data caffeine-scCO2-water were determined with a static-analytic method. A high-pressure stirred tank (NOVA, Switzerland) of 5L and MAWP 30 MPa at 300°C was equipped with two sampling ports (see Fig. 5). The vessel was thoroughly cleaned, preheated and partly filled with an aqueous caffeine or a coffee solution. Subsequently the vessel and all valves were closed and Carbon Dioxide fed to the vessel with a high-pressure diaphragm pump. The system was de-aerated by venting down to atmospheric pressure and refilling several times. After that temperature and pressure were adjusted and sufficient contact time passed to reach phase equilibrium. Vigorous stirring accelerated the process and to establish homogeneous conditions throughout the vessel volume. Stirring was then terminated and phase separation took place. The necessary stirring and settling times were determined in preliminary tests. The caffeine content of the CO2-rich and the aqueous phase were determined by sampling both phases. In order to minimize influence on the system parameters, samples of the CO2-rich phase were pulled first. A very small quantity of the CO2 phase passed a three-way valve and bubbled in expanded state through a glass trap vial previously filled with water. CO2 flow was controlled with a needle valve and visual observation of the bubbling in the trap vial. Total CO2 gas flow was recorded with drum gas meter (Ritter, Germany). Once the required amount of the CO2-rich phase had been let out, the three way valve was switched to shut-off the vessel and open a water supply. Possibly precipitated caffeine was washed with water into the trap vial. Mass of the collected water phase, its caffeine content (measured via UV-VIS at 273nm) and the reading from the gas meter allowed the determination of the caffeine content in the CO2-rich phase. First draw was discarded always. The tiny sampling tubing (1/16") as well as the large equilibrium vessel in relation to the sample quantity allowed multiple measurements without significant pressure loss of the system. Finally samples of the aqueous phase were obtained in a similar way but without the necessity for water rinsing. Pure caffeine was obtained from Merck, Germany, the used water was of demineralized lab quality (conductivity < 1µS) and carbon dioxide of a purity >99.95 vol%. For tests with coffee constituents commercially available instant coffee powder (spray dried) with a caffeine content of 3.2% was used. Caffeine content in clean water samples was determined photometrically (UV extinction at 273nm, Shimadzu UV120-02, 10mm glass cuvette) and in coffee solutions with isocratic HPLC (pump Perkin Elmer 250, 11.5% acetonitrile, 88.5% H_2O; column Superspher 100 RP18 125+4; 0.8 ml/min; detection at 272 nm Waters M480).

RESULTS

Obtained data given as loadings X (aqueous phase) and Y (CO_2-rich phase) in ppm (mg caffeine/kg CO2 or water) and depicted in Fig.6. Polynomic fits are added for illustrating purposes only. The mutual miscibility of the two phases has not been investigated by the later on quoted authors. In isobaric cycle processes both phases will be saturated with the other fluid and therefore determination of caffeine loadings is the main focus. Not surprisingly caffeine concentration in the CO2-rich phase is affected by the concentration in the water phase. It shall be noted, that these values are much lower than the solubility in pure CO2 (binary equilibrium, Fig.2). Or in other words, binary solubility data overestimate the caffeine content in the supercritical phase by roughly one order of magnitude (in the technical relevant data range). Since caffeine is highly water soluble at elevated temperatures (Fig.3) this result is comprehensible and in accordance with literature data [17,22,23].

The partition coefficient K of caffeine between the coexisting two phases is defined as the relationship of the loadings Y/X (Fig.9). Determined values of the investigated system are significantly below unity (0.02-0.08). A nearly linear relationship between Y and X leading to a constant partition coefficient was can be used for systems with caffeine loadings in the CO_2-rich phase up to ~100 ppm or the aqueous phase up to ~ 1000 ppm (see Fig.6 left). For higher loadings though a non-negligible influence of caffeine loadings in the system was found (see Fig.6 right).
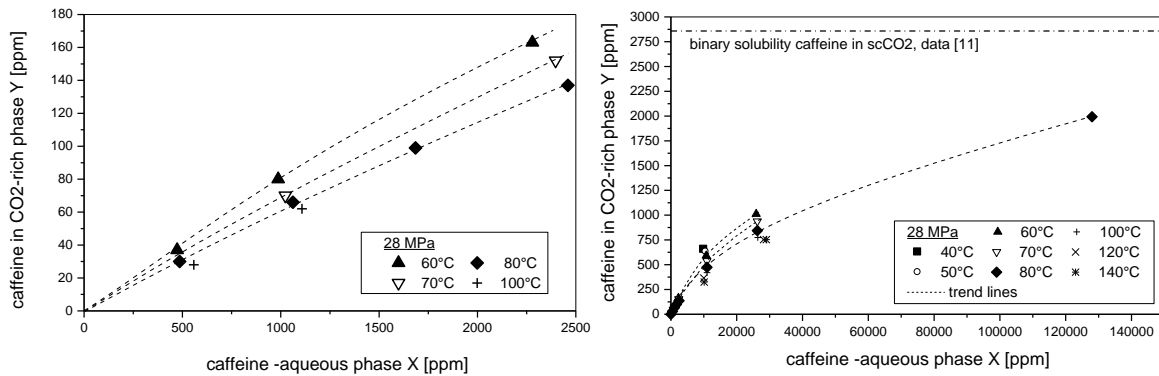

Figure 6. Ternary data caffeine in $scCO_2$-H2O, influence of caffeine content.
left: lower CO_2 loadings, right: higher loadings

A Gibb´s triangular diagram is depicted in Fig.7. The left part of the bimodal curve is extremely close to 100% CO_2 and is not recognizable in this plot. On the right side the bimodal shows a nearly constant mass fraction of CO_2, the slight tilt against the right edge of the triangle is due to the increasing caffeine fraction. The experimental determination of the CO_2 concentration in the H_2O-rich phase did not show a significant influence of caffeine: the mean concentration was 0.0569 $gCO_2/(gH_2O+gCO_2)$ with a SD of 0.24%. This value corresponds well with interpolated literature data of 0.565. The phase diagram is not completely explored yet, some speculative lines are shown.
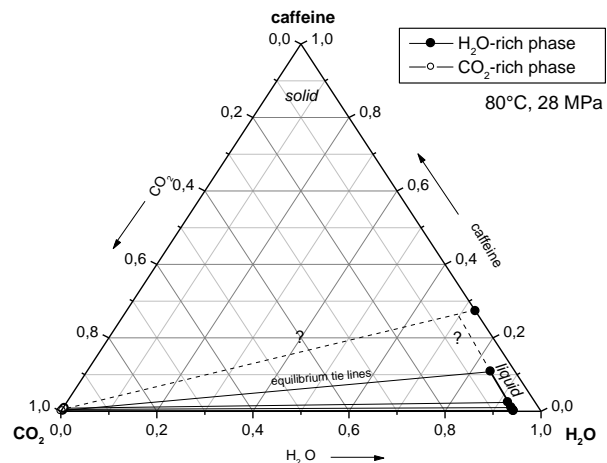

Figure 7. Gibb´s triangular diagram
CO_2 – water - caffeine

Not finally known was so far the temperature-influence on the partition coefficient in the technical important pressure range around 30 MPa (see Fig.8). Brudi [22] found no significant temperature influence and Birtigh et al. [17] stated comprehensibly that the partition coefficient decreases with increasing temperature although the presented data was not overall consistent. n order to investigate the impact of further components, some equilibrium data with added coffee solubles and isopropanol were measured. Repeatability was poor (± 8%) probably due to foaming problems in the equilibrium vessel and the data in Tab.2 is shown to illustrate qualitative trends only. But surely it can be stated that coffee solubles decrease the partition

coefficient significantly. Addition of 2% isopropanol as modifier increases the partition coefficient but not beyond values of the purely ternary system.
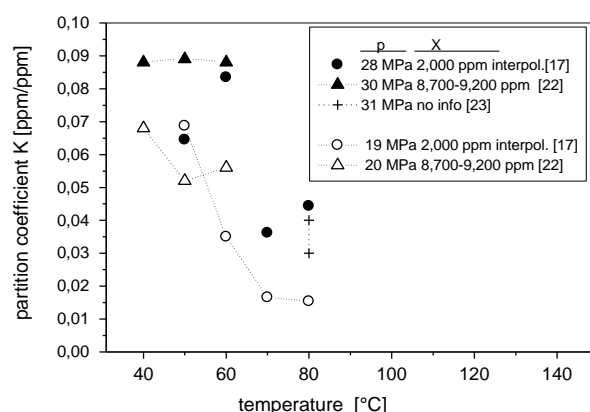
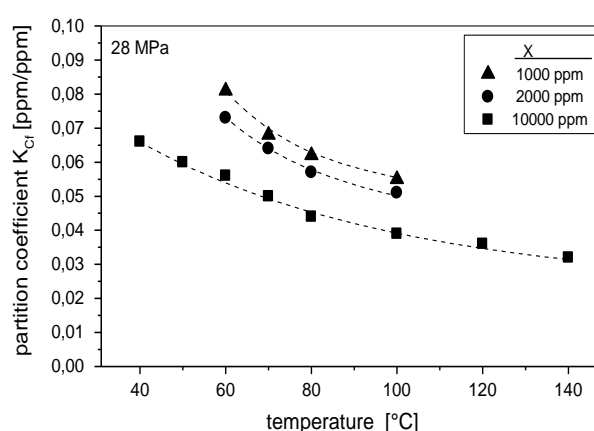**Figure 8**. Caffeine partition coefficients, calculated or interpolated from literature data

Figure 9. Caffeine partition coefficients, this work

Table 2 partition coefficients K=Y/X of the quasi-ternary system caffeine-scCO2-water with added substances

X	partition coefficient K at 28 MPa, 90°C				
	ternary	quasi-ternary, with coffee solubles and isopropanol			
	caffeine, CO_2, H_2O, interpol.	+19% coffee solubles in aqueous phase	+19% coffee solubles in aqueous phase +2% isopropanol CO_2 phase	+28% coffee solubles in aqueous phase	+26% coffee solubles in aqueous phase +2% isopropanol CO_2 phase
~5.000 ppm	0.049	0.028	0.032	0.028	
~9.000 ppm	0.044			0.020	0.039

DISCUSSION

Despite the industrial relevance of the equilibria with caffeine and scCO2 the existing data is surprisingly still not very concordant. But this is even true for the apparently trivial solubility measurements of caffeine in water. Thorough investigations by Cammenga[12] in the 1980s have shown that caffeine in contact with water forms a 4/5 hydrate below 51.5°C and an anhydrate above that temperature. The anhydrate state can aggregate by base stacking to di-, tri- and even tetramers and thereby enhance solubility in water significantly. It has to be noted that this process is slow and can thereby lead to wrong data if in phase equilibrium experiments sufficient contact time is not ensured. Additionally an influence of pH is theoretically conceivable but has not been shown or published yet. Looking at systems with scCO2 base stacking is not expected due to the rather nonpolar character of CO2 molecules. Nevertheless the morphology of the solid caffeine material in the equilibrium cell can influence the measurements and obviously presence of water traces will impair measurements. Besides, caffeine can adsorb to stainless steel surfaces. All these effects may be reasons for inconsistent data in this field.

The determined partition coefficients show, that a wash tower is an adequate unit operation to regenerate the supercritical CO_2 from decaffeination processes. Caffeine take-up of the water phase is high and caffeine concentrations in the wash water can be higher than in the supercritical phase what is helpful for a subsequent caffeine isolation process. For a process attempting to decaffeinate an aqueous extract either from coffee or tea the opposite is true: large amounts of the supercritical phase are necessary to extract the caffeine. The ratio of the contacting flows is given as MFR – mass flow ratio in (kg CO_2/h)/(kg aqueous flow/h).
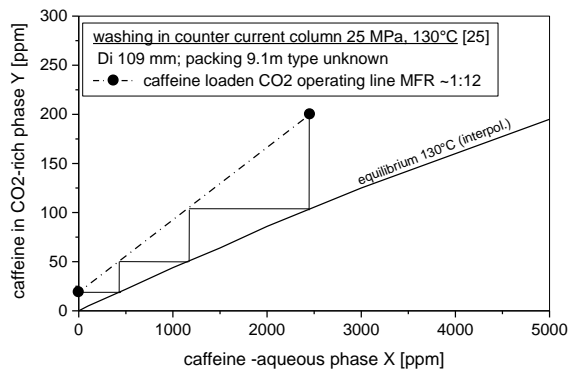

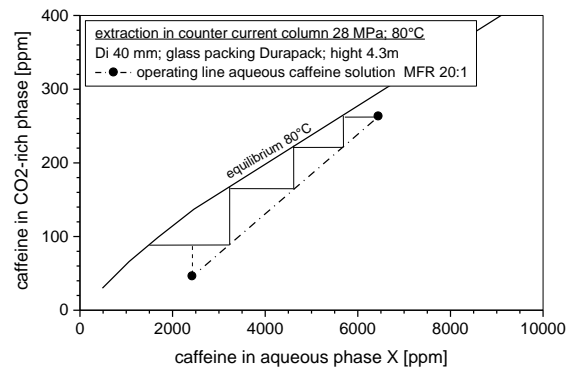**Figure 10** McCabe-Thiele diagram for a wash tower

Figure 11 McCabe-Thiele diagram for the decaffeination of an aqueous liquid

In Fig.10 and 11 the use of ternary equilibrium data is shown exemplarily. The data is used for the determination of the number of theoretical equilibrium stages according to the McCabe-Thiele method[5]. Data for the operating line of a caffeine scrubber is taken from a patent[25] and graphical determination (Fig.11) renders three theoretical equilibrium stages. With a total packing height of 9.1m the height of one equilibrium stage is roughly 3m. Although the patent probably does not give the optimum parameters (lower temperatures are preferable for the wash process) it is recognizable, that scrubbing wash towers have to be tall (see Fig.1 right). Own experimental results of column separation experiments for the decaffeination of aqueous solutions are displayed in Fig.12. In the case of a model-system with caffeine and water the task to reduce the caffeine loading from 6500ppm to 2400ppm (filled circles) requires 3.5 stages and thus the height of one equilibrium stage is ~1.3m. It must be noted, that very large CO_2 flows are necessary.

The same process with real systems with soluble coffee substances will be hindered by the unfavorable shift of the phase equilibrium: the partition coefficient is lowered significantly (see Tab. 2). This is a serious drawback for this process concept. The clear impact of added coffee solubles needs an explanation. As before mentioned, caffeine reacts with other coffee brew components and can form complexes, e.g. a caffeine-chlorogenate complex [24] and because of that caffeine solubility in water can be enhanced. The effect was confirmed by first screening experiments: caffeine showed roughly a four-fold solubility in water at room temperature when 20% of coffee solubles were added.

Another aspect of the shape of the equilibrium line can be mentioned although its effect is not substantial for the investigated system: if we classify a constant partition coefficient and thus a straight equilibrium line as neutral, the curved shape of the real equilibrium line is not beneficial for the wash-tower process but for extraction of caffeine from aqueous solution.

Finally the choice of temperature and pressure can be addressed. The partition coefficients show that the scrubbing process is enhanced by lower pressures and lower temperatures. This is proposed by Linning et al.[26]. But in practice the process is dominated by the optimum parameters for the extraction of tea of coffee beans and an isobaric process is preferred. Only

alone a temperature change for the wash column would probably lead to costly heat exchange systems to handle the large CO_2 flows. For the "opposite" process the opposite is true for parameter choice: $scCO_2$-extraction of aqueous caffeine solutions is enhanced by higher pressures and higher temperatures. Coffee solubles hinder this process concept significantly.

CONCLUSION

Partition coefficients of caffeine in the ternary system with $scCO_2$ and water are influenced by caffeine concentration, pressure and temperature. Binary literature data of the solubility of caffeine in supercritical CO_2 overestimate the quantity of caffeine in the supercritical phase in a ternary system with water by far (technical relevant data range). In case of a water wash tower for CO_2 regeneration this is beneficial, for decaffeination of liquid coffee extract or aqueous caffeine solutions this effect is a serious drawback. A clear temperature influence on the partition coefficient of caffeine in a two-phase system with water and supercritical CO_2 was found: scrubbing is enhanced with lower, extraction with elevated temperatures.

REFERENCES

[1] ZOSEL K., Verfahren zur Entcoffeinierung von Kaffee, German patent 2905239, 1970
[2] STAHL, E., QUIRIN K.-W., GERARD, D., Dense gases for extraction and refining, Springer-Verlag, Berlin, 1987
[3] LACK E., SEIDLITZ H., Commercial scale decaffeination of coffee and tea using supercritical CO_2, in: King, M. B.,
    Bott, T.R., (Eds.), Extraction of natural products using near-critical solvents, Blackie Academic Professional, p. 101, 1993
[4] McHUGH, M.A., KRUKONIS, V.J., Supercritical Fluid Extraction – Principles and Practice, Butterworth-Heinemann, Boston, 2nd Ed.,
    1994
[5] BRUNNER, G., Gas Extraction, Steinkopf NewYork 1994
[6] EGGERS R. (Ed.), High Pressure Processes, Wiley-VCH Verlag, 2012
[7] PRASSAD R., Decaffeination of aqueous extracts, US patent 4,246,291, 1981
[8] ZOSEL K., Process for the direct decaffeination of aqueous coffee extract solutions, US patent 4,348,422, 1978
[9] PIETSCH A., Decaffeinating coffee – processes and quality; in Follmer, B. (Ed.) The Craft and Science of coffee. Academic Press,
    Elsevier 2017
[10] BRUNNER, G., Mass transfer from solid material in gas extraction, Ber.Bunsenges. Phys.Chem. 88, 887-891, 1984
[11] JOHANNSEN M., BRUNNER G.; Solubilities of the xanthines caffeine, theophylline and theobromine in supercritical carbon dioxide,
    Fluid Phase Equilibria, Vol 95, pp. 215-226, 1994
[12] Cammenga, H. K.: Coffein, Theophyllin und Theobromin: physikalisch-chemische Untersuchungen für Lebensmitteltechnologie und Pharmazie, 41. Diskussionstagung FEI 4./5.11.82 in Würzburg, Germany,1982 (in german)
[13] KOPCAK, U., RMOHAMMED, R.S., Caffeine solubility in supercritical carbon dioxide/co-solvent mixtures, J.Sup. Fluids 34, pp.209-214, 2005
[14] KURZHALS, H.A.: Decaffeination of Coffee and Tea, in: Hirata, M., Ishikawa, T.: The Theory and Practice in Supercritical Fluid Technology, Kap.4, New Technology & Science, Tokyo, Japan, 1986
[15] LENZ, H.: Dynamic Solubility Measurements of Caffeine in Carbon Dioxide and in Carbon Dioxide Saturated with Water, Physica 139&140B, pp.70-72, 1986
[16] GADKARI, P.V., BALARAMAN, M., Solubility of caffeine from green tea in supercritical CO2: a theoretical and empirical approach, J. Food Sci Technol 52 (12), 2015
[17] BIRTIGH, A., LIU K., JOHANNSEN M., BRUNNER G.: Regeneration Methods for Caffeine-Loaded CO_2, Sep. Sci. Technol., 30, p.325, 1995
[18] GEHRIG, M.: Verfahren zur Abtrennung von Coffein aus verflüssigtem oder überkritischem Kohlendioxid, German patent DE 3443 390 C2, 1984
[19] ZOSEL K., Verfahren zur Entcoffeinierung von Kaffee. German patent DE2732103, 1977
[20] BIRTIGH, A., STOLDT, J., BRUNNER G., New method for supercritical fluid regeneration, J. Sup. Fluids, 8 Vol.2, p.162-166, 1995
[21] Pietsch, A., Eggers, R.: The Mixer-Settler Principle as a Separation Unit in Supercritical Fluid Processes, J. Sup. Fluids, 14, p.163-171, 1999
[22] BRUDI K., DAHMEN N., SCHMIEDER, H.; Partition Coefficients of Organic Substances in Two-Phase Mixtures of Water and Carbon Dioxide at Pressures of 8 to 30 MPa and Temperatures of 313 to 333 K, J. Sup. Fluids, 9, S. 146, 1996
[23] KRUKONIS V.J.: unpublished, quoted from McHugh M.A., Krukonis V.J.: Supercritical Fluid Extraction, 2.nd edition, Butterworth-Heinemann, Boston, 1994
[24] D'AMELIO N., FONTANIVE L.,UGGERI F., SUGGI-LIVERANI F., NAVARINI l., NMR Reinvestigation of the Caffeine–Chlorogenate Complex in Aqueous Solution and in Coffee Brews, Food Biophysics, Vol4, Issue 4, pp 321–330, 2009
[25] KATZ, S.N., Method for Decaffeinating Coffee with a Supercritical Fluid, US patent 4,820,537, 1989
[26] LINNIG D.A., LEYERS W.E.,NOVAK R.A., Decaffeination with supercritical carbon dioxide. In: proceedings of the 14th ASIC Colloquium, pp.357-364, ASIC, Paris, France
[27] SPENCE J.E., KATZ S.N., VOGEL G.J., PRASSAD R., Method for decaffeinating coffee materials including a reverse osmosis permeate cycle, US patent 5,266,342, 1993
[28] PIETSCH A., EGGERS R., Basic investigation of integrating a membrane unit into high-pressure decaffeination processing; Separation and Purification Technology 14 pp.107-115, 1998
[29] MARGOLIS, G., CHIOVINI, J.: Decaffeination Process, US Patent 4,251,559, 1981