HIGH PRESSURE EQUIPMENT FOR DETERMINATION OF P-V-T-X DATA OF GAS-LIQUID PHASE EQUILIBRIA

ALTIN MELE[1,2], MARIZA ANDONI[1,2], ARDITA MELE[1,2], ELVA DURO[3], JETA LICA[2], LORENCI GJURGJAJ[2], ISUELA KARÇINI[2], ANTONINA MEMA[3]

[1]Department of Chemistry, Faculty of Natural Sciences,

University of Tirana, Tirana, Albania

[2]Center of Techniques Studies, Faculty of Dental Techniques,

Ivodent Academy, Tirana, Albania

[3]Department of Prosthetics, Faculty of Dental Techniques,

Ivodent Academy, Tirana, Albania

e-mail: altin.mele@fshn.edu.al

Abstract

High pressure phase equilibria measurements are important in several industrial applications where pure substances or mixtures thereof coexist in different phases (McHugh et al., 1983). Determination of the phase's composition and density (or molar volume) at certain temperatures and high pressures is shown in this study to be carried out in a high pressure steel apparatus equipped with calibrated measurement instruments. In the carbon dioxide – ethanol – water mixtures, the chemical composition of coexisting liquid and gaseous phases is done using difference weighing for the carbon dioxide mole fraction before and after its release, and pycnometers for the remaining ethanol-water mixtures. Measurements of the P-V-T-x Data in the CO_2-EtOH-H_2O system were carried out in this high-pressure apparatus at 10.2 MPa and three different temperatures 308.15 K, 333.15 K and 353.15 K. The results were presented in a molar volume – composition diagram. At 308.15 K, this ternary system shows an equilibrium between a CO_2-rich and a H_2O-rich liquid phase, running from the CO_2-H_2O binary system to a common critical point. Liquid and gas phases coexist in the ternary system at 333.15 K and 353.15 K. The gas phase shows molar volumes and composition

running from the CO_2-rich phase of the CO_2-H_2O to the CO_2-EtOH binary system, while in the liquid from H_2O-rich to the EtOH-rich phases of the same binary systems.

Key words**:** *High pressure phase equilibria, CO_2-EtOH-H_2O, molvolume-concentration diagram.*

Përmbledhje

Matjet e ekuilibrit fazor në presion të lartë janë të rëndësishme në disa aplikime industriale ku substancat e pastra ose përzierjet e tyre bashkëekzistojnë në ekuilibër në fazë të lëngët dhe të gaztë (McHugh et al., 1983). Përcaktimi i përbërjes së fazave dhe dendësisë (ose vëllimit molar) të tyre në temperatura të caktuara dhe presione të larta është kryer në këtë studim në një aparaturë çeliku inoks të pajisur me instrumente matëse të kalibruara. Në përzierjet dioksid karboni – etanol – ujë, përbërja kimike e fazave të lëngshme dhe të gazta në ekuilibër përcaktohet duke matur diferencën në peshë për thyesin molar të dioksidit të karbonit para dhe pas lirimit të tij, si dhe piknometria për përzierjet e mbetura etanol-ujë. Matjet e të dhënave P-V-T-x në sistemin CO_2-EtOH-H_2O u kryen në presionin 10.2 MPa dhe tre temperatura të ndryshme; 308.15 K, 333.15 K dhe 353.15 K. Rezultatet janë paraqitur në një diagramë vëllim molar – përbërje. Në 308.15 K, ky sistem ternar tregon një ekuilibër midis një faze të lëngshme të pasur me CO_2 dhe një faze të lëngshme të pasur me H_2O, që shtrihet nga sistemi binar CO_2-H_2O deri në një pikë kritike të përbashkët. Fazat e lëngshme dhe të gazta bashkëekzistojnë në sistemin ternar në 333.15 K dhe 353.15 K. Përbërja e fazës së gaztë ndryshon duke nisur nga faza e pasur me CO_2 e sistemit binar CO_2-H_2O deri te faza e pasur me CO_2 e sistemit binar CO_2-EtOH. Përbërja e fazës së lëngshme ndryshon nga fazat e pasura me H_2O në ato të pasura me EtOH të të njëjtave sisteme binare të sipërpërmendura.

Fjalë kyçe: *Ekuilibra fazorë, përzierje ujë-etanol-dioksid karboni, diagramë fazore vëllim molar-përbërje.*

Introduction

For the design and development of high-pressure extraction processes (e.g. the sizing of separation equipment), the qualitative and quantitative knowledge of the phase behavior of the mixtures occurring in these processes is of particular importance. The literature contains is rich in experimental and theoretical

investigations of high-pressure vapor–liquid equilibria in binary mixtures. However, mixtures of three or more components are of greater interest from an application point of view. In the literature, ternary phase equilibria are predominantly investigated with the aim of utilizing extraction for downstream processing in biotechnology.

Various publications examine the biotechnological production of ethanol or other alcohols from biomass (among others (McHugh et al., 1983)). Since distillation would consume a large proportion of the energy supplied for separating the resulting water–alcohol mixture, the question arises of an alternative downstream processing method, such as high-pressure extraction, which requires significantly less thermal energy. Several authors (e.g. (Brunner & Kreim, 1986), (Horizoe et al., 1993), (McHugh et al., 1983), (Paulaitis et al., 1984), (Takishima et al., 1986)) have measured ternary mixtures of carbon dioxide or ethane, water and alcohol as the basis for high-pressure extraction of alcohol from aqueous solutions. Investigations using test or pilot plants have shown that high-pressure extraction of ethanol and other alcohols from aqueous solutions with near-critical carbon dioxide is efficient (de Filippi & Moses, 1982), (Ikawa et al., 1993).

Significantly less energy is required compared to distillation. However, the investment costs are higher than for distillation due to the more complex high-pressure technology, so that – at current energy prices – the process is not economically viable. In this work, the phase boundaries of the ternary system water–ethanol–carbon dioxide and its constituent binary systems are investigated. Most commonly, the phase boundaries of such mixtures are presented in P–x (isotherms), T–x (isobars) or P–T (isopleths) diagrams (Prausnitz, 1999). The densities or molar volumes of the phases are very rarely measured and, even when they are, the volume–concentration diagram is not the chosen form of representation. Yet the coexisting phases of a system usually differ in molar volume and composition, but not in pressure or temperature. Therefore, the V–x diagram, although very rarely used, is a very informative way of presentation.

The aim of this work is to measure the P–T–x_1–x_2 data in the ternary system water–ethanol–carbon dioxide and the molar volumes of the coexisting phases at the pressure 10.2 MPa and three different temperatures 308.15 K, 333.15 K

and 353.15 K. The representation of the measured phase boundaries is done using quantitative molar volume–concentration diagrams (V–x_1–x_2).

Literature review

The system water–ethanol–carbon dioxide (H_2O-EtOH-CO_2) has been investigated with respect to P–T–x_1–x_2 data by various authors. The first P–T–x_1–x_2 data in the ternary system were measured by Baker and Anderson in 1957 (Baker & Anderson, 1957). In the following years, other authors also dealt with the phase behavior of this system (Schwarts & Efremova, 1970), (Kuk & Montagna, 1983), (Nagahama, 1988), (Gilbert & Paulaitis, 1986), (Y.S. Feng, 1988), (Inomata et al., 1989), (de la Ossa et al., 1990), (Hirohama et al., 1993), (Lim et al., 1994), (Yoon et al., 1994), (Yao et al., 1994), (Budich & Brunner, 2003), (Durling et al., 2007), (Fornari et al., 2009). In most studies, the pressure and temperature ranges surround the critical point of pure carbon dioxide. Data on the molar volumes of the coexisting phases in this system are available from literature source (Schwarts & Efremova, 1970).

Methodology

Experimental setup

The high-pressure apparatus (Figure 1) was constructed analogously to earlier works (Lentz, 1969), (Nünnerich, 1999) and consists essentially of a cylindrical autoclave serving as the measuring cell. It is made of stainless steel (material no.: 1.4571) and has been honed on the inside. The cell is 300 mm long with an inner diameter of 25.59 ± 0.01 mm and an outer diameter of 50 mm. At the front face, the measuring cell is equipped with a window (30 mm diameter), which is sealed with an O-ring and fixed by a screw connection. Through the opening in the screw connection, the entire measuring volume is visible. Inside the autoclave there is a freely movable piston. An O-ring in a groove on the piston seals the measuring volume against the pressure medium. The piston is made of stainless steel and has a diameter of 25.24 mm. It can be moved using a spindle press and mineral oil as the pressure transmission medium. At the rear of the piston there is a stainless-steel rod with a magnet at the end. To measure the position of the piston, a slide caliper with a Hall probe is mounted on the rear connection of the autoclave.

The maximum volume of the sample chamber is approximately 80 cm^3. Near the front face of the autoclave, two high-pressure capillaries (6 × 1.5 mm) are

welded in, at the ends of which are two control valves. They allow evacuation, filling, and sampling. The measuring cell is connected horizontally to the pressure branch of the experimental setup, so that the two side connections point upward and downward. This way, when sampling from two phases, one connection is available for each phase. To avoid dead volumes, thinner capillaries with an outer diameter of 0.5 mm and an inner diameter of 0.2 mm have been hard soldered into the main capillaries. The measuring cell is surrounded by a temperature-control jacket in which ethylene glycol circulates as the thermostat fluid. The temperature inside the measuring cell is measured with a NiCr–Ni sheathed thermocouple, which is fed into the measuring cell together with one of the sampling capillaries. The desired pressure is generated by a diaphragm pump and a spindle press connected in series. The pressure is measured directly in the measuring cell. A thin high-pressure capillary connects the measuring cell to the pressure transducer. Additionally, the pressure was measured in the pressure branch.For sampling, two small pressure vessels with internal volumes of 10.23 cm^3 and 10.35 cm^3 were used.

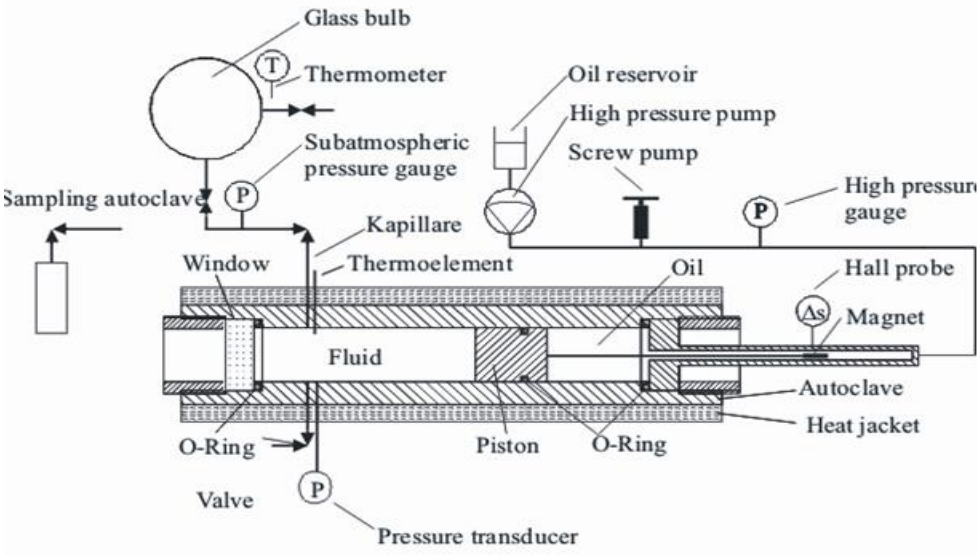

Figure 1. High pressure cell for determination of density and composition of coexisting phases at constant pressure and temperature

Substances used

Below is a list of the substances used and their purity. The substances were used without further purification.

Table 1. Substances used in this study, including purity and supplier information.

Substance	Purity *	Supplier
Water	1	–
Ethanol	> 99 % [2]	Merck
Carbon dioxide	99.996 %	Messer Griesheim

*Supplier specifications

[1] Water was prepared in a double distillation apparatus.

[2] Gas chromatographic analysis showed a purity of 99.9%.

Experimental procedure

At the beginning of each experiment, the cell was evacuated while being heated. Subsequently, the cell was filled twice with gaseous CO_2 and then emptied again down to atmospheric pressure. The amount of CO_2 remaining in the cell was calculated according to the ideal gas law. First, the desired ethanol–water mixture was prepared and filled into the cell. For this purpose, a valve connection was screwed on, the mixture of water and ethanol was filled in from a syringe, and the cell was immediately closed again. Then, liquid CO_2 was filled in from a 100 mL bottle. Both the syringe and the bottle were weighed before and after filling. The first difference in weight gave the exact amount of water and ethanol in the cell, and the second – with a small correction – gave the mass of CO_2. The CO_2 bottle was reconnected to the filled cell and the bottle valve opened.

A further difference-by-weighing method then allowed determination of the CO_2 loss in the connecting capillaries between the bottle and the cell. After filling the substances, the cell was thermostated to the measurement temperature. By moving the piston, the desired pressure was set. The mixture in the measuring cell was stirred with a 1 cm long Teflon-coated magnetic stir

bar to accelerate the establishment of equilibrium. This stir bar was driven by an externally rotating magnet. The stirring was normally carried out for 3 hours. After stirring, the system was allowed to stand for approximately 30 minutes. The phases were then well separated, and samples could be taken. The sample pressure vessels are equipped with needle valves.

They are evacuated and weighed. After the pressure vessel is connected to the apparatus, the control valve is slowly opened while at the same time the piston is advanced. The pressure remained constant to within ±0.5 % during sampling – an indication that the equilibrium was not disturbed. Through the window in the autoclave, the entrainment of another phase during sampling could be observed and prevented. After sampling, the pressure vessel is weighed again, and thus the mass of the withdrawn sample is determined.

Error Analysis

The error in measurement of pressure was diminished by using two electronic pressure sensors (ranges 0–10 MPa and 0–40 MPa). They were regularly calibrated against a Bourdon precision manometer. The error in pressure measurement in the range up to 10 MPa is estimated at 0.005 MPa. Between 10 MPa and 40 MPa, the error corresponds to the reading accuracy of 0.01 MPa. The temperature measuring instrument has a resolution of 0.1 K. It is calibrated using certified precision mercury thermometers readable to 0.05 K. At 353.15 K, a temperature difference of 0.1 K was measured between the inlet and outlet of the tempering jacket. It can therefore be assumed that temperature fluctuations inside the measurement cell do not exceed this value. No temporal temperature fluctuations were observed.

The absolute error in temperature measurement is thus estimated to be less than 0.15 K. The error in determining the mole fractions depends primarily on the precision of the weighing. For the CO determination, a balance with a capacity of 250 g and a resolution of 0.1 mg is used. The smallest measured CO□ mass was 0.285 g and the largest 2.517 g. Since the CO mass fraction is obtained by differential weighing, the relative error in this determination ranges from 0.1% to 0.04%, or 1 mmol in the CO mole fraction of 1 mmol. The mole fractions of ethanol and water are derived from the pycnometrically determined density of the mixture. According to the manufacturer, the pycnometers have a volume accuracy of 10 (relative).

Calibrations with water in the laboratory confirmed that, at the 0.1 mg resolution of the precision balance used, no volume-related error is detectable. The density of the ethanol–water mixture can thus be determined with an uncertainty of ±0.0002 g/cm³. From the tables, this corresponds to an error in the ethanol and water mass fractions of 0.2%. The largest masses of ethanol and water in the liquid phase were 1.0096 g and 1.0180 g, respectively. This results in a maximum error in mole fraction determination of 1.12 mmol for water and 0.43 mmol for ethanol. In the ternary system ethanol–water–carbon dioxide, five samples were withdrawn from the same mixture and analyzed. From these, the standard deviation for both volume and mole fraction was calculated. It amounts to less than 0.8 % for the volume and 0.0025 mol (0.65 %) for the mole fraction at medium concentrations.

The measured values from this work for the ternary system ethanol–water–carbon dioxide at 308.15 K and 10.2 MPa were also compared with literature data. The maximum deviation in mole fraction in an isothermal–isobaric diagram was 0.003 mol. Paulaitis [14] states an uncertainty of 0.002 mol for his measurements at medium concentrations. This is of the same order of magnitude as the deviation between his data and the measurements of the present work.

Analysis and discussion

The isobaric surface at 10.2 MPa is shown in Figure 2. The 308.15 K, 333.15 K, and 353.15 K isotherms run across the surface. Molar volumes and composition of coexisting phases are given in Table 2. The isotherms at 353.15 K and 333.15 K follow a similar course in both branches. At these temperatures, the system is in a vapor–liquid equilibrium. The isotherm at 308.15 K is open only toward the water–carbon dioxide system. At this temperature, the system exhibits a liquid–liquid equilibrium.

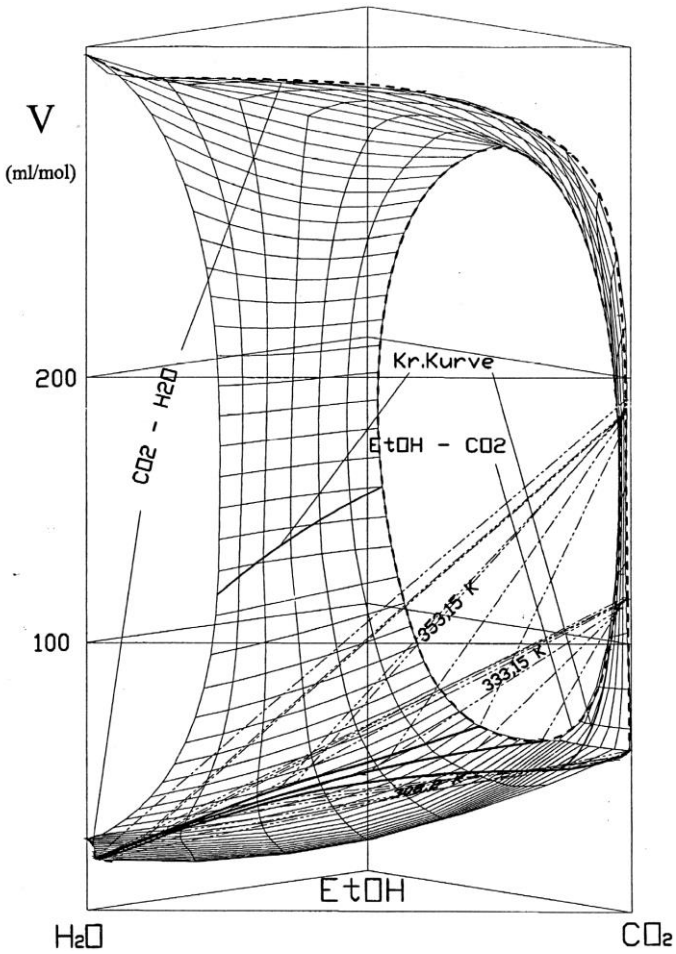

Figure 2: Isobar surface (net) at P = 10.2 MPa with isotherms (———), critical curve (———), measured gas-liquid - or liquid-liquid-node lines (— ·· — ·· —) and binary isotherms (– – – –).

The transition from one type of equilibrium to the other proceeds continuously at 10.2 MPa. At 10.2 MPa, the shape of the grid changes compared to 7 MPa because the binary system ethanol–carbon dioxide possesses both an upper and a lower critical point. This results in an almost circular course of the grid in this binary subsystem. At 10.2 MPa, two critical curves exist. The first curve

starts with decreasing temperature, from the CO_2-rich critical volume of the ethanol–carbon dioxide system and passes through the ternary critical point at 308.15 K. Initially, it represents the critical states of vapor–liquid equilibria. of the ethanol–carbon dioxide system and passes through the ternary critical point at 308.15 K. Initially, it represents the critical states of vapor–liquid equilibria.

Table 2: Measured mole fractions and molar volumes (V_m) of the coexisting liquid-vapor and liquid-liquid phases in the ternary system H_2O-EtOH-CO_2 at the pressure 10.2 MPa and 3 different temperatures.

T = 308.15 K							
Mole fraction liquid 1			V_m^{l1}	Mole fraction liquid 2			V_m^{l2}
X_{CO2}	X_{H2O}	X_{EtOH}	(cm^3/mol)	X_{CO2}	X_{H2O}	X_{EtOH}	(cm^3/mol)
0.978	0.0052	0.0168	57.84	0.034	0.8482	0.1178	22.04
0.9585	0.0108	0.0307	55.99	0.0474	0.7765	0.1761	24.89
0.941	0.0101	0.0489	56.01	0.101	0.6197	0.2793	30.35
0.93	0.0132	0.0569	56.17	0.1417	0.5394	0.3189	33.62
0.9155	0.0162	0.0683	55.17	0.1971	0.4447	0.3582	36.62
0.8755	0.0261	0.0984	51.94	0.3711	0.2514	0.3775	43.28
T = 333.15 K							
Mole fraction gas			V_m^{l1}	Mole fraction liquid			V_m^{l2}
Y_{CO2}	Y_{H2O}	Y_{EtOH}	(cm^3/mol)	X_{CO2}	X_{H2O}	X_{EtOH}	(cm^3/mol)
0.9833	0.007	0.0097	117.39	0.0375	0.8441	0.1184	23.34
0.9754	0.0086	0.016	115.49	0.0563	0.7562	0.1875	27.20
0.9745	0.0094	0.0161	115.01	0.0874	0.6648	0.2478	28.42
0.9691	0.0079	0.023	113.26	0.2913	0.286	0.4227	44.18
0.964	0.0059	0.0301	112.82	0.4992	0.0852	0.4156	53.68
T = 353.15 K							
Mole fraction gas			V_m^{l1}	Mole fraction liquid			V_m^{l2}
Y_{CO2}	Y_{H2O}	Y_{EtOH}	(cm^3/mol)	X_{CO2}	X_{H2O}	X_{EtOH}	(cm^3/mol)

0.982	0.007	0.011	186.94	0.0358	0.8456	0.1186	23.82
0.9805	0.0075	0.012	186.25	0.0415	0.8181	0.1404	25.53
0.972	0.007	0.021	185.14	0.1737	0.4132	0.4131	40.77
0.9692	0.0078	0.023	185.43	0.1552	0.4533	0.3915	39.96
0.9655	0.0075	0.027	182.49	0.2996	0.1988	0.5017	45.09

Along the isobaric surface, it shows an exponential decline, and at 308.15 K it constitutes the critical curve of a liquid–liquid equilibrium. The second critical curve is that of the vapor–liquid equilibrium. This curve appears in the ternary system at high temperatures. With increasing temperature, it runs from the ethanol-rich critical volume of the ethanol–carbon dioxide system into the critical volume of the ethanol–water system. In Figure 2, the presumed course of this curve is shown.

Conclusion

High-pressure phase equilibria in the ternary system water-ethanol-carbon dioxide at the pressure 10.2 MPa are presented in this work using molar volume–composition diagrams. The measurement temperatures were 308.15 K, 333.15 K, and 353.15 K and the molar volumes measured ranged between 12.8 cm^3/mol and 186.9 cm^3/mol. For experimental investigations, a phase equilibrium apparatus with a horizontal cylindrical autoclave serving as the measuring cell is used.

The ternary system ethanol–water–carbon dioxide exhibits simple phase behavior at pressure 10.2 MPa. At 308.15 K two liquid phases are in equilibrium with one critical point connecting the phase lines. At 333.15 K and 353.15 K the gas phase line and the liquid phase line are separated. The molar volumes run from those of the water–carbon dioxide system across to the molar volumes of the ethanol–carbon dioxide system. A critical curve starts from the critical point in the ethanol–carbon dioxide system and extends into the ternary region. At this pressure, the transition from a vapor–liquid equilibrium to a liquid–liquid equilibrium occurs continuously.

References

Baker, L. C., & Anderson, T. F. (1957). Some phase relationships in the three component liquid system CO_2–H_2O–C_2H_5OH at high pressures. Journal of the American Chemical Society 79, 2071–2074. doi:https://doi.org/10.1021/ja01566a013

Brunner, G., & Kreim, K. (1986). Separation of ethanol from aqueous solutions by gas extraction. German Chemical Engineering 9, 246–250. Retrieved from

https://www.osti.gov/etdeweb/biblio/7146792

Budich, M., & Brunner, G. (2003). Supercritical fluid extraction of ethanol from aqueous solutions. The Journal of Supercritical Fluids 25, 45–55. doi:https://doi.org/10.1016/S0896-8446(02)00091-8

de Filippi, R. P., & Moses, J. M. (1982). Extraction of organics from aqueous solutions using critical-fluid carbon dioxide. Biotechnology and Bioengineering Symposium Series 12, 205–219.

de la Ossa, E. M., Brandani, V., del Re, G., di Giacomo, G., & Ferri, E. (1990). Binary and ternary phase behaviour of the system water–ethanol–carbon dioxide. Fluid Phase Equilibria 56, 325–340. doi:https://doi.org/10.1016/0378-3812(90)85112-N

Durling, N. E., Catchpole, O. J., Tallon, S. J., & Grey, J. B. (2007). Measurement and modelling of the ternary phase equilibria for high pressure carbon dioxide–ethanol–water mixtures. Fluid Phase Equilibria 252 (1–2), 103–113.

doi:https://doi.org/10.1016/j.fluid.2006.12.014

Fornari, T., Hernández, E. J., Ruiz-Rodriguez, A., Señorans, F. J., & Reglero, G. (2009). Phase equilibria for the removal of ethanol from alcoholic beverages using supercritical carbon dioxide. The Journal of Supercritical Fluids 50(2), 91–96.

doi:https://doi.org/10.1016/j.supflu.2009.05.012

Gilbert, M. L., & Paulaitis, M. E. (1986). Gas–liquid equilibrium for ethanol–water–carbon dioxide mixtures at elevated pressures. ournal of Chemical & Engineering Data 31, 296–298. doi:https://doi.org/10.1021/je00045a012

Hirohama, S., Takatsuka, T., Miyamoto, S., & Muto, T. (1993). Phase equilibria for the carbon dioxide–ethanol–water system with trace amounts of organic components. Journal of Chemical Engineering of Japan 26(3), 247–253. doi:https://doi.org/10.1252/jcej.26.247

Horizoe, H., Tanimoto, T., Yamamoto, I., & Kano, Y. (1993). Phase equilibrium study for the separation of ethanol–water solution using subcritical and supercritical hydrocarbon solvent extraction. Fluid Phase Equilibria 84, 297–320.

doi:https://doi.org/10.1016/0378-3812(93)85129-A

Ikawa, N., Nagase, Y., Tada, T., Furuta, S., & Fukuzato, R. (1993). Separation process of ethanol from aqueous solutions using supercritical carbon dioxide. Fluid Phase Equilibria 83, 167–174. doi:https://doi.org/10.1016/0378-3812(93)87019-W

Inomata, H., Arai, K., Saito, S., Ohba, S., & Takeuchi, K. (1989). Measurement and prediction of phase equilibria for the CO_2–ethanol–water system. Fluid Phase Equilibria 53, 23–30. doi:https://doi.org/10.1016/0378-3812(89)80069-X

Kuk, M. S., & Montagna, J. C. (1983). Solubility of oxygenated hydrocarbons in supercritical carbon dioxide. In J. M. Mark E. Paulaitis (Ed.), Chemical engineering at supercritical fluid conditions (pp. 101–111). Ann Arbor Science Publishers, Ann Arbor.

Lentz, H. (1969). A method of studying the behaviour of fluid phases at high pressures and temperatures. Review of Scientific Instruments 40, 371–372.

doi:https://doi.org/10.1063/1.1683948

Lim, J. S., Lee, Y. Y., & Chun, H. S. (1994). Phase equilibria for carbon dioxide–ethanol–water system at elevated pressures. The Journal of Supercritical Fluids 7, 219–230.

doi:https://doi.org/10.1016/0896-8446(94)90009-4

McHugh, M. A., Mallett, M. W., & Kohn, J. P. (1983). High pressure fluid phase equilibria of alcohol-water-supercritical solvent mixtures. In J. P. Michael E. Paulaitis (Ed.), Chemical Engineering at Supercritical Fluid Conditions (pp. 113-137). Michigan: Ann Arbor Science Publishers, Ann Arbor.

Nagahama, K. J. (1988). High pressure vapour–liquid equilibria for the supercritical CO_2 + ethanol + water system. Proceedings of the International Symposium on Supercritical Fluids, 1, pp. 143–150. Nice, France.

Nünnerich, P. (1999). Die Nodenlinien im V-x-Diagramm binärer Mischungen am Beispiel Argon–Ammoniak und Methan–n-Decan.

Paulaitis, M. E., Kander, R. G., & DiAndreth, J. R. (1984). Phase equilibria related to supercritical-fluid solvent extraction. Berichte der Bunsengesellschaft für Physikalische Chemie 88, 869–875. doi:https://doi.org/10.1002/bbpc.19840880920

Prausnitz, J. M. (1999). Molecular Thermodynamics of Fluid-Phase Equilibria (3rd ed.). Pearson Education.

Schwarts, A. V., & Efremova, G. D. (1970). Critical phenomena of the highest order in an ethanol–water–carbon dioxide system. Zhurnal Fizicheskoi Khimii 44(4), 1105–1107.

Takishima, S., Saiki, K., Arai, K., & Saito, S. (1986). Phase equilibria for CO_2–C_2H_5OH–H_2O system. Journal of Chemical Engineering of Japan 19, 48–56.

doi:https://doi.org/10.1252/jcej.19.48

Y.S. Feng, X. D. (1988). An apparatus for determining high pressure fluid phase equilibria and its applications to supercritical carbon dioxide mixtures. Proceedings of the International Symposium on Supercritical Fluids, 1, 75–84.

Yao, S., Guan, Y., & Zhu, Z. (1994). Investigation of phase equilibrium for ternary systems containing ethanol, water and carbon dioxide at elevated pressures. Fluid Phase Equilibria 99, 249–259. doi:https://doi.org/10.1016/0378-3812(94)80035-9

Yoon, J.-H., Lee, H.-J., & Chung, B.-H. (1994). High pressure three phase equilibria for the carbon dioxide–ethanol–water system. Fluid Phase Equilibria 102, 287–292.

doi:https://doi.org/10.1016/0378-3812(94)87081-0