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Публикации в списания с ISI импакт-фактор

1. Fornari, T., P. Luna, R.P. Stateva: The vdW EoS Hundred Years Later, Yet Younger than Before. Application to the Phase Equilibria Modeling of Food-Type Systems for a Green Technology”. *J Supercritical Fluids* **55**, 579–593 (2010).

Abstract

The relevant applications that supercritical fluid extraction (SFE) has attained in the food industry in the last decades increased the interest in the development of thermodynamic models to represent the phase equilibria of systems comprising food-related substances and supercritical carbon dioxide (SCCO₂). The targets are twofold: (i) calculation of solid solubilities in SCCO₂ pure or with polar co-solvents (mainly ethanol in food applications), what directly affects the selectivity of one of the most applied processes, e.g. the semi-batch SFE of plant material, and (ii) calculation of vapor–liquid equilibrium compositions of liquid raw materials processed in countercurrent packed columns, what is straightforwardly related with the number of theoretical stages necessary to achieve the desired separation. Cubic equations of state derived from the equation proposed by van der Waals (vdW-type EoSs, e.g. Peng–Robinson and Soave–Redlich–Kwong EoS) are the most common thermodynamic models applied to achieve these objectives. In this work, the application of vdW-type EoSs to food-type substance + SCCO₂ is reviewed. More than 100 systems, comprising lipids, antioxidants, pigments, alkaloids, vitamins, etc. were investigated from 2003 up today. Even though phase equilibria modeling of SCCO₂ + food-related systems involves serious difficulties, the extensive and, in many cases, successful application of vdW-type EoSs demonstrates that though developed 100 years ago the van der Waals equation is lively and younger than before.

2. Sovová, H., A.A. Galushko, R.P. Stateva, K. Rochová, M. Sajfřtová, M. Bártlová: “Supercritical Fluid Extraction of Minor Components of Vegetable Oils: *beta*-sitosterol”. *J. Food Engineering* **101**, 201-209 (2010).

Abstract

The extracts of valuable vegetable oils containing a number of minor components (sterols, tocopherols, carotenoids, etc.) have added value as pharmaceuticals and food additives. Beta-sitosterol (BS) as minor component of vegetable oil was extracted from ground seeds of sea buckthorn with supercritical CO₂ at pressures 15–60 MPa and temperatures 40–80 C. The changes in the BS content in extract in the course of the extraction were evaluated using HPLC and described in terms of phase equilibrium. It was shown that the separation factors used in counter-current fractionation of oils apply also to the initial period of oil extraction from ground seeds. The equilibrium compositions of a model BS + trilinolein + CO₂ mixture were calculated using SRK and PSRK equations of state. The BS to triacylglycerol separation factor, ranging from 1.0 to 3.1, was correlated with CO₂ density.

3. Shacham, M., G.St. Cholakov, R.P. Stateva, N. Brauner: “Quantitative Structure-Property Relationships for Prediction of Phase Equilibrium Related Properties”. *Ind. Eng. Chem. Res.* **49**, 900-912 (2010).

Abstract

In this work, novel techniques for predicting vapor pressure and binary interaction coefficients for homologous series are developed based on the previously proposed targeted quantitative structure-property relationship (TQSPR) and QS2PR methods. For predicting vapor pressure variation as a function of temperature, a two reference compound (TRC) QSPR method is suggested. This method uses two, structurally similar predictive compounds with available vapor pressure data to predict point by point the vapor pressure or the saturation temperature of a target compound. For the target compound, only structural

information is required. The two variants of the method were applied to several homologous series. They demonstrate prediction of vapor pressure within experimental uncertainty, depending on the level of similarity between the predictive compounds and the target compound. A targeted QSPR method for prediction of the binary interaction coefficients (k_{ij}) in cubic equations of state for a compound with the members of its homologous series is also presented. The coefficients for the Soave-Redlich-Kwong and Peng-Robinson equations, used to test the method, were reproduced within the deviation of those obtained from regressed experimental data.

4. Justo-Garcia, D.N., F. Garcia-Sanchez, R.P. Stateva, B.E. Garcia-Flores: "Modeling of the Multiphase Behavior of Nitrogen-Containing Systems at Low Temperatures with Equations of State". *J. Chem. Eng. Data* **54** (9), 2689–2695 (2009).

Abstract

In this work, we present the modeling of the vapor-liquid-liquid equilibria (VLLE) for three ternary systems that are of interest in the natural gas and oil industry: nitrogen + methane + *n*-pentane, nitrogen + methane + *n*-hexane, and nitrogen + methane + *n*-heptane. The capabilities of the PC-SAFT and SRK equations of state to predict the complex phase behavior exhibited at low temperatures by the systems studied were compared and analyzed. The computer algorithm performing the isothermal multiphase flash calculations in the first case is based on the minimization of the Gibbs energy, while the second is based on the minimization of a modified tangent-plane distance function. The results obtained demonstrate that both equations of state predict with reasonable accuracy the experimentally observed phase behavior of the ternary systems considered.

5. Yankov, D.S., J.P.M. Trusler, R.P. Stateva, G.St. Cholakov: "Influence of pH and Acid Solutes on the Phase Behaviour of Aqueous Solutions Containing Poly(ethylene glycol) and Poly(ethyleneimine)". *Biochemical Engineering Journal* **48**, 104–110 (2009).

Abstract

In this paper, which forms part of a study on aqueous two-phase systems (ATPS) for separation of low molar-mass organic acids in the biotechnology industry, we examine the phase behaviour of ATPSs containing poly(ethylene glycol) (PEG) and poly(ethyleneimine) (PEI) as a function of pH, the nature of the acid used for titrating PEI, and the addition of lactic acid. We show that increasing the pH leads to contraction of the two-phase regions and that titrating PEI with a higher polyvalent acid results in a larger two-phase region. We propose a mechanism explaining the experimentally observed phase behaviour. Finally, we demonstrate that the lactic acid partition coefficient is very favourable (the acid partitions preferentially to the PEI-rich phase), which confirms that the (PEG + PEI) ATPSs could be used to advantage as a medium for lactic acid bio-transformation.

6. Cháfer, A., T. Fornari, R.P. Stateva, A. Berna: "Trans-Cinnamic Acid Solubility Enhancement in the Presence of Ethanol as a Supercritical CO₂ Cosolvent". *J. Chem. Eng. Data* **54**, 2263–2268 (2009).

Abstract

Trans-3-phenyl-2-propenoic acid (cinnamic acid; *trans*-cinnamic acid) is widely used in food, cosmetics, and pharmaceuticals because of its reported antimicrobial, antifungal, and antioxidant properties. This paper is devoted to the experimental measurement of the solubility of solid *trans*-cinnamic acid in pure supercritical CO₂ and in supercritical CO₂ with ethanol as a cosolvent. Measurements were carried out at T (313.15 to 343.15) K and at p (10 to 40) MPa. Two different thermodynamic models were applied to represent the solubility data obtained: a cubic type equation of state, the Soave-Redlich-Kwong (SRK-EoS) was employed to correlate the solubility data and the group contribution associating EoS (GCA-EoS) was also applied but in a completely predictive manner. In addition, values for the thermophysical properties of *trans*-cinnamic acid are also advocated.

7. Montanes, F., T. Fornari, R.P. Stateva, A. Olano, E. Ibanez: "Solubility of carbohydrates in supercritical carbon dioxide with (ethanol+water) cosolvent." *J. Supercritical Fluids* **49**, 16-22 (2009).

Abstract

Prebiotic carbohydrates are defined as non-digestible carbohydrates that beneficially affect the host by selectively stimulating the growth and/or activity of a limited no. of bacteria in the colon. The present study is focused on two prebiotic ketosugars: tagatose and lactulose, which are currently obtained by alk. isomerization of their resp. aldoses-galactose and lactose. It is a part of a broader research devoted to examg. the possibility of complex solid carbohydrate mixts. fractionation using supercrit. carbon dioxide and alc.-type cosolvents. We report new exptl. soly. data of tagatose, galactose, lactulose and lactose in supercrit. carbon dioxide with ethanol:water (95:5, vol./vol.) used as a cosolvent at T = (60 and 100) °C, P = (10-30) MPa and cosolvent content from 6 to 21% (wt./wt.). The soly. measured was in the range (0.02-1.09) mg g⁻¹. Addnl., the exptl. data was correlated using the Soave-Redlich-Kwong cubic equation of state with the modified Huron-Vidal second order (MHV2) mixing rule. The latter employs the mS-UNIFAC, which introduces two new groups in the original UNIFAC parameter matrix to represent the sugar mols.

8. Coelho, J.P., K. Bernotaityte, M.A. Miraldes, A.F. Mendonsa, R.P. Stateva: "Solubility of Ethanamide and 2-Propenamide in Supercritical Carbon Dioxide. Measurements and Correlation". *J. Chem. Eng. Data* **54**, 2546-2549 (2009)

Abstract

Solubilities of ethanamide (acetamide) and 2-propenamide (acrylamide) in supercrit. carbon dioxide were measured at T = (308.2, 318.2, and 333.2) K over the pressure range (9.0 to 40.0) MPa by a flow-type app. The soly. of acetamide (2.3.10⁻⁴ to 31.3.10⁻⁴) in the overall region of measurements is approx. twice that of acrylamide (1.2.10⁻⁴ to 16.3.10⁻⁴). The soly. of both components increases with pressure, and the relative location of the crossover region is obsd. at about 12.0 MPa. The exptl. data were correlated by using the Soave-Redlich-Kwong equation of state (EOS) with the one-fluid van der Waals mixing rule. In addn., the pure compd. properties required for the modeling were also estd.

9. Cholakov, G.St., R.P. Stateva, N. Brauner, M. Shacham: "Estimation of Properties of Homologous Series with Targeted Quantitative Structure Property Relationships". *J. Chem. Eng. Data* **53**, 2510-2520 (2008).

Abstract

The ability of the targeted quant. structure-property relationships (TQSPR) method to predict properties for groups of congeneric compds. was tested with Tc and pc data for five homologous series: n-alkanes, 1-alkenes, 1-alkanols, n-alkylbenzenes, and n-alkanoic acids. Training sets were identified from a database of 326 hydrocarbon and oxygen compds. with different structures, described with 1664 descriptors, or from the resp. series only. It has been established that the TQSPR method can identify descriptors collinear with the property studied and develop linear equations for the series from measured data. In most cases, the resp. collinear descriptors could be identified with the controls imbedded in the TQSPR program. Comparison with presently available methods shows that TQSPR achieves deviations from measured data in most cases within the av. exptl. uncertainties, like the best ABC methods, but it needs smaller amts. of measured data and provides higher statistical confidence in long-range prediction. The method has been tested with only five homologous series, but the existence of descriptors collinear with properties found in the present work is relevant to all homologous series. When applied to simple mols., TQSPR can also provide insight into the way compds. are selected by structural similarity and outline eventual inefficiencies in this selection.

10. Fornari, T., R.P. Stateva, F.J. Senorans, G. Reglero, E. Ibanez: "Applying UNIFAC-Based Models to Predict the Solubility of Solids in Subcritical Water". *J. Supercritical Fluids* **46**, 245-251 (2008).

Abstract

This work explores the capabilities of UNIFAC-based models to predict the soly. of different solid solutes in subcrit. water as a function of temp. The original UNIFAC, its modified (Dortmund) version and the A-UNIFAC model, which explicitly includes assocn. effects between groups, are applied to calc. the soly. of solid compds. in subcrit. water in the temp. range 298-500 K. The comparison between the three models is carried out using polycyclic arom. hydrocarbons (PAHs) as test substances and for which reliable phys. properties and exptl. data are available in the literature. The results obtained indicate that modified UNIFAC (Dortmund) provides the best representation of the arom. compds.' soly. as a function of temp. In addn., the application of the A-UNIFAC model confirms the hypothesis that a decrease in the level of assocn. between the subcrit. water mols. (in accordance with the dielec. const. decrease with temp.), greatly improves the soly. of hydrophobic org. compds.

11. Yankov, D.S., J.P.M. Trusler, B.Y. Yordanov, R.P. Stateva: "Influence of Lactic Acid on the Formation of Aqueous Two-phase Systems Containing Poly(ethylene glycol) and Phosphates". *J. Chem. Eng. Data* **53**, 1309-1315 (2008).

Abstract

This is a part of aq. two-phase system (ATPS) study for sepn. of low-molar-mass org. acids in the biotechnol. industry. The paper presents exptl. results on the phase equil. of ATPS contg. poly(ethylene glycol) (PEG) and either K₂HPO₄ or KH₂PO₄ or a fixed mixt. of the two phosphates. The measurements were made at a temp. of 298.15 K and a pressure of 1 bar. The PEG had a mass-av. molar mass of either 10,000 g/mol-1 or 20,000 g/mol-1 and a polydispersity index of 1.05. The influence of 2-hydroxy-propanoic acid (lactic acid) on the formation of the ATPS was studied, and the partition coeff. for this compd. between the coexisting phases was found to be close to unity.

12. Kahrs, O., N. Brauner, G.St. Cholakov, R.P. Stateva, W. Marquardt, and M. Shacham: "Analysis and Refinement of the Targeted QSPR Method". *Comp. & Chem. Eng.* **32**, 1397-1410 (2008).

Abstract

The targeted quant. structure-property relationship (TQSPR) method of N. Brauner et al.(2006) is analyzed in this study with respect to its various algorithmic steps. It is shown that accurate QSPRs for predicting the crit. temp. can be developed using a training set of 10 compds. that exhibit the highest level of similarity with the target compd. (the compd. for which a property has to be predicted). Alternative methods to compute the similarity of compds. and to assemble the training set are compared. The potential of a principal component anal. of the mol. descriptor data to improve the TQSPR performance is assessed and a new stopping criterion for QSPR refinement based on the discrepancy principle is introduced. It is shown that collinearity between mol. descriptors and the increase of the no. of compds. and descriptors in the database do not have adverse effects on the performance of the TQSPR method.

13. Brauner, N., G.St. Cholakov, O. Kahrs, R.P. Stateva, M. Shacham: "Linear QSPRs for Predicting Pure Compound Properties in Homologous Series". *AIChE J.* **54** (4), 978-990 (2008).

Abstract

Linear QSPRs, contg. 1 through 4 descriptors, are developed for predicting the normal boiling temp., m.p. temp., and crit. properties for the n-alkane, 1-alkene, n-alkylbenzene, 1-alc., and alkanolic monocarboxylic acid homologous series. Property values for which exptl. data are available can be predicted within exptl. error level (with very few and very small exceptions), irresp. of whether interpolation or extrapolation is involved. Property values for which predicted literature data are available can be matched within the reported reliability level, even when extrapolation is carried out from very small training sets contg. exptl. data. Thus, the linear QSPRs developed represent well the nonlinear variation of the particular property with the carbon no., and increase the confidence in the values predicted when extrapolation is involved.

14. Sovova, H., R.P. Stateva, A.A. Galushko: "High-pressure Equilibrium of Menthol +CO₂". *J. Supercritical Fluids* **41**, 1-9 (2007).

Abstract

Data on menthol + CO₂ phase behavior and menthol soly. in dense CO₂ are needed to optimize supercrit. extn. of peppermint oil. The paper presents novel exptl. data for the phase diagram of (-)-menthol + CO₂ binary system in the temp. range 5-40 °C and pressures up to 8.2 MPa, including menthol m.p. depression, as well as data on menthol soly. in dense CO₂ in the temp. range 30-60 C and pressure range 6.6-14.4 MPa. The system exhibits quadruple point from which four three phase loci originate; The soly. data obtained in this work confirm previous results of Maier and Stephan. Both the soly. of menthol and the pressure-temp. diagram of the system menthol + CO₂ were modelled with the Soave-Redlich-Kwong equation of state and good agreement with the exptl. data was achieved.

15. Balogh, J., R.J.B. Craven, R.P. Stateva: "The AREA Method for Phase Stability Analysis Revisited – Further Developments. Formulation in Terms of the Convex Hull of the Free Energy". *Ind. Eng. Chem. Res.*

46, 1611-1631 (2007).

Abstract

The area method for phase stability anal. is re-examd. from the viewpoint of the topol. of thermodyn. surfaces. A new generalization of the area method objective function and the max. area criterion is proposed in terms of the convex envelope of thermodyn. surfaces. Several special cases for two-component, single- and two-phase systems are analyzed and the results generalized to hypersurfaces, characteristic of the Gibbs energy of multicomponent, multiphase systems. It is shown conclusively that the area (or more generally hypervolume) between the free energy hypersurface and a hyperplane that intersects the hypersurface is maximal when the hyperplane coincides with the convex envelope of the hypersurface. Extension of the max. area criterion to four basic thermodyn. surfaces for pure fluids and mixts. is discussed. The authors believe the approach adopted here sets the area method on secure theor. foundations, answers criticisms concerning its validity, and will stimulate fresh research.

16. Cholakov G.St., R.P. Stateva, M. Shacham, N. Brauner: "Prediction of Properties in Homologous Series with A Short-Cut QS2PR Method". *AIChE J.* **53**(1), 150-159 (2007).

Abstract

For prediction of properties of pure compds. in homologous series a shortcut version of the QS2PR technique is introduced. The structure-structure relation between a target compd. and three predictive compds. from its homologous series is described in the short version with the no. of carbon atoms and one easily calcd. noncollinear mol. descriptor. This correlation provides predictions of high precision for properties of members of the homologous series, if property data for interpolation are available. It can also be used for short-range extrapolation with precision similar to that of asymptotic relations. The advantages of the proposed method over the existing methods are that with the structural correlation parameters it predicts all structure-dependent properties of the target and enables estn. of its missing properties even if properties for only three predictive compds. are available. The method can also use as a descriptor the normal boiling temp.

17. Cháfer, A., T. Fornari, R.P. Stateva, A. Berna, J. García-Reverter: "On the Solubility of the Natural Antioxidant Gallic Acid in Supercritical CO₂ + Ethanol as a co-Solvent". *J. Chem. & Eng. Data* **52**(1), 116-121 (2007).

Abstract

Soly. data of solid 3,4,5-trihydroxybenzoic acid (gallic acid) in supercrit. CO₂ + ethanol as a cosolvent are reported in this work. Measurements were carried out in the temp. range (313.15 to 333.15) K, pressures ranging from (10 to 40) MPa, and different ethanol modifier content ranging from (0.7 to 6) %. The exptl. data were correlated using the Soave-Redlich-Kwong equation of state and the group contribution assocg. equation of state. The thermodyn. modeling anal. includes also the soly. representation of an important class of natural antioxidants (e.g., gallic acid esters) in supercrit. CO₂.

18. Yankov, D.S., R.P. Stateva, J.P.M. Trusler, G.St. Cholakov: "Liquid-Liquid Equilibria in Aqueous Two-phase Systems of Poly(ethylene glycol) and Poly(ethyleneimine). Experimental Measurements and Correlation". *J. Chem. & Eng. Data* **51**, 1056-1061 (2006).

Abstract

In this paper, which forms part of a study on aq. two-phase systems (ATPS) for sepn. of low molar mass org. acids in the biotechnol. industry, the authors present exptl. and modeling results on the phase equil. of an ATPS contg. poly(ethylene glycol) (PEG) and poly(ethyleneimine) (PEI). The measurements were made at a temp. of 25 C and a pressure of 1 bar, at pH = 5.3, 7.5, and 9.2. The PEG had a mass-av. molar mass of 4000 gmol⁻¹ and a polydispersity index of 1.05, while the PEI had a mass-av. molar mass of 25 000 gmol⁻¹ and a polydispersity index of about 2.5. A UNIQUAC model, incorporating the polydispersity of the PEI, was found to give a satisfactory correlation of the exptl. data. The expt. results demonstrated that the polymers are distributed unevenly in the two phases, and this suggests that org. acids (e.g., lactic acid) will partition preferentially to the PEI-rich phase through acid-base assocn.

19. Brauner, N., R.P. Stateva, G.St. Cholakov, M. Shacham: "A Structurally "Targeted" QSPR Method for Property Prediction". *Ind. Eng. Chem. Res.* **45**, 8430–8437 (2006).

Abstract

Prediction of unknown properties for a target compd. using quant. structure-property relationships (QSPRs) is reliable only if the compd. is within the model applicability domain. To improve the prediction reliability, a "targeted" QSPR (TQSPR) method is developed in which a training set contg. only compds. structurally similar to the target compd. is first identified. Similarity is measured by the partial correlation coeffs. between the vectors of the mol. descriptors of the target compd. and each potential predictive compd. Available property data in the training set are then used in the usual manner to select mol. descriptors for QSPRs, predicting the properties of the target and the rest of the compds. in the set. Preliminary results show that the method proposed yields predictions within the exptl. error for compds. well represented in the database and fairly reliable ests. for complex compds. that are sparsely represented. The cutoff value of the partial correlation coeff. provides an indication of the expected prediction error.

20. Chafer, A., T. Fornari, R.P. Stateva, A. Berna: "D-pinitol Solubility in Supercritical CO₂ – Experimental Data and Correlation". *J. Chem. & Eng. Data* **51**, 612-615 (2006).

Abstract

Measurements of D-pinitol soly. in supercrit. CO₂ in the temp. range (313 to 333) K and pressures ranging from 10 to 40 MPa are reported for the first time in this work. Two different thermodyn. models are applied to correlate the exptl. D-pinitol solubilities: a cubic-type equation of state (the Soave-Redlich-Kong, SRK) and a model based on the group contribution approach (the Group Contribution Equation of State, GC-EoS). Both models demonstrate high capability to describe the solid-gas-phase equil. of this system. In addn., values for the thermophys. properties, sublimation pressure, and solid molar volume of D-pinitol are also given.

21. Fornari, T., A. Chafer, R.P. Stateva, G. Reglero: "A New Development in the Application of the Group Contribution Associating Equation of State To Model Solid Solubilities of Phenolic Compounds in SC-CO₂". *Ind. Eng. Chem. Res.* **44** (21), 8147–8156 (2005).

Abstract

The potential of the Group Contribution Assocg. Equation of State (GCA-EoS) to correlate and predict the solubilities of solid phenolic compds., e.g. phenols, arom. ethers, and arom. acids, in supercrit. carbon dioxide is explored in this work. The Carnahan-Starling type repulsive term of the GCA-EoS equation contains a mol. parameter, the hard sphere diam. d_i , which is assumed to be temp.-dependent in the original model and is calcd. following a generalized expression. In the present study, this expression is singled out as a target for improvement, since it was established that the low-volatile solid compd. diam. value influences to a great extent the phase equil. calcns. The paper demonstrates that a d_i -dependent solute d_i parameter can better represent the exptl. soly. data of the compds. studied and maintains the group contribution character of the model.

22. Chafer, A., T. Fornari, A. Berna, R.P. Stateva: "Solubility of Quercetin in Supercritical CO₂+Ethanol as a modifier: Measurements and Thermodynamic Modelling". *J. Supercritical Fluids*, **32**, 89–96 (2004).

Abstract

Grape seeds exts. have shown a broad range of pharmacol. activities including, among others, antiulcer and antioxidant properties, which are mainly attributed to the phenolic compds. present. To date, the most abundant phenolic compds. isolated from grape seeds are catechins and their derivs., e.g. quercetin. The present study is devoted to the exptl. measurement and thermodyn. modeling of the soly. of quercetin in supercrit. CO₂ + ethanol as a co-solvent. The soly. of quercetin was measured at 313.15 K, pressures ranging from 80 to 120 bar, and at different content of the modifier ethanol-from 5 to 30%. Two types of thermodyn. models were applied to model the soly. of quercetin-the group contribution equation of state (GC-EoS), developed by Skjold-Jogensen, and the Soave-Redlich-Kwong (SRK) EoS.

23. Shacham, M., N. Brauner, G.St. Cholakov, R.P. Stateva: "Property Prediction by Correlations Based on Similarity of Molecular Structures". *AIChE J.* **50** (10), 2481-2492 (2004).

Abstract

A new approach for predicting a wide range of phys. and thermodyn. properties is proposed. It involves calculn. of the mol. descriptors of a target compd. of unknown properties, followed by regression of this vector of mol. descriptors vs. a database of compds. with known descriptors and measured properties. The regression model, obtained for the target descriptors in terms of predictive compds. and their coeffs., is then used for prediction of properties of the target compd. The precision of the prediction can be estd. from the std. deviation of the correlation and the known precision of the property data of the predictive compds. The proposed method was tested in predicting 31 properties of 18 compds. representing different hydrocarbon structures. The results show that the method has several unique advantages, such as the use of one structural correlation to predict all properties; estn. of the prediction error for compds. without measured data; opportunities to find alternative solns. to different problems and means to est. their adequacy. The method can be used also for checking the consistency of measured data and data predicted by other methods.

24. Peeva, L.G., E. Gibbins, S.S. Luthra, L.S. White, R.P. Stateva, A.G. Livingston: "Effect of Concentration Polarisation and Osmotic Pressure on Flux in Organic Solvent Nanofiltration". *J. Membrane Science* **236**, 121-136 (2004).

Abstract

The sepn. of mols. present in org. solvents by nanofiltration has potential application in several industries, and org. solvent stable nanofiltration (NF) membranes have recently become available. There is a rapidly growing body of information available on the processes controlling solvent fluxes and solute rejections in solvent nanofiltration. However, previous work has mainly been carried out with dil. solns. (<1 wt.% solute in solvent), whereas in actual applications, solutes will be more concd. (>5 wt.%) and phenomena such as concn. polarization and osmotic pressure may contribute to the solvent flux, as in aq. systems. In order to improve our understanding of org. solvent nanofiltration phenomena, expts. were performed in a cross-flow rig in which NF was carried out in a continuous mode. Solns. of different concns. (up to 20 wt.%) of tetraoctylammonium bromide and docosane in toluene were used. Description of the exptl. data, including prediction of solute rejection, was performed using the soln. diffusion model for membrane transport and the film theory for liq. mass transfer effects. The results show that the org. systems cannot always be described by a simple osmotic pressure model. The flux through the membrane is affected by the cross-flow velocity, indicating that concn. polarization induces mass transfer limitations. The fit between the model and the exptl. data is markedly improved by allowing the activities of the soln. components to vary, indicating that these systems are non-ideal.

25. Wakeham, W.A., R.P. Stateva: "Numerical Solution of the Isothermal Multiphase Flash Problem". *Reviews in Chemical Engineering* **20**, 1-56 (2004).

Abstract

A review. The application of a wide range of numerical methods and optimization techniques for the soln. of the phase equil. problem is demonstrated. After a brief discussion of the thermodyn. of the phase equil. of multicomponent systems, the multiphase isothermal, isobaric flash problem is outlined followed by the direct minimization of the Gibbs free energy. Next, the minimization of the tangent-plane distance function (TPDF) is treated. Then, Michelsen's approach and global optimization methods are described. Results are presented for the H₂S/CH₄ system at T = 190 K and P = 40.53 bar. Further phase equil. calculns. were carried out in a stage-wise and nonstage-wise manner. Results are given for the ethylene glycol, lauryl alc., and nitromethane system at T = 295 K and P = 0.1 MPa. Finally, the area method is illustrated.

26. Polishuk I, R.P. Stateva, J. Wisniak, H. Segura H: "Simultaneous prediction of the critical and sub-critical phase behavior in mixtures using equations of state IV. Mixtures of chained *n*-alkanes". *Chem. Eng. Sci.* **59**, 633-643 (2004).

Abstract

The present study compares the ability of two semi-predictive approaches, namely the global phase diagram approach (GPDA) and the predictive Soave-Redlich-Kwong model (PSRK), for describing the exptl. data in the binary homologous series of *n*-alkanes. A method to expand the application of the GPDA model to the heavy *n*-alkanes, absent in the Design Institute for Phys. Property Data (DIPPR) data base, is proposed. Since both models do not implement the binary data of the systems under consideration for evaluation of

their parameters, they appear here as entirely predictive. Both models are reliable in predicting the data of sym. systems and they yield deviations that do not significantly exceed the possible exptl. uncertainties. The robustness and reliability of GPDA in comparison with PSRK becomes evident predicting the data of asym. systems. PSRK tends to overestimate the liq.-liq. immiscibility range and as a result it over predicts the phase equil. pressures and fails to describe the global phase behavior. In contrast, GPDA describes the global phase behavior exactly and yields accurate predictions of both the crit. and the sub-crit. data even for asym. systems, such as propane-n-hexatetracontane.

27. Balogh, J., T. Csendes, R.P. Stateva: "Application of a Stochastic Method to the Solution of the Phase Stability Problem: Cubic Equations of State". *Fluid Phase Equilibria* **212**, 257-267 (2003).

Abstract

Phase equil. calcns. and phase stability anal. are of fundamental importance in various chem. engineering applications, such as azeotropic and three-phase distn., supercrit. extrn., petroleum and reservoir engineering, etc. Phase stability is often tested using the tangent plane criterion, and a practical implementation of this criterion is to minimize the tangent plane distance function (TPDF), defined as the vertical distance between the molar Gibbs energy surface and the tangent plane for given phase compn. In the present work, we use a modified TPDF and an equation of state as the thermodyn. model. We advocate a stochastic sampling and clustering method to locate the min. of the TPDF and compare its reliability with some of the most promising global optimization methods. Our method is user-friendly and not computationally demanding regarding the no. of function evaluations, and CPU time.

28. Polishuk, I., R.P. Stateva, J. Wisniak, H. Segura: "Prediction of High Pressure Phase Equilibria Using Cubic EOS. What Can Be Learned?". *Can. J. Chem. Eng.* **80**, 927-942 (2002).

Abstract

Modern semi-empirical cubic equation of states (EOSs) are usually attached by complex functionalities, such as Huron-Vidal (HV)-type mixing rules. Although this practice improves the flexibility of the models, it also complicates consideration of an overall picture of phase behavior. As a result, excess Gibbs energy (GE)-based equations are usually adjusted to the exptl. data by way of a local fit. The latter approach tends to ignore that different regions of the thermodyn. phase space are closely inter-related. The present study demonstrates that the contribution of (HV)-type mixing rules to predicting high-pressure phase equil. can be quite modest and that in addn. they may generate non-realistic phase diagrams.

29. Wakeham, W.A., G.St. Cholakov, R.P. Stateva: "Liquid Density and Critical Properties of Hydrocarbons Estimated from Molecular Structure". *J. Chem. Eng. Data* **47**(3), 559-570 (2002).

Abstract

The paper provides new correlations for the estn. of the relative liq. d. and crit. parameters of hydrocarbons. The correlations employ mol. descriptors from computer simulation of mol. mechanics, which proved valuable in our previous work. High precision is achieved, without the use of unduly complex descriptors and rules, as a result of improved methodol. The new methodol. includes a limit upon the functionality of the property database and its pre-design by expanding the range and improving the distribution of the repeating structural features in the selected compds. A compilation of estd. data for the liq. d. and crit. properties of some hydrocarbons of industrial importance for which no values have been available before is provided.

30. Wakeham, W.A., G.St. Cholakov, R.P. Stateva: "Consequences of property errors on the design of distillation columns". *Fluid Phase Equilibria* **185** (1-2), 1-12 (2001).

Abstract

In modern design simulators, the initial input for the estn. of the phase behavior of mixts. is a series of characteristic parameters of the pure species, such as the normal b.p. T_b , the crit. temp. T_c and the crit. pressure P_c . For many components encountered in practice, these parameters are not available from expt., and therefore, they must be estd. The study of the propagation of errors in these estd. parameters through to the final design of an item of process plant - a distn. column sepg. binary and ternary mixts. - is the purpose of the present work. The likely magnitude of uncertainties in the input T_b , T_c and P_c is generated

by the application of several popular and accepted methods. Considerable uncertainties in the predicted designs are demonstrated. Greater attention should be devoted to the development and employment in modern simulators of more sophisticated methods ensuring better description of mol. structures and intermol. interactions.

31. Sovova, H., R.P. Stateva, A.A. Galushko: "Solubility of β -carotene in supercritical CO₂ and the effect of entrainers". *J. Supercritical Fluids* **21**, 195-203 (2001).

Abstract

Solubilities of trans- β -carotene in supercrit. CO₂, both pure and modified, were measured at temps. 313.2, 323.2 and 333.2 K and pressures up to 28 MPa using a one-pass flow app. The soly. data measured in pure CO₂ were correlated by the d.-based equation proposed by Chrastil, and modelled using the Soave-Redlich-Kwong cubic equation of state. Most of the literature data were in good agreement with our results; smaller discrepancies were ascribed mostly due to β -carotene degrdn. While ethanol entrainer increased the soly. of beta-carotene in supercrit. CO₂ by one order of magnitude, vegetable oil was less efficient. In both cases, the increase in soly. was proportional to square root of entrainer concn.

32. Sovova, H., R.P. Stateva, A.A. Galushko: "Essential Oils from Seeds. Solubility of limonene in supercritical CO₂ and how it is affected by fatty oil". *J. Supercritical Fluids* **20**, 113-129 (2001).

Abstract

Fatty oil influence on the soly. of limonene in CO₂ was investigated under pressures 8-12 MPa at 313.2 K, a temp. typically applied in supercrit. fluid extrn. of essential oils. Soly. in CO₂ was measured using the dynamic method both for limonene and for the mixt. of limonene and black currant seed oil. In the whole range of pressures applied, the concn. of fatty oil in the vapor phase is negligible in comparison with the concn. of limonene. Limonene is distributed between the liq. phase rich in fatty oil and the vapor phase rich in CO₂, and its equil. concn. in the latter decreases with the diminishing limonene-to-oil ratio in the saturator. There is a steep increase of the limonene partition coeff. with pressure between 8 and 10 MPa, near the crit. pressure of the binary mixt. of limonene and CO₂. The obsd. behavior of the three-component system was confirmed and explained by thermodyn. modeling. The thermodyn. model applied was the Soave-Redlich-Kwong cubic equation of state with either the one fluid linear van der Waals mixing rule or with the MHV2 mixing rule. Appropriate conditions for an efficient supercrit. fluid extrn. of essential oils from seeds follow from the results obtained. Extn. pressure should be approx. 20% larger than the crit. pressure of the essential oil+CO₂ binary mixt. and rather tight packing of the ground seed in the bed should be applied.

33. Stateva, R.P., G.St. Cholakov, A.A. Galushko, W.A. Wakeham: "A Powerful Algorithm for Liquid-Liquid-Liquid Predictions and Calculations". *Chem. Eng. Sci.* **55**, 2121-2129 (2000).

Abstract

The paper describes a new robust and efficient algorithm for liq.-liq.-liq. equil. (LLE) predictions and calcn. The architecture of the algorithm is a two-level, one, and a judicious combination of a stability anal., carried out in the first stage, with phase identification routines and liq. flash calcns., carried out in the second stage, is realized. The numerical routines require modest computational efforts and demonstrate excellent convergence characteristics. The thermodyn. model applied to a system does not influence the robustness of the new algorithm, which can treat any model and handle any no. of components and phases. The usefulness and efficiency of the new algorithm is exemplified by using two model systems, a water + oil + non-ionic surfactant system and the system ethylene glycol + lauryl alc. + nitromethane.

34. Cholakov, G.St., W.A. Wakeham, R.P. Stateva: "Estimation of Normal Boiling Points of Hydrocarbons from Descriptors of Molecular Structure". *Fluid Phase Equilibria* **163**, 21-42 (1999).

Abstract

Correlations for estn. of thermophys. properties are needed for the design of processes and equipment related to phase equil. The normal b.p. (NBP) is a fundamental characteristic of chem. compds., involved in many correlations used to est. important properties. Modern simulation packages usually require the NBP and a std. liq. d. from which they can est. all other necessary properties and begin the design of particular

processes, installations and flowsheets. The present work contributes a correlation between the mol. structure and the normal b.p. of hydrocarbons. Its main features are the relative simplicity, sound predictions, and applicability to diversified industrially important structures, whose b.ps. and nos. of carbon atoms span a wide range. An achievement of particular interest is the opportunity revealed, for reducing the no. of the compds. required for the derivation (the learning set), through multivariate anal. and mol. design. The high accuracy achieved by the correlation opens up a possibility for systematic studies of chem. engineering applications in which the effects of small changes are important. This also defines a path towards the more general problem of the influence of uncertainties in calcd. thermophys. parameters on the final outcome of computer aided simulation and design.

35. Elhassan, A.E., St.G. Tsvetkov, R.J.B. Craven, R.P. Stateva, W.A. Wakeham: "A Rigorous Mathematical Proof of the Area Method for Phase Stability". *Ind. Eng. Chem. Res.* **37**, 1483-1489 (1998).

Abstract

The paper introduces new developments of the original AREA method. A rigorous math. proof that the equil. points are the only ones which satisfy the max. AREA criterion in the case of a two-component, two-phase system is given for the first time. A rigorous proof that the max. AREA criterion is a necessary but not a sufficient condition for equil. in the case of an N-component, two-phase system is given also for the first time in the paper. Two test examples which reinforce the validity of the theor. results obtained are presented and discussed.

36. Stateva, R.P., W.A. Wakeham: "Phase Equilibrium Calculations for Chemically Reacting Systems". *Ind. Eng. Chem. Res.* **36**, 5474-5482 (1997).

Abstract

An overall strategy for phase equil. calcns. within chem. reacting multicomponent nonideal systems is presented. The strategy involves three stages and employs an indirect method to det. the phase configuration of the reacting system at equil. The latter is based on an existing technique for the soln. of the phase equil. problem extended to include chem. reacting systems. Independently, a new algorithm for chem. equil. calcns. in any prescribed no. of phases is advocated. A detailed anal. of its computational efficiency on the basis of multiplication operations required is provided. Results for three chem. reacting systems, two of which exhibit complex phase equil., are given and compared with the results of other authors.

37. Tsvetkov, St.G., R.P. Stateva: "A Computationally Efficient Algorithm for Simultaneous Phase and Chemical Equilibrium Calculations". *Coll. Czech. Chem. Comm.* **62**, 558-574 (1997).

Abstract

The paper recommends a particularly effective modification of the K-value approach to simultaneous phase and chem. equil. Three examples are presented - the esterification reaction of ethanol with acetic acid, the synthesis of methanol, and the butylation of m-xylene. Discussed are the reliability and computational efficiency of the new algorithm.

38. Stateva, R.P., A.E. Elhassan, R.J.B. Craven, K.M. de Reuck: "Predicting and Calculating Complex Phase Equilibria from Equations of State Models: A Case Study of a Prototype Liquefied Natural Gas System". *Chemical Engineering Research and Design* **73**, 582-588 (1995).

Abstract

Two methods, a Soave-Redlich-Kwong cubic equation of state and a two-fluid corresponding states procedure, models A and B, resp., were used to predict the three-phase equil. compns., pressures and liq. molar vols. for binary ethane-nitrogen and the three-phase equil. compns. and liq. molar vols. for ternary methane-ethane-nitrogen mixts. Each method uses its own phase equil. algorithm which incorporates robust stability anal. procedures. Comparisons of the predictions with exptl. results showed that both models gave good agreement with the data.

39. Stateva, R.P.: "Predicting and Calculating Complex Phase Equilibrium in Supercritical Fluid Systems with a New Technique". *Coll. Czech. Chem. Commun.* **60**, 188-210 (1995).

Abstract

A general approach to multiphase equil. calcns. with particular application to vapor-liq.-liq. and liq.-liq.-liq. systems is presented. The capabilities of the new technique to correctly predict and calc. complex phase equil. are tested on five highly non-ideal systems, relevant to supercrit. fluid extn. The thermodyn. models applied are the recently proposed Huron-Vidal second-order (MHV2) model and the Redlich-Kwong-Soave cubic equation of state.

40. Stateva, R.P., St.G. Tsvetkov: "A Diverse Approach for the Solution of the Isothermal Multiphase Flash Problem. Application to Vapor-Liquid-Liquid Systems", *Can. J. Chem. Eng.* **72**, 772-734 (1994).

Abstract

A novel approach is presented for the soln. of isothermal multiphase flash problem with particular application to systems exhibiting liq.-liq.-vapor equil. The approach includes a rigorous method for thermodyn. stability anal. as a first step and an efficient phase identification procedure. The stability anal., exercised only once, uses a modification of the Gibbs tangent plane criterion. The identification procedure implements the results of the stability test in a sequence of liq.-liq. and liq.-vapor calcns. only till the phase configuration with a min. Gibbs energy is detd. The efficiency and reliability of the proposed method is illustrated by solving three typical problems encountered in enhanced oil recovery, natural gas processing and petrochem. industry.

Публикации в международни списания без ISI импакт-фактор

1. Galushko, A.A., H. Sovova, R.P. Stateva: "Solubility of Menthol in Pressurised Carbon Dioxide – Experimental Data and Thermodynamic Modelling". *Chemical Industry and Chemical Engineering Quarterly (CI&CEQ)* **12**, 152-158 (2006).

Abstract

The paper reports new exptl. data and the results of the thermodyn. modeling of menthol soly. in pressurized CO₂. The soly. was measured using the dynamic method and modeled with the Soave-Redlich-Kwong equation of state in the temp. range 30-60 °C and pressure range 66-144 bar. The results obtained were compared with the soly. data published by Maier and Stephan and by Sovova and Jez. The agreement with Maier and Stephan was very good. The deviation of the solubilities, published by Sovova and Jez, from the other data sources was explained and revised accordingly. The paper also presents for the 1st time exptl. and modeling data for the m.p. depression of menthol in the presence of CO₂ in the pressure range of interest. The exptl. data was obtained comparing the appearance of menthol particles before and after their exposure to pressurized CO₂.

2. Sovova, H., S.A. Aleksovski, M. Bocevska, R.P. Stateva: "Supercritical Fluid Extraction of Essential Oils – Results of a Joint Research". *Chemical Industry and Chemical Engineering Quarterly (CI&CEQ)*, **12**, 168-174 (2006).

Abstract

Peppermint, creeping thyme, and sage herbs, as well as yarrow flowers were extd. with supercrit. and liq. carbon dioxide at 9-13 MPa and 25-60 °C. Two extn. periods were distinguished except in the case of thyme extn. Almost pure essential oil was extd. in the first, fast period. The extn. was retarded in the second period controlled by essential oil-matrix interaction, and waxes and water prevailed over the essential oil in the ext. To est. the effect of essential oil-vegetable oil interaction during the extn. of essential oils from seeds, the limonene + vegetable oil + CO₂ equil. was investigated using thermodyn. modeling. Changes in the compn. of the essential oil in the exts. are demonstrated on the example of sage oil. Compared to hydrodistn., the exts. contained less monoterpenes, the most volatile components, because the sepn. of the ext. from gaseous CO₂ in the cold trap was incomplete. The yield of sesqui- and di-terpenes in the exts., however, was higher than their yield by hydrodistn. The extn. of sage essential oil was most efficient at 13 MPa and 50 °C, when the yield of diterpene manool was more than two times higher than its yield by hydrodistn.

3. Stateva, R.P., A.A. Galushko, G.St. Cholakov, W.A. Wakeham: "Towards a strategy for the computer management of water + oil + surfactant systems in industrial applications". *Bulgarian Chemistry and Industry* **72**, 117-125 (2001).

Abstract

This study outlines the organization and constituent elements of a new strategy for computer management of water-oil-surfactant systems in industrial applications. Such a methodol. has not been developed before largely because of the lack of an adequate thermodyn. model but also because of the numerical difficulties assocd. with the robust soln. for any thermodyn. model. The procedure includes a thermodyn. model, a method of pure component property estn., and an algorithm of multiphase liq. equil. predictions and calcns. In order to demonstrate the application of the strategy in a clear-cut form the discussion is limited to systems with non-ionic surfactants only. The influence of different factors on phase behavior patterns of these complex systems is studied, and comparison with exptl. data available is given. The present study is a first attempt toward the development of an effective strategy for scientific selection and assessment of surfactant systems suitable for particular industrial applications.

4. Sovova, H., R.P. Stateva: "Biologically active substances treated with supercritical fluids". *Bulgarian Chemical Communications* **33**, 247-258 (2001).

Abstract

A review. Supercrit. fluids are nowadays finding application both in labs. and in large-scale technologies. Their properties make them useful as extremely versatile solvents possessing very good transport properties. Pressurized carbon dioxide is the most frequent supercrit. solvent, which is inert, non-toxic, environmentally friendly in comparison with org. solvents and it can be easily removed by depressurization. This survey is focused on the possibilities of handling biol. active materials with supercrit. fluids. In addn. to already conventional processes such as supercrit. fluid extn. and fractionation, new areas of application open in diverse fields such as pharmaceutical industry (micronization of solid materials), enzymic reactions (esp. when the reaction mixt. contains non-polar substances like lipids), and food/beverage sterilization at low temps. As the research in this field has been very extensive and a large amt. of scientific papers have been published during the last decades, the refs. in this paper had to be limited to review papers and to a selection of most recent publications.

5. Balogh, J., T. Scendes, R.P. Stateva: "Phase stability analysis using a new objective function and a global optimization method". *Magy. Kem Foly* **107** (2), 82-89 (2001).

Abstract

In the last decade there has been a considerable interest in developing (both theor. and algorithmically) new methods for the soln. of a no. of problems in chem. engineering process design, synthesis, optimization and control. The phase stability anal. problem is among the most challenging, because its formulation, either as a tangent plane distance function minimization or as a Gibbs energy minimization, requires robust and reliable numerical techniques to det. the global soln. A modified tangent plane distance function is used and a stochastic sampling and clustering method to optimize it is advocated. The efficiency and robustness of the method are demonstrated on the example of the hydrogen sulfide-methane system, which is modeled by a Redlich-Kwong-Soave cubic equation of state. The obtained results demonstrate the high level of reliability of the method in comparison with other stochastic techniques. The procedure is user-friendly and it can well be tuned by the user. The new method significantly decreases the computational cost regarding the no. of function-evaluations, and CPU time requirements which compare very favorably with other stochastic optimization methods, like plain Newton methods.