Introduction

The present issue contains some papers presented during the 21st European Symposium on Applied Thermodynamics that was held in Jurata, Poland, June 1–5, 2005. This Symposium was organized jointly by the Laboratory of Applied Thermodynamics of the Faculty of Chemistry, Warsaw University of Technology, and by the Thermodynamics Laboratory for Environmental Purposes (TALES) of the Institute of Physical Chemistry, Polish Academy of Sciences.

The idea of Symposium is bring together academic, government and industrial researchers from many countries to focus on fundamentals and applications of physical properties and phase equilibria in a wide range of industries, such as oil, gas, chemicals, pharmaceuticals, materials, biotechnology and foods. Thermodynamics is the main source of inspiration.

One hundred two lectures and posters devoted to the following subjects: Thermodynamics for Process Design; Supercritical Fluids; Petroleum Fluids; Chemical and Phase Equilibria; Interfacial Phenomena; Experimental Techniques, Data; Molecular-Based Models (Molecular Simulation); Computational Thermodynamics of Real Systems; Ionic Liquids; Environmental Applications; Bio- and Micellar Systems were presented at this meeting.

The present issue of the Polish Journal of Chemistry contains papers presented at this Symposium, only of these authors who decided to publish their contributions in Poland. These manuscripts went through the standard Polish Journal of Chemistry reviewing process. The complete list of lectures and posters presented follows this introduction.

The Symposia have a long tradition. First was organized, twenty-five years ago in 1975, second in 1976 both at the Technische Universität Berlin (Germany). The idea pointed out by the organizer, Helmut Knapp was to start free, unhampered discussion of academia and industry how to apply contemporary knowledge of thermodynamics for energy saving in the industrial practice. At that time, this was an important task. The first energy crisis just hit the world. The series of European Seminars devoted to this problem started. The organization was spontaneous. The third European seminar was organized in 1978 at the Institutted for Kemiteknik, Danmarks Tekniske Højskole, Lyngby, Denmark by late Åge Fredenslund. To ensure free exchange of ideas a Steering Committee of the Seminars consisting of chairmen of earlier seminars was formed. The seminars were organized by Academia (15) and Industry (6). Among industrial organizers were Royal Dutch/Shell, Linde AG, Norsk Hydro, ICI and Bayer AG. The seminars stimulate the flow of ideas and methods developed in Academia to industrial organizations.

The idea was widespread and in addition to European Symposia based on the same principle American – European Conferences started. The first on Phase Equilibria and Fluid Properties in Chemical Industry was held in 1977 in California (Asilomar, Pacific Grove). These Conferences are organized each third year in USA, Europe and recently also in Japan.

In 2006, the 22-nd European Symposium will be organized by Danmarks Tekniske Universitet in Lyngby.

December, 2005   *S.K. Malanowski*

Calculation of Petroleum Processes Using the Modified Distillation Package

by P. Gierycz

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A modified distillation package, elaborated in the Institute of Physical Chemistry, Polish Academy of Sciences, has been used for modelling of the existing petroleum process. The package employs a local composition model NRTLmKW [1] for calculation of multicomponent VLE equilibria. The obtained results have been compared with results given by the use of the NRTL model and discussed from the point of view of its practical applications. Some recommendations have been made on the use of the distillation package for modelling and optimization of the industrial processes.

Key words: modelling of distillation columns, multicomponent VLE calculation, NRTLmKW model

The Generalized NRTL Model Associated with the Peng-Robinson Equation of State to Predict Liquid-Liquid Equilibria Between Hydrocarbons, Water and Ethylene Glycol

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In this study, the generalized NRTL model is combined with the Peng-Robinson equation of state in order to predict the liquid-liquid equilibrium of binary systems containing hydrocarbons, water and glycols. In the proposed model, the binary interaction parameters of the NRTL model are predicted by means of a group contribution method, while the volume and surface-area parameters of pure components introduced in the generalized NRTL version are estimated from the UNIFAC group contribution method. The results obtained in this paper are compared with those provided by well known models described in the literature.

Key words: liquid-liquid equilibria, equation of state, g^E model, water + hydrocarbon systems

Parametrization of Molecular-Based Equations of State: The PC-SAFT, soft-SAFT, PHSC and PSCT Models

by F. Castro-Marcano[1], C.M. Colina[2] and C. Olivera-Fuentes[1]

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We examine the parametrization of four molecular-based equations of state (MBEOS): PC-SAFT, soft-SAFT, PHSC and PSCT. In each case, scaled critical and saturation properties are calculated and related to critical temperature T_c, critical pressure P_c and acentric factor ω through equivalent polynomial expressions. A parametrization strategy matching experimental data of T_c, P_c and ω gives good fits of saturation pressures, but deviations in saturated liquid densities reflect the limitations of each MBEOS in representing the critical region. Nevertheless, the method presented provides a simple way to determine the MBEOS parameters for a wide variety of fluids and can be extended to other models.

Key words: phase envelope, PC-SAFT, soft-SAFT, PHSC, PSCT

Numerical Algorithms for Determination of Retrograde Region of Gas Condensate Reservoir

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Two mathematical algorithms based on a cubic EOS are developed to determine the retrograde region for reservoir fluids. The first method is based on marching and the second one utilizes regression analysis. In marching method, a series of flash calculations is performed to calculate maximum L/F (moles of liquid/moles of feed). In the regression method, a non-linear regression and an optimization method in addition to a limited number of flash calculations are used to determine the maximum L/F. Based on these mathematical algorithms a computer program to predict a full phase envelope containing the retrograde curve was developed. The computer program consists of three basic parts of bubble point, dew point, and flash calculations. These three basic parts are used to determine the retrograde region. In the course of determination of the retrograde condensation region, the coordinates of critical point and cricondentherm point were also determined and used to speed up the search method. Several cases were studied and it was found that the regression method is faster and more accurate.

Key words: retrograde region, phase envelope, equation of state, critical point

Vapor-Liquid (VLE) and Liquid-Liquid (LLE) Phase Equilibria Calculations for Polystyrene + Methylcyclohexane and Polystyrene + Cyclohexane Solutions

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This paper presents the vapor-liquid (VLE) and liquid-liquid (LLE) phase equilibria pre-dictions for polystyrene in two theta solvents: cyclohexane and methylcyclohexane. VLE calculations were performed with the Elbro free volume method and a modified version of the PC-SAFT method, as well as with three UNIFAC type group contribution models: Entropic Free Volume + UNIFAC VLE 1coeff., Entropic Free Volume + UNIFAC VLE 2coeff., and Oishi-Prausnitz + UNIFAC VLE 2coeff. Solvent activities were calculated for the polystyrene + cyclohexane and polystyrene + methylcyclohexane solutions, and compared with experimental data. LLE predictions were performed with PC-SAFT method and compared with experimental data. The obtained results show that the PC-SAFT method gave the most accurate predictions for both VLE as well as LLE for the systems studied.

Key words: UNIFAC, PC-SAFT and Elbro free volume methods, solvent activities, polystyrene

An Energy-Based Cohesion Function
for Cubic Equations of State

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A cohesion function is derived for cubic equations of state of van der Waals type, based on the behaviour of the residual internal energy of pure fluids; it contains two fluid-specific constants and is therefore suitable for nonpolar and polar fluids. The characteristic constants are obtained for the van der Waals, Redlich-Kwong and Peng-Robinson equations for 846 fluids by fitting cohesion parameters computed from vapour pressures taken from the DIPPR database. Comparison with similar functions proposed in the literature shows that the new function is generally better. A corresponding states generalization is presented using the acentric and critical compressibility factors.

Study of Extraction of Cinnamon Oils from the Bark of *Cinnamomum cassia presl* by Supercritical Carbon Dioxide

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Cinnamon oils were isolated from the bark of *Cinnamomum cassia presl* by supercritical fluid extraction (SFE) and compared with steam distillation (SD). The extracts were analyzed with GC-MS. The yield from SFE was around four times as that from SD. The results from GC-MS revealed that the constituent components obtained from SFE and SD are similar while the distributions of individual compounds are different. In SFE, effects of various factors such as time (t), extraction pressure (P), extraction temperature (T), particle size (S) and flow rate of supercritical carbon dioxide (F) on the yield of target components were investigated. Favorable operation conditions were found at t = 2 h, P = 22.5 MPa, T = 50°C, S < 0.3 mm and F = 9.0 l/h.

Key words: cinnamon oils, *Cinnamomum cassia presl*, supercritical fluid extraction

VLE in (C_6H_{14} + $C_{16}H_{34}$) Mixture.
Prediction with Elbro Free Volume Method

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The main purpose of this work was a search for the dependence of VLE prediction quality on the kind of chosen *n*-alkane model system. The activities and total vapour pressure for (*n*-C_6H_{14} + *n*-$C_{16}H_{34}$) mixture at 293.15 K, 313.15 K and 333.15 K were successfully predicted with Elbro free volume method using three sets of UNIQUAC A_{ij} interaction parameters: (1) A_{ij} obtained with the semi-empirical quantum mechanical method AM1 (Austin Model 1) for (*n*-C_6H_{14} + *n*-$C_{16}H_{34}$) system, (2) A_{ij} adjusted to (*n*-C_6H_{14} + *n*-$C_{16}H_{34}$) VLE experimental data, (3) A_{ij} obtained with the CFF (Consistent Force Field) method for the chosen (*n*-alkane + *n*-alkane) model system. The predicted curves were compared with experimental data. It has been found that when sizes of the solvent molecule and a chosen segment in the second long chain molecule are comparable to the model system size then the UNIQUAC interaction parameters obtained with molecular mechanics quantitatively describe the real intermolecular forces in *n*-hexane + *n*-hexadecane system.

Key words: *n*-hexane, *n*-hexadecane, Elbro free volume method, activity, vapour pressure

Modeling of the Liquid-Liquid Equilibrium for Aqueous Solutions of Nonionic Surfactants C_iE_j

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A new thermodynamic model was developed to calculate the liquid-liquid equilibria (LLE) of aqueous solutions of nonionic surfactants. It is based on continuous thermodynamics and on Flory-Huggins theory. Besides the micellization the self association of water is taken into account in the framework of a mass-action law approach. The polydisperse mixture of micelles and water associates is described by two continuous size distribution functions depending on temperature and surfactant concentration. First, the model is applied to several aqueous solutions of *n*-alkyl polyglycol ethers (C_iE_j) with tail length i from 6 to 8 and head length j from 3 to 6, showing lower critical solution temperatures (LCST) only. Furthermore, LLE was calculated for the aqueous solutions of C_4E_1, $C_{10}E_4$ and $C_{10}E_5$ with closed-loop miscibility gaps. The agreement between calculated and experimental data is very good for nearly all systems of both types.

Key words: nonionic surfactants, aqueous solutions, liquid-liquid equilibrium, continuous thermodynamics

Experimental and Predicted Thermodynamic Properties of Mixtures Containing Corn Oil with Ketones and Alkanes Employed in Their Refine

by J.M. Resa, C. González, R.G. Concha and J.M. Goenaga

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We present new experimental data of density, refractive index, speed of sound and viscosity for the binaries of corn oil + (*n*-hexane, *n*-heptane, *n*-octane, 2-butanone, 3-pentanone and 4-methyl-2-pentanone) at T = 298.15 K and standard conditions, and the corresponding computed derived magnitudes (change of isentropic compressibility, change of refractive index on mixing and excess molar volume). A good agreement among experimental data and the values estimated by theoretical procedures was obtained.

Modelling the Solubility of Gases in Saturated and Substituted Perfluoroalkanes

by A.M.A. Dias[1], J.C. Pamies[2], L.F. Vega[2], J.A.P. Coutinho[1] and I.M. Marrucho[1]

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The importance of the study of fluorinated molecules is justified by the innumerous applications that these compounds are founding in many diverse and interesting areas as a consequence of their unusual properties. They are being used as substitutes for chlorinated solvents, surfactants in supercritical solvents, environmental probes, and in numerous biomedical applications. The choice of the best fluoroalkane to be used for a given application depends on its properties and in some cases, such as in biomedical applications, that choice has to be precise. Thus, the knowledge of the thermodynamic properties of these compounds is of extreme importance as well as the ability to describe and predict them at different conditions using thermodynamic models. In this work, the soft-SAFT EoS is used to describe the solubility of gases as oxygen, xenon and radon in saturated and substituted perfluoroalkanes. The conclusions reached in this work corroborate the experimental evidences reported in the literature indicating that the interaction between the oxygen and the CF_3 terminal group is stronger than the interaction between the oxygen and other fluorinated groups in the molecule.

Key words: solubility, modelling, perfluoroalkanes, oxygen, xenon, radon, soft-SAFT EoS

Activity Coefficients of Potassium Hydrogen Tartrate in Aqueous Solutions with Potassium Chloride at Temperatures Between 278.15 and 298.15 K

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The activities of the potassium salt of tartaric acid were obtained by an indirect potentiometric method that requires the presence in the solution of a second salt with a common ion and for which a specific electrode is available. In this study, KCl was used as the second electrolyte. Experimental data were obtained for KHT concentrations varying from 0.005 to 0.015 m, with concentrations in KCl ranging from 0.01 to 0.03 m between 278.15 and 298.15 K. To describe the non-ideal behaviour of the electrolytes in single-salt and in mixed systems, the molal ion-interaction model proposed by Pitzer was used.

Solid-Liquid Equilibria in the Quaternary System NaCl–KCl–NH$_4$Cl–H$_2$O

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The mixture parameters of the mole-fraction model of Pitzer-Simonson-Clegg pertaining to the aqueous salt pair NH$_4$Cl + KCl were obtained by fitting the semi-empirical equations to the solid-liquid distribution data measured for KCl and NH$_4$Cl, at 293, 313 and 333 K, as well as to experimental solubilities of NaCl in the quaternary system NaCl + KCl + NH$_4$Cl + H$_2$O. The fitted parameters and the solid-liquid equilibria (SLE) data were used to estimate the activity coefficients of KCl and NH$_4$Cl in the solid phases, thus allowing the calculation of the eutonic points of the discontinuous series of solid solutions precipitated from aqueous solutions containing both chlorides.

Thermochemical Study of Indium Nitride

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Fluorine bomb calorimetry was applied for determination of the standard molar enthalpy of formation $\Delta_f H_m^0$(InN, 298.15 K). The combustion reaction of InN with fluorine was following: $InN(cr) + \frac{3}{2} F_2(g) = InF_3(s) + \frac{1}{2} N_2(g)$. Standard molar enthalpy of formation $\Delta_f H_m^0$ (InN, 298.15 K) = –(146.5 ± 4.6) kJ/mol has been calculated from the measured standard massic energy of reaction: $\Delta_c u$(InN) = –(8396.1 ± 7.6) J/g. Indium nitride was analysed for trace levels of metals and other elements.

H/D Isotope Effects on Miscibility of Nitrobenzene with *n*-Hexane

by E. Starościak, A. Siporska, A. Makowska and J. Szydłowski

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The miscibility of nitrobenzene with *n*-hexane and their deuterated forms over a broad concentration range has been determined. All the measured systems present the phase diagrams with the upper critical solution temperature (UCST). It appears that deuterium substitution in CH bonds in either molecule leads to the remarkable upward shift of the UCST, increasing the domain of the limited miscibility. The phase diagrams were described by a scaling equation with a critical exponent β close to the theoretically predicted value and practically independent of isotope substitution. The origin of the isotope effects on the miscibility in the systems studied was briefly discussed.

Key words: phase diagram, deuterium, nitrobenzene, hexane

Conductivity of 1-Butyl-3-methyl-imidazolium Chloride Solutions in Alcohols

by U. Domańska and E. Bogel-Łukasik

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This work presents the ionic conductivity of 1-butyl-3-methylimidazolium chloride [bmim][Cl]'s solutions in alcohols (ethanol, 1-butanol, 1-hexanol, 1-octanol, 1-decanol, 2-butanol, 2-methyl-2-propanol) and that of pure alcohols measured in wide range of temperature and concentration. The values of limiting conductance were determined by the Onsager limiting law. The molar conductivities of these systems were presented as a function of temperature and concentration. The mathematical description of ionic conductivities data by the Vogel-Tammen-Fulcher equation was made. It was shown that the conductivity of [bmim][Cl]'s solutions in the relatively low dielectric constant media is affected by the length of an alcohol carbon chain.