Proceedings

Colloquium to promote experimental work in Thermophysical Properties for Scientific Research and Industry

September 3 - 4, 2009 at Mines ParisTech, Paris, FRANCE.

In Honor of the 60th Birthday of Prof. Dominique Richon

Dominique Richon’s laboratory, after more than 30 years has developed several apparatuses for measurements of thermodynamics properties in regions where the behavior of fluids and fluids mixtures are quite complex (see: http://www.fcep.ensmp.fr/Accueil_Eng.htm). Of course the quality of experimental data, published by his laboratory in more than 200 papers, is well considered by scientific and industrial communities.
Honorary Chairman: Prof. John M. Prausnitz

Citations

"Models come and go, but good data are forever!" (John M. Prausnitz)

"Theory suggests but experiment decides" (Izaak M. Kolthoff).

Chair: Luis A. Galicia-Luna

Co Chairs: Henry V. Kehiaian, Christophe Coquelet, Amir H Mohammadi
Organizing committee

Luis A. Galicia Luna
Henry V. Kehiaian
Amir H. Mohammadi
Christophe Coquelet

Secretary

Dominique Blondeau

Special thanks to Instituto Politécnico Nacional, Armines and Mines Paristech for their helps and advice in the organization of this colloquium
# Scientific Committee

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<td>Josefa Fernandez</td>
<td>Universidad de Santiago (Spain)</td>
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<td>John P. O’Connell</td>
<td>University of Virginia (USA)</td>
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<td>Giancarlo Scalabrin</td>
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<td>Jürgen Gmehling</td>
<td>Universität Oldenburg (Germany)</td>
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<td>Michael Frenkel</td>
<td>NIST, Boulder (USA)</td>
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<td>Hiroshi Inomata</td>
<td>Tohoku University (Japan)</td>
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<td>Christophe Coquelet</td>
<td>Mines ParisTech (France)</td>
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<td>Amir H. Mohammadi</td>
<td>Mines ParisTech (France)</td>
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SPONSORS

The organizing committee wishes to express special thanks to ARMINES, Instituto Politécnico Nacional, EXXONMOBIL and SHELL for their financial support.

http://www.ensmp.fr/Accueil

http://www.armines.net

http://www.ipn.mx

http://www.shell.com

http://www.exxonmobil.com
## Technical program

*Thursday, September 3rd, 2009*

Auditorium "Amphi" of the Ecole des Mines de Paris located at 60 bd Saint Michel, 75006, Paris (France)

### Opening Ceremony: Honorary Chairman: John M Prausnitz

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<td>Directeur Mines ParisTech</td>
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<tr>
<td>9h20-9h40</td>
<td>Didier Mayer</td>
<td>Directeur Centre Energetique et Procédés</td>
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<td>9h40-9h50</td>
<td>Luis A. Galicia-Luna</td>
<td>Colloquium Chairman</td>
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### Opening Lectures

Chair: Kai Fischer and Luis A. Galicia-Luna

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<td>10h50-11h40</td>
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<tr>
<td>11h45-12h05</td>
<td>Giancarlo Scalabrin</td>
<td>A Fundamental Equation of State for the Ammonia-Water System in the Extended Equation of State Format</td>
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<td>12h05-12h25</td>
<td>Fernando García</td>
<td>Modeling of the Three-Phase Vapor-Liquid-Liquid Equilibria of a Natural-Gas System Rich in Nitrogen with the PC-SAFT EoS</td>
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<td>Patrice Paricaud</td>
<td>Hydrogen production by the sulfur-iodine cycle: modeling the phase equilibria of the HIX mixture using the SAFT-VRE equation of state</td>
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<td>Antonin Chapoy</td>
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### Lecture

Chair: Josefa Fernandez and Amir H. Mohammadi

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<td>Fernando del Rio</td>
<td>Beyond corresponding states: a successful nonconformal theory</td>
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<td>Alexander Bolotov</td>
<td>Electrostriction of Magnesium Perchlorate Solutions</td>
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<td>Luis Galicia-Luna</td>
<td>New Analytic Apparatus for experimental determinations of VLE and Saturation Densities</td>
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<td>Vicente Gomis</td>
<td>Isobaric Vapour-Liquid-Liquid Equilibrium Determination</td>
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<td>Katsumi Tochigi</td>
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<td>Erlin Sapei</td>
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<td>Compressibility of Liquids. Rule of Noncrossing P-V Curvatures</td>
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Auditorium "Amphi" of the Ecole des Mines de Paris located at 60 bd Saint Michel, 75006, Paris (France)

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<td>Antonio Marcilla</td>
<td>Capabilities and Limitations of Local Composition Models and Methods for Condensed Phase Equilibrium Calculations</td>
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<td>Mauricio E. Flores</td>
<td>Topological Approach to Barotropic Phenomena in Asymmetric Mixtures</td>
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<td>Silvia A. Wilinski</td>
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<td>Yoshiyuki Sato</td>
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<td>Jean-Yves Coxam</td>
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Lectures
Chair: Christophe Coquelet and Olivier Baudouin

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<td>Josefa Fernandez</td>
<td>Gas solubility and Volumetric Behaviour of Carbon dioxide+lubricant systems</td>
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<td>Luis A.</td>
<td>Vapor-Liquid Equilibria and Saturation Densities of Carbon Dioxide + 1-Butanol</td>
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<td>Esther Rilo</td>
<td>Densities and Derived Thermodynamic Properties of Ternary Mixtures BMIM-BF4 + water + ethanol at Seven Pressures and Two Temperatures</td>
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<td>Ricardo Hernandez-Tinoco</td>
<td>Measurement of compressed liquid densities of n-heptane + n-octane and n-heptane + n-nonane binary mixtures up to 25 MPa</td>
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<td>High-pressure vapor-liquid equilibria and densities of ternaries mixtures of carbon dioxide + nonane + benzothiophene</td>
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<td>Jose F. Martinez-Zaragoza</td>
<td>Application of Artificial Neural Networks to Modeling Experimental P ,V, T Data Obtained by Vibrating Tube Densimeter for Refrigerant R134a, at Temperatures Ranging Between 253.15 K and 423.15 K and Pressures up to 70 MPa</td>
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<td>Compressed liquid densities for binary mixtures of octane + undecane and octane + tetradecane at pressures up to 25 MPa and temperatures from (313 to 363) K</td>
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<td>Elise El Ahmar</td>
<td>Isothermal vapor-liquid equilibrium study of three binary systems: N₂ -SO₂, O₂ -SO₂ and Ar-SO₂</td>
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Chien Bin Soo | Study of Biofuels: development of specific thermodynamic models
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Farid Brahim Belaribi | Excess molar enthalpies at 298.15 K and 1 atm of 1,2-Dichloroethane + Ethers binary systems
Veronica Belandria | Volumetric Properties of the (Tetrahydrofuran + Water) and (Tetra-n-butyl Ammonium Bromide + Water) Systems: Experimental Measurements and Correlations
Veronica Belandria | A Static-Analytic Apparatus with a Mobile Sampler for Simultaneous Compositional and Gas Hydrate Phase Equilibrium Measurements
Waheed Afzal | Solubility of Carbonyl Sulfide in Glycols: Experimental Data, and Modeling Using the Cubic-Plus-Association Model

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| Industry: |
| O. Baudouin (Prosim, France), P. Arpentinier (Air Liquide, France), P. Mougin (IFP, France), F. Montel (TOTAL, France), D. Amoros (Rhodia, France), G. Lauhermann (Linde, Germany), K. Fischer (Shell, Netherlands) and S. Northrop (Exxon Mobil, USA) |

"The Essential Importance of Experimental Research and the use of experimental thermodynamics to the benefit of industry"

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Banquet

Nos ancêtres les Gaulois

Friday September 4th at 7.30 pm

http://www.nosancetreslesgaulois.com

"Ile Saint-Louis"
39, rue Saint-Louis-en-l’Ile
75004 Paris
Tél : (33)1 46 33 66 07 / (33)1 46 33 66 12
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LECTURES
The Essential Importance of Experimental Research for Advancing Chemical Engineering Thermodynamics

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Abstract

In chemical process design, we like to calculate required thermodynamic properties from correlations such as equations of state, excess Gibbs energy models and a variety of semi-empirical equations for vapor pressures, densities, surface tensions, etc. However, we sometimes forget that all of these relations depend on results from experimental measurements. Our correlations cannot exist without an experimental-data base.

To illustrate the essential importance of experimental data, some examples show new phase-behavior phenomena that cannot be predicted from theory or correlations. Further, while molecular simulation often provides a powerful tool, it too can fail to represent nature unless good experimental data are available to establish the all-important force field.

Experimental studies are especially important for quantitatively giving the physical properties of complex fluid mixtures that are often encountered in the chemical and related industries. For complex mixtures, we have few, if any, truly reliable theories. The required experimental studies are difficult; they demand much patience, ingenuity and painstaking attention to details. Fortunately, the laboratory for physical properties and phase behavior at the École des Mines is able to produce excellent experimental results due to its gifted director, Professor D. Richon. His laboratory is a jewel of French science.
The Universal Group Contribution Equation of State VTPR - Present Status and Potential for Process Development

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A prerequisite for the synthesis, design and optimization of unit operations or whole plants in the chemical, pharmaceutical, food, gas processing and petrochemical industry is a reliable knowledge of the thermophysical properties, in particular the phase equilibrium behavior of the systems considered. Since the measurement of the required but missing thermophysical properties is very time-consuming, reliable predictive models are required.

Already more than 30 years ago powerful predictive $g^E$-models, such as ASOG and UNIFAC for the prediction of vapor-liquid equilibria were developed. With the development of modified UNIFAC the range of applicability was even extended to other phase equilibria and excess enthalpies. But $g^E$-models in contrast to equations of state show the disadvantage, that they cannot be applied to supercritical compounds and that they can not be used to calculate enthalpies, heat capacities, densities (e.g. excess volumes), entropies, etc. for the pure compounds and their mixtures as a function of temperature, pressure and composition.

After the development of $g^E$-mixing rules, the group contribution concept could be applied for equations of state. The result was a group contribution equation of state, such as LCVM, PSRK ... In the meantime these group contribution equations of state were further revised by using an improved equation of state and improved mixing rules. At the same time all kind of thermodynamic data were used to fit the required reliable temperature dependent group interaction parameters simultaneously to all kind of phase equilibrium data (VLE, $\gamma^\infty$, LLE, SLE, gas solubilities, azeotropic data) and excess properties ($h^E, c_p^E$) stored in the Dortmund Data Bank.

The result of our activities is the universal group contribution equation of state VTPR. In the lecture after a short outline about the historical development of predictive thermodynamic models, typical results of the group contribution equation of state VTPR for pure components properties as well for the mixtures and further applications of industrial interest should be presented.
Global Information System in Thermodynamics:
Magnifying the Value of Experimental Thermophysical Property Data

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Global Information Systems can be defined as information systems designed to collect, process, integrate, evaluate, and communicate the entire “body of knowledge” pertaining to a field and to support any application requiring this knowledge in an “on-demand” mode with definitive information quality assessments. The presentation will outline the major components of the global information system in thermodynamics, ThermoGlobe, developed at the U. S. National Institute of Standards and Technology. The impact of the ThermoGlobe in “magnifying” the value of experimental thermophysical property data will be discussed emphasizing such aspects as quality and integrity of the process of the data “production”, efficiency of the data communication, critical data evaluation, “bundling” with engineering applications, and strategic experiment planning.

Keywords: Expert Systems, Information Management, Properties, Thermodynamics, Thermophysics, ThermoGlobe
Complex Phase Behaviour at High Pressure

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In the chemical industry and in the oil and gas industry high-pressure processes and operations frequently occur. Examples are reactions with compressed gases, the synthesis of acetic acid and methanol, hydrogenation and oxosynthesis, polymerization reactions, and the recovery of oil and gas. In all these processes high-pressure phase equilibria play an important role. In most cases this concerns two-phase equilibria, but sometimes more complex phase behaviour is encountered.

I this contribution I will discuss some examples of multiphase behaviour in systems of (potential) industrial importance. These examples are related to the production of oil and gas, supercritical processing, the production of polyolefins and the removal of carbon dioxide from process streams.
Reflections on the interplay of experiment, theory, molecular simulation, and modeling of chemical engineering properties

John P. O'Connell

The role of chemical engineering properties modeling is to provide reliable and accurate descriptions of thermodynamic and transport properties, as well as molecular and mesoscopic structure, for process and product design. While theories and molecular simulation give simplified results for systems of varying idealization, it is experiment which quantitatively demonstrates Nature's richness and provides the benchmark information that models must capture to adequately serve for the task at hand.

The presentation will describe a view about the objectives of modeling, strategies for model development including parameterization and regression, and the influences that experiment should impose on the process. Examples from a variety of systems and conditions will be illustrated.
Heuristic Modeling for Thermodynamics: State of the Art and Prospects

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The heuristic methods began to be used in thermodynamic modeling more than 25 years ago and from then on several developments have been set up and high accuracy dedicated equations of state (DEoS) according to these methods have been made available up to now for a large number of fluids. In this context only DEoS in fundamental form, i.e., in the Helmholtz energy form, are considered.

In the present lecture it is at first discussed the sound technique for the optimisation of the functional form of a pure fluid DEoS, historically developed by W. Wagner and coworkers. For the extension of the technique to mixtures the method of Tillner-Roth is then considered. These methods are synthetically presented and their advantages and disadvantages are then discussed.

In the last few years the research group of the author proposed a substantial improvement of the historic extended corresponding states method transforming it into a heuristic one to be applied both to pure fluids and mixtures and indicated with the acronym ECS-NN.

The same authors have then overcome this method presenting a completely general technique, known as ‘extended equation of state – neural network’, indicated with the acronym EEoS-NN, which has been extended to the mixtures as well. For a mixture the method does not require the preliminary set up of any mixing rule.

Through the EEoS-NN method the DEoSs for the pure fluids sulfur hexafluoride (SF$_6$) and 2-propanol (i-C$_3$H$_8$O) and for the strongly deviating mixture NH$_3$-H$_2$O have been obtained.

Applying the same EEoS-NN method the research activity has been furthermore addressed toward the modeling of the ternary mixture 2-propanol – water – propylene in a large range of temperatures and pressures. This mixture is suitable to study an extraction operation case in which a light solvent (propylene) selectively extracts a component (2-propanol) from a homogeneous liquid mixture (2-propanol – water). Once the DEoS of this target system could be obtained it can be used to search for the more effective sequence of thermodynamic transformations to get a more efficient extraction from the energetic point of view. It is noteworthy that the thermodynamics of this system cannot be representing through the conventional literature methods.

Moreover, the studies about these modeling methods have pointed out the necessity of an analysis of the set up of the data base from which to start the heuristic development of a DEoS. This analysis has shown a particular hierarchy of the type of experimental data required to obtain the Helmholtz energy form of the DEoS, depending on which $\partial^i$ derivatives are involved in the expression of each thermodynamic quantity.

For a heuristic method primary quantities for the composition of the training data base are single phase densities and coexistence in terms of phase equilibria and saturation densities of the coexisting phases. In particular, from these data the EEoS-NN method allows to get a good quality DEoS for the representation of all the thermodynamic quantities. These characteristics of the method lead to an optimization of the experimental effort needed to obtain a DEoS for a target system. These innovative modeling methods, together with the coordinated experimental activities, create the prospects both for setting up an accurate DEoS for a target mixture inside a particular window of interest with the lower experimental effort, and for studying the thermodynamic optimization of a unit operation involving such target mixture inside that window. The study also indicates which equipments the experimenter should primarily use to set up the more effective data base for the EEoS-NN training. Consequently, the lines of development of innovative experimental equipments for the present purpose become also evident, encouraging the experimenter to follow them.
Gas Solubility and Volumetric Behaviour of Carbon Dioxide + Lubricant Systems

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Abstract

The use of biodegradable lubricants, such as polyol esters and polyalkylene glycols (PAG), have been proposed for applications in air conditioning and refrigeration industries using different refrigerants, as HFCs and carbon dioxide. These lubricants have properties friendly to the environment; most of them do not evaporate, are not toxic and are stable as liquids over a very wide temperature range [1-3]. Also, they are miscible with refrigerants, such as carbon dioxide, which makes them appropriate candidates for use in refrigeration systems. However, thermophysical properties are generally not available. Therefore it is necessary to study these properties before testing a specific lubricant in a CO\textsubscript{2} refrigeration system.

In the last years, our research group has been working in lubricants (PAGs and esters) as well as their mixtures with CO\textsubscript{2} [1-3]. We have recently measured the solubility of CO\textsubscript{2} in several polyol ester oils and a PAG lubricant from 283 K to 348 K up to 8 MPa with an isochoric technique [2]. Moreover, the densities for compressed CO\textsubscript{2} + polyol esters with an Anton Paar HPM densimeter from 278.15 K to 398.15 K up to 120 MPa have been also determined. For this purpose computer-operated-densimetric equipment [4] was coupled to an isobaric loading system equipped with syringe pumps ISCO Teledyne. In this work, we will present and analyze our last results on solubility and volumetric behaviour of carbon dioxide+lubricant systems.

Key words: Density, solubility, carbon dioxide, lubricant, polyol esters, polyalkylene glycols

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ORAL
COMMUNICATIONS
A Fundamental Equation of State for the Ammonia-Water System in the Extended Equation of State Format

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An innovative method for the regression of a fundamental equation of state of a mixture was recently proposed. The technique, indicated as extended equation of state, adopts a framework similar to the extended corresponding states method, but a one-fluid model cubic equation for the target mixture is assumed instead of the equation of state of the reference fluid and the shape functions are expressed through a multilayer feedforward neural network. The use of a neural network assures a very high flexibility of the functional forms to be regressed, allowing the resulting model to represent the thermodynamic properties of a mixture with an accuracy comparable to that attained by the state-of-the-art multiparameter equations of state for mixtures. The technique has been applied here to the water-ammonia system drawing its dedicated equation of state in a heuristic mode directly from the available experimental data.

The majority of the data covers the range for temperatures from 250 to 525 K and for pressures up to 40 MPa and this is also the validity ranges of the developed equation.

For the present case, primarily due to the unfavorable situation of the data, all the available thermodynamic properties have been used for the regression procedure in order to get the expected accuracy.

The model has been successively validated for the data sets of coexistence, density, isobaric and isochoric heat capacities, and enthalpy differences. The obtained results are satisfactory because the proposed equation of state represents the available data within their mean experimental uncertainty.
Modeling of the Three-Phase Vapor-Liquid-Liquid Equilibria of a Natural-Gas System Rich in Nitrogen with the PC-SAFT EoS†

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In this work, we present the modeling of the vapor-liquid-liquid equilibria for a mixture of natural gas containing very high concentrations in nitrogen (51.8 mole fraction %) from the PC-SAFT equation of state. The interest of studying this mixture is due to the experimental evidence of the occurrence of multiple equilibrium liquid phases for this mixture over certain ranges of temperature and pressure. The calculation of the multiphase equilibria was carried out by using an efficient numerical procedure based on the minimization of the system Gibbs energy and thermodynamic stability tests to find the most stable state of the system. The results of the calculated vapor-liquid-liquid equilibria showed that the PC-SAFT equation of state predicts satisfactorily the phase behavior that experimentally exhibits this mixture. In addition, we have determined the phase envelope for this mixture through isothermal flash calculations whereas the calculation of the critical point was performed by using the algorithm of Heidemann and Khalil. In this case, the obtained results showed that this mixture does not present vapor-liquid critical point, which indicates that the calculated two phase envelope is essentially a dew-points curve.

† Paper dedicated to Professor Dominique Richon on the occasion of his 60th anniversary
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Hydrogen production by the sulfur-iodine cycle: modeling the phase equilibria of the HIx mixture using the SAFT-VRE equation of state.

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Hydrogen as an energy carrier is a possible answer to the increasing demand for energy and to the decrease of CO₂ emissions. The Sulfur-Iodine (SI) cycle is a promising way of producing hydrogen industrially. The SI process is a series of chemical reactions and separation operations that sum as the decomposition of water into hydrogen and oxygen. The design and optimisation of separation units of the sulfur-iodine (SI) process for hydrogen production requires a thorough understanding of the thermodynamic behaviour of the involved mixtures. Here, we apply the SAFT-VRE equation of state for electrolyte solutions to represent the phase equilibria of the HIx mixture (HI+H₂O+I₂) encountered in the reactive distillation column where hydrogen is produced. The SAFT-VRE model is a molecular based equation of state that takes hydrogen bonding, ion-solvent, and ion-ion interactions into account. One key advantage of the SAFT-VRE model is the possibility to predict densities and the effect of pressure on thermodynamic properties. The vapour-liquid, liquid-liquid and solid-liquid equilibria of the binary mixtures (I₂+H₂O, HI+I₂ and H₂O+HI) are accurately represented with the SAFT-VRE model using a few adjusted parameters.
In this communication, new experimental data are reported for the water content of methane and two synthetic gas mixtures in equilibrium with hydrates at pressures range from 5 MPa to 40 MPa and temperature down to 251.65 K. The measurements have been made on equilibrated samples taken from a high-pressure variable volume hydrate cell using a new analyser based upon Tuneable Diode Laser Absorption Spectroscopy (TDLAS) technology. A statistical thermodynamic approach, with the Cubic-Plus-Association equation of state, is employed to model the phase equilibria [1]. The hydrate-forming conditions are modelled by the solid solution theory of van der Waals and Platteeuw [2]. The thermodynamic model was used to predict the water content of methane and synthetic gases in equilibrium with gas hydrates.

Keywords: Gas Hydrate; Water; Methane; Water Content; CPA Equation of State; Experimental Data; Thermodynamic Modelling


In spite of the diversity of molecular interactions, thermodynamic evidence shows that many substances have systematic deviations from the Principle of Corresponding States, PCS. For instance, values of the compression factor $Z = \frac{PV}{NkT}$ at the critical point, $Z_c$, and reduced values of $Z$ along orthobaric states can be modelled by simple empirical parameters such as Pitzer’s acentric factor. On the face of this situation: Is it possible to construct a theory to explain quantitatively and from physical principles the deviations from the PCS? How good is this theory? What types of molecule are covered by it? We dare say that thermodynamic behaviour shows regularities that are not directly accounted for by the large variety and specificity of All-Atom potential models. These specific potentials, although very useful in simulating a great variety of fluid properties, are too complicated to lead to explicit equations of state, EOS. Moreover, that same specificity implies that there would be as many different EOS as there are distinct force fields. An alternative is to simplify the detailed molecular interaction and use instead less-specific effective potentials. These are usually spherically symmetric, simpler, and also constitute a generic approach by which many substances can be handled in a unified way. In this work we establish a direct link between a set of nonconformal potentials and the EOS explaining systematic departures from the PCS. To do this we use the approximate nonconformal theory, ANC, that identifies a single dimensionless form parameter to quantify the lack of conformality between potentials –besides the usual molecular energy and size. The ANC family of potential functions contain the most popular effective interactions, such as the Lennard-Jones 12/6 and the hard-sphere potentials, as special cases. The molecules treated thus far –already close to a hundred– include noble gases, alkanes and halogenated hydrocarbons, as well as diatomic, linear, tetrahedral and polar molecules. We apply the ANC theory to exhibit the influence of polarity, polarizability and three-body forces on second and third virial coefficients, and also critical temperatures, volumes and pressures.
Electrostriction of Magnesium Perchlorate Solutions

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It is well known that reactions of cycloaddition are essentially accelerated in the presence of Lewis acids [1]. Interaction with Lewis acids and complex formation are accompanied with substantial exothermal effects and volume decreases. The effect of acceleration of reactions was observed for magnesium perchlorate [2]. In present work we measured enthalpies of solution and partial molar volumes of magnesium perchlorate in solvents for studying of electrostriction of solvent in strong electrostatic field of magnesium cation, understanding the nature of processes of solvation and prediction of possibilities of catalytic effects for interaction of salt as catalyst.

For waterless magnesium perchlorate the heats of solution and partial molar volumes were determined: -45.5 and 81.0 in formamide; -37.0 and 68.9 in water, -56.7 and 65.8 in DMSO; -58.7 and 46.1 in DMFA; -45.6 and -0.8 in acetone; no data and 23.7 in ether; -34.0 kcal/mol and 47.9 cm$^3$/mol in ethyl acetate, respectively. Clear correlation was obtained ($R = 0.99$) between the values of partial molar volumes of magnesium perchlorate ($V_{MP}$) and lithium perchlorate; between ($V_{MP}$) and compressibility coefficient of the solvents ($\beta_T$), ($R = 0.96$); between ($V_{MP}$) and electrostriction parameter of the solvents ($\partial(1/\varepsilon)/\partial p$), ($R = 0.97$).

The differences of the heat of solution (-34– -59 kcal/mol) and partial molar volume (-0.8 – +81 cm$^3$/mol) for solutions of magnesium perchlorate were much greater than for lithium perchlorate solutions (-6 – -18 kcal/mol and -2.0 – +47 cm$^3$/mol) which previously was obtained in our laboratory. These results are in a good agreement with the greater catalytic effect of magnesium perchlorate solutions.

The work was supported by the grant RFBR No 08-03-00219.

Keywords: enthalpy of solution, partial molar volume, electrostriction


Laying the ghost of twin paradox

Marko Popovic

Someone’s age is not written in his ID as date, but in his biomarkers. Aging process is not caused by time passing, but by plenty of thermodynamically laws. Entropy, extent of metabolic reaction (f.e. free radicals reaction), temperature are Lorentz invariant, so these facts make twin paradox impossible because there is no way for one twin to age slower than the other. So twin paradox is a logical mistake based on wrong first premise and there is no need for Bergson symmetry.

Key words: Twins paradox, Aging, Extent of the reaction, Entropy, reaction rate constant, STR
Collaboration between Kwazulu-Natal University and the CEP/TEP laboratory in the frame of the thermodynamics of fluorinated component systems

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South Africa, as part of a developmental strategy in its chemical sector cluster, has launched a programme to beneficiate fluorspar. Fluorspar is the starting point for the manufacture of chemicals that are fluorine based and this has led to the Fluorochemical Expansion Initiative (FEI). The initiative has a number of research trusts, one of which is the production and development of applications for fluorochemicals. Under the umbrella of FEI, our two teams have collaborated since 2005 on the measurement, interpretation and modeling of phase equilibria and thermophysical properties of systems involving fluorochemicals, and in particular refrigerants. These properties are required for the effective design of separation equipment and are critical in the design of separation processes and eventually chemical plants.

The collaboration has grown from strength to strength with initially two students from South Africa and Pr. Deresh Ramjugernath spending 3 and 2 months respectively in France. Pr. Dominique Richon and Dr. Christophe Coquelet have travelled three times each to South Africa. Currently there are a number of joint projects, including jointly supervised PhD and Masters students.

The joint projects have to date involved experimental measurements using equipment developed at CEP/TEP such as the static-analytic apparatus with a ROLSI sampler for vapour-liquid equilibrium measurements and a vibrating tube densitometer for the determination of the volumetric properties. Several systems were studied and some of them have been published in international journals and presented at international congress. Some of the components studied have been R116, HFP, HFPO and hydrocarbons.
New Analytic Apparatus for Experimental Determination of VLE and Saturation Densities

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Abstract

The aim of this work is to present vapor-liquid equilibria of carbon dioxide + alkanol mixtures. CO\textsubscript{2} + 1-propanol, and CO\textsubscript{2} + 2-propanol binary mixtures were measured at (313, 333 and 363) K. The new static analytic apparatus focused on perform VLE measurements was modified by adding an Anton Paar vibrating tube densitometer to obtain simultaneously saturation densities for the carbon dioxide + alkanol mixtures. Depending on which phase (vapor or liquid) was going to be sampled, vapor or liquid phase was flowed through the densitometer by using a recirculating pump. Experimental results agree well with those reported in literature for the studied range.
Isobaric Vapour-Liquid-Liquid Equilibrium Determination

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Equilibrium data (LV, LL y LLV) are necessary to calculate, design and optimize an azeotropic distillation process. In recent years, great effort has been put into improving the thermodynamic models, but without experimental data it is not possible to obtain good parameters and check the goodness of predictions [1]. It is difficult to find VLLE data in the literature because there are no commercial devices available with which to carry out the required determinations. On the one hand, some authors have adapted equipment based on the static method, which permits determination of isothermal VLLE. On the other hand, when an isobaric VLLE determination is needed, most authors modify equipment based on the dynamic method.

For the determination of such data it is important that the two phases are in intimate contact with each other, either by simple agitation or by recirculation. There are systems that can be analyzed using simple equipment since they are easily homogenized. An example is the water-butanol system. However, other systems, such as those constituted of water and hydrocarbon mixtures, require more sophisticated equipment because it is difficult to obtain a good phase homogenization by mere agitation. In most cases this type of heterogeneous mixture could be dispersed by coupling an ultrasonic homogenizer to the boiling flask of a Labodest device based on the design by Gillespie [2].

The above apparatus has been used to study water-butanol, water-cyclohexane and water-toluene binaries in order to compare the influence of the characteristics of the systems whose VLLE are to be determined. These three systems were analyzed with and without the ultrasonic homogenizer using mixtures made up of different proportions of the two phases. The butanol-water binary could be determined simply using the stirring unit of the apparatus. It is for this reason that this type of system can be determined with equipment based on this technique, as is the case with, for example, the one developed by Iwakabe and Kosuge [3]. However, the other binaries presented problems during the homogenization that caused large oscillations in pressure, temperature and vapour compositions. These oscillations decreased considerably when the mixture was dispersed with the help of an ultrasonic homogenizer, which then facilitated analysis of the VLL equilibrium of the mixture. Therefore, the properties of heterogeneous mixtures limit the use of commercial VLE determination equipment, since it is not always suitable for obtaining VLLE data. Mixtures that are easily homogenized (high solubility, similar densities, low interfacial tension, etc.) can be determined by recirculation and mechanical agitation with simple equipment. In contrast, mixtures that are difficult to homogenize (low solubility, different densities, high interfacial tension, etc.) should be analyzed using an apparatus as the one described here, which allows proper dispersal of the liquid phases.

Keywords: Vapour-liquid-liquid equilibrium, determination, ultrasound homogenizer

Measurement of Isochoric Vapor-Liquid Equilibria for Binary Systems Containing Tetrahydrofuran

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Tetrahydrofuran (THF) is produced by the dehydrocyclization of 1,4-butanediol. The key step in purification is breaking of the THF + water azeotrope. The n-paraffines like n-pentane, n-hexane and n-heptane are considered as the azeotropic solvents. The vapor-liquid equilibria for the systems containing THF are important for discussing the azetropic distillation process.

This paper deals with the measurement of bubble points for four binary systems, THF + water, + n-pentane, + n-hexane, + n-heptane at reduced pressure using automatic VLE equipment. It is confirmed that THF + water and THF + n-hexane systems are azeotropic mixtures, though THF + n-pentane and THF + n-heptane are non-azeotropic mixtures. The NRTL parameters have been then determined using experimental bubble points. The NRTL parameters will be useful for discussing distillation process.
Isothermal Vapor-Liquid Equilibrium for Binary Systems of Tetrahydrothiophene with Aromatic Hydrocarbons at 368.15 K and 378.15 K

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Tetrahydrothiophene is used as an odorant in natural gas and also found as one of the organic sulfur compounds present in Fluid Catalytic Cracking (FCC) products. The organic sulfur compounds should be removed to meet the standards of new environmental legislation and ultra-low-sulfur fuel is required by 2010 in many countries.

As continuation of our sulfur measurement project, in this work we have measured VLE for systems tetrahydrothiophene + toluene and tetrahydrothiophene + \textit{o}-xylene at 368.15 K and 378.15 K with a recirculation still. No other VLE of the binaries studied in this work have been found in the literature. The liquid vapor pressure of tetrahydrothiophene was measured and the behavior of tetrahydrothiophene with aromatic hydrocarbons was studied.

The sulfur containing group for tetrahydrothiophene is not available in original UNIFAC and UNIFAC-Dortmund as the behavior of existing sulfide group does not work well with a sulfide group in a ring, thus these measurements are valuable for the development of predictive models.

Keywords: Vapor-liquid equilibrium, tetrahydrothiophene, toluene, \textit{o}-xylene
Binary Parameter Sensitivity in Correlating Vapor-Liquid Equilibrium of the Supercritical Water-Heavy Hydrocarbon Mixtures for Bitumen Conversion

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The petroleum oil crises lead us to the diversification in the fuel resources and also to the effective utilization of the super-heavy crude bitumen. There are many reports on upgrading super-heavy hydrocarbon resources via decomposition at high temperature. However coking is always big problem for high conversion yield. One possible technology, which is expected to reduce the coking, is the decomposition in supercritical water. The operation temperature is above 400 C and the pressure is above 20 MPa, where no VLE data for the related water-undefined mixtures exist because of experimental difficulties. This does not mean the unnecessary of phase equilibrium information in the reactor, but the importance of estimation method of the phase equilibria.

Since the crude heavy crude bitumen is actually multi-component mixtures, we have to specify the component composition for the phase equilibrium calculation by using such as equations of state(EOS). Normally the fractions in distillation of the mixtures are considered to be pseudo-components and of which the critical properties for calculating EOS parameters are estimated from their boiling points and densities. However, there is no way to estimate the intermolecular binary parameters \( k_{ij} \) \( l_{ij} \) in EOS method.

In this work, we correlated the high pressure vapor-liquid equilibrium data for water-heavy hydrocarbon (C10–C30) binary mixtures above 300 C by P-R EOS with varying binary parameters\( k_{ij} \) \( l_{ij} \), and made sensitivity maps by plotting the correlation deviations against the parameters. It was revealed from the maps that both parameters are very effective in correlation and \( k_{ij} \) showed clear temperature dependence than \( l_{ij} \).

KEYWORD: Equation of State, Heavy oil, VLE, Binary parameter, Sensitivity
Liquid-liquid equilibrium of (Water+ 1-Propanol+ 1-Pentanol) system at 298.15K and 323K.

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Liquid-liquid extraction is an operation unit well known in chemical engineering. The understanding of this separation process needs accurate model and consequently accurate experimental data. In this study, the system of interest concerns water+ 1-propanol+ 1-pentanol. Liquid-liquid equilibrium data for the ternary system have been determined experimentally at 298.15 and 323K. The experimental data were correlated by the NRTL model for the activity coefficient. The results obtained have shown the superiority of the NRTL model for the determination of liquid-liquid data of the studied system.

Keywords: Liquid-liquid equilibrium, NRTL model, Experimental.
Vapour Pressure Measurements, PVT and Vapor-Liquid Equilibria Modeling of Dipentaerythritol Ester Lubricants

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The aim of this work is to present new vapour pressure measurements and to provide a good description of the volumetric and phase behaviour of dipentaerythritol ester (DiPEs) lubricants using SAFT model (PC-SAFT and SAFT-VR versions). Characteristic parameters of these versions were optimized for dipentaerythritol hexapentanoate (DiPEC5), dipentaerythritol hexaheptanoate (DiPEC7) and dipentaerythritol isononanoate (DiPEiC9) using experimental vapor pressures and densities [2]. With these parameters compressed densities will be predicted.

Experimental vapor pressures, determined by a gas saturation apparatus [2], range between 2.10⁻⁵ Pa and 16 Pa, whereas the absolute deviations obtained in the correlations for both versions of the model (PC-SAFT and SAFT-VR) are between 10⁻⁶ Pa and 1 Pa. In the case of saturated densities the average absolute deviations are for PC-SAFT and SAFT-VR, respectively 1.3%, and 0.5% for DiPEC5; 0.6% and 1.1% for DiPEC7; 1.0% and 0.2% for DiPEiC9. SAFT-VR version gives slightly better correlations, although we must point out that this version has four parameters whereas PC-SAFT has three. These deviations are higher than expected due (probably to the difference of temperature range for both properties: vapor pressure temperature ranges are 392.71 K to 534.15 K for DiPEC5, 473.15 K to 534.15 K for DiPEC7 and 473.15 K to 553.15 K for DiPEiC9 whereas saturated densities temperature range is 283.15 K to 398.15 K for the three compounds.

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Keywords: Vapor pressures, density, SAFT, modeling, dipentaerythritol ester, lubricants

Compressibility of Liquids. Rule of Noncrossing P-V Curvatures

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Compressibility is a fundamental and inherent property of liquids, which expresses by how much the volume decreases as external pressure is applied to the liquid. We have proposed a new and precise method for determination of compressibility of liquids by measuring the differences in weights of hydraulic oil injected into the high pressure device. Weight analysis of the liquid introduced into the stainless steel bomb under pressures up to 1 kbar in the temperature range of 293.15K to 323.15K at the interval of 10K was performed for 1,4-dioxane, acetonitrile, toluene, ethyl acetate, chlorobenzene, n-hexane, propylene carbonate and decahydronaphthalene. The error of determination of compressibility values does not exceed 0.3% and can be reduced by increasing level of control of temperature, mass and pressure.

We found clear linear relation between tangent bulk modulus at atmospheric pressure and secant bulk modulus at 1 kbar in a wide range of temperature for 270 different liquids. This represents the rule of noncrossing P-V curvatures for the liquids. Using the correlation it is possible to predict the coefficients (C, B) of Tait equation from experimental data of $\beta_T$ at 1 bar. We have predicted unknown coefficients C and B for 34 liquids and obtained $V$-$P$ curves in this pressure interval [1].

The work was supported by the grant RFBR No 08-03-00219.

Keywords: compressibility, high pressure, propylene carbonate, decahydronaphthalene

Under the concept of reducing greenhouse gas emissions, carbon dioxide capture technologies are gaining a great interest within the scientific research community. In the case of post-combustion capture, it involves removing carbon dioxide from a multi-component stream mainly composed of nitrogen and oxygen. The high energy demand of amine facilities widely expanded in natural gas treatment plants, has motivated researchers to further investigate on efficient and cost effective carbon dioxide capture processes development [1,2,3]. Carbon dioxide removal through gas hydrate formation is a novel approach that offers a promising route towards lowering carbon dioxide emissions. As we need to selectively capture carbon dioxide, the efficiency of such process is basically assessed by the carbon dioxide concentration in the hydrate phase [2,3]. In the present work, we have established an experimental protocol that allows measuring the composition of hydrate and vapour phases once the thermodynamic equilibrium is reached. Hydrate formation experiments are carried out in a high pressure cell properly instrumented with temperature and pressure sensors allowing to accurately measure the thermodynamic conditions. The Isochoric technique [4] has been followed to obtain the hydrate-vapour phase boundary of the ternary CO$_2$-N$_2$-water system with carbon dioxide concentrations ranging from 5 to 17% mol. The upper value, well reported in literature, corresponds to conventional power plant emissions and has been our basis for the validation of the experimental procedure. The effect of a promoter, Tetrahydrofuran, on the thermodynamic equilibrium and on the selectivity of the process is also investigated. The measurements have been compared to a thermodynamic model coupling the classical van des Waals hydrates approach and the CPA equation of state for the fluid phases.

Keywords: carbon dioxide capture, post-combustion, gas hydrate, hydrate-vapour phase boundary, tetrahydrofuran, process selectivity

Capabilities and Limitations of Local Composition Models and Methods for Condensed Phase Equilibrium Calculations

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Local composition models like UNIQUAC and NRTL, and the UNIFAC group contribution method are used the world over in the synthesis and design of separation processes, as well as for a large number of other applications of industrial interest. The impacts of and the benefits derived from these equations have been amply demonstrated, but: a) new capabilities of these models have yet to be investigated, and b) their limitations must be clearly defined and recognized.

As part of the work undertaken by our research group, we are developing a robust calculation algorithm to compute phase equilibria between condensed phases (LLE, LLLE, LLSE, etc.), that avoids inconsistencies and improves the results obtained. We are using it as a tool to investigate new applications of the existing models in areas such as LLE data correlation of complex systems, for example, island type (type 0) ternary systems [1] and type 3 ternary systems including LLLE that are not usually correlated in the bibliography [2], and simultaneous correlation of all the equilibrium regions for LLSE of water + solute + organic solvent + inorganic salt systems with anhydrous and hydrated salts [3,4].

Existing models like NRTL can qualitatively describe the complex behaviour of these types of systems but, in general, not with the precision required for the design of separation equipment. Regrettably, this precision is not even achieved for the LLE of many conventional type 1 ternary systems. Given this fact, the goal of investigation must be to improve these equations or to develop newer more powerful ones. We believe study of the topology of the Gibbs energy of mixing function to be an indispensable tool in the carrying out of this type of research, so as to verify the results obtained, avoid inconsistencies, and to ascertain the capabilities and limitations of the models.

Keywords: phase equilibria, correlation, NRTL, local composition models, LLE, LLSE

Topological Approach to Barotropic Phenomena in Asymmetric Mixtures

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The barotropic phenomena is a significant effect in chemical processes, where gravimetric effects dominate. This is the case of CO$_2$ injection to enhance recovery from reservoir oil and for automobiles cooling systems based on mixtures of refrigerants and lubricants. In all these cases, knowing a priori the conditions for mass density inversion is fundamental to achieve optimal operation [1].

This paper proposes an analysis of the barotropic inversion phenomena in binary mixtures, produced by the molecular asymmetry of its components. The asymmetric systems studied correspond to binary mixtures of (1) CO$_2$ and n-alkanes and (2) perfluoromethane and n-alkanes. Both systems have observed, experimentally, the presence of barotropy [2,3]. The PC-SAFT EOS is used for the occasion, not only for its industrial relevance, but because from a theoretical point of view is explicitly applicable to chain molecules [4].

Starting from the analysis of the barotropic point movement with increasing molecular chain length, a transitional mechanism was developed capable of identifying the existence of Type systems, according to the classification of van Konynenburg and Scott [5], which may or not show mass densities inversion. In the context of a Global Phase Diagram (GPD) for the systems studied, there exists predicted regions of barotropic Type III and IV. Experimental data show that both are qualitatively and quantitatively in agreement.

This work has found that the tricritical transition does not affect the barotropic behavior, unlike Double Critical End Point, which combined with the transitional mechanism shown here, explains the shift between different branches of the barotropic triphasic as the chain length of the series varies.

Keywords: barotropic phenomena, equations of state, phase equilibria, Global Phase Diagram, PC-SAFT

Dimensionless Characterization of the Capillary Flow at Corners

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The properties of transport and interfacial are important to characterize systems. One of the primordial objectives of investigating them is to promote the full understanding of the phenomena and the development of technologies. Forces that define the behavior of a system are calculated of those properties and other characteristics of the same one. Commonly, the relative magnitude of these forces is related with dimensionless numbers used in the design of equipments and processes. The handling of small quantities of liquids with a lot of interfacial area is characterized by properties of transport, properties in interfaces and geometric [1]. A very attractive case for certain industrial applications is the capillary flow through corners [2]; which occurs under specific conditions [1, 3, 4, 5]. In this investigation this flow was characterized by dimensionless numbers, facilitating its incorporation in the development of equipments and technologies. They were carried out experimental tests and a mathematical analysis to corroborate the results. It was ratified the effect of certain geometric parameters and properties on the capillary flow [1,5] and included another parameters for effects of the gravity force [2]. A total of eight dimensionless numbers was obtained to correlate the properties of transport and properties in interface of this phenomenon. The intervals recommended for each dimensionless number were also determined. The results obtained with this investigation have importance in the design of equipments and processes with capillary flow; they allow guaranteeing the similarity: geometric, dynamics and of movement to different scales, interfacial properties and properties of transport.

Keywords: properties in interfaces, capillary flow at corner, dimensionless numbers.

Relativistic compression as a form of isenthalpic compression

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Abstract: Thermodynamic aspect of relativistic compression is analyzed. This process Planck understood as isobaric, Ott and Einstein as adiabatic and Popovic as isothermal. Having in mind fact that no external work is performed during the process of relativistic compression in vacuum, it is concluded that relativistic compression is good example of isenthalpic compression. Gravitational effect of relativistic mass may cause internal work, necessary for this type of process. So the relativistic compression can be described with known relations for isenthalpic process.

Key words: STR, isenthalpic process, entropy, enthalpy, relativistic temperature transformation
Experimental Determination and Modelling of Gas Solubilities in Certain Ionic Liquids Using a Group Contribution Equation of State

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Abstract

This study presents results of the experimental determination and the thermodynamic modelling of gas solubilities in the homologous [-mim][Tf$_2$N] family using a Group Contribution Equation of State (GC-EoS). A Caillet et al. apparatus was used for the measurement of the solubility data. Our own experimental data cover a temperature range of 300 – 380 K and pressures up to 15 MPa. The model parameters were estimated on the basis of 1400 experimental data points in the temperature range 278-460 K and pressures up to 4.5 MPa. Results show that the GC-EoS is a suitable model to describe gas solubilities in this family of room temperature ionic liquids. The solubility of various gases like CO$_2$, H$_2$, CH$_4$ and CO were studied. It was found that the IL-family under study has an excellent solvent power for CO$_2$. However, the solubility of H$_2$, CH$_4$ and CO is very limited. Comparison with experimental data shows excellent agreement with model predictions.
Compact Apparatus for Rapid Measurement of High Pressure Phase Equilibria of Carbon Dioxide Expanded Liquids

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A new apparatus based on a synthetic method was developed for phase equilibrium measurements. The characteristic features of the apparatus are its light weight (ca. 288 g), variable volume with a free piston, position sensing device for the piston, precise pressure and temperature control, and a window for visual observation. Inner volume of the cell can vary from 2.5 to 8.8 cm$^3$. The cell was constructed from titanium (JIS Class 2) so that composition of sample can be determined from direct weighing of the cell. Temperature and pressure range of the apparatus was designed up to 473 K and 25 MPa, respectively.

To confirm reliability of the apparatus, vapor-liquid equilibria of the carbon dioxide - methanol system was measured. The estimated uncertainties of temperature, pressure, and composition of carbon dioxide were less than ±0.05 K, ±0.015 MPa, ±0.20wt%, respectively. Bubble point pressures obtained in this work agreed well with the literature data[1,2]. Since the apparatus is compact, the time required for making measurements can be reduced. About 22 h was required to make 16 bubble point pressure measurements. Some new data of bubble point pressure for carbon dioxide expanded liquid of acetone and methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK) were obtained in this work at temperatures ranging from 313 to 353 K, and could be correlated well with the Peng-Robinson equation of state. The P-x diagrams for acetone, MEK, and MIBK binaries with carbon dioxide were found to be practically identical over the given range of temperatures.

Keywords: Bubble point pressure, carbon dioxide, expanded liquid, ketones

CO$_2$ capture by aqueous solution of amine: experimental measurements and thermodynamic model for the enthalpy of solution.

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To fight against the global earth warning, the international community agrees on a reduction of the emissions of the so-called greenhouse gases. This reduction concerns mainly CO$_2$ resulting from fossil fuels combustion, or present as constituent of natural gas. One of the options to reduce the greenhouse gas emissions is the capture in industrial effluents. One possible process is a gas separation by absorption in a solution that can be regenerated. For CO$_2$ capture the classical absorbent solutions are aqueous solutions of amine. The gas separation process consists in gas dissolution in absorbent solution following by regeneration of the absorbent solution. However the regeneration step represents an important economic cost in the treatment of post combustion effluents. This cost is mainly due to the energy required for desorption of CO$_2$. It is of interest to study this energy that is directly related to the enthalpy of solution of the gas in the aqueous solvent. The objective of our work is to obtain reliable thermodynamic data in order to develop a thermodynamic model for the representation of the absorption properties of CO$_2$ in aqueous solutions of amines. The thermodynamic properties of absorption reported are enthalpies of solution and gas solubilities [1, 2]. Measurements of enthalpy of solution are carried out using a customized flow mixing unit adapted to a SETARAM C-80 calorimeter [2]. The energy of mixing of CO$_2$ in aqueous solution of amine is determined at constant temperature and pressure as a function of loading charge $\alpha$ (moles CO$_2$ / mole amine). The enthalpy of solution $H_s$ expressed as kJ·mol$^{-1}$ of CO$_2$ or kJ·mol$^{-1}$ of amine are derived from the energy of mixing using molar flow rate of CO$_2$ or molar flow rate of amine, respectively. Solubility limits are directly deduced from the analysis of the enthalpic data. The thermodynamic model representative of \{gas - amine - water\} system is adjusted using literature data of gas solubility data and equilibrium constants of chemical reactions and phases equilibriums. The aptitude of the model to predict enthalpies of solution is tested using our experimental values.

Vapor-Liquid Equilibria and Saturation Densities of Carbon Dioxide + 1-Butanol and Carbon Dioxide + 2-Butanol System from (313 to 363) K

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Abstract

In this work, an apparatus based on the static-analytic method with liquid and vapor phase sampling, was used to measure Vapor-Liquid Equilibria (VLE) and Saturation Density data for the carbon dioxide CO\textsubscript{2} + 1-butanol and carbon dioxide + 2-butanol systems, the measurements were carried out at (313, 333, 363) K. The suitability of the experimental apparatus has already been confirmed for VLE and saturation density measurements in previous publications. VLE data were fitted to the Peng-Robinson equation of state (EoS) using the Wong-Sandler mixing rules.
Absorption with alkanolamine solutions is the major process used to remove acid gases such as CO$_2$ or H$_2$S from natural gas. To optimize the cost and the efficiency of this process, new solvents are developed, adding a physical solvent to the chemical solvent. A realistic thermodynamic modelling of such systems requires, in addition to the usual VLE data, data that are sensitive to the liquid phase composition. In order to acquire these data, an original experimental device has been developed in our laboratory. This device combines a FT-IR spectroscopy analysis of the liquid phase with a VLE measurement cell [1].

In this work, the system CO$_2$/water/ Diethanolamine/ Polyethyleneglycol400, was studied. The CO$_2$ partial pressure and the liquid phase speciation were determined at T=298.15K, for various PEG400 concentrations (10.3, 20.2 and 29.3 wt%), the concentration of DEA being 30%wt. At fixed pressure, the CO$_2$ solubility decreases for increasing PEG400 concentrations, traducing the solvent polarity decrease. For a given loading, the CO$_2$ molecular concentration increases with the PEG400 composition, whereas the ions repartition is not significantly influenced by the solvent composition. Comparison with solutions containing methanol instead of PEG400 in the same proportion shows that, at a fixed loading, the CO$_2$ partial pressure is lower with methanol than with PEG400, whereas the CO$_2$ molecular concentration remains constant.

The experimental results have been modelled using an electrolyte equation of state.

Keywords : Absorption, Acid gas, Alkanolamine, PEG400

POSTER SESSION
Densities and Derived Thermodynamic Properties of Ternary Mixtures BMIM-BF$_4$ + water + ethanol at Seven Pressures and Two Temperatures

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Ionic liquids (ILs) are molten salts composed by an organic cation and usually an inorganic anion with particular physicochemical properties, as wide liquid range and extremely low vapor pressure, that make them suitable for multiple applications[1], like extraction and separation processes, synthesis and catalysis reactions, electrodeposition, etc. The measurement and interpretation of physical properties of ionic liquids and their mixtures are necessary to develop those applications and to obtain theoretical models capable to explain the physical chemistry of ILs.

As a continuation of our studies [2], we present experimental measurements of density for ternary mixtures of 1-butyl-3-methyl-imidazolium tetrafluoroborate (BMI$\text{M-BF}_4$) with water and ethanol. Let us note that BMIM-BF$_4$ is the only IL of the family CnMIM-BF$_4$ (where Cn represents the alkyl chain) that can be mixed with water and ethanol in all range of concentrations. The measurements have been performed at 298.15 K and 323.15 K and at seven pressure conditions between 0.1 to 30 MPa. They were measured using a digital vibrating tube densimeter [3]. From the data measured we will extract derived thermodynamic properties such us excess molar volumes, isothermal compressibility and isobaric expansivity, which will be discussed and compared with data from the corresponding binary mixtures and also with suitable theoretical models.

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Keywords: ionic liquid, ethanol, water, density, ternary mixture, pressure.


Measurement of compressed liquid densities of $n$-heptane + $n$-octane and $n$-heptane + $n$-nonane binary mixtures up to 25 MPa

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Abstract
In this work, liquid densities of the $n$-heptane + $n$-octane and $n$-heptane + $n$-nonane binary mixtures have been experimentally measured from (313 to 363) K and in the pressure range of 1 - 25 MPa. Measurements were performed by means of a vibrating tube densitometer (Anton Paar). Excess molar volumes were calculated from density data using the five parameter equation used in a previous work. Uncertainty in measured densities was within 0.2 kg/m$^3$. 

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In this communication we report the measured values of excess molar enthalpies for ternary mixture of MTBE + ethanol + decane and the involved binary mixture ethanol + decane, over the whole mole fraction range at 298.15 K and atmospheric pressure. It is part of our systematic program of research concerning the experimental study of several thermodynamic and transport properties of binary and ternary liquid mixtures containing 2-Methoxy-2-Methylpropane (MTBE), alkan-1-ol and alkane used as oxygenating agents in gasoline technology. These ethers are also increasingly used as solvents or chemical reactants.

Earlier works from our laboratory has been published reporting experimental excess molar enthalpies of the ternary mixtures containing MTBE, alkanols and alkanes, as components [1-9]. Excess molar enthalpy provides direct information about the energetic effects arising between the molecules present in the mixture. The sign, magnitude, and symmetry of this quantity is a direct result of bond breaking and rearranging during the mixing process, and any effect arising from energetic interactions between both like and unlike molecules will be directly reflected in the enthalpy data and their representations.

The series including the ternary systems MTBE + ethanol + hexane [5], MTBE + ethanol + heptane [2] and MTBE + 1-ethanol + octane [3], is now continued, considering decane as the third component in this case. Experimental data of MTBE+ propanol or pentanol +decane were reported in early papers [1,9]. This should help to study the molecular interactions of these mixtures and to examine the effect of the enlargement of the CH₂ unit in the alkanol or n-alkane.

Keywords: enthalpies, binary mixture, ternary system, 2-Methoxy-2-Methylpropane, ethanol, nonane.

High-pressure vapor-liquid equilibria and densities of ternaries mixtures of carbon dioxide + nonane + benzothiophene

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Vapor-liquid equilibria (VLE) for a CO2 + nonane + benzothiophene system was measured at three different temperatures (313, 343 and 374) K and at pressures up to 15.08 MPa. Densities for three CO2 + nonane + benzothiophene mixtures were also obtained in the (313 to 363) K temperature range at pressures up to 25 MPa. VLE measurements were performed by using an apparatus based on the static-analytic method. Obtained VLE data were correlated with the Peng-Robinson equation of state using the classical and Wong-Sandler mixing rules. Density data were obtained by means of an apparatus based on the static-synthetic method that includes a vibrating tube densimeter (VTD) as the main part. Densities were correlated with an empirical five-parameter equation. Good agreement between experimental and correlated data was observed.

Keywords: Vapor–liquid equilibria; Density; Nonane; Benzothiophene; Carbon dioxide
Application of Artificial Neural Networks to Modeling Experimental \( P,V,T \) Data Obtained by Vibrating Tube Densimeter for Refrigerant R134a, at Temperatures Ranging Between 253.15 K and 423.15 K and Pressures up to 70 MPa.

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Considerable literature describing the use of artificial neural networks (ANNs) [1] has evolved for a diverse range of applications such as fitting experimental data, modeling of thermodynamics properties [2], prediction of physical properties for both pure components or their mixtures [3,4] among many others of interest for chemical engineering. In this communication we describe the application of feed-forward ANNs technique in order to obtain densities from the oscillation period of our based vibrating tube densimeter, designed by ARMINES (France) [5]. The used original experimental data are arranged along 18 isotherms regularly measured every 10 degrees in the interval between 253.15 K and 423.15 K and at pressures up to 70 MPa for pure compound R-134a. Two different NN models were conveniently selected in order to study the subcritical and supercritical state separately. In both cases the set of data points was divided in two subsets, the training set and the validation set (alternate isotherms). We will show in poster presentation the results obtained in a more detailed manner for all cases (tables and graphics).

Finally the modeling of some VLE and thermodynamics properties has been carried out by means of ANNs. The obtained results are, in general terms, in good agreement when comparing with reference data [6]. More detailed results will be presented in poster presentation (tables and graphics).

Keywords: Vibrating tube, neural networks, isothermal compressibility

Compressed liquid densities for binary mixtures of octane + undecane and octane + tetradecane at pressures up to 25 MPa and temperatures from (313 to 363) K
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Compressed liquid densities were determined for mixtures of octane + undecane and octane + tetradecane at temperatures from 313 to 363 K and pressures up to 25 MPa. A vibrating tube densitometer, with two reference calibration fluids, was used to obtain density. The global uncertainty was estimated to be 0.2 kg·m⁻³. The experimental densities for both binaries systems were in agreement with those reported in literature as expected. A 6-parameter equation was used to correlate the mixture densities within the experimental uncertainty.
Isothermal vapor-liquid equilibrium study of three binary systems: \( \text{N}_2\text{-SO}_2 \), \( \text{O}_2\text{-SO}_2 \) and \( \text{Ar}\text{-SO}_2 \)

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Within the fight against global warming and the reduction of greenhouse-gas emission, research has been particularly intense over the last years to develop efficient processes of carbon dioxide captures. The capture step addresses the main cost of data processing sequence: capture/transportation/storage. According to the concerned industrial sector (energy production, cement factory, refining…) and to the type of capture process that is retained, the compositions of gases accompanying produced \( \text{CO}_2 \) can vary considerably, on both qualitative and quantitative levels. Indeed, along with carbon dioxide and water, a great number of compounds such as \( \text{O}_2 \), \( \text{N}_2 \), \( \text{Ar} \), \( \text{SO}_x \), \( \text{NO}_x \), \( \text{H}_2 \) and \( \text{CO} \) can be present at different levels of concentration. The objective of this communication is to provide new sets of data to characterize phase equilibrium of these systems for the development of geological storage technologies. We focus here on binary systems containing sulphur dioxide, ie: \( \text{SO}_2\text{-N}_2 \), \( \text{SO}_2\text{-O}_2 \) and \( \text{SO}_2\text{-Ar} \), for which only very few data are available in open literature. Isothermal “Vapor-Liquid” equilibrium data were generated for these binary systems in the \((323\text{ to }413)\text{ K}\) temperature range at pressures from 2 to 20 MPa. All Measurements were carried out using an apparatus based on the “static-analytic” method especially designed* and built for this project. This apparatus is equipped with two electromagnetic ROLSI\textsuperscript{TM} serving for micro sampling of liquid and vapor phases.

* This work is supported by French National Agency for Research (ANR) and the “Conseil régional d’Ile de France”.
Compressed liquid densities and excess volumes of hexane + undecane and heptane + undecane mixtures at temperatures from (313 to 363) K and pressures up to 25 MPa

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Abstract

Compressed liquid densities for the hexane + undecane and heptane + undecane binary mixtures were measured at temperatures from 313 to 363 K and pressures up to 25 MPa with an uncertainty of ±0.2 kg/m3. Densities measurements were performed in an apparatus based on the static-synthetic method, it consists of a sapphire visual cell and a vibrating tube densimeter. Also excess volumes were calculated for each composition. The experimental densities obtained were correlated with two empirical equations, good representation of this set of data was observed.

Keywords: densities, alkanes, excess volumes.

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Vapor liquid equilibrium and Partition coefficients of n-Propylmercaptan, n-Butylmercaptan and Dimethyl sulfide in MDEA aqueous solution

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This investigation was carried out to determine the “Vapor-liquid” equilibria and partition coefficients of n-Propylmercaptan, n-Butylmercaptan and Dimethyl sulfide in Methyldiethanolamine (MDEA) 50 wt % aqueous solutions while using a “static-analytic” apparatus, with pneumatic capillary samplers (Rolsi™, Armines' patent) used for fluid sampling at equilibrium conditions. Measurements were made in the presence/absence of acid gases, H$_2$S and CO$_2$, with individual acid gases present, and with mixtures of acid gases present. The total pressure for most of the experiments was about 6.8-7.4 MPa, which was mentioned by methane. These experiments were carried out at 333.15 and 365.15 K. The inlet n-PM, n-BM and DMS concentration in most of the experiments was mentioned at 1000 ppm mol. The reaction between organic sulfur species and N-Methyldiethanolamine (MDEA) aqueous solutions will be presented by using the acid base neutralization approach.

Key words: n-Propylmercaptan, n-Butylmercaptan, Dimethylsulfide, MDEA, static analytic technique, Vapor liquid equilibra, Acid-Base neutralization approach.

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Study of Biofuels: development of specific thermodynamic models

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The rapid rise of biofuels in the energy market has stimulated a renewed interest in the research of oxygenated compounds such as alcohols esters, ethers, ketones, etc… At least two types interactions can be identified: those of associative (hydrogen bonding) and dipolar types. Until now, these interactions have rarely been features of petroleum simulations. Thus, there is a need for experimental data involving compounds with such interactions among, or without, hydrocarbons – systems which are generally not well-described by cubic equations of state. The scope of this work involves the measurement of thermodynamic properties pertaining to associating mixtures, for the study of specific thermodynamic models covering a large domain of applications. Such developments are under achievement via experimentations using several of the technologies available the CEP/TEP laboratory.
Excess molar enthalpies at 298.15 K and 1 atm of 1,2-Dichloroethane + Ethers binary systems

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Excess molar enthalpies, $h_{\text{mix}}^\circ$, for the binary mixtures of 1,2-dichloroethane (1,2-DCE) with diethyl ether (DEE), diisopropyl ether (DIPE), methyl 1,1-dimethylethyl ether (MTBE), 1,4-dioxane (1,4-DOXA), tetrahydropyran (THP), 1,3-dioxolane (1,3-DOXO), diethylene glycol dimethyl ether (DEGDME), 2-methoxyethyl ether (2-MOxEE), and 2-ethoxyethyl ether (2-EOxEE), have been measured at 298.15 K and atmospheric pressure, using a Setaram Tian-Calvet C80 microcalorimeter. All the binary systems investigated are characterized by exothermic mixing over the entire composition range, except for 1, 2-DCE + DIPE which presents a S-shape $h_{\text{mix}}^\circ$ behavior. The experimental $h_{\text{mix}}^\circ$ data have been correlated using the two empirical equations of Redlich-Kister and Margules. Also, NRTL and UNIQUAC models were applied. The experimental results are analyzed in terms of intermolecular interactions.
Volumetric Properties of the (Tetrahydrofuran + Water) and (Tetra-n-butyl Ammonium Bromide + Water) Systems: Experimental Measurements and Correlations

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In this communication, we report experimental density data for the binary mixtures of (water + tetrahydrofuran) and (water + tetra-n-butyl ammonium bromide) at atmospheric pressure and various temperatures. The densities were measured using an Anton Paar™ digital vibrating-tube densimeter. For the (tetrahydrofuran + water) system, excess molar volumes have been calculated using the experimental densities and correlated using the Redlich–Kister equation. The Redlich–Kister equation parameters have been adjusted on experimental data. The partial molar volumes and partial excess molar volumes at infinite dilution have also been calculated for each component. A simple density equation was finally applied to correlate the measured density of (tetra-n-butyl ammonium bromide + water) system.

Keywords: Tetrahydrofuran, tetra-n-butyl ammonium bromide, water, density, excess molar volume.
Gas hydrates are solid crystalline compounds stabilized by the inclusion of suitably sized guest molecules inside cavities, of different sizes, formed by water molecules through hydrogen bonding under low temperatures and elevated pressures. They resemble ice in appearance, but unlike ice, they may form at temperatures well above the ice point. The low temperatures and elevated pressures conditions required for formation of gas hydrates commonly occur in petroleum industry. Gas hydrates can block the production, transportation and processing facilities giving rise to operational problems and safety concerns. On the other hand, gas hydrate technology has been proposed as a means for positive applications. Examples are carbon dioxide separation from industrial flue gases, natural gas and hydrogen storage, carbon dioxide sequestration, methane production from natural gas hydrate reservoirs and etc.

Accurate knowledge of gas hydrate phase behavior is important to avoid hydrate formation risks in petroleum industry and also to design and optimize the facilities to be used for positive applications of gas hydrates. Traditionally, the pressure – temperature values corresponding to dissociation conditions of gas hydrates are measured using an isochoric pressure search method and then considered as hydrate phase equilibrium data. No compositional analysis of the equilibrium phases is traditionally reported.

In this work, we report the details of an experimental setup adapted to perform compositional and gas hydrate phase equilibrium measurements. Briefly, the main part of the apparatus is a cylindrical vessel with two sapphire windows, which can withstand pressures higher than 40 MPa. The volume of the vessel is 57.5 cm³. A stirrer has been installed in the vessel to agitate the fluid and gas hydrate crystals inside it. The vessel is immersed inside a temperature controlled bath to maintain the temperature inside it at a prescribed level. Two platinum resistance thermometers (Pt100) inserted into the vessel are used to measure temperature and check for equality of temperatures within temperature measurement uncertainties, which is estimated to be less than 0.1 K. The pressure in the vessel is measured with two pressure transducers (Druck type PTX611). Using the equilibrium cell, an isochoric pressure search method is applied to measure gas hydrate dissociation points. A mobile Rolsi™ sampler is used to take samples from the equilibrium phases and send them to a gas chromatograph for compositional analysis. Some recent obtained results are presented.
Natural gas is produced with several unwanted impurities from reservoirs including water, sulfur species, carbon dioxide (CO$_2$), etc. During the production, transportation and processing of raw gases, large quantities of chemicals are used for specific applications. For example, glycols and methanol are often used for inhibiting gas hydrate and ice formation in gas facilities. Glycols are also widely used in gas dehydration for dew point suppression in order to avoid water condensation at high pressures. In addition to absorbing water during dehydration process, and inhibiting hydrate and ice formation during transportation, glycols also absorb hydrocarbons and gas impurities. Solubility of natural gas components in glycols creates serious economic, operational, and environmental problems. Knowledge of phase behavior of systems involving natural gas components and glycols is therefore necessary to address these problems. The sulfur species like carbonyl sulfide (COS) and hydrogen sulfide (H$_2$S) along with CO$_2$ are often be the major impurities in natural gas and natural gas liquids. For this work, an experimental setup based on “static-synthetic” technique was used to measure solubility of COS in three glycols namely, monoethylene glycol (MEG), diethylene glycol (DEG), and triethylene glycol (TEG). An efficient multiple-phase magnetic agitator, inside equilibrium cell to facilitates fast equilibria. With respect to data correlation, an appropriate thermodynamic model capable of handling associating fluids like glycols is necessary. We have shown the Cubic-Plus-Association Equation of State model (CPA EoS) allows satisfactory representation of measured solubility data.