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Fields of research

- Thermophysical properties of pure ionic liquids and their liquid phase behavior in mixtures with molecular solvents
- Experimental determination of vapor–liquid equilibria in mixtures containing components of low and high molecular mass
- Data processing with activity coefficient models and equations of state
- Prediction of phase behavior using models based on group contribution methods
- Density functional study of interfacial phase transitions and nanodrops
- Dynamic properties of simple and complex fluids on a molecular scale
- Molecular simulations and perturbation theories for model fluids and fluid mixtures
- Development of equations of state based on molecular theory
- Molecular simulations of solid–liquid interfaces
- Molecular simulations of ionic liquid interfaces
- Mesoscale simulations of polymeric and energetic systems
- Density functional study of interfacial phase transitions and critical phenomena at non-planar surfaces
- Dynamic non-equilibrium properties of complex fluids and their mixtures

Applied research

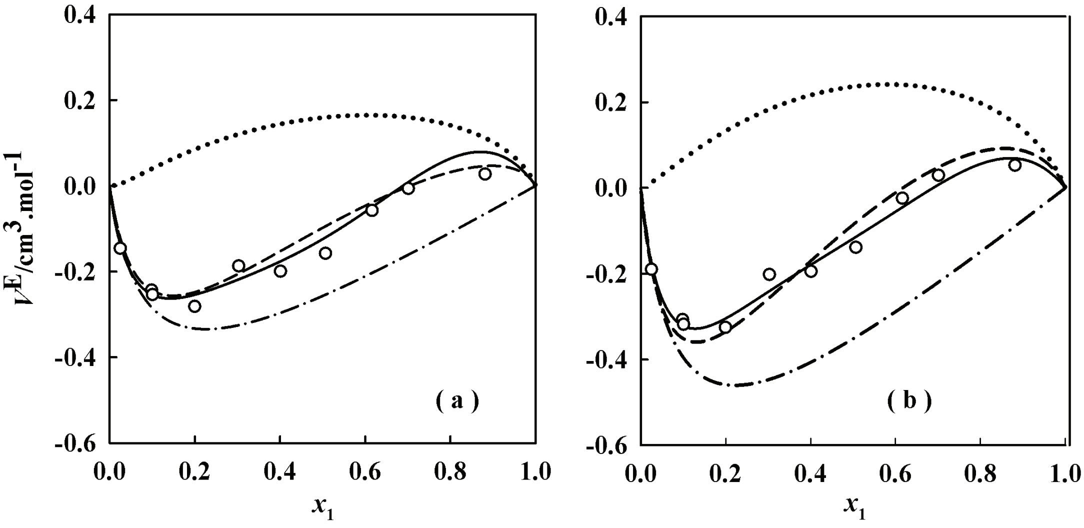
- Technology for the preparation of molecularly imprinted polymeric materials – Project: *Novel technology of molecularly imprinted polymeric materials preparation*, MoSES Republic of Croatia (2007–2014)

Research projects

Excess molar volumes and excess molar enthalpies in binary systems N-alkyl-triethylammonium bis{(trifluoromethyl)sulfonyl}imide + methanol [1]

(M. Bendová, bendova@icpf.cas.cz; joint project with QUILL Belfast, UK and Laboratory of Thermophysics, Department of Applied Physics, Universidade de Vigo, supported by ICPF)

A study on the influence of the alkyl chain length in N-alkyl-triethylammonium bis{(trifluoromethyl)sulfonyl}imide ionic liquids, $[N_{R,222}][Tf_2N]$ (R = 6,8 or 12), on the excess molar enthalpy at 303.15 K and excess molar volume within the temperature interval (283.15–338.15 K) of ionic liquid + methanol mixtures was performed. Small excess molar volumes with highly asymmetric curves (i.e. S-shape) as a function of mole fraction composition were obtained, with negative values showing in the methanol-rich regions. The excess molar volumes increase with the increase of the alkyl-chain length of the ammonium cation of the ionic liquid and decrease with temperature. The excess enthalpies of selected binary mixtures are positive over the whole composition range and increase slightly with the length of the alkyl side-chain of the cation on the ionic liquid. Both excess properties were subsequently correlated using a Redlich–Kister-type equation, as well as by using the ERAS model. From this semipredictive model the studied excess quantities could be obtained from its chemical and physical contribution. Finally, the COSMOThermX software has been used to evaluate its prediction capability on the excess enthalpy for investigated mixtures at 303.15 K and 0.1 MPa. From this work, it appears that COSMOThermX method predicts this property with good accuracy of approx. 10%, providing at the same time the correct order of magnitude of the partial molar excess enthalpies at infinite dilution for the studied ILs $\overline{H}_1^{E,\infty}$, and methanol, $\overline{H}_2^{E,\infty}$.



Excess molar volume in system $[N_{6,222}][Tf_2N]$ (1) + methanol (2) at T = 298.15 K (a) and T = 328.15 K (b). (○) experimental data; full line – Redlich-Kister expansion; dash line – ERAS prediction; dotted line – ERAS chemical contribution; dash-dotted line – ERAS physical contribution

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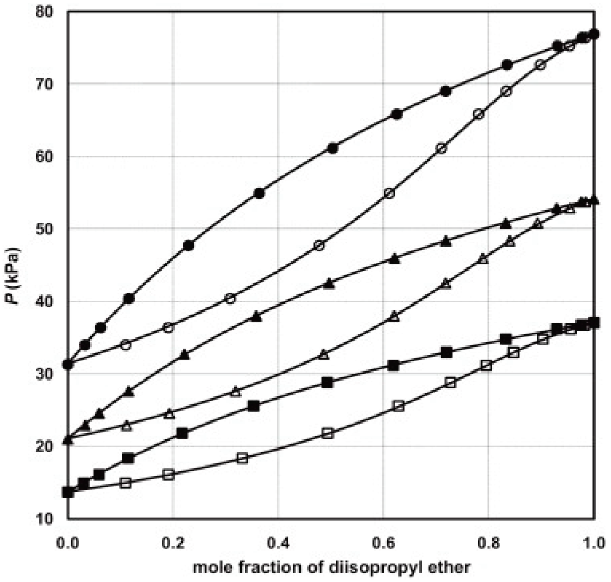
[1] Machanová, K.; Troncoso, J.; Jacquemin, J.; Bendová, M. *Fluid Phase Equilibria*, paper in press as of December 2013

Vapour − liquid equilibrium – measurement and data processing

(I. Wichterle, wichterle@icpf.cas.cz supported by ICPF)

a) Systems containing low molecular mass components

Isothermal vapour−liquid equilibrium data were measured in there binary and one ternary systems containing alcohol, ether and ketone. [Ref. 16]

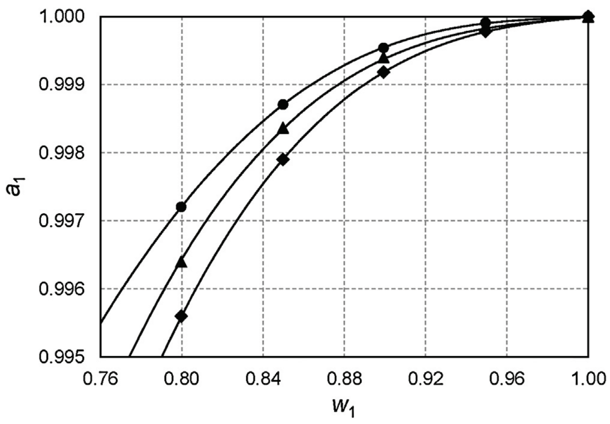


Isothermal vapour – liquid equilibrium in the diisopropyl ether + 3-methyl-2-butanone system (*x–y–P* plot). Experimental data: 313.15 K (■, □), 323.15 K (▲, △), 333.15 K (●, ○); (solid points) liquid phase; (open points) vapour phase; (—) NRTL correlation

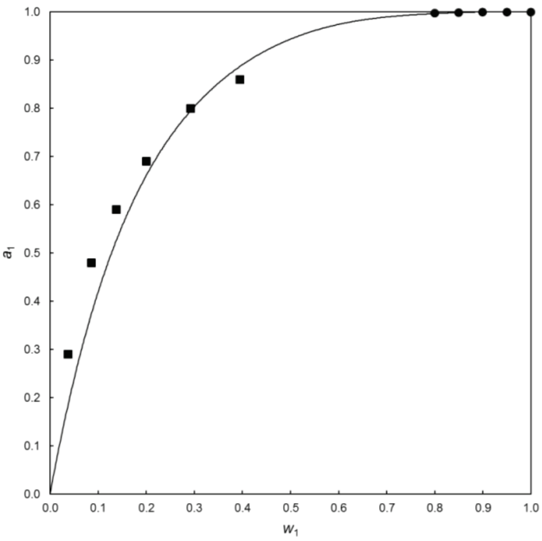
b) Systems containing polymers

Vapour–liquid equilibria have been determined in systems composed of poly(acrylic acid) with water, and poly(methyl methacrylate) with acetone by ebulliometric (total pressure measurement) method. Ebulliometer has been redesigned and experimental procedure has been upgraded. Experiments have been carried out isothermally, the measured data were correlated by the UNIQUAC equation, and compared with available literature data. It should be stressed that this type of measurements, *i.e.* ebulliometry in the high-concentration region of solvent, is unique and is presently carried out only at ICPF. Results were published in journal [17] and presented at 13th International Conference on Properties and Phase Equilibria for Products and Process Design, Iguazu Falls, Argentina.

Microebulliometer – new design



Activity a_1 of water in PAA as a function of water mass fraction w_1.
Experimental data at (●) 353.15 K;
(▲) 363.15 K and (◆) 373.15 K.
Solid lines represents correlated activities using the UNIQUAC model at 353.15, 363.15 and 373.15 K



Activity a_1 of water in PAA as a function of water mass fraction w_1.
Experimental data at (●) 353.15 K [ref. 17], (—) correlated activities using the UNIQUAC model at 353.15 K; experimental data at (■) 303.15 K [Arce A., Fornasiero F., Rodrigues O., Radke C.R., Prausnitz J.M., Phys. Chem. Chem. Phys. 6, 103-108 (2004)].

c) Prediction of properties of petroleum fluids

A simplified method for characterizing petroleum fluids (crude oil and gas condensate) and for predicting phase equilibria developed earlier was presented as invited lecture at World Congress on Petrochemistry and Chemical Engineering, San Antonio, USA and at 38th Croatian Invention Exhibition with International Participation, INOVA 2013, Zagreb, Croatia.

Molecular-level simulations aqueous electrolytes

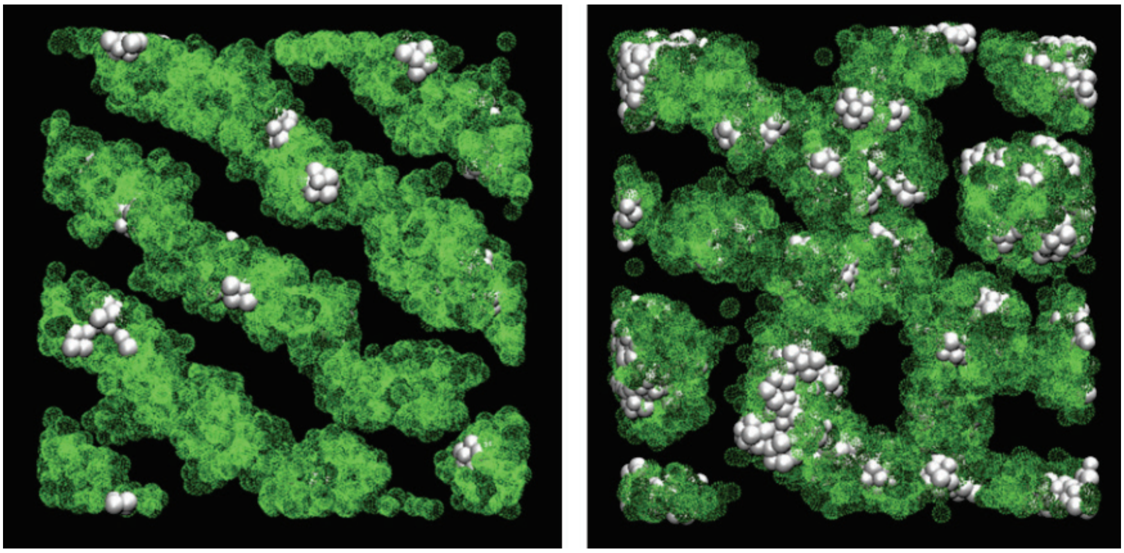
(I. Nezbeda, ivonez@icpf.cas.cz, joint project with the University of Ontario, Institute of Technology, Oshawa, ON, Canada and UJEP; supported by UJEP)

This series of papers deals with common non-polarizable models of electrolytes with the goals to (i) assess their appropriateness, (ii) find ranges of their applicability, and (iii) examine the possibility of their improvement by a reparametrization. Consistency tests of available literature data for the chemical potential were also performed. All simulations used the recently developed MPM-MC method demonstrating thereby its efficiency. [Refs. 10-13]

Tailored self-assembly of polyelectrolyte copolymers with surfactants in aqueous solutions

(Z. Posel, M. Lísal, posel@icpf.cas.cz, lisal@icpf.cas.cz; supported by GACR, project No. 13-02938S)

Multidisciplinary study of the tailored self-assembly of branched polyelectrolyte copolymers with surfactants in aqueous solutions aimed at deeper understanding of the relationship between the chain architecture and the structure, stability, thermodynamic behavior and properties of nanostructures formed under different conditions (pH, ionic strength, temperature) was carried out. A combination of dissipative particle dynamics and newly developed hybrid Monte Carlo method with experiments was used. [Ref. 18]



Effect of nanofiller loading in a *PS_2PVP_{18}* (f = 0.1). *PS* domain is represented as dotted green spheres and *NPs* as white spheres. *PVP* domain is omitted for clarity

A controlling of diffusion processes in pores with varying permeability

(A. Malijevský, M. Lísal, malijevsky@icpf.cas.cz, lisal@icpf.cas.cz; supported by GACR, project No. 13-09914S)

Interfacial phase transitions at non-planar surfaces have been studied in the framework of a density functional theory and effective Hamiltonian theory. New hidden connections (covariances) between adsorption phenomena at different substrate geometries have been found and explained. While most of the results obtained by the two theories give mutually consistent conclusions, the molecular-based density functional theory whose implementation was newly extended for the geometries possessing nontrivial symmetries, provides a more microscopic insight into the understanding of the interfacial phenomena and revealed some new and surprising predictions. These results are not only interesting by their own rights but also serve as a pre-requisite for a further study of dynamical properties of fluids (such as diffusive processes) at modified surfaces and between patterned walls. [Refs. 5-7, 15]

Mesoscopic modeling of protein - surface interactions

(A. Malijevský, Z. Posel, and M. Lísal, malijevsky@icpf.cas.cz, posel@icpf.cas.cz, and lisal@icpf.cas.cz; supported by Grant Programme of the MEYS, project No. LH12020)

Mesoscopic modeling using dissipative particle dynamics was employed to systematically study the effect of shape, size and hydrophobicity / hydrophilicity of proteins on their adsorption kinetics. Mesoscale models of proteins and surfaces were obtained from atomistic simulations of individual proteins in water and individual proteins close to walls using mapping from the atomistic to mesoscopic level. [Refs. 3, 4]

International co-operations

Imperial College London, London, UK: Confined fluids

INA, Research and Development, Zagreb, Croatia: Novel technology of molecularly imprinted polymeric materials preparation

Penn State University, State College, PA, USA: Dissipative particle dynamics simulations of adsorption behavior of model proteins on surface

Queen's University Ionic Liquids Laboratory (QUILL), Belfast, UK: Liquid–liquid phase equilibria in systems of ionic liquids
University of Loughborough, Loughborough, UK: Dynamic density functional theory
University of Ontario Institute of Technology, Oshawa, ON, Canada: Macroscopic and molecular-based studies in the statistical mechanics of fluids
U.S. Army Research Laboratory, Weapons and Materials Research Directorate, MD, USA: Mesoscale simulations of energetic and reactive materials
Wrocław University of Technology, Department of Chemical Engineering, Poland: Solubility behavior of chiral ionic liquids in water and 1-octanol, and their tendency to bioaccumulation
Laboratoire TIM, Institut de chimie de Clermont-Ferrand, CNRS UMR 6296 / Université Blaise Pascal, France: How the presence of a molecular component will affect the structure, interactions and ionicity of an ionic liquid?
Laboratory of Thermophysics, Department of Applied Physics, Universidade de Vigo, Spain: Excess molar properties in systems of ionic liquids with methanol

Visits abroad

M. Lísal: Pennsylvania State University, State College, PA, USA (1 month)
A. Malijevský: Imperial College London, London, UK (3 months)
A. Malijevský: University of Loughborough, Loughborough, UK (2 weeks)

Visitors

A. Archer, University of Loughborough, Loughborough, UK
C. Hardacre, Queen's University Ionic Liquids Laboratory (QUILL), Belfast
J. Jacquemin, Queen's University Ionic Liquids Laboratory (QUILL), Belfast
J. Troncoso, Laboratory of Thermophysics, Department of Applied Physics, Universidade de Vigo
B. Rathke, Faculty of Engineering, Bremen University
J. Feder-Kubis, Department of Chemical Engineering, Faculty of Chemistry, Wrocław University of Technology

Teaching

M. Bendová: ICT, Faculty of Chemical Engineering, postgraduate course "Physical Chemistry for Technological Practice"
J. Jirsák: UJEP, Faculty of Science, courses "Introduction to Chemistry", "Physical Chemistry", "Physical Chemistry Seminar" and "Free Software in Natural Sciences"
M. Kotrla, M. Předota: CU, course “Advanced Computer Simulations in many Particle Systems”
M. Lísal: UJEP, Faculty of Science, courses “Parallel Programming”, “Numerical Mathematics”, “Molecular Simulations” and “Mesoscale Simulations”
A. Malijevský: ICT, Faculty of Chemical Engineering, courses “Physical Chemistry I”, “Physical Chemistry of the Micro-World", "Introduction to a Modern Theory of Phase Transitions", "Mathematics for Physical Chemistry" and "Statistical Thermodynamics"
M. Předota: University of South Bohemia, České Budějovice, courses “Lectures from Physics Oriented to Particle and Nuclear Physics” and “Selected Lectures from Physics”

Publications

Original papers

[1] Houšková H., Morávková L., Sedláková Z., Boublík T., Kolská Z.: Volumetric Behavior of the Ternary System Benzene – 2-Methoxy-2-Methylbutane – 2,2,4-Trimethylpentane and All Binary Sub-Systems at Temperature Range (298.15 – 318.15) K. *Fluid Phase Equil.* 337, 156-164 (2013).

[2] Kárászová M., Šimčík M., Friess K., Randová A., Jansen J.C., Růžička M., Sedláková Z., Izák P.: Comparison of Theoretical and Experimental Mass Transfer Coefficients of Gases in Supported Ionic Liquid Membranes. *Sep. Purif. Technol.* 118, 255–263 (2013).

[3] Lísal M.: The Liquid Surface of Chiral Ionic Liquids as Seen from Molecular Dynamics Simulations Combined with Intrinsic Analysis. *J. Chem. Phys.* 139(21), 214701-15 (2013).

[4] Lísal M., Izák P.: Molecular Dynamics Simulations of n-Hexane at 1-Butyl-3-Methylimidazolium bis(trifluoromethylsulfonyl) Imide Interface. *J. Chem. Phys.* 139(1), 014704 (2013).

[5] Lísal M., Předota M., Brennan J.K.: Molecular-Level Simulations of Chemical Reaction Equilibrium and Diffusion in Slit and Cylindrical Nanopores: Model Dimerization Reactions. *Mol. Simul.* 39(13), 1103-1120 (2013).

[6] Malijevský A., Parry A.O.: Density Functional Study of Complete, First-Order and Critical Wedge Filling Transitions. *J. Physics-Condensed Matt.* 25(30), 305005 (2013).

[7] Malijevský A., Parry A.O.: Critical Point Wedge Filling. *Phys. Rev. Lett.* 110(16), 166101 (2013).

[8] Morávková L., Troncoso J., Machanová K., Sedláková Z.: Volumetric Behaviour of the (2,2,4-Trimethylpentane + Methylbenzene + Butan-1-ol) Ternary System and Its Binary Sub-Systems within the Temperature Range (298.15–328.15) K. *J. Chem. Thermodyn.* 64, 137–150 (2013).

[9] Moučka F., Nezbeda I.: Gibbs Ensemble Simulation on Polarizable Models: Vapor-liquid Equilibrium in Baranyai-Kiss Models of Water. *Fluid Phase Equilib.* 360, 472-476 (2013).

[10] Moučka F., Nezbeda I., Smith W.R.: Computationally Efficient Monte Carlo Simulations for Polarizable Models: Multi-Particle Move Method for Water and Aqueous Electrolytes. *Mol. Simul.* 39(14-15), 1125-1134 (2013).

[11] Moučka F., Nezbeda I., Smith W.R.: Molecular Force Field Development for Aqueous Electrolytes: 1. Incorporating Appropriate Experimental Data and the Inadequacy of Simple Electrolyte Force Fields Based on Lennard-Jones and Point Charge Interactions with Lorentz-Berthelot Rules. *J. Chem. Theory Comput.* 9(11), 5076-5085 (2013).

[12] Moučka F., Nezbeda I., Smith W.R.: Molecular Simulation of Aqueous Electrolytes: Water Chemical Potential Results and Gibbs-Duhem Equation Consistency Tests. *J. Chem. Phys.* 139(12), 124505-7 (2013).

[13] Moučka F., Nezbeda I., Smith W.R.: Molecular Force Fields for Aqueous Electrolytes: SPC/E-Compatible Charged LJ Sphere Models and Their Limitations. *J. Chem. Phys.* 138(15), 154102-9 (2013).

[14] Nezbeda I., Rouha M.: Extended Excluded Volume: Its Origin and Consequences. *Pure. Appl. Chem.* 85(1), 201-210 (2013).

[15] Pařez S., Guevara-Carrion G., Hasse H., Vrabec J.: Mutual Diffusion in the Ternary Mixture of Water Plus Methanol Plus Ethanol and Its Binary Subsystems. *Phys. Chem. Chem. Phys.* 15(11), 3985-4001 (2013).

[16] Pavlíček J., Andresová A., Bogdanić G., Wichterle I.: Vapour–Liquid Equilibria in the Binary and Ternary Systems Composed of 2,3-Dimethylbutane, Diisopropyl Ether, and 3-Methyl-2-Butanone at 313.15, 323.15 and 313.15 K. *Fluid Phase Equilib.* 344, 59-64 (2013).

[17] Pavlíček J., Bogdanić G., Wichterle I.: Vapour–Liquid Equilibria in the Polymer + Solvent System Containing Lower Concentrations of Solute at Normal or Reduced Pressures. *Fluid Phase Equilib.* 358, 301-303 (2013).

[18] Posel Z., Posocco P., Fermeglia M., Lísal M., Pricl S.: Modeling Hierarchically Structured Nanoparticle/Diblock Copolymer Systems. *Soft Matter* 9(10), 2936-2946 (2013).

Review papers

[19] Morávková L., Sedláková Z.: Excess Molar Volume of Binary Systems Containing Mesitylene. *Kemija u industriji* 62(5-6), 159-170 (2013).

[20] Wichterle I.: Editorial. *Kemija u industriji* 62(5-6), 2 (2013).