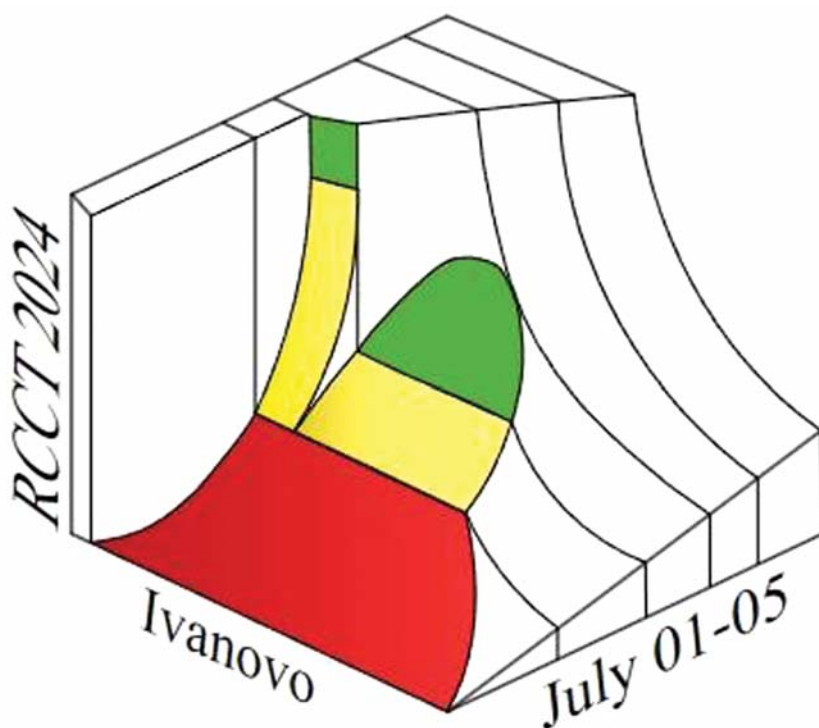


# **XXIV International Conference on Chemical Thermodynamics in Russia**

**July 1-5, 2024  
Ivanovo, Russia**



**RCCT-2024**

# **BOOK OF ABSTRACTS**

**POLY(DIALYLDIMETHYLAMMONIUM) CATION MOBILITY AND  
COUNTERION DISTRIBUTION IN WATER AND AQUEOUS SALT SOLUTION  
FROM MD SIMULATION AND EXPERIMENT**

I.Yu. Gotlib, E.A. Safonova, P.A. Korchak  
Saint Petersburg State University, Russian Federation  
*i.gotlib@spbu.ru*

Polyelectrolytes' behavior in solutions depends on interactions between the charged polymeric chain and its environment, including counterions, solvent molecules, (optionally) co-ions and other additives. Typically, a double electric layer is formed around the chain, including condensed counterions near it and a more extended diffuse "cloud" with an excess of counterions. Structural, (electro)kinetic and other characteristics of the polyelectrolyte, including properties important in practical applications, depend on its concentration as well as on the presence of additional components (e.g. a low-weight electrolyte that causes screening of electrostatic interactions). In the present work, we have studied these dependences in dilute ( $0.00289m$  in terms of monomer units) and semi-dilute ( $0.0289m$ ) solutions of poly(diallyldimethylammonium) chloride (PDADMAC) in water and water+NaCl, using atomistic molecular dynamics (MD) simulation and comparing MD results with experimental data obtained both from the literature and from our own measurements.

The MD simulation has shown that adding the salt to the aqueous solution makes the polycation chain only slightly less stretched, despite significant counterion condensation, while the diffuse counterion "cloud" becomes much more compact. At the same time, the calculated polyion electrophoretic mobility decreases significantly, in comparison with a salt-free solution, already at low salt concentrations. In a more concentrated (semi-dilute) PDADMAC solution, the polycation mobility calculated by MD becomes somewhat lower (Figure 1), as the effective charge of the polycation with a "cloud" of counterions decreases due to an additional contraction of the "cloud". Our simulation results agree with the behavior of the electrophoretic mobility observed experimentally, thus providing a good complement to the experiment and suggesting probable molecular mechanisms for these effects.

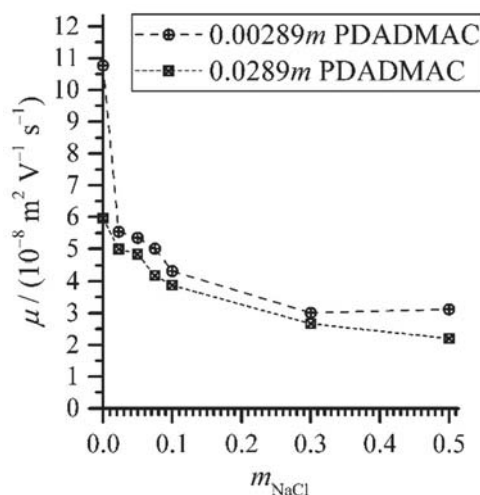


Figure 1. The electrophoretic mobility  $\mu$  of poly(diallyldimethylammonium) 40-mer cations in water and NaCl aqueous solutions ( $m_{\text{NaCl}}$  is the molality) from MD simulations.

We thank Russian Science Foundation (project 20-13-00038) for financial support.

**DIFFUSION OF COMPONENTS IN COACERVATE PHASE OF AQUEOUS-SALT SYSTEMS CONTAINING POLYMERIZED IONIC LIQUID**

E.A. Safonova, P.A. Korchak, A.S. Koneva, P.S. Yarchenko, I.Yu. Gotlib  
*Saint Petersburg State University, Russia*  
*e.a.safonova@spbu.ru*

In recent decades, ionic liquids (ILs) with their unique properties are of special interest for synthesis of polymerized ionic liquids [1-3]. Polymerized ILs are the polyelectrolytes composed IL as a monomer unit. Due to the combination of properties of ILs and polyelectrolytes, polymerized ILs are used for the preparation of functional materials, the development of methods for analysis, synthesis and catalysis, the design of electrochemical devices, etc. [1-3]. A particular attention is paid to apply such polyelectrolytes in the composition of aqueous-salt biphasic systems for the extraction of biomolecules [4]. For their specific application, structural design is required [5]. Indeed, the rational design may help to find the polymerized ILs structures with different phase behavior in aqueous or aqueous-salt solutions. For water-soluble polymerized ILs, an addition of salting out salts results in formation of aqueous biphasic systems (ABSs) [6]. ABSs are considered as media for the highly effective extraction of various solutes including biomolecules. In general, the extraction efficiency is determined by the affinity of the polyelectrolyte-rich (i.e. coacervate) phase to the solute and, in particular, is up to the structural behavior of the phase.

In this work, we consider the structural behavior of aqueous and aqueous-salt solutions of the polymerized IL, poly(1-butyl-3-vinylimidazolium bromide), in the presence/absence of L-tryptophan and vanillin (as model biocomponents). Polymerized IL was synthesized and characterized by  $^1\text{H}$  - NMR and by thermogravimetric analysis. Moreover, the viscosities and surface tension data were obtained for aqueous and aqueous-salt solutions of poly(1-butyl-3-vinylimidazolium bromide) in the dilute concentration range. Diffusion of the components have been studied experimentally by dynamic light scattering and PGSTE - NMR spectroscopy and simulated by Molecular Dynamics. By means of MD modeling, we obtain the data on conformation and local structure of polyelectrolyte chains, diffusion and binding of counterions (bromide, L-tryptophanate). We discuss the results for two concentration regimes, i.e. dilute and concentrated. Note that the compositions of the studied concentrated solutions are close to the composition of the polymer-rich phase of the ABS.

- [1] A. Eftekhari and T. Saito, *Eur. Polym. J.*, 2017, 90, 245.
- [2] D. Mecerreyes, *Prog. Polym. Sci.*, 2011, 36 (12), 1629.
- [3] A.S. Shaplov, D.O. Ponkratov, Y.S. Vygodskii, *Polym. Sci. - Ser. B*, 2016, 58 (2), 73.
- [4] Y. Ke et al., *ChemSusChem*, 2020, 13 (7), 1906.
- [5] O. Green et al. *Polym. Rev.*, 2009, 49 (4), 339.
- [6] K.G. João et al. *Phys. Chem. Chem. Phys.*, 2015, 17 (41) 27462.

The financial support of the reported study was provided by the Russian Science Foundation, project number 20-13-00038. NMR measurements were performed at the Center for Magnetic Resonance of the Research Park of St. Petersburg State University.

**XXIV Международная конференция  
по химической термодинамике в России**

*Тезисы докладов опубликованы в авторской редакции*

**ISBN 978-5-6051371-2-2**

Подписано в печать 05.06.2024.

Формат 60×84 1/8. Бумага офсетная №1, пл. 80 г/кв.м.

Печать плоская. Печ. л. 46,63. Усл. печ. л. 43,36.

Тираж 30 экз. Заказ № 26127.

Отпечатано в АО «Ивановский издательский дом».

153000, г. Иваново, ул. Степанова, 5. Тел. (4932)301411, 303237

e-mail: 301411@rambler.ru