

# Advances in the study of gas hydrates by dielectric spectroscopy

Lunev I., Kamaliev B., Shtyrlin V., Gusev Y., Kiamov A., Zaripova Y., Galiullin A., Farhadian A., Varfolomeev M., Kelland M.

Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

---

## Abstract

The influence of kinetic hydrate inhibitors on the process of natural gas hydrate nucleation was studied using the method of dielectric spectroscopy. The processes of gas hydrate formation and decomposition were monitored using the temperature dependence of the real component of the dielectric constant  $\epsilon'(T)$ . Analysis of the relaxation times  $\tau$  and activation energy  $\Delta E$  of the dielectric relaxation process revealed the inhibitor was involved in hydrogen bonding and the disruption of the local structures of water molecules.

<http://dx.doi.org/10.3390/molecules26154459>

---

## Keywords

Dielectric relaxation, Dielectric spectroscopy, Gas hydrates, Kinetic hydrate inhibitors

## References

- [1] Hammerschmidt, E.G. Formation of Gas Hydrates in Natural Gas Transmission Lines. *Ind. Ing. Chem.* 1934, 26, 851–855. [CrossRef]
- [2] Paz, P.; Netto, T.A. On the Rheological Properties of Thermodynamic Hydrate Inhibitors Used in Offshore Oil and Gas Production. *J. Mar. Sci. Eng.* 2020, 8, 878. [CrossRef]
- [3] Chong, Z.R.; Chan, A.H.M.; Babu, P.; Yang, M.; Linga, P. Effect of NaCl on methane hydrate formation and dissociation in porous media. *J. Nat. Gas. Sci. Eng.* 2015, 27, 178–189. [CrossRef]
- [4] Walker, V.K.; Zeng, H.; Ohno, H.; Daraboina, N.; Sharifi, H.; Bagherzadeh, S.A.; Alavi, S.; Englezos, P. Antifreeze proteins as gas hydrate inhibitors. *Can. J. Chem.* 2015, 93, 839–849. [CrossRef]
- [5] Talaghat, M.R. Experimental investigation of induction time for double gas hydrate formation in the simultaneous presence of the PVP and L-Tyrosine as kinetic inhibitors in a mini flow loop apparatus. *J. Nat. Gas. Sci. Eng.* 2014, 19, 215–220. [CrossRef]
- [6] Daraboina, N.; Pachitsas, S.; von Solms, N. Experimental validation of kinetic inhibitor strength on natural gas hydrate nucleation. *Fuel* 2015, 139, 554–560. [CrossRef]
- [7] Farhadian, A.; Varfolomeev, M.A.; Abdelhay, Z.; Emelianov, D.; Delaunay, A.; Dalmazzone, D. Accelerated Methane Hydrate Formation by Ethylene Diamine Tetraacetamide as an Efficient Promoter for Methane Storage without Foam Formation. *Ind. Eng. Chem. Res.* 2019, 58, 7752–7760. [CrossRef]
- [8] Ke, W.; Kelland, M.A. Kinetic Hydrate Inhibitor Studies for Gas Hydrate Systems: A Review of Experimental Equipment and Test Methods. *Energy Fuels* 2016, 30, 10015–10028. [CrossRef]
- [9] Asami, K. Characterization of heterogeneous systems by dielectric spectroscopy. *Prog. Polym. Sci.* 2002, 27, 1617–1659. [CrossRef]
- [10] Di Biasio, A.; Cametti, C. On the dielectric relaxation of biological cell suspensions: The effect of the membrane electrical conductivity. *Colloids Surf. B* 2011, 84, 433–441. [CrossRef] [PubMed]

- [11] Agranovich, D.; Ishai, P.B.; Katz, G.; Bezman, D.; Feldman, Y. Microwave dielectric spectroscopy study of water dynamics in normal and contaminated raw bovine milk. *Colloids Surf. B* 2017, 154, 391–396. [CrossRef] [PubMed]
- [12] Maeda, N. Development of a high pressure electrical conductivity probe for experimental studies of gas hydrates in electrolytes. *Rev. Sci. Instrum.* 2013, 84, 015110. [CrossRef]
- [13] Priegnitz, M.; Thaler, J.; Spangenberg, E.; Rücker, C.; Schicks, J.M. A cylindrical electrical resistivity tomography array for three-dimensional monitoring of hydrate formation and dissociation. *Rev. Sci. Instrum.* 2013, 84, 104502. [CrossRef] [PubMed]
- [14] Zatsepina, O.Y.; Buffett, B. Nucleation of CO<sub>2</sub>-hydrate in a porous medium. *Fluid Phase Equilib.* 2002, 200, 263–275. [CrossRef]
- [15] Faizullin, M.Z.; Vinogradov, A.V.; Koverda, V.P. Hydrate formation in layers of gas-saturated amorphous ice. *Chem. Eng. Sci.* 2015, 130, 135–143. [CrossRef]
- [16] Johari, G.; Whalley, E. The dielectric properties of ice Ih in the range 272–133 K. *J. Chem. Phys.* 1981, 75, 1333–1340. [CrossRef]
- [17] Popov, I.; Lunev, I.; Khamzin, A.; Greenbaum, A.; Gusev, Y.; Feldman, Y. The low-temperature dynamic crossover in the dielectric relaxation of ice Ih. *Phys. Chem. Chem. Phys.* 2017, 19, 28610–28620. [CrossRef] [PubMed]
- [18] Geil, B.; Kirschgen, T.M.; Fujara, F. Mechanism of proton transport in hexagonal ice. *Phys. Rev. B Condens. Matter Mater. Phys.* 2005, 72, 014304. [CrossRef]
- [19] Popov, I.; Puzenko, A.; Khamzin, A.; Feldman, Y. The dynamic crossover in dielectric relaxation behavior of ice Ih. *Phys. Chem. Chem. Phys.* 2015, 17, 1489–1497. [CrossRef]
- [20] Khamzin, A.A.; Lunev, I.V.; Popov, I.I.; Greenbaum, A.M.; Feldman, Y.D. Mechanisms of dielectric relaxation of hexagonal ice. *Radioelektron. Nanosistemy Inf. Tehnol.* 2020, 12, 87–94.
- [21] Manakov, A.Y.; Khlystov, O.; Hachikubo, A.; Minami, K.; Yamashita, S.; Khabuev, A.; Ogienko, A.; Il'yakov, A.; Kalmychkov, G.; Rodionova, T. Structural Studies of Lake Baikal Natural Gas Hydrates. *J. Struct. Chem.* 2019, 60, 1437–1455. [CrossRef]
- [22] Röttger, K.; Endriss, A.; Ihringer, J.; Doyle, S.; Kuhs, W. Lattice constants and thermal expansion of H<sub>2</sub>O and D<sub>2</sub>O ice Ih between 10 and 265 K. *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* 1994, 50, 644–648. [CrossRef]
- [23] Jonscher, A.K. Dielectric relaxation in solids. *J. Phys. D Appl. Phys.* 1999, 32, R57–R70. [CrossRef]
- [24] Dyre, J.C.; Maass, P.; Roling, B.; Sidebottom, D.L. Fundamental questions relating to ion conduction in disordered solids. *Rep. Prog. Phys.* 2009, 72, 046501. [CrossRef]
- [25] Klein, R.J.; Zhang, S.H.; Dou, S.; Jones, B.H.; Colby, R.H.; Runt, J. Modeling electrode polarization in dielectric spectroscopy: Ion mobility and mobile ion concentration of single-ion polymer electrolytes. *J. Chem. Phys.* 2006, 124, 144903. [CrossRef]
- [26] Pal, P.; Ghosh, A. Dynamics and relaxation of charge carriers in poly(methylmethacrylate)-based polymer electrolytes embedded with ionic liquid. *Phys. Rev. E Stat. Nonlinear Soft Matter Phys.* 2015, 92, 062603. [CrossRef] [PubMed]
- [27] Serghei, A.; Tress, M.; Sangoro, J.R.; and Kremer, F. Electrode polarization and charge transport at solid interfaces. *Phys. Rev. B Condens. Matter Mater. Phys.* 2009, 80, 184301. [CrossRef]
- [28] Ishai, P.B.; Talary, M.S.; Caduff, A.; Levy, E.; Feldman, Y. Electrode polarization in dielectric measurements: A review. *Meas. Sci. Technol.* 2013, 24, 102001. [CrossRef]
- [29] Kremer, F.; Schönhals, A. Broadband Dielectric Spectroscopy, 1st ed.; Springer: Berlin/Heidelberg, Germany, 2003; pp. 91–93.
- [30] Khamzin, A.A.; Popov, I.I.; Nigmatullin, R.R. Correction of the power law of ac conductivity in ion-conducting materials due to the electrode polarization effect. *Phys. Rev. E Stat. Nonlinear Soft Matter Phys.* 2014, 89, 032303. [CrossRef] [PubMed]
- [31] Popov, I.I.; Nigmatullin, R.R.; Khamzin, A.A.; Lounev, I.V. Conductivity in disordered structures: Verification of the generalized Jonscher's law on experimental data. *J. Appl. Phys.* 2012, 112, 094107. [CrossRef]
- [32] Liu, S.H. Fractal model for the ac response of a rough interface. *Phys. Rev. Lett.* 1985, 55, 529–532. [CrossRef] [PubMed]
- [33] Kaatze, U. The dielectric properties of water in its different states of interaction. *J. Solut. Chem.* 1997, 26, 1049–1112. [CrossRef]
- [34] Sizikov, A.A.; Manakov, A.Y.; Aladko, E.Y. Pressure dependence of gas hydrate formation in triple systems water-2-propanol-methane and water-2-propanol-hydrogen. *Fluid Phase Equilib.* 2016, 425, 351–357. [CrossRef]
- [35] Fouconnier, B.; Komunjer, L.; Ollivon, M.; Lesieur, P.; Keller, G.; Clausse, D. Study of CCl<sub>3</sub>F hydrate formation and dissociation in W/O emulsion by differential scanning calorimetry and X-ray diffraction. *Fluid Phase Equilib.* 2006, 250, 76–82. [CrossRef]

- [36] Semenov, M.Y.; Ivanova, I.; Koryakina, V. Peculiarities of natural gas hydrate formation from ice in reactors under high pressure. *IOP Conf. Ser. Earth Environ. Sci.* 2018, 193, 012061. [CrossRef]
- [37] Kashchiev, D.; Firoozabadi, A. Induction time in crystallization of gas hydrates. *J. Cryst. Growth* 2003, 250, 499–515. [CrossRef]
- [38] Kashchiev, D.; Firoozabadi, A. Nucleation of gas hydrates. *J. Cryst. Growth* 2002, 243, 476–489. [CrossRef]
- [39] Zhao, X.; Qiu, Z.; Huang, W. Characterization of Kinetics of Hydrate Formation in the Presence of Kinetic Hydrate Inhibitors during Deepwater Drilling. *J. Nat. Gas. Sci. Eng.* 2015, 22, 270–278. [CrossRef]
- [40] McNamee, K. Evaluation of Hydrate Nucleation Trends and Kinetic Hydrate Inhibitor Performance by High-Pressure Differential Scanning Calorimetry. In Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011), Edinburgh, Scotland, UK, 17–21 July 2011; Curran Associates, Inc.: Red Hook, NY, USA, 2016.
- [41] Ivall, J.; Pasieka, J.; Posteraro, D.; Servio, P. Profiling the Concentration of the Kinetic Inhibitor Polyvinylpyrrolidone throughout the Methane Hydrate Formation Process. *Energy Fuels* 2015, 29, 2329–2335. [CrossRef]
- [42] Liu, J.; Feng, Y.; Yan, Y.; Yan, Y.; Zhang, J. Understanding the inhibition performance of polyvinylcaprolactam and interactions with water molecules. *Chem. Phys. Lett.* 2020, 761, 138070. [CrossRef]
- [43] Dirdal, E.G.; Kelland, M.A. Does the Cloud Point Temperature of a Polymer Correlate with Its Kinetic Hydrate Inhibitor Performance? *Energy Fuels* 2019, 33, 7127–7137. [CrossRef]
- [44] Lim, V.W.; Metaxas, P.J.; Stanwix, P.L.; Johns, M.L.; Haandrikman, G.; Crosby, D.; Aman, Z.M.; May, E.F. Gas hydrate formation probability and growth rate as a function of kinetic hydrate inhibitor (KHI) concentration. *Chem. Eng. J.* 2020, 388, 124177. [CrossRef]
- [45] Liu, J.; Wang, H.; Guo, J.; Chen, G.; Zhong, J.; Yan, Y.; Zhang, J. Molecular insights into the kinetic hydrate inhibition performance of Poly(N-vinyl lactam) polymers. *J. Nat. Gas. Sci. Eng.* 2020, 83, 103504. [CrossRef]