STUDY OF ELECTROLYTE PARTITIONING BETWEEN PHASES OF DIFFERING POLARITY: EXPERIMENTAL AND COMPUTATIONAL APPROACHES

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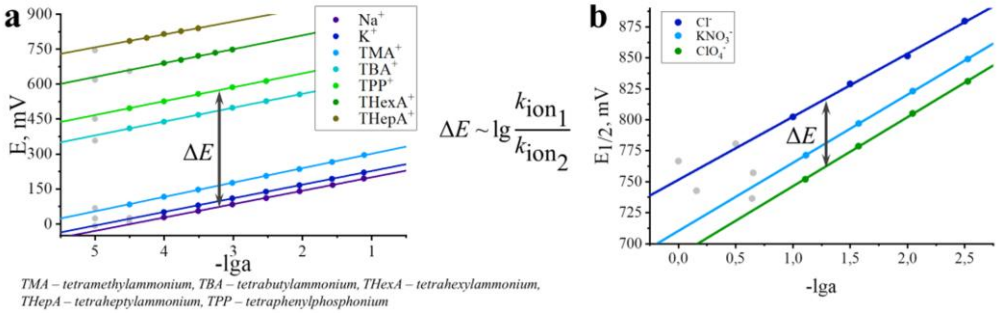
Partition coefficients may be of interest when considering equilibrium in multiphase systems. Lipophilicity of ions governs partitioning of electrolytes and ion exchange. There are several methods which can be applied to measure corresponding equilibrium constants. The shake-flask method [1] and calculation from solubility data [2] are applicable to both ionic and non-ionic substances, while ion exchange constants can also be determined voltammetrically [3] and potentiometrically [1]. However, consistency between different methods is not always observed [1,2], and each technique is suitable for a specific range of partition coefficient values.

In our study we estimated partition coefficients of ions between an aqueous phase and plasticized poly(vinyl chloride), a typical matrix for ion-selective sensors. Both hydrophilic inorganic and lipophilic organic ions were of interest. The shake-flask method and potentiometry (Fig. a) were employed as techniques typically used for such systems. To our knowledge, voltammetry was applied for the first time to a system with a polymeric matrix to obtain the ratios of partition coefficients (Fig. b).



Experimental data used to obtain ratio of partition coefficients:
a) potentiometric, b) voltammetric

Molecular dynamics offers access to properties difficult to obtain experimentally. For partition coefficients far from unity, free energy calculation methods are required. We used umbrella sampling with the Weighted Histogram Analysis Method to obtain partition coefficients of electrolytes between water and nonpolar organic solvents.

1. Siamionau A.V., Egorov V.V., *Membranes*, 2022, 12(10)
2. Samec Z., Langmaier J., Trojánek A., *J. Electroanal. Chem.*, 1996, 409(1–2)
3. Scholz F., Komorsky-Lovrić Š., Lovrić M., *Electrochem. Commun*, 2000, 2(2)

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