# Unusual concentration dependence of ion-exchange membrane conductivity in ampholyte-containing solutions: Effect of ampholyte nature

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## ARTICLE INFO

## ABSTRACT

Electric conductivity of homogeneous cation-exchange (CMX) and anion-exchange (AMX, AX) membranes in the salt solutions of some organic (lysine hydrogen chloride and potassium hydrogen tartrate (KHT)) and inorganic (sodium dihydrogen phosphate) ampholytes was measured as a function of their concentration. In all cases, an increase in membrane conductivity with diluting external solution was observed at concentrations $< 0.04$ mol L$^{-1}$. This trend is not observed in the presence of strong electrolytes, such as NaCl. The effect is explained by a shift in ionic equilibriums caused by decreasing external concentration: increasing Donnan exclusion of H$^+$ ions from an anion-exchange membrane (AEM) as co-ions and increasing fraction of OH$^-$ ions in the external solution when it is diluted under a constant pH. This leads to an increase in pH of the internal charged solution in the membrane gel phase and transformation of a part of singly charged ampholyte anions (e.g. H$_2$PO$_4^-$) into doubly charged ones (HPO$_4^{2-}$). The conductivity increases when one doubly charged counterion replaces two singly charged ones. The mathematical simulation of membrane conductivity concentration dependence provides a good accordance with experimental data. The effect was also simulated by measuring and calculating the conductivity of mixed KHT$-$K$_2$T external solutions as a function of the equivalent fraction of the tartrate ion (T$^{2-}$) under condition that the total equivalent electrolyte concentration was maintained constant. The shape of the conductivity vs. concentration curve strongly depends on the ampholyte nature, namely, on the $(pK_2 - pK_1)/2$ value.

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## 1. Introduction

Electromembrane processes of purification, separation and concentration in combination with other membrane methods are being actively implemented in "green" chemistry systems [1–6]. This is a rapidly developing industry based on complex processing of ampholyte-containing biomass and organic wastes [7] for the production of nutrients, monomers for synthesis of biodegradable packaging materials, bio-based chemicals and other valuable products. Electrodialysis (ED) allows the separation of particles by using the difference in a rather large number of their properties, such as size/mobility of particles (as in ultrafiltration), their charge (separation of charged and uncharged species, as in reverse osmosis and nanofiltration), possibility to control pH via water splitting at membrane/solution interface. This variety of leverage presents an important advantage of this process in comparison with other membrane methods. Especially, wide opportunities open when

treating ampholyte solutions. Ampholyte substances contain both acidic and basic groups [8] (e.g., carboxylic acid and amine groups), which can enter into protonation–deprotonation reactions in aqueous solutions. As a result, the charge of ampholyte particles depends on the pH of the environment. That allows one to use the shift in pH as an additional tool in ED separation [9]. This shift may be obtained by adding acid/base [6] or applying bipolar membranes [10]. On the other hand, this peculiarity gives rise to the transport mechanisms not observed in the case of strong electrolytes like NaCl. Circulation [11] and barrier effects [12] of ampholyte species transport in ED desalination channel as well as effects of ampholyte-facilitated diffusion [13] and electrodiffusion [14,15] through ion exchange membranes are discussed in literature. All these effects are essentially related to the transformation of the uncharged form of an ampholyte into its charged forms and vice-versa due to protonation–deprotonation reactions.

Among numerous examples of ED applications in separation of ampholyte species (most of them were reviewed by Xu and Huang [2] and Nagarale et al. [1]), let us cite regeneration of carbon dioxide absorbents (monoethanolamine, polyenanolamin, etc.) used in life support systems [16,17]; extraction of boric acid from water

[18,19]; regeneration of pickling solutions [20]; separation and demineralization of amino acids [1,6,21], production of carboxylic acids [1,2,22,23]; fine purification and fractionation of proteins [5,24], phosphorus-containing acids [25]; conditioning juices [26], wine [27] and dairy products [28].

ED efficiency strongly depends on the electrical conductivity of ion-exchange membrane (IEM). This property has been experimentally studied in details for IEM in strong electrolyte solutions [29–32]. The concentration dependence of conductivity in this case is well described by the microheterogeneous model [29], which links structural and kinetic parameters of membrane with its transport properties. However, we know a quite limited amount of studies dedicated to the electrical conductivity of membranes in ampholyte solutions [33–37].

For the first time, the concentration dependence of IEM in ampholyte-containing solution was studied by Pismenskaya et al. [33]. It was shown that in the range of low concentrations ( < 0.05 M), the conductivity of homogeneous anion-exchange membranes (AEM) increased with decreasing $NaH_2PO_4$ external solution concentration, in contrast with strong electrolytes, such as NaCl or $NaNO_3$, where the membrane conductivity always decreased with lowering external concentration. Similar results were obtained later in the case of $NaH_2PO_4$ and heterogeneous MA-41 anion-exchange membrane (Shchekinoazot, Russia) [36], as well as in the case of lysine hydrochloride solution with homogeneous CMX Neosepta and heterogeneous MK-40 Shchekinoazot cation-exchange membranes (CEM) [36,38].

In this paper, we present a rather comprehensive study of the concentration dependence of electrical conductivity for several homogeneous AEMs and CEMs in ampholyte solutions as well as in NaCl solutions for comparison. We use a larger number of different electrolytes than earlier: potassium hydrogen tartrate (denoted as KHT), lysine hydrochloride ($H_2LCl$), which are salts of a carbonic acid and an amino acid, respectively, and monosodium phosphate ($NaH_2PO_4$). These organic and inorganic ampholytes have one uncharged molecular ($H_2T$ and $H_3PO_4$) or zwitterion ($Lys^{\pm}/HL^{\pm}$) form, and several charged forms. The proposed earlier [33] hypothesis that the unusual trend of the membrane conductivity concentration dependence in ampholyte-containing solutions is due to the enrichment of the membrane with double charged ampholyte ions is re-examined. We analyze some experiments from literature supporting this hypothesis. As well, we describe our own experiment in solution simulating the behavior of an AEM. We propose some new approximations describing changes in an ion-exchange membrane when the external solution concentration is diluted, as well as a full description of ionic equilibriums in the system.

## 2. Experimental

### 2.1. Membranes

Commercial homogeneous anion-exchange (AMX and AMX-SB) and cation-exchange (CMX) membranes by Astom, Japan, as well as a homogeneous anion-exchange membrane AX were studied. The main properties of these ion-exchange membranes are listed in Table 1.

The ion-exchange capacity of CEM was determined by acid–base titration of the $H^+$ ions produced in the course of base neutralization [39] and that of AEM by precipitation titration [40].

**Table 1**
Some characteristics of the membranes under study.

| Membrane | Fixed charged groups | [a]Thickness in $H_2O$ (μm) | [b]Ion-exchange capacity (mmol $g^{-1}$) | [c]Fraction of the «inter-gel» solution ($f_2$) | [d]Electric conductivity at the iso-conductivity point, $\kappa_{iso}$ (mS $cm^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | NaCl | $H_2LCl$ | $NaH_2PO_4$ | KHT |
| **Anion-exchange membranes** | | | | | | | | |
| AX | $-N^+(R)_3$ | 170 | *2.68, **1.84 | 0.12 | 6.3 | – | 2.6 | 2.1 |
| AMX-SB | $-N^+(R)_3$ | 170 | *1.71, **1.28 | 0.12 | 3.9 | – | 1.7 | 1.3 |
| AMX | $-N^+(R)_3$ | 150 | *1.61, **1.22 | 0.10 | 3.3 | – | 0.8 | 1.0 |
| **Cation-exchange membrane** | | | | | | | | |
| CMX | $-HSO_3^-$ | 170 | *2.17, **1.86 | 0.11 | 1.4 | 0.20 | – | – |

[a] The average deviation (a.d.) is equal to $\pm 10$ μm.
[b] Values are given for the dry* and the swollen** membranes in $Cl^-$ (AEM) or $H^+$ (CEM) forms. The a.d. is $\pm 0.02$ mmol $g^{-1}$.
[c] The a.d. is $\pm 0.01$.
[d] The relative deviation is 5%.

**Table 2**
Some characteristics of the electrolytes used in the study. The data relate to infinite dilution and temperature 298 K.

| Electrolyte, pH | Equivalent conductivity at infinite dilution, $\lambda_i^0$ (S $cm^2$ $eq^{-1}$) | | Diffusion coefficients at infinite dilution, $D_i \times 10^5$ $cm^2$ $s^{-1}$ | | | Stokes radius, $r_i$ (nm) | |
|---|---|---|---|---|---|---|---|
| | Cation | Anion | Cation | Anion | Electrolyte | Cation | Anion |
| NaCl pH $\approx 6.15$ | 50.08 [43,44] | 76.31 [43,44] | 1.334 [43,44] | 2.032 [43,51] | 1.61 [45] | 0.18 | 0.12 |
| $NaH_2PO_4$ pH $\approx 4,80$ | | 36.0 [43,44] | | 0.958 [43] | 1.11 [44] | | 0.26 |
| $Na_2HPO_4$ pH $\approx 10.30$ | | 57.0 [44] | | 0.759 [43] | 1.06 [44] | | 0.32 |
| KHT pH $\approx 3.60$ | 73.48 [43,44] | 31.75 [46] | 1.957 [44] | [b]0.852 | [c]1.19 | 0.13 | 0.29 |
| $K_2T$ pH $\approx 6.20$ | | 59.6 [43] 60.49[47] | | 0.794 [43] [b]0.805 | [c]1.32 | | 0.31 |
| $H_2LCl$ pH $\approx 5.60$ | [a]25.17 | 76.31 [43,44] | 0.67 [48] | 2.032 [43,44] | [c]1.01 | 0.37 | 0.12 |
| $H_3LCl_2$ pH $\approx 2.50$ | [a]45.08 | | [d]0.60 [36] | | [c]1.13 | 0.41 | |

[a] Calculated by using the ionic diffusion coefficients at infinite dilution, Eq. (A16).
[b] Calculated by using the ionic equivalent conductivity at infinite dilution, Eq. (A16).
[c] Calculated by using the ionic diffusion coefficients at infinite dilution, Eq. (A17).
[d] Reported for a mixed $H_2L^+$, $H_3L^{2+}$ solution at pH=2.5 and ionic strength=5 mmol $L^{-1}$.