

Solvent polymeric membranes based on tridodecylmethylammonium chloride studied by potentiometry and electrochemical impedance spectroscopy

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Abstract

Solvent polymeric membranes based on quaternary ammonium salt tridodecylmethylammonium chloride (TDDMACl) with different concentration were investigated. Potentiometric measurements confirmed the deviation of selectivity of the membranes with low TDDMACl concentration from Hofmeister lipophilicity series likely caused by pH-dependence of response. Electrochemical impedance spectroscopy (EIS) was applied to study conductivity and to determine energetic parameters of conductivity (activation energy and pre-exponential factor) for the first time for this type of materials. The dissociation degree and association constants of TDDMACl in the membrane as well as membrane relative permittivities were calculated on the basis of EIS data.

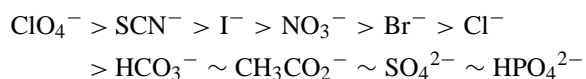
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1. Introduction

Quaternary ammonium salts (QAS) are known from the late sixties of 20th century [1] as components for ion-selective electrodes (ISE). However, they still continue attracting attention of many research groups. The sensors for chloride [2–4] and nitrate [5–7] are the main areas of application of these compounds. QAS-based anion sensors for significant number of different other analytes such as anionic metal complexes, organic anions and poly-ions were also reported [8,9].

Selectivity of anion sensors based on solely QAS was originally considered being governed by Hofmeister lipophilicity sequence [2]:



Selectivity in this case is determined by the free energies of ion hydration without taking into account any specific interactions between ion-exchanger and ions. Theoretical examination of response of liquid ion-exchange membranes was performed by Sandblom et al. [10]. The effect of ionic association on solvent polymeric membrane selectivity was studied by Egorov et al. [11,12]. A number of researches reported deviations of selectivity of QAS-based membranes from Hofmeister pattern [3–5,13]. These deviations depended on the concentration and structure of QAS and the additives present in the membrane, but only recently the nature of these deviations was explained by pH-sensitivity [14].

Ionic additives and particularly QAS are strongly recommended [15] as components for neutral carrier based anion-selective electrodes. Incorporation of QAS into anion sensor membranes generates cationic sites in organic phase that prevents counter-ion interference and provides Nernstian sensitivity to the ion of interest. Such ionic additives or ion-exchangers are also assumed to influence the selectivity and reducing membrane resistance. QAS can also improve the performance of potentiometric sensors such

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as cation-selective electrodes based on charged ionophores [16].

Different techniques for measurement of ionophore–ion complex formation constants in solvent polymeric membranes have been developed and improved recently [17,18]. Still there is a lack of experimental data regarding association constants of simple ion-exchangers, though an attempt to make numerical simulation was performed [19]. The direct data may be beneficial for optimization of composition of ion-selective membranes as well as for better understanding of the processes taking place in the membrane phase. While the association in cation-selective solvent polymeric membranes was intensively studied by Armstrong et al. [20,21], much less attention was paid to anion sensors. In the present work, the study of the sensors based on different concentrations of tridodecylmethylammonium chloride (TDDMACl) was performed by potentiometry and electrochemical impedance spectroscopy (EIS) in order to clarify the influence of TDDMACl content on electrochemical properties of membranes.

2. Experimental

2.1. Materials

Tridodecylmethylammonium chloride (TDDMACl), bis(2-ethylhexyl)sebacate (DOS) and *o*-nitrophenyloctyl ether (NPOE) in Selectophore[®] grade; high molecular weight poly(vinyl chloride) (PVC), purum, were obtained from Fluka (Buchs, Switzerland). Tetrahydrofuran (THF) from Merck (Darmstadt, Germany) was freshly distilled prior to use. Tris(hydroxymethyl)aminomethane (Tris) and all salts were of p.a. grade from Merck. Milli-Q water (18 M Ω cm) was used throughout all experiments.

2.2. Membrane preparation

Concentrations of components in the membranes are shown in the Table 1. Two concentration scales: weight per-

cent (wt.%) and molality units (mmol kg⁻¹) are presented for convenience. Weighted amounts of membrane components: TDDMACl, plasticizer (DOS or NPOE) and polymer (PVC) were mixed in freshly distilled THF. Membrane cocktail was intensively stirred for approximately 15 min until all components were dissolved. The resulting homogeneous liquid was poured into Teflon ring mounted on the glass plate and left for 48 h for solvent evaporation. The disks were punched from the resulted film. The thickness of the membranes was determined with the scaled microscope and was found to be 0.60 \pm 0.02 mm. The diameter of membranes for impedance measurements was 10 mm and of those for sensor preparation 7 mm. The sensors were made according to conventional procedure. The membranes were glued onto PVC tubes. 0.01 M solution of sodium chloride as internal filling and internal reference Ag/AgCl electrodes were used. All sensors and membranes for impedance studies were conditioned in 0.01 M of sodium chloride for 5 days before measurements.

2.3. Potentiometric measurements

Potentials were measured with a custom-made multi-channel mV-meter with high input impedance, connected to PC for data acquisition and processing. The reference electrode Metrohm (Ag/AgCl, type 6.0729.100) had 3 M KCl internal filling and 1 M CH₃COOLi bridge electrolyte.

Selectivity coefficients were determined by separate solution method (SSM) in unbuffered 0.1 M solutions of sodium salts. Ion activity coefficients were calculated according to the second approximation of Debye–Hückel theory, acetate-ion parameters being applied for salicylate. Calibrations in sodium chloride solutions were carried out in the range 10⁻⁵–10⁻¹ M. All presented data shows the averaged responses of three replica sensors of each type. Potentiometric measurements were performed at room temperature (20 \pm 1 °C).

2.4. Electrochemical impedance measurements

Electrochemical impedance measurements were made using Agilent Technologies 4284A and 4285A L,C,R meters governed by a PC. Electrical impedance spectra were recorded in the temperature range 275–300 K and in the frequency range from 20 Hz to 1 MHz. The amplitude of the sinusoidal excitation signal was 50 mV. Temperature was adjusted with a temperature controller connected to cryostat-thermostat. The accuracy of preset temperature was 0.05 K. Impedance measurements were carried out in a custom-made symmetrical set-up shown in Fig. 1. The distance between membrane and disk-shaped platinum working electrodes was 4 mm. 0.01 M solution of sodium chloride was in contact with membrane on both sides. The contact area of 0.5 cm² was determined by the cell geometry. At least three replica membranes of each type were studied.

Table 1
Membrane compositions

Sensor membrane	TDDMACl		DOS (wt.%)	NPOE (wt.%)	PVC (wt.%)
	wt.%	mmol kg ⁻¹			
1	–	–	67.0	–	33.0
2	0.5	8.6	66.5	–	33.0
3	1.0	17	66.0	–	33.0
4	2.0	35	65.0	–	33.0
5	5.0	87	62.0	–	33.0
6	–	–	–	67.0	33.0
7	0.5	8.6	–	66.5	33.0
8	1.0	17	–	66.0	33.0
9	2.0	35	–	65.0	33.0
10	5.0	87	–	62.0	33.0

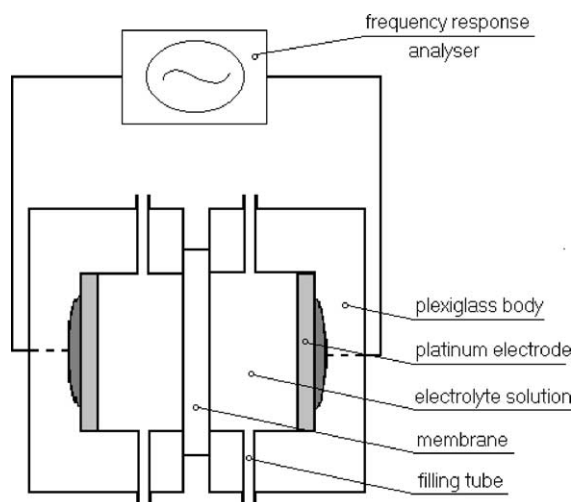


Fig. 1. Electrochemical cell for impedance measurements.

3. Results and discussion

3.1. Potentiometric measurements

Previously reported concentrations of QAS in the sensor membranes selective to chloride, nitrate and other anions were usually high (up to 16.7 wt.%) [3]. Only the works [13,14] were focused on membranes with rather low QAS concentration (10 mmol kg^{-1} of plasticizer). According to [13] selectivity of membranes can differ from Hofmeister pattern at QAS's concentration $1\text{--}10 \text{ mmol kg}^{-1}$ of plasticizer. Sensitivity to chloride of membranes based on TDDMACl with 10 mmol kg^{-1} of plasticizer was reported being sub-Nernstian (-43.1 mV per decade and -35.3 mV per decade for DOS and NPOE-plasticized membranes, respectively). Therefore, the authors used biionic potentials as characteristics of selectivity instead of selectivity coefficients [13]. A possible explanation of anti-Hofmeister behaviour was published recently [14]. The proposed reason

for such behaviour is OH-response of the sensors with low TDDMACl concentration.

We received similar results: chloride calibration slopes of -48.4 ± 0.5 and $-46.2 \pm 0.6 \text{ mV}$ per decade were observed for DOS- and NPOE-plasticized membranes, respectively, at TDDMACl concentration of 8.6 mmol kg^{-1} . Therefore, the selectivity coefficients presented in Fig. 2 are also complemented with biionic potentials (BIP[NaCl–NaX], mV). The analysis of the selectivity shows that increase of ion-exchanger concentration in the membrane leads to a smooth decrease of selectivity towards lipophilic anions and increase of selectivity to hydrophilic ones. This confirms the expectation that the lower is the lipophilicity of the ion the higher should be the content of ion-exchanger in the membrane. At high TDDMACl concentrations selectivity pattern of the membranes corresponds to Hofmeister series and remains constant. Another important conclusion is that the membranes plasticized with NPOE are more selective toward chloride in the presence of hydrophilic anions, while DOS membranes demonstrate better selectivity in the presence of lipophilic anions. As it was mentioned above these data should be treated with certain care since the membranes with low QAS concentration do not exhibit Nernstian sensitivity to the most of interfering ions. The values of selectivity coefficients for membranes with relatively high TDDMACl concentration are in a good agreement with [22].

However, behaviour of sensors based on DOS-plasticized membranes with low TDDMACl concentration in bicarbonate and acetate solutions is significantly different. The decrease of TDDMACl concentration in DOS-membrane from 87 mmol kg^{-1} down to 8.6 mmol kg^{-1} gives an apparent gain in selectivity to bicarbonate of about two-orders of magnitude. The effect towards acetate is also high (1.8 in logarithmic scale). Apparent non-Hofmeister behaviour of QAS-based DOS-membranes becomes evident that agrees well with the results from [13,14]. These observations indicate the role of factors other than anion lipophilicity influencing DOS membrane selectivity at low QAS concen-

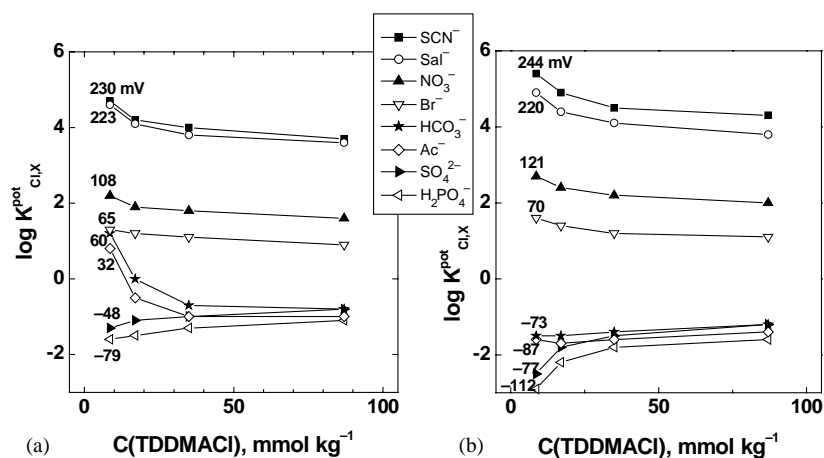


Fig. 2. Selectivity coefficients ($\log K_{\text{Ci,X}}^{\text{pot}}$) and biionic potentials (in mV) of sensors based on TDDMACl, plasticized with DOS (a) and NPOE (b).

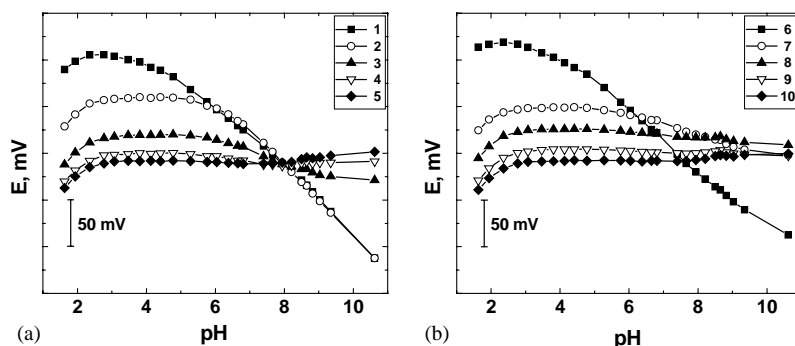


Fig. 3. Influence of pH on response of the sensors, plasticized by DOS (a) and NPOE (b).

trations. At the same time the membranes plasticized with NPOE do not exhibit non-Hofmeister selectivity. The influence of pH on the responses of the sensors with varied concentrations of TDDMACl was measured by drop-wise adding of H_2SO_4 to 0.01 M solution of NaCl and 0.01 M Tris, the results being presented in Fig. 3. “Dummy” DOS- and NPOE-plasticized membranes exhibit remarkable pH sensitivity, which decreases with the increase of concentration of ion-exchanger. In case of NPOE this sensitivity disappears at 8.6 mmol/kg of TDDMACl, but in case of DOS it does not. Since sodium bicarbonate and sodium acetate solutions have higher pH (8.4 and 8.9, correspondingly) than other solutions of sodium salts the observed pH sensitivity leads to the decreased membrane potentials and to apparent gain in selectivity to carbonate and acetate anions. These results confirm previous observations [14], but on the basis of the present study we may particularly emphasize that the plasticizer is the main source of possible pH-sensitivity of membranes.

3.2. Electrochemical impedance analysis

Electrochemical impedance spectroscopy (EIS) was applied to study ac conductivity of materials and also to derive characteristics of ionic equilibria in the membrane. A typical Nyquist plot for PVC membranes, plasticized with DOS is presented in Fig. 4. Only the first semicircle, which is referred to bulk resistance of the membrane, was observed for all samples. The standard electrical conductivity of membranes was calculated from membrane resistance (real part of the electrochemical impedance) recorded at 100 Hz. Temperature dependence of conductivity obeys Arrhenius law. Typical plots are presented in Fig. 5. Activation energy of conductivity (E_a), pre-exponential factors ($\log \sigma_0$) and standard conductivities at 298 K ($\log \sigma_{298}^0$) were calculated by least squares method from Arrhenius-type equation: $\sigma T = \sigma_0 \exp(-E_a/kT)$. The results are summarized in the Table 2 and Fig. 6.

The standard conductivity of “dummy” membrane plasticized with NPOE is about 15 times higher than that of DOS-plasticized (logarithmic conductivities are -6.81 and -5.62 , correspondingly). A stepwise increase of conduc-

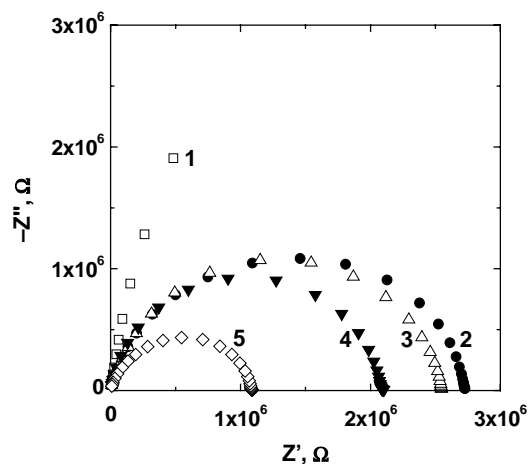


Fig. 4. Nyquist plots of impedance of DOS-plasticized membranes. The membrane compositions are presented in Table 1.

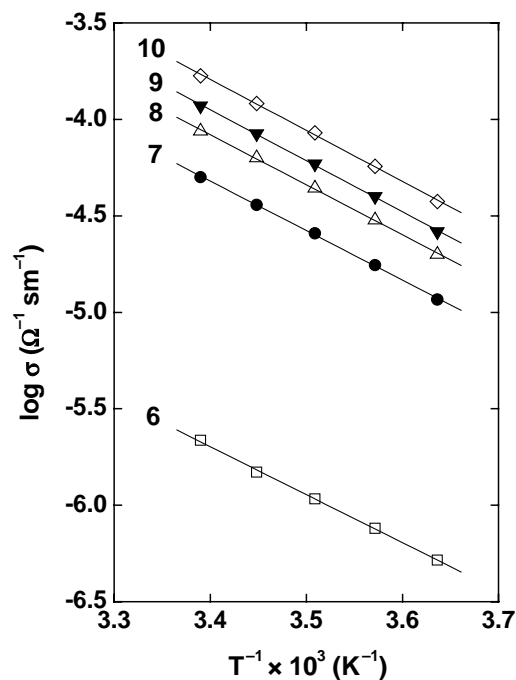


Fig. 5. Conductivity Arrhenius plots of NPOE-plasticized membranes. See Table 1 for membrane compositions.

Table 2
Membrane conductivity parameters

Sensor membrane	$-\log \sigma_{298}$ ($\Omega^{-1} \text{sm}^{-1}$)	E_a (eV)	$\log \sigma_0$ ($\Omega^{-1} \text{sm}^{-1} \text{K}$)
1	6.81 (7)	0.44 (1)	0.6 (1)
2	5.53 (5)	0.528 (6)	3.4 (1)
3	5.48 (5)	0.538 (6)	3.6 (1)
4	5.41 (6)	0.556 (6)	4.0 (1)
5	5.13 (4)	0.596 (6)	4.9 (1)
6	5.62 (8)	0.48 (2)	2.5 (3)
7	4.21 (4)	0.534 (7)	4.8 (2)
8	3.96 (6)	0.536 (7)	5.1 (2)
9	3.83 (5)	0.55 (1)	5.5 (2)
10	3.67 (5)	0.55 (1)	5.6 (2)

tivity by more than an order of magnitude is observed when the first portion of TDDMACl (0.5 wt.%) is being added to “dummy” membrane. This can be explained by different charge carriers in “dummy” membranes and materials with QAS. According to [23] “dummy” membranes made from PVC are assumed of containing endogenous negative fixed ion-exchange sites with typical concentration of 0.05–0.6 mmole kg^{-1} . These sites ensure affinity to cations, e.g. sodium or potassium, that are responsible for conductivity of the membrane. The increase of QAS concentration results in significant increasing of chloride-ion content. Furthermore, the presence of QAS may partly lead to charge compensation of endogenous membrane sites by the lipophilic quaternary ammonium-cations. Thus, chloride is assumed of being main charge carrier in QAS containing membranes. Sharp changes of E_a and σ_0 at the first QAS addition provide an additional prove of different conductivity mechanisms in ‘dummy’ and QAS-containing membranes. Activation energies of conductivity and pre-exponential factors of TDDMACl-based membranes are presented in Table 2.

Pre-exponential factor ($\log \sigma_0$) that is related to concentration and mobility of charge carriers in the membrane increases by an order of magnitude with ion-exchanger con-

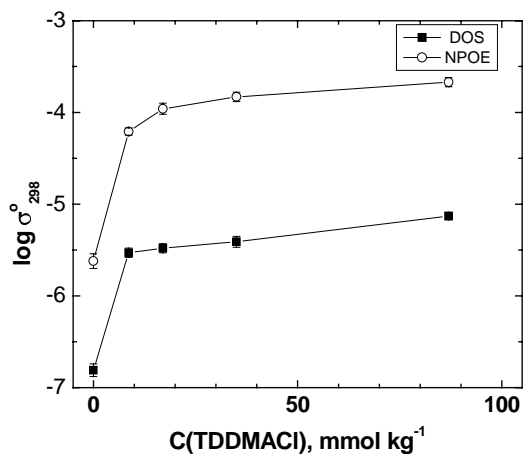


Fig. 6. Dependence of standard conductivity from concentration of TDDMACl in membranes plasticized with DOS and NPOE.

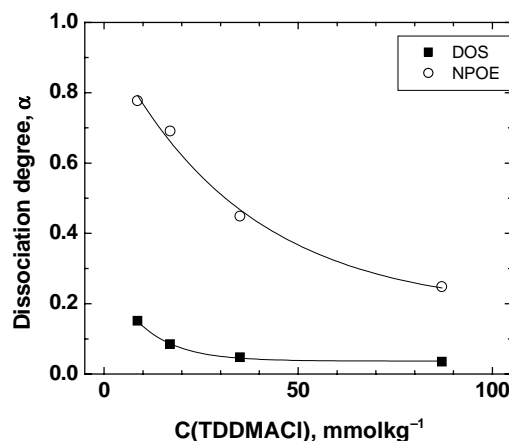


Fig. 7. Dissociation degree α of TDDMACl in membranes plasticized with DOS (■) and NPOE (○).

centration increase. This growth, which closely follows QAS concentration change, may be attributed to the increase of charge carrier net content. However, the change of σ_0 by an order of magnitude does not correspond directly to only three-fold enhancement of conductivity value. Partial association of QAS in the membrane is likely an explanation for such behaviour. It may be logically supposed that degree of association increases with the growth of QAS content. This supposition is confirmed by the observed behaviour of activation energy (E_a) value. In QAS-containing materials, E_a slightly grows with the increase of ion-exchanger content that can be considered as an evidence of partial inhibition of TDDMACl dissociation at higher contents, especially for less polar DOS membranes.

The values of association constants of TDDMACl (K_a) were calculated according to Ostwald's dilution law: $K_a = \lambda_m^0(\lambda_m^0 - \lambda_m)/\lambda_m^2 C$, where λ_m^0 is limiting molar conductivity, λ_m the equivalent molar conductivity and C is electrolyte (TDDMACl) concentration. Ternary ion interactions were neglected. Limiting molar conductivities (λ_m^0) were determined by extrapolation of $\lambda_m = f(C^{1/2})$ to infinite dilution ($C = 0$). Dissociation degree of TDDMACl ($\alpha = \lambda_m/\lambda_m^0$) versus concentration is plotted in Fig. 7. When the concentration of ion-exchanger is 8.6 mmol kg^{-1} , almost 80% of TDDMACl in NPOE membrane is in the dissociated form, while in DOS membrane this value is only about 15%. Calculated logarithms of association constants ($\log K_a$) of TDDMACl were 3.7 ± 0.2 for DOS- and 1.6 ± 0.3 for NPOE-plasticized membranes. Higher error in the latter case is caused by concentration dependence of K_a , which is more significant for stronger electrolytes since TDDMACl is better dissociated in polar NPOE membrane.

For calculating association constant theoretically we applied Fuoss equation [24]:

$$K_a = \frac{4\pi N_A a^2}{3000} \exp\left(\frac{|z_1 z_2| e^2}{4\pi \epsilon \epsilon_0 a k T}\right),$$

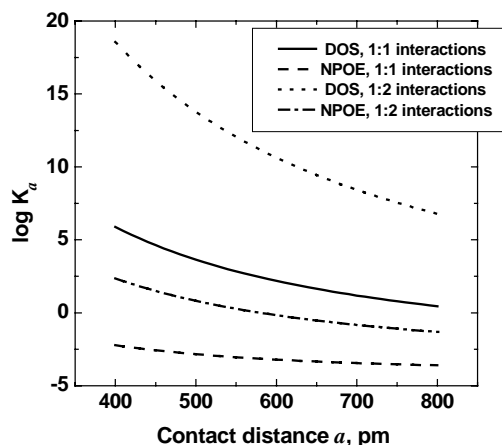


Fig. 8. Dependence of association constant, calculated according Fuoss equation, from contact distance at 1:1 and 1:2 ions interactions at different relative permittivities of the solvent.

where a is center-to-center distance of the ions in a pair (the so-called contact distance), z_1 and z_2 the charges of interacting ions, e the elementary charge, k the Boltzmann's constant, N_A the Avogadro's number, ϵ_0 the relative permittivity of vacuum and T is temperature.

Relative permittivities (dielectric constants, ϵ) of membranes were estimated on the basis of our impedance data at 1 MHz and 300 K. The values of ϵ were found being 4.8 ± 0.2 and 13.3 ± 0.3 for DOS and NPOE membranes, correspondingly. They did not depend on concentration of QAS in the membrane. These ϵ values are in agreement with literature data (4.8 for DOS and 14 for NPOE membranes with 33 wt.% of PVC [25]).

The analysis of Fuoss equation shows the dependence of association constant from contact distance at different relative permittivities of the membrane (Fig. 8). The lower is ϵ the higher is association constant and the stronger its dependence from contact distance a . Furthermore, the association between highly charged ions should be even stronger. Thus, the influence of contact distance or anion size on association constant must be higher in membranes plasticized with less polar DOS. It should be mentioned that the direct calculation of association constants according to Fuoss equation is somewhat difficult as the contact distance of TDDMACl in the plasticizers that were used in this work can be only roughly estimated. Using the estimates of a , the resulted association constants are overvalued (up to four-orders of magnitude for DOS- and about one-order of magnitude for NPOE-plasticized membranes). The influence of PVC on ion pairing was discussed earlier by Armstrong et al. for cation-exchanger membranes [20] and the solvation of sodium-ions by chlorines on the PVC chain was suggested to decrease ionic association. Evidently, in the case of anion-selective membranes this explanation is inappropriate. Harrison et al. showed that PVC matrix does not play a specific role in solvation and dissociation of the electrolytes in solvent polymeric membranes

Table 3

Ionic radii (r), absolute standard molar enthalpies of hydration ($\Delta H_{\text{hyd}}^\circ$) and experimental values of the molar Gibbs energies of hydration of ions (ΔH_{hyd}^*) [28]

Ion	r (pm)	$\Delta H_{\text{hyd}}^\circ$ (kJ/mol)	ΔH_{hyd}^* (kJ/mol)
OH ⁻	133	-520	-430
Br ⁻	196	-335	-315
Cl ⁻	181	-365	-340
CH ₃ CO ₂ ⁻	190	-425	-365
CO ₃ ²⁻	178	-1395	-1315
HCO ₃ ⁻	185	-380	-335
H ₂ PO ₄ ⁻	238	-520	-465
NO ₃ ⁻	179	-310	-300
SCN ⁻	213	-310	-280
SO ₄ ²⁻	240	-1035	-1080

[26]. An explanation might be that “the primitive model” [27] does not take into account a number of parameters, such as asymmetry of TDDMA⁺ ion, extremely high viscosity of media and so on. At least the model enables evaluating the influence of relative permittivity on association constant.

Table 3 contains ionic radii, enthalpies and Gibbs energies of hydration of selected anions studied in this work. Evidently, the free energies of hydration are responsible for Hofmeister behaviour of sensor membranes. As mentioned above the observed anti-Hofmeister behaviour of DOS-plasticized membranes with low TDDMACl content is due to inherent pH-dependence of sensor response. However, the membranes sensitivity to hydroxyl ions may also be explained by the formation of ionic pairs of quaternary ammonium cations with hydroxyl ions. According to [28], the hydroxyl ion radius is almost 50 pm smaller than that of chloride and hydration energies are not that different. This factor along with low polarity of DOS membranes causes deviation of selectivity in favour of hydroxyl. Precise confirmation of this statement requires the measurement of association constants of the TDDMA⁺ with hydroxyl ion. For other hydrophilic anions no selectivity increase was observed since the radii of these anions are much greater and hydration energies are significantly higher than those for chloride. Even 1:2 charge interactions for divalent sulphate-ion cannot compensate this gap in hydration energies.

4. Conclusions

Concentration dependence of potentiometric properties and conductivity parameters of solvent polymeric membranes based on two plasticizers—DOS and NPOE and containing 0.5–5% of TDDMACl were investigated. The values of conductivities, the changes in activation energy and pre-exponential factor were determined and discussed in terms of ionic association in membrane phase. The calculated dissociation degrees and association constants

of TDDMACl in solvent polymeric membranes are presented, the latter being 3.7 ± 0.2 for DOS- and 1.6 ± 0.3 for NPOE-plasticized membranes. Apparent deviations of membrane selectivity from Hofmeister lipophilicity sequence at low TDDMACl concentration in DOS-plasticized membranes were explained by pH-dependence of the sensor response.

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