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Abstract

Full Text

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ION-EXCHANGE AND ELECTROCHEMICAL PROPERTIES OF SULFOCATIONITES IN SOLUTIONS OF CERTAIN 1–1 CHARGE ELECTROLYTES

In the preceding communication (^{1}) an approximate equation was discussed which expresses the dependence of the e.m.f. of the cell

$$\mathrm{Ag}\,|\,\mathrm{AgCl,\ ACl,\ BCl}\underset{\text{solution I}}{\Big|}\ \text{cationite membrane}\,\Big|\,\mathrm{ACl,\ BCl,\ AgCl}\underset{\text{solution II}}{\Big|}\ \mathrm{Ag} \tag{1}$$

on the compositions of solutions I and II:

$$E = \frac{RT}{F}\ln\frac{a^2_{\pm(\mathrm{BCl})_2} + K_{\mathrm{A-B}}\frac{U_A}{U_B}a^2_{\pm(\mathrm{ACl})_2}}{a^2_{\pm(\mathrm{BCl})_1} + K_{\mathrm{A-B}}\frac{U_A}{U_B}a^2_{\pm(\mathrm{ACl})_1}}. \tag{2}$$

Here $a_{\pm(\mathrm{ACl})_1}$, $a_{\pm(\mathrm{ACl})_2}$, $a_{\pm(\mathrm{BCl})_1}$, and $a_{\pm(\mathrm{BCl})_2}$ are the mean activities of the corresponding chlorides in solutions I and II; U_A and U_B are the mobilities of ions A^+ and B^+ in the membrane; $K_{\mathrm{A-B}} = \dfrac{C_A a_B}{C_B a_A}$ is the exchange constant of ions A^+ and B^+ between the cationite and the solution; C_A and C_B are the concentrations of ions A^+ and B^+ in the cationite, and a_A and a_B are their activities in the solution.

Fig. 1. Cell for measuring transport numbers (schematic)

Fig. 2. Setup for measuring electrical conductivity (schematic)

Figure 2: Fig. 2. Setup for measuring electrical conductivity (schematic)

This equation can be obtained from the general thermodynamic relation given in (²). The assumptions made in deriving equation (2) were discussed in detail in (¹). For the systems investigated in the present work, the most important is the following: it is assumed that the membrane is impermeable to anions, that the activity coefficients and mobilities of the cations inside the membrane are constant, and that solvent transport may be neglected.

For the special case in which each of the solutions contains only one electrolyte, i.e., for the galvanic cell

$$\mathrm{Ag}\,|\,\underset{\text{solution I}}{\mathrm{AgCl,\ ACl}\ \Big|}\ \text{cationite membrane}\ \Big|\,\underset{\text{solution II}}{\mathrm{BCl,\ AgCl}\ \Big|}\ \mathrm{Ag} \qquad (3)$$

equation (2) is transformed into the following:

$$E = \frac{RT}{F}\ln\frac{a^2_{\pm(\mathrm{BCl})_2}}{K_{\mathrm{A-B}}\frac{U_A}{U_B}a^2_{\pm(\mathrm{ACl})_1}} = \frac{2RT}{F}\ln\frac{a_{\pm(\mathrm{BCl})_2}}{a_{\pm(\mathrm{ACl})_1}} - \frac{RT}{F}\ln K_{\mathrm{A-B}}\frac{U_A}{U_B}. \qquad (4)$$

The present communication is devoted to studying the applicability of equations (2) and (4) to specific systems including HCl–NaCl, HCl–KCl, NH_4Cl–KCl solutions and heterogeneous membranes based on KU-2 and SBS-1 sulfocationites.*

On the basis of the results of independent measurements, the parameters K_{A-B} and $\frac{U_A}{U_B}$, entering equations (2) and (4), were determined. From these data the e.m.f. of galvanic cells (1) or (3) containing solutions of known composition was calculated. The values obtained were compared with the e.m.f. values determined experimentally. K_{A-B} was calculated from data on the equilibrium compositions of the solution and the corresponding granular ion exchanger; the ratio of the activity coefficients of the cations in solution was calculated by Harned' s method (⁴).

The ratio of the mobilities of cations inside the ion exchanger was determined on the basis of measurements of transport numbers through a membrane (or resin) in mixed form, or from the change in the electrical conductivity of the membrane when it was converted from one ionic form into another. The ion transport numbers (H^+, Na^+, Cl^-) were determined analytically from the change in their content in the cathodic solution after passing a definite quantity of electricity through the system. The cell in which the measurements were carried out is shown in Fig. 1a.

Fig. 2. Setup for measuring electrical conductivity (schematic)

When calculating the ratio of the mobilities of H^+ and Na^+ ions inside the membrane from the values of their transport numbers, it was assumed that the ionic composition of the membrane corresponds to equilibrium with the anodic solution.** The latter condition is not fulfilled if concentration polarization arises at the boundary between the membrane and the anodic solution. To avoid its possible influence, we investigated ion transport through a layer of granular ion exchanger (packed membranes). In this case, between the chambers of the cell (Fig. 1b) there was placed a layer of ion exchanger of known ionic composition, separated from the solutions by the corresponding heterogeneous membranes. During the experiment, the constancy of the composition of the ion-exchanger layer adjacent to the cathodic solution was monitored. Under this condition, possible polarization at the membrane boundary with the anodic solution will not affect the results.

The electrical conductivity was measured using direct current. The layout of the apparatus is presented in Fig. 2. The resistance of the layer of solution adjacent to the membrane was taken into account by a blank experiment in which the membrane was removed from the cell. During resistance measurements the system was thermostated; all other quantities were determined at room temperature (18–20°).

When measuring the e.m.f. of cell (1) or (3), the solutions separated by the membrane were buffered by adding to them 10–20 g of resin previously brought into equilibrium with the given solution. The contents of the chambers were stirred vigorously. The results obtained are presented in Table 1.

In the last three columns of the table are given the e.m.f. values of the cells

* The characteristics of these resins and membranes are given in work ([3]).

** The theoretical and experimental justification of this assumption will be given in a more detailed communication.

Table 1

Resin	Electrolyte system	Equilibrium solution composition m_1	Equilibrium solution composition m_2	K_{1-2}	Transport, heterogeneous membrane: composition of anode solution m_1	Transport, heterogeneous membrane: composition of anode solution m_2	Transport, heterogeneous membrane u_1/u_2	Transport, saturated membrane: membrane composition c_2/c_1	Transport, saturated membrane u_1/u_2	u_1/u_2 from electrical conductivity in an equilibrium solution with 0.1 M total concentration at 20°	EMF of elements (1) or (3), mV: solution I (m)	EMF of elements (1) or (3), mV: solution II (m)	E_{exp}	E'_{theor} at K_{1-2} and u_1/u_2 (mean)	E''_{Te}
KU-2	HCl – NaCl	0.0497	0.0496	0.68	0.284	0.285	7.0	1.16	6.5	6.2	3.0 NaCl	0.3 HCl	38	42	−4
KU-2	HCl – NaCl	0.0237	0.0733	0.72	0.0497	0.0496	6.8	1.38	6.5	6.2	0.1 NaCl	0.1 HCl	37	39	−7
KU-2	HCl – NaCl	0.0497	0.0496	0.68	0.126	0.392	5.8	3.64	6.4	6.2	0.01 NaCl	0.01 HCl	38	38	−8
KU-2	HCl – NaCl	0.0237	0.0733	0.72	0.0237	0.0733	6.5	3.9	6.0	6.2	0.001 NaCl	0.001 HCl	40	38	−8
KU-2	HCl – NaCl	0.0497	0.0496	0.68	0.284	0.285	7.0	1.16	6.5	6.2	0.0667 NaCl + 0.0333 HCl	0.0333 NaCl + 0.0667 HCl	10	11	−3

Resin	Electrolyte system	Equilibrium solution composition m_1	Equilibrium solution composition m_2	K_{1-2}	Transport, heterogeneous membrane composition of anode solution m_1	Transport, heterogeneous membrane: composition of anode solution m_2	Transport, heterogeneous membrane u_1/u_2	Transport, saturated membrane: composition c_2/c_1	Transport, saturated membrane u_1/u_2	u_1/u_2 from electrical conductivity in an equilibrium solution with 0.1 M total concentration at 20°	EMF of elements (1) or (3), mV: solution I (m)	EMF of elements (1) or (3), mV: solution II (m)	E_{exp}	E'_{theor} at K_{1-2} and u_1/u_2 (mean)	E''_{Te}
KU-2	HCl – KCl	0.050	0.050	0.49	–	–	–	–	–	4.3	0.1 KCl	0.1 HCl	23	22	−14
KU-2	HCl – KCl	0.025	0.075	0.56	–	–	–	–	–	4.3	0.01 KCl	0.01 HCl	25	20	−16
KU-2	HCl – KCl	0.050	0.050	0.49	–	–	–	–	–	4.3	0.001 KCl	0.001 HCl	30	20	−16
KU-2	NH_4Cl – KCl	0.050	0.050	0.75	–	–	–	–	–	1.3	0.1 NH_4Cl	0.1 KCl	6	5	11
KU-2	NH_4Cl – KCl	0.050	0.050	0.75	–	–	–	–	–	1.3	0.01 NH_4Cl	0.01 KCl	5	2	8
KU-2	NH_4Cl – KCl	0.050	0.050	0.75	–	–	–	–	–	1.3	0.001 NH_4Cl	0.001 KCl	3	1	7

Resin	Electrolyte system	Equilibrium solution composition m_1	Equilibrium solution composition m_2	K_{1-2}	Transport, heterogeneous membrane: composition of anode solution m_1	Transport, heterogeneous membrane: composition of anode solution m_2	Transport, heterogeneous membrane u_1/u_2	Transport, saturated membrane: membrane composition c_2/c_1	Transport, saturated membrane u_1/u_2	u_1/u_2 from electrical conductivity in an equilibrium solution with 0.1 M total concentration at 20°	EMF of elements (1) or (3), mV: solution I (m)	EMF of elements (1) or (3), mV: solution II (m)	E_{exp}	E'_{theor} at K_{1-2} and u_1/u_2 (mean)	E''_{Te}
SBS-1	HCl – NaCl	0.0497	0.0496	1.13	0.284	0.285	8.2	0.64	5.1	5.7	0.3 NaCl	0.3 HCl	56	56	10
SBS-1	HCl – NaCl	0.0237	0.0733	1.36	0.0497	0.0496	9.5	1.62	4.7	5.7	0.1 NaCl	0.1 HCl	54	53	7
SBS-1	HCl – NaCl	0.0497	0.0496	1.13	0.126	0.392	6.3	0.84	7.3	5.7	0.01 NaCl	0.01 HCl	52	52	6
SBS-1	HCl – NaCl	0.0237	0.0733	1.36	0.0237	0.0733	6.0	2.03	4.8	5.7	0.001 NaCl	0.001 HCl	52	52	6
SBS-1	HCl – NaCl	0.0497	0.0496	1.13	0.284	0.285	8.2	0.64	5.1	5.7	0.0667 NaCl + 0.0333 HCl	0.0667 HCl + 0.0333 NaCl	14	13	2

Resin	Electrolyte system	Equilibrium solution composition m_1	Equilibrium solution composition m_2	K_{1-2}	Transport, heterogeneous membrane composition of anode solution m_1	Transport, heterogeneous membrane: composition of anode solution m_2	Transport, heterogeneous membrane: u_1/u_2	Transport, saturated membrane: membrane composition c_2/c_1	Transport, saturated membrane: u_1/u_2	u_1/u_2 from electrical conductivity in an equilibrium solution with 0.1 M total concentration at 20°	EMF of elements (1) or (3), mV: solution I (m)	EMF of elements (1) or (3), mV: solution II (m)	E_{exp}	E'_{theor} at K_{1-2} and u_1/u_2 (mean)	E''_{Te}
SBS-1	HCl – NaCl	0.050	0.050	0.78	–	–	–	–	–	3.6	0.1 KCl	0.1 HCl	42	31	–4
SBS-1	HCl – NaCl	0.025	0.075	1.02	–	–	–	–	–	3.6	0.01 KCl	0.01 HCl	40	29	–3
SBS-1	HCl – NaCl	0.050	0.050	0.78	–	–	–	–	–	3.6	0.001 KCl	0.001 HCl	39	29	–3
SBS-1	NH_4Cl – KCl	0.050	0.050	0.92	–	–	–	–	–	1.0	0.1 NH_4Cl	0.1 KCl	2	6	6
SBS-1	NH_4Cl – KCl	0.050	0.050	0.92	–	–	–	–	–	1.0	0.01 NH_4Cl	0.01 KCl	1	3	3

SBS-1	NH_4Cl–KCl	0.050	0.050	0.92	–	–	–	–	–	1.0	0.001 NH_4Cl	0.001 KCl	3	2	2

Note. In all cases, subscript 1 refers to that electrolyte or cation which is written first in the second column.

(1) or (3), obtained experimentally (E_{expt}), calculated from equation (2) or (4) (E'_{theor}), and also from the equation of the ion-exchange theory of the glass electrode (^{5}), which does not take into account the influence of ion mobilities on the magnitude of the e.m.f. (E_{theor}). The agreement between the values of E_{expt} and E'_{theor} may be considered satisfactory if one takes into account the considerable scatter in the values of the exchange constants and the ratios of the ion mobilities, especially for the SBS-1 resin.* The e.m.f. values calculated from the equation of ion-exchange theory for all systems containing the hydrogen ion show greater discrepancies with experiment, clearly exceeding the experimental error. Consequently, in this case the diffusion potential inside the membrane, caused by the different mobilities of counterions, makes a substantial contribution to the e.m.f. of the cell.

The satisfactory agreement between the e.m.f. values determined experimentally and calculated from equations (2) and (4) indicates the applicability of these equations to the systems studied: HCl–NaCl, NH_4Cl–KCl, and, to a lesser extent, HCl–KCl. Consequently, the assumptions (^{1}) made in deriving these equations may, for the first two systems, be considered valid within the accuracy of our experiment.

As has already been noted in the literature (see, for example, (^{6})), the magnitude of the bi-ionic potential (or of the e.m.f. of cell (3) in our case) is a measure of the specificity of the membrane electrode with respect to ion B^+ in the presence of ion A^+. In the systems we studied, one can speak only of a certain slight specificity of the membrane electrodes with respect to the hydrogen ion, which is determined by its increased mobility in the ionite phase.

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* The low accuracy of the results obtained for the SBS-1 resin is evidently due to the fact that the latter has lower chemical stability, lower capacity than the KU-2 resin, and is also not strictly monofunctional.

Note: Figure translations are in progress. See original paper for figures.