EQUILIBRIUM SORPTIONS IN HETEROGENEOUS ION EXCHANGE MEMBRANES

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The equilibrium sorption of uni-univalent electrolytes (NaCl, KCl) in heterogeneous cation exchange membranes with various contents of the ion exchange component and in ion exchange membranes Ralex was investigated. Using experimental data which express the concentration dependence of equilibrium sorption, validity of the Donnan relation for the systems under investigation was tested and values of the Glueckauf inhomogeneity factor for Ralex membranes were determined. Determination of the equilibrium sorption allows the effect of the total content of internal water and of the ion-exchange capacity on the distribution coefficients of the electrolyte to be determined.

Interest in the utilization of membrane processes in, untraditional directions and attempts to use transport phenomena in biotechnologies, medical applications and the like stimulate the necessity of a thorough knowledge of the mechanism of all processes which occur when a substance passes through the membrane. They can be investigated from various viewpoints[1]; one of important factors are conditions of establishment of the concentration equilibrium of the transported substance at the phase boundary at a certain place and time. Such state of equilibrium is difficult to define and therefore most often expressed by means of a distribution coefficient.

The equilibrium distribution of single electrolytes and ions between polymeric ion exchange membranes and aqueous solutions of electrolytes has been studied quite often[2-6]. Quantitatively, it is expressed through the distribution coefficients defined by

$$k = c_m/c, \qquad k_i = c_{mi}/c_i, \tag{1a, b}$$

where c_m, c_{mi} is the concentration of the substance and ion in the membrane, respectively, and c, c_i is the respective concentration of the substance and ion in the external solution in contact with the membrane.

Polymeric ion exchangers which form the membrane are electrolytes with ions of one charge fixed at the polymer chain, while ions of the opposite type are mobile. In most cases, where the polymer has been swollen in water, both mobile and fixed ions can be regarded as dissolved in the swelling water. The latter, together with the sorbed ions, forms a separate phase in the membrane (an internal solution). This allows us to apply relations of the solution thermodynamics also to the membrane and to express the distribution coefficients[7] in the form of Eqs (2) – (4):

$$k_i = K_i \Lambda^{\nu_i} \gamma_i/\bar{\gamma}_i \tag{2}$$

$$\Lambda = \exp(-F\Delta\psi/RT) \tag{3}$$

$$K_i = \exp[-(\Delta\mu_i^0 + \bar{V}_i \Delta p)/RT], \tag{4}$$

where ν_i is the valency of the ion, $\bar{\gamma}_i$ is its activity coefficient in the membrane, γ_i is its activity coefficient in the external solution, Δp is the pressure difference, $\Delta\psi$ is the difference of electric potentials, F is the Faraday constant, R is the universal gas constant, T is the absolute temperature, $\Delta\mu_i^0$ is the chemical affinity of the ion, $\bar{V}_i$ is the partial molar volume of the ion.

In the sorption of electrolytes, if there are no specific interactions with the membrane and properties of internal water approach those of ordinary water, the nonelectrolyte concentration in the membrane does not differ from that of the external solution. At a sufficient ion-exchange capacity of the ion exchanger and in the case of a sufficiently dilute electrolyte the sorption is very low, because the presence of fixed charged groups causes exclusion of co-ions. Quantitatively, this phenomenon is expressed in terms of the Donnan equilibrium (5):

$$(c_{mi} + c_F)\, c_{mj} = k\, c^2(\gamma/\bar{\gamma})^2, \tag{5}$$

where c_F is the ion exchange capacity of the membrane, $\gamma, \bar{\gamma}$ are the mean activity coefficients in solution or in the membrane. If $c_m << c_F$ and γ/γ is constant, relation (5) assumes a simple form

$$c_m \sim c^2 . \tag{6}$$

In the treatment of experimental data it is always possible to keep the Donnan relation formally valid and to include all deviations in the ratio of the activity coefficients. Of course, in many cases where the ratio of the activity coefficients varies within the range of several orders of magnitude without any apparent reason the utility and justification of such approach are very weak.

This fact has stimulated hypotheses of the sorption of electrolytes in the membrane, e.g. in the form of a "bound cation"[7], where one part of sorbed atoms is bound onto fixed groups of the polymeric ion exchanger. A conception of local concentrations of fixed groups which involve all possible types of inhomogeneity of the membrane, such as the irregular ordering of polymer chains, crosslinking, and the like, underlies the Glueckauf model frequently used,

$$c_m \sim c^{2-z} \tag{7}$$

in which the constant z characterizes inhomogeneity of the internal membrane solution, assuming values between 0 and 1. At $z = 0$ the relation becomes the Donnan equilibrium (*6*). The z values are determined as the slopes of the log c_m vs log c dependence. The dependence defined by Eq. (*7*) adequately describes experimental data within a broad concentration range, up to six orders of magnitude. Petropoulos et al. showed[7] that data concerning the individual ions, especially in systems where $z \rightarrow 1$, are more sensitive to deviations from relation (*7*). In some cases the log c_{mi} vs log c_i dependence is not linear, assuming the form of an inflexion curve.

An alternative approach to Glueckauf's conception of inhomogeneity is a twophase model – "variable V_D" – introduced by Sivaraja-Iyer[8]. In this theory the imperfect exclussion of co-ions from the membrane is explained by the solution being divided into two types: the "Donnan" one, where the exclusion od co-ions corresponds to the Donnan equilibrium, and the other, defined as the "internal sloution", approaching by its properties the external solution, where, consequently, no exclusion of the co-ion takes place ($k_i = 1$). This approach adequately reflects experimental data also as relatively high concentrations of the electrolytes, where Glueckauf's relation fails. Modification of the two-phase model can be found in studies by several authors[9 – 12].

Possibilities of the application of various solutions described above in the characterization of application domains of heterogeneous ion exchange membranes in connection with the amount of the ion exchanger in the membrane and with the concentration of ions in solutions are studied experimentally in this work.

EXPERIMENTAL

Heterogeneous Ion Exchange Membranes

Ralex membranes (Mega, Stráž pod Ralskem, Czechoslovakia), products R-K2 and R-A2. Further test samples of heterogeneous ion exchange membranes were made by the calandering and pressing technique from high-pressure polyethylene (Bralen FB4, Czechoslovakia), atactic polypropylene and powdery ion exchange materials based on styrene–divinylbenzene copolymers (type Ostion KS, manufactured by the Union, Ústí nad Labem, Czechoslovakia). The preparation procedure was analogous to the production technology of Ralex membranes; the samples under investigation with varying content of the ion exchange component in their composition were also compared with membranes intended for electrodialysis. The ratio between the content of ion exchange components and polyolefins varied between 20 and 70 wt.% of the ion exchange fraction in the mixture. The particle size in this fraction was 5 – 30 μm. At the same time, membranes were prepared containing 55 wt.% of the ion exchange fraction, particle size above 30 μm or very small, below 5 μm. All compositions were transformed into membranes by employing a uniform procedure, the calandered foil was pressure-moulded at 120 °C and 30 MPa with a two-sided addition of the polyamide reinforcing network. Prior to the measurement, the membranes were alternately activated in 1 M-HCl and 1 M-NaOH solutions, in the final stage of the salt form they were thoroughly washed with water. For basic characteristics see Table I.

Determination of Distribution Coefficients

The distribution coefficients were determined by the equilibrium sorption and desorption method. The membranes swollen to equilibrium were exposed in an electrolyte solution for 40 h, weighted under defined conditions, transferred into a defined volume (30 – 50 ml) of distilled water, and after another 40 h the concentration of ions was determined in the solutions after desorption by using calibration dependences.

The distribution coefficients were calculated using equation

$$k = V c_2 / m (c_1 - c_2), \qquad (8)$$

where V is the volume of distilled water for desorption, c_1 is the concentration of solution for sorption, c_2 is the concentration of solution after desorption, m is the mass of the membrane.

The distribution coefficients of ion exchange materials used in the production of membranes in the form of particles having the average diameter 1 mm (with great polydispersity of particle size), activated similarly to the membranes, were determined in a similar manner. A reproducible determination of the mass of swollen particles was accomplished by removing the solution in excess by suction.

TABLE I

Basic properties of the membranes: I content of ion exchanger in dry membrane, C ion exchange capacity in dry membrane, W equilibrium water content in g per 1 g of swollen membrane in Na^+ form, d membrane thickness

Membrane	I mass %	C mequiv/g	W g/g	d mm
1	20	0.853	0.083	0.41 – 0.43
2	30	1.12	0.183	0.34 – 0.37
3	40	1.59	0.246	0.54 – 0.57
4	55	1.95	0.312	0.58 – 0.67
5	54	2.23	0.324	0.60 – 0.65
6	53	2.21	0.330	0.70 – 0.73
7	56	2.13	0.340	0.59 – 0.64
8	63	2.63	0.394	0.79 – 0.80
9	66	2.55	0.391	0.66 – 0.75
10	70	2.81	0.402	0.76 – 0.78
11[a]	56	2.25	0.313	0.58 – 0.64
12[b]	56	2.17	0.369	0.58 – 0.64
R-K2		2.33	0.745[c]	0.75 – 0.80
R-A2		1.1	0.695[c]	0.58 – 0.66

[a] Membranes containing particles above 30 μm. [b] Membranes containing particles below 5 μm. [c] Calculated per 1 g of dry membrane.

RESULTS AND DISCUSSION

The equilibrium sorption of uni-univalent electrolytes NaCl and KCl in ion exchange membranes was investigated at 25 °C within a broad concentration range; the distribution coefficients of membranes R-K2 and R-A2 for the concentration range 0.05 – 0.9 mol l^{-1} are given in Table II. The coefficients of the series of samples prepared in this study at the concentration 0.5 M-NaCl are summarized in Table III.

The concentration of external solution and that of solution in the membrane are correlated in Fig. 1. The slopes of the straight lines differ considerably from the theoretical value 2, which leads to a conclusion that conditions of the Donnan relation have not been fulfilled. Inhomogeneity factors z were calculated from the slopes using the Glueckauf relation and are summarized in Table IV. To determine an exact value of the inhomogeneity factor, work should be carried out in a wider concentration range. Petropoulos and coworkers showed[9] that suitability of the application of the Glueckauf model could be tested more adequately using the distribution coefficients of the individual ions in the low concentration range. Direct comparison of z values of membranes which have often been purposefully prepared and are of theoretical interest is questionable; in spite of this, however, the measured degrees of heterogeneity are comparatively high. For this reason the z factors were also determined for starting ion exchange materials. The sorption characteristics made possible determination of the concentration dependences (Fig. 2), and inhomogeneity factors for ion exchangers K and A in Table IV show that the equilibrium behaviour of the membranes is a direct consequence of properties of the ion exchangers used.

TABLE II
Distribution coefficients (K) of membranes R-K2 and R-A2

R-K2				R-A2			
c_{NaCl} mol l^{-1}	K	c_{KCl} mol l^{-1}	K	c_{NaCl} mol l^{-1}	K	c_{KCl} mol l^{-1}	K
0.856	0.151	0.7	0.140	0.5	0.184	0.7	0.126
0.342	0.127	0.6	0.124	0.5	0.180	0.6	0.118
0.342	0.120	0.4	0.130	0.3	0.166	0.4	0.105
0.171	0.112	0.3	0.124	0.2	0.158	0.3	0.110
0.171	0.116	0.2	0.116	0.1	0.133	0.2	0.098
0.171	0.117	0.1	0.124	0.1	0.105	0.1	0.081
0.044	0.099	0.1	0.115	0.125	0.124		
0.044	0.098			0.065	0.120		
0.009	0.076						

TABLE III

Distribution coefficients of membranes with varying content of ion exchange material at NaCl concentration 0.5 mol l^{-1}. S sulfur content, C_s ion exchange capacity of swollen membrane, C_W ion exchange capacity related to the amount of water in the membrane, K_1 distribution coefficient of the swollen membrane, K_2 distribution coefficient of water in the membrane, K_3 distribution coefficient K_2 related to the unit of ion exchange capacity

Membrane	S mass %	C_s mequiv/g	C_W mequiv/g	$K_1 . 10^2$	K_2	$K_3 . 10^2$ g/mequiv
1	2.73	0.782	9.42	1.06	0.13	1.4
2	3.54	0.915	5.00	2.2	0.12	2.4
3	5.10	1.20	4.87	4.2	0.17	3.5
4	6.24	1.34	4.30	5.4	0.17	4.0
5	7.14	1.51	4.66	5.7	0.20	4.2
6	7.07	1.48	4.48	6.4	0.19	4.2
7	6.80	1.41	4.15	6.7	0.20	4.8
8	8.43	1.59	4.05	8.1	0.21	5.2
9	8.17	1.55	3.96	8.9	0.23	5.8
10	9.00	1.68	4.18	8.9	0.23	5.5
11[a]	6.94	1.37	3.71	7.3	0.21	5.7
12[b]	7.21	1.55	4.94	5.7	0.18	3.8

[a] Membranes containing particles above 30 μm. [b] Membranes containing particles below 5 μm.

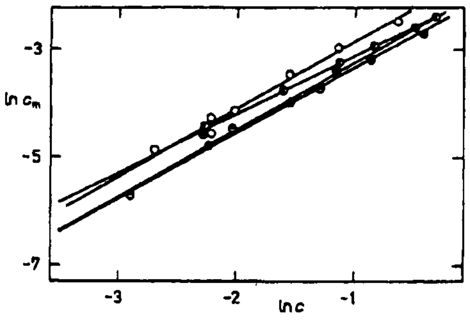

FIG. 1

Dependence of the electrolyte concentration in the ion exchange membrane (c_m in g l^{-1}) on the concentration of external solution (c_{MCl} in g l^{-1}): ◓ RK-2/NaCl, ○ RA-2/NaCl, ◐ RK-2/KCl, ● RA-2/KCl

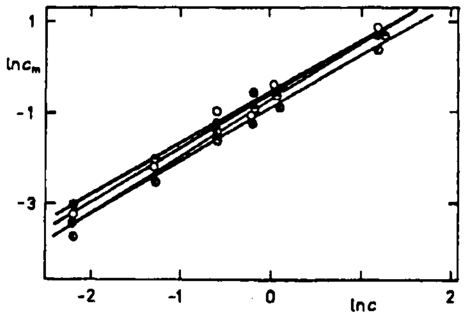

FIG. 2

Dependence of the electrolyte concentration in the ion exchange material (c_m in g l^{-1}) on the concentration of external solution (c_{MCl} in g l^{-1}): ◐ Ostion/NaCl, ○ Varion/NaCl, ◓ Ostion/KCl, ● Varion/KCl

Another procedure of verification of the Glueckauf model consists in the determination of the distribution coefficient for zero concentration of the electrolyte[10]. If the relation is valid, this distribution coefficient is zero, unlike models in which one part of solution in the membrane has properties very close to the external solution, and the distribution coefficient is nonzero. In the case of the membranes under investigation extrapolation to zero concentration leads to nonzero values, however, with the accuracy of data used such method cannot be regarded as reliable. The basic finding consist in that the inhomogeneity factor is a valuable characteristic of the membrane, in spite of essential differences in theoretical approaches to its evaluation.

The samples of heterogeneous membrane systems prepared in this study differ from the production types of membranes in the variable ion exchange capacity, which gradually increases to three times the original value. The hypothesis of aqueous domains in the membrane and of their basic influence upon the equilibrium sorption of the electrolyte in the membrane is supported by the ion exchange capacity expressed in the volume unit of water or in the unit of the membrane mass. Table I and dependences in Fig. 3 show that the equilibrium water content in a certain range of the content of the ion exchange component is proportional to the concentration of the latter. This is agreement with the degree of hydration of ion exchange materials with a low degree of crosslinking. Only at a high degree of crosslinking of sulfonated polystyrene ion exchangers (20%) there is no hydration for steric reasons[13]. It should be pointed out, of course, that due to the water content, which increases proportionately to the ion exchange capacity, this capacity, related to the mass unit of internal water, varies very little.

According to the rule of Donnan equilibrium, the distribution coefficients are proportional to the ion exchange capacity for the concentrations $c_{mi} << c_F$. Table III shows that the distribution coefficient vs exchange capacity ratio is not constant and increases gradually with increasing content of functional groups. The exclusion effect

TABLE IV
Values of Glueckauf factor z (f denotes correlation coefficient)

Sample	NaCl		KCl		$\bar{z}$
	z	f	z	f	
R-K2	0.86	0.999	0.93	0.998	0.90
R-A2	0.76	0.996	0.79	0.999	0.77
Ion exchanger K[a]	0.84	0.997	0.98	0.996	0.91
Ion exchanger A[b]	0.83	0.993	0.88	0.995	0.85

[a] Ostion KS-8. [b] Varion AT-400.

of the membranes is higher at a lower water content. The cause may consist in an increased heterogeneity of the membrane at a higher content of the ion exchange material due to the formation of aggregates. Such macroheterogeneity may also lead to a higher degree of microheterogeneity, i.e. to the distribution of fixed functional groups in the membrane. This would result in a decrease in the Donnan exclusion in the sense of the Glueckauf model. To support this view by determining heterogeneity in the dry

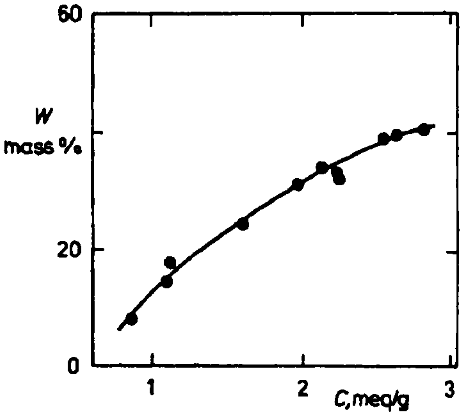

FIG. 3
Dependence of the equilibrium water content in membranes (W in mass %) on their ion exchange capacity (C)

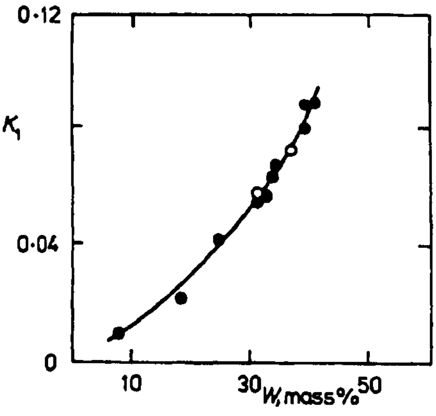

FIG. 4
Dependence of the distribution coefficient K_1 on the equilibrium water content (W in mass %) in the membrane (c_{NaCl} = 0.5 mol l^{-1}): ● membranes 1 – 10, ○ membranes 11 and 12

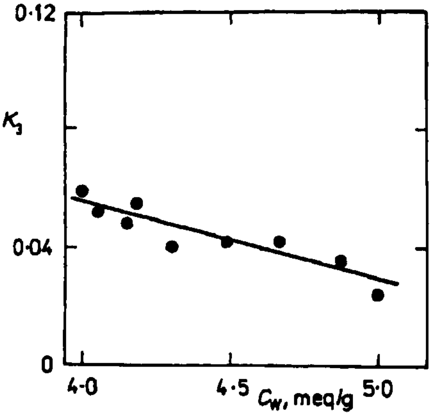

FIG. 5
Dependence of the distribution coefficient related to the exchange capacity and the equilibrium water content in the membrane (K_3) on the ion exchange capacity C_W (c_{NaCl} = 0.5 mol l^{-1})

state of the membrane is even more difficult than to determine exactly the heterogeneity coefficient z within a broad concentration range.

The distribution coefficients of membranes prepared from particles of atypical sizes show (Fig. 4) that the decisive role in reaching a certain degree of equilibrium sorption is played by the water content in the membranes, and thus by the type of the ion exchange material used, characterized by its ion exchange capacity.

With increasing amount of the ion exchange material in the membrane, and thus with decreasing fraction of the hydrophobic component of the binding agent the factor of formation of "free" spaces in the membrane may also become operative. These spaces contain the aqueous phase without fixed functional groups with properties of external solution. If the hydration of functional groups is constant, the distribution coefficients related to the amount of water in the membrane decrease linearly with incresing exchange capacity. Experimental data satisfy this idea (Fig. 5). Such possibilities may be confirmed by a detailed study of the character of internal water in the membrane using physical procedures, e.g. differential scanning calorimetry[14].

CONCLUSIONS

1. Heterogeneous ion exchange membranes investigated from the viewpoint of the Glueckauf model by describing the equilibrium sorption of uni-univalent electrolytes are of relatively low homogeneity with respect to properties of internal membrane solution, mainly due to the nonuniform distribution of fixed functional groups. This nonhomogeneity is a direct result of properties of ion exchange materials used in the production of membranes. At the same time, alternative interpretations of the experiment bearing in mind several structural types of internal membrane solution cannot be ruled out.
2. The nonhomogeneity observed in this study is directly related to dynamic, i.e. transport properties of the membranes. Their investigation should allow us to characterize the applicability of the model used, especially with respect to the steric distribution of hydrophobic and hydrated domains.
3. The distribution coefficient related to the water content in the membrane increases with the increasing ratio of the ion exchange component in the membrane; it is quite probable that the equilibrium sorption is not affected by the structural distribution of water domains, by their sizes and linkage, in contrast with the properties which influence their membrane transport properties.

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