Ion Exchange of Liquid and Solid Cation Exchangers with Ethylammonium Ions

AVENERI V. MIKULICH,[a] VLADIMIR S. SOLDATOV[a] and ERIK HÖGFELDT[b]

[a] Institute of Physico-Organic Chemistry, Academy of Sciences BSSR, 220603 Minsk, USSR and [b] Department of Inorganic Chemistry, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

We have recently investigated the thermodynamics, ion exchange and structural properties of the liquid cation exchanger dinonylnaphthalene sulfonic acid (HD). A summary covering about 10 years research has recently been published.[1] In the present paper the exchange between primary, secondary, tertiary and quarternary ethylammonium ions are briefly reported. Besides HD in the diluents: heptane, nitrobenzene and 2-ethylhexanol also the solid cation exchanger KRS-8 has been studied.

The experimental results have been communicated in the Russian literature[2] with a slightly different set of equilibrium constants from those reported in the present paper.

Experimental. The amines were of reagent grade quality. They were treated with HCl and the salts further purified by recrystallization.

The source of HD was a commercial sample, further purified according to the method of Danesi *et al.*[3]

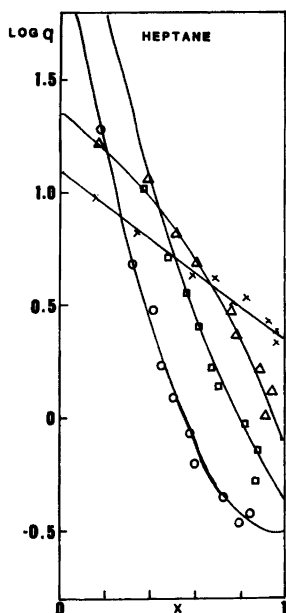The resin KRS-8 had been prepared from 99.8 % paradivinylbenzene and was of high purity.

Fig. 1. log q plotted against x for HD in heptane. ×, $R^+=C_2H_5NH_3^+$; △, $R^+=(C_2H_5)_2NH_2^+$; □, $R^+=(C_2H_5)_3NH^+$; O, $R^+=(C_2H_5)_4N^+$. The curves have been computed from the constants in Table 1 using eqn. (2).

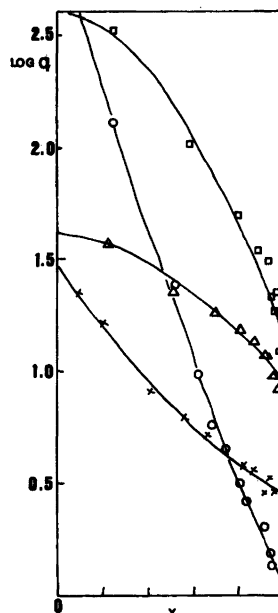*Fig. 2.* log q plotted againsts x for HD in nitrobenzene. ×, $R=C_2H_5NH_3^+$; △, $R^+=(C_2H_5)_2NH_2^+$; □, $R=(C_2H_5)_3NH^+$; O, $R^+=(C_2H_5)_4N^+$. The curves have been computed from the constants in Table 1 using eqn. (2).

Table 1. Equilibrium quotients [*cf.* eqn. (5)] and water uptake [*cf.* eqn. (6)] for reaction (4) at 298 K. I=Ionic strength=0.1 (R,H)Cl.[a]

Diluent	R^+	$\log q_1$	$\log q_2$	$\log q_{12}$	w_1	w_1	w_{12}
Heptane	$C_2H_5NH_3^+$	0.36	1.10	0.73	2.6	10.3	2.3
	$(C_2H_5)_2NH_2^+$	−0.09	1.34	1.12	3.7	10.3	1.7
	$(C_2H_5)_3NH^+$	−0.33	2.77	0.19	8.9	10.3	1.5
	$(C_2H_5)_4N^+$	−0.50	2.20	−0.65	−	−	−
Nitrobenzene	$C_2H_5NH_3^+$	0.47	1.50	0.75	1.8	6.1	2.9
	$(C_2H_5)_2NH_2^+$	0.98	1.62	1.55	0.9	6.1	1.6
	$(C_2H_5)_3NH^+$	1.20	2.61	2.56	0.8	6.1	1.6
	$(C_2H_5)_4N^+$	0.08	2.99	1.19	1.8	6.1	1.4
2-Ethyl-hexanol	$C_2H_5NH_3^+$	−0.63	−0.63	−0.63	1.8	2.7	2.2
	$(C_2H_5)_2NH_2^+$	−0.37	−0.37	−0.37	1.1	2.7	1.3
	$(C_2H_5)_3NH^+$	−0.49	−0.36	−0.42	1.6	2.7	3.1
	$(C_2H_5)_4N^+$	−1.10	−0.71	−0.90	2.0	2.7	2.4
KRS-8	$C_2H_5NH_3^+$	0.12	1.12	0.21	7.2	12.8	9.2
	$(C_2H_5)_2NH_2^+$	−0.15	1.50	0.25	5.9	12.8	7.2
	$(C_2H_5)_3NH^+$	−1.03	1.77	0.37	5.2	12.8	5.5
	$(C_2H_5)_4N^+$	−1.03	3.00	−1.11	5.2	12.8	3.9

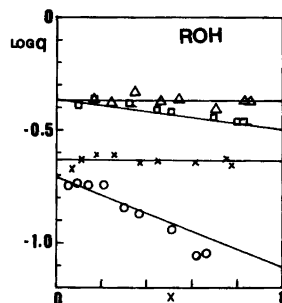[a] The estimated uncertainty in $\log q \sim \pm(0.02$ to $0.03)$ and in $W \sim \pm(0.1$ to $0.2)$.

Fig. 3. log q plotted against x for HD in 2-ethylhexanol (ROH). ×, $R^+=C_2H_5NH_3^+$; △, $R^+=(C_2H_5)_2NH_2^+$; □, $R^+=(C_2H_5)_3NH^+$; ○, $R^+=(C_2H_5)_4N^+$. The curves have been computed from the constants in Table 1 using eqn. (2).
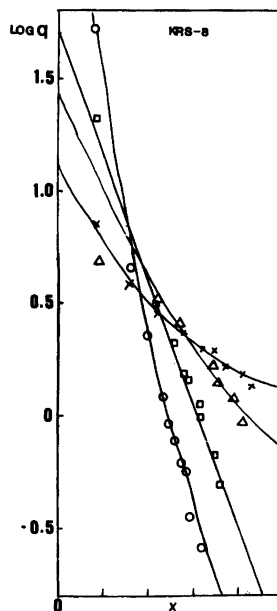
Fig. 4. log q plotted against x for the resin KRS-8. ×, $R^+=C_2H_5NH_3^+$; △, $R^+=(C_2H_5)_2NH_2^+$; □, $R^+=(C_2H_5)_3NH^+$; ○, $R^+=(C_2H_5)_4N^+$. The curves have been computed from the constants in Table 1 using eqn. (2).

The hydrochloric acid was of reagent grade quality and used as such. The equilibrium measurements were carried out as batch experiments. Samples of HD($\sim$0.1 mol dm^{-3}) in the different diluents (2−5 cm^3) or solid resin (0.3−0.5 g) were shaken with 10−20 cm^3 aqueous phase. This phase contained the two cations in their chloride form with an ionic strength of 0.100 mol dm^{-3}. The samples were shaken for two days in a room kept at 298.0±0.25 K. After settling or filtration of the resin the two phases were analysed for H$^+$ by titration with standard alkali using methyl orange as indicator (aqueous phase) or by potentiometric titration with standard alkali (organic phase). In some cases the ethylammonium ions were determined by titration of Cl$^-$ according to Mohr after evaporation of HCl.

Water in the organic phase was determined by Karl Fischer titration.

The model. The model has been reported elsewhere.[4,5] It assumes three constants, one for each pure ionic form and one for their mixtures. For any molar property, Y, this gives

$$Y = y_1 x_1^2 + y_2 x_2^2 + 2y_m x_1 x_2 \tag{1}$$

In the equation it is assumed that the fraction of ion exchanging sites associated with ion (1) is proportional to x_1^2, where x_1 is the equivalent fraction of ion (1) and similarly for ion (2) *etc.*, corresponding to a random distribution of ions over the available sites. The quantities y_1, y_2 are Y in pure (1) and (2), while y_m refers to the mixture.

For convenience eqn. (1) can be compared with

$$Y = y_1 x_1 + y_2 x_2 + B x_1 x_2 \tag{2}$$

where B is a constant accounting for deviations from linearity in the plot of Y against x.

From eqns. (1) and (2)

$$y_m = \tfrac{1}{2}(y_1 + y_2 + B) \tag{3}$$

By fitting the data $Y-x$ by least squares methods, the constants y_1, y_2 and B are obtained, finally y_m is computed from (3).

In the present study Y is $\log q$ or W (*cf.* below). q is the equilibrium quotient of the reaction

$$R^+ + HX \rightleftarrows RX + H^+ \tag{4}$$

$$q = \frac{[RX][H^+]}{[HX][R^+]} = \frac{x \cdot [H^+]}{(1-x)[R^+]} \tag{5}$$

where $R^+ = (C_2H_5)_n H_{4-n}^+$ ($n=1$ to 4), $X^- =$ sulfonate group of liquid or solid ion exchanger. $x =$ equivalent fraction of RX.

The other quantity studied, W, the number of water molecules per sulfonate group is given by

$$W = (n_{H_2O} - n_{H_2O}(\text{dil}))/n_{HD} \text{ or } W = n_{H_2O}/n_{res} \tag{6}$$

where $n =$ mmol of the various compounds, n_{HD} for HD and n_{res} for resin.

$n_{H_2O}(\text{dil}) =$ water extracted by the diluent.

Results and discussion. In Figs. 1−4 $\log q$ and in Figs. 5−6 W are plotted against x for the systems studied. Except for the water uptake in the system $(C_2H_5)_4N^+-H^+$ and HD in heptane can the data be fitted by the model. In this system pure $(C_2H_5)_4ND$ extracts about 26 water molecules per sulfonate group. This suggests a structure very different from that of pure HD in heptane. It has been found by vapor phase osmometry that this salt forms large aggregates (micelles) in heptane.[6] It seems that the structural changes are too drastic to be accommodated by our simple model. The free energy ($\log q$) can nevertheless be fitted by the model. This quantity thus seems to be less sensitive to structural changes than W.
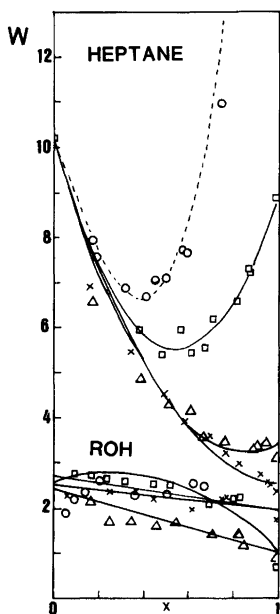
Fig. 5. W plotted against x for HD in heptane (upper set) and for HD in ethylhexanol (ROH) (lower set). The symbols are the same as in Figs. 1 and 3. The curves have been computed from the constants given in Table 1 with the exception of the system $(C_2H_5)_4N^+ - H^+$ in heptane. The dashed curve for this system refers to a third degree polynomial in x.
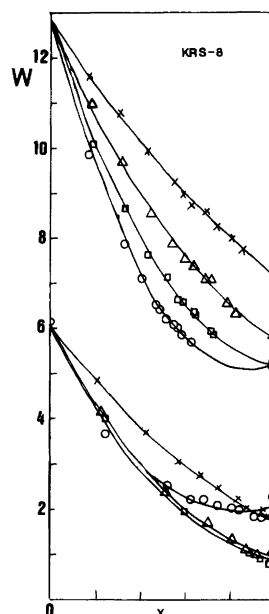
Fig. 6. W plotted against x for KRS-8(upper set) and HD in nitrobenzene (lower set). The symbols are the same as in Figs. 2 and 4. The curves have been computed from the constants in Table 1.

In 2-ethylhexanol the variation is small. Most of the data can be fitted by straight lines. This difference in behavior can be attributed to formation of a 1:1 complex between alcohol and HD.[1] Aggregation also seems to be negligible in this diluent as distinguished from the others.

Systems where $B=0$, i.e. where $\log q$ is a straight line when plotted against x, the activity coefficients in the exchanger phase can be described by the regular solution model.[7] In earlier publications[2,8] data for KRS-8 were fitted by straight lines, i.e. the regular solution model, In the present study this model has only been applied to the system $(C_2H_5)_3NH^+ - H^+$.

A detailed account of this work together with studies of methyl- and butylammonium ions at various temperatures and diluents is published elsewhere.[9]

1. Högfeldt, E., Chiarizia, R., Danesi, P.R. and Soldatov, V.S. Chem. Scr. 18 (1981) 13.
2. Mikulich, A.V. and Soldatov, V.S. Izv. Akad. Nauk SSSR vol. 2 (1979) 39.
3. Danesi, P.R., Chiarizia, R. and Scibona, G. J. Inorg. Nucl. Chem. 35 (1973) 3926.
4. Högfeldt, E. and Soldatov, V.S. J. Inorg. Nucl. Chem. 41 (1979) 575.
5. Högfeldt, E. Acta Chem. Scand. A 33 (1979) 557.
6. Soldatov, V.S. and Mikulich, A.V. Dokl. Akad. Nauk BSSR 25 (1981) 724.
7. Högfeldt, E. In Naden, D. and Streat, M., Eds., Ion Exchange Technology, Ellis Horwood, Chichester 1984, p. 170.
8. Högfeldt, E. Reactive Polymers 2 (1984) 19.
9. Soldatov, V.S., Mikulich, A.V. and Högfeldt, E. To be published.