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On the log $[H_2O]/[HX]$ vs. log a_{HX} Relationships of Aqueous Solutions of Acids

O zależności log $[H_2O]/[HX]$ vs. log a_{HX} wodnych roztworów kwasów

Об зависимости log $[H_2O]/[HX]$ vs. log a_{HX} водных растворов кислот

In an attempt to elucidate the perchlorate effect in chloride and nitrate ion exchange systems [1] I have noticed parallel variations of R_M vs. log a_{HX} (for perchlorate ions) and log $[H_2O]/[HX]$ vs. log. a_{HX} in the investigated range of concentrations of the acids. This observation could be interpreted by assuming that the differences in the behaviour of perchlorates in chloride and nitrate systems [2] are due to different activity of perchlorates relative to the activity of the ionic medium. Therefore, the mean mole numbers of water corresponding to one mole of the acid were calculated from the density and concentration of aqueous solutions of HCl, HNO_3 and $HClO_4$ [3, 4] for the whole ranges of their concentrations. The results are presented in Table 1.

It follows from the data that the number of moles of water per one mole of acid is:

a) within calculation error identical for HCl, $HClO_4$ and HNO_3 at a given molar concentration,

b) decreasing with the concentration of electrolyte approximating in the limit 4 in the case of HCl and 3 for $HClO_4$ and HNO_3.

Constant molar amount of water obtained for one mole of all three acids suggests that the hydration of the proton H^+ seems to be the predominant process.

Graphical relationships of log $[H_2O]/[HX]$ vs. log a_{HX} (values of a_{HX} were taken from Ref. [5] presented in Fig. 1, have two characteristic

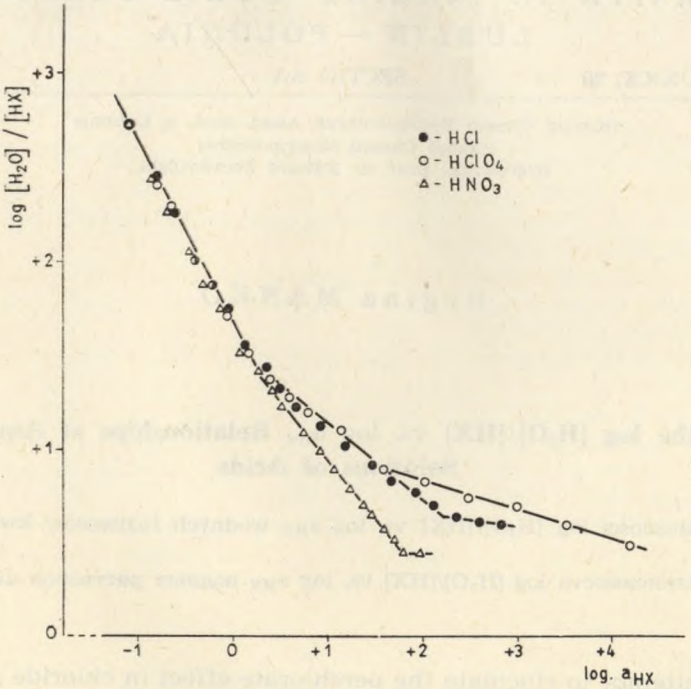

Fig. 1. Relationships between log $[H_2O]/[HX]$ (Mole/Mole) and log a_{HX}[5]) of the aqueous solution of the acids: 1 — HCl; 2 — $HClO_4$; 3 — HNO_3

break points: the first, at ca 2 M concentrations of HX, when the molar ratio H_2O:HX is about 25, is observed for all three acids; the second occurs at high concentrations of the acids and corresponds to H_2O:HX ratios ca. 8 in the case of $HClO_4$, ca 4 for HCl and ca 3 for HNO_3.

In certain concentration ranges the log $[H_2O]/[HX]$ relationships are linear; for low concentrations (lower than 2 M) the plot is common to all three acids; for higher concentrations the line of HNO_3 deviates from the common line of HCl and $HClO_4$ and at the highest concentrations (above 5 M) the latter acids also behave in an individual manner. These effects can be interpreted in terms of Azzan's theory [5].

REFERENCES

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Table 1

Molarity of acids	Log a_{HX} [5]			$[H_2O]/[HX]$ Mole/Mole		
	HCl	$HClO_4$	HNO_3	HCl	HNO_3	$HClO_4$
0.1	−1.096	−1.091	−1.100	—	552	554
0.2	−0.812	−0.802	−0.817	277	250	278
0.3	−0.640	−0.630	−0.651	184	181	183
0.5	−0.416	−0.403	−0.436	110	105	109
0.7	−0.259	−0.244	−0.289	78	77	78
1.0	−0.081	−0.059	−0.125	55	53	53
1.5	0.147	0.186	0.078	36	34	35
2.0	0.333	0.395	0.237	27	25	26
2.5	0.497	0.588	0.376	21	19	21
3.0	0.649	0.776	0.500	17	16	17
4.0	0.933	1.166	0.723	13	11.5	12
5.0	1.198	1.579	0.912	10	8	10
6.0	1.469	2.026	1.076	8	7	7.5
7.0	1.707	2.508	1.221	7	5.5	6.2
8.0	1.956	3.027	1.352	6	5	5.2
9.0	2.185	3.584	1.468	5	4	4.5
10.0	2.368	4.234	1.578	4.4	3	3.8
11.0	2.630	—	1.679	4.3	—	3.2
12.0	2.850	—	1.779	4.2	—	2.8
14.0	—	—	1.970	—	—	2.8

STRESZCZENIE

W zakresie niskich stężeń roztworów (niższych od 2 m) zależność log $[H_2O]/[HX]$ vs. log a_{HX} jest liniowa i identyczna dla trzech badanych kwasów: HCl, $HClO_4$, HNO_3. W obszarze stężeń 2—5 m analogię wykazują roztwory HCl i $HClO_4$; w bardziej stężonych roztworach oba kwasy wykazują różny przebieg zależności log $[H_2O]/[HX]$ vs. log a_{HX}.

Zaobserwowane efekty odgrywają istotną rolę w procesie ekstrakcji i wymiany jonowej i mogą być wyjaśnione w oparciu o teorię Azzana.

РЕЗЮМЕ

В пределах низких концентраций растворов (ниже 2 м) зависимость log $[H_2O]/[HX]$ vs. log a_{HX} бывает линейной и идентичной для трех исследованных кислот: HCl, $HClO_4$, HNO_3.

В зоне концентрации 2—5 и провяляют аналогию растворы HCl и $HClO_4$; в более сконцентрированных растворах обе кислоты проявляют разные зависимости log $[H_2O]/[HX]$ vs. log a_{HX}.

Полученные результаты играют существенную роль в процессе экстракции и ионного обмена и могут быть объяснены при помощи теории Аззана.