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ACTIVITY COEFFICIENTS OF LiNO_3 , HNO_3 AND NH_4NO_3 IN
DOWEX-1 ANION-EXCHANGE RESIN

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When an ion exchange resin is immersed in an electrolytic solution, a given amount of electrolyte penetrates the resin phase. The difference in ionic composition between the two phases depend on the type of resin, its degree of cross-linking and on the activity of the ions of the aqueous solution. These systems can be treated by thermodynamic methods by considering a two-phase equilibrium and it is thus possible to calculate the activity coefficients of the electrolyte in the resin phase.

With anion-exchange resins such measurements were made mostly with chloride systems ^{1,2,3}. In the present work we have extended these studies to the nitrate systems. Anion-exchange resins have been used for the investigation of nitrate complexes and the quantitative treatment of these results depend on the knowl

edge of the activities of the electrolytes in the resin phase ^{4,5}:

We assume with Nelson and Kraus ² that J is an electrolyte of the type $M_{\nu^+} X_{\nu^-}$ where ν^+ and ν^- are the number of positive ions (M) and negative ions (X). The equilibrium distribution of J is described by the equality of the thermodynamic activities in the two phases:

$$a_J = a_{J(r)} \quad (1)$$

where the subscript (r) denotes the resin phase. Equality (1) implies that the same standard states are selected for J in the two phases.

Relation (1) can be written as a function of data on electrolyte invasion:

$$a_J = m_M^{\nu^+} \cdot m_X^{\nu^-} \cdot \gamma_{\pm}^{\nu} = m_{M(r)}^{\nu^+} \cdot m_{X(r)}^{\nu^-} \cdot \gamma_{\pm}^{\nu}(r) \quad (2)$$

where m represent the modal concentration of the ions and γ_{\pm} the mean activity coefficients.

Experimental

The amount of electrolyte in the resin was measured by the volumetric method ¹. Dowex-1 resin, 8% DVB, 50-100 mesh was washed with 4 M HCl in order to remove impurities and converted to the nitrate form with diluted HNO_3 . After being washed with water the resin was dried over anhydrous at 60°C until constant weight.

About 1 gr. of resin was placed in a small sintered glass

funnel. Nitrate solutions of known composition were passed through the funnel until partition equilibrium was attained. The funnel was next centrifuged to constant weight and the resin was washed with water in order to remove the ambibed electrolyte.

HNO_3 was titrated with standard NaOH . LiNO_3 was determined by flame photometry in an ElectroSelenium photometer which was previously calibrated with solutions of known concentrations of LiNO_3 prepared from standard LiCO_3 . NH_4NO_3 was determined by displacing NH_4OH with concentrated NaOH in a distillation apparatus and the products collected over H_2SO_4 of known molarity. All determinations were made, at least, twice. Analytical reagents were used through.

The determination of the interstitial volume of the resin bed was made with spherical glass beads of the same mesh. The value obtained 0.0345 l. per l. of bed is slightly higher than that found for 200-230 mesh Dowex-1 (0.033 l/l). This difference is probably a consequence of the difference in mesh of the two batches.

The water content of the resin was determined by the difference in weight of the dry resin and the resin equilibrated with water after centrifugation and corrected for the interstitial water. The value obtained 1.465 ± 0.005 kg of wet resin per kg of dry resin gives a water content of the wet resin of 31.85%.

The volume of the resin bed in the several media investigated was determined by measuring with a cathetometer the height of the bed after centrifugation in a calibrated sintered funnel.

The value found averaged 2.12 ± 0.08 l. per kg of dry resin. The changes of this observed value with the various electrolytes are within the experimental error in the measurement of the volumes.

The capacity of the resin for nitrate ions was measured by two different procedures. The resin was converted to the chloride form with NaCl solution and the chloride ion was next eluted with NaClO_4 and titrated with AgNO_3 solution of known molarity. Other measurements were made by eluting the nitrate ion with NaClO_4 . The nitrate was next reduced with Devarda's alloy and NaOH and the NH_4OH formed in ten determinations was 2.952 ± 0.005 moles per kg of dry resin. This yields a molality of the nitrate functional group of the resin of 6.325 equivalents per kg of resin water.

All determinations were made at room temperature ($25 \pm 3^\circ\text{C}$).

Results and discussion

The results obtained are summarized in table 1.

The results obtained for the nitrate systems show a close similarity with other systems.

For LiNO_3 the relation Γ between the activity coefficients in the resin and the aqueous solution remain essentially constant and close to 0.7 as m_j changes from 3 to 13. The value of Γ is notably close to that found for LiCl^2 (~ 0.8).

The values of $\gamma_{\pm}(r)$ for NH_4NO_3 are also constant in the molality range 1 to 23. Although the value of Γ increases it

Table 1 *

LiNO_3				
m_J	$m_{J(r)}$	$m_{X(r)}$	Γ	$\gamma_{\pm}(r)$
0.077	0.010	6.434	0.298	0.261
0.736	0.333	6.712	0.492	0.359
1.506	0.993	7.513	0.551	0.432
2.922	2.006	8.720	0.697	0.668
4.14	3.54	10.55	0.68	0.78
5.97	5.79	13.25	0.68	1.02
8.50	9.00	17.07	0.69	1.42
11.38	12.61	21.38	0.70	1.94
12.84	14.15	23.21	0.70	2.24
NH_4NO_3				
1.05	0.45	6.92	0.59	0.30
2.85	1.52	8.32	0.80	0.30
4.99	2.70	9.86	0.96	0.29
6.65	3.43	10.82	1.09	0.29
10.09	5.11	12.95	1.23	0.27
22.80	9.21	18.43	1.74	0.25
HNO_3				
0.068	0.034	6.360	0.147	0.121
0.317	0.235	6.615	0.254	0.186
1.816	2.743	9.582	0.354	0.275
2.684	4.664	11.880	0.360	0.313
3.043	5.491	12.850	0.362	0.330
5.504	11.62	20.23	0.36	-
10.28	29.00	41.77	0.29	-
15.06	63.35	85.36	0.20	-

* Values of mean activity coefficients in aqueous solutions were taken from Robinson and Stokes "Electrolytic Solutions" - Butterworths Publications - London 1955.

remains close to unity until very high molalities of the aqueous phase.

The constancy of Γ at values not far from unity confirm the conclusions of previous studies ^{1,2} that the internal media of the exchanger behaves like a concentrated aqueous solution without a notable interaction between the embibed electrolyte and the "resin-electrolyte".

With HNO_3 as well as for HCl and H_2SO_4 ², a strong interaction between the electrolyte and the resin is demonstrated by the excess uptake of acid even at moderate concentrations of the external electrolyte. This is reflected on the values of Γ which are quite below the unity for all range of m_J values. A comparison between the values of Γ obtained for the three acids show that for a given molality of the aqueous phase we have

$$\Gamma_{\text{HNO}_3} < \Gamma_{\text{H}_2\text{SO}_4} < \Gamma_{\text{HCl}}$$

This decrease of the value of Γ follows the increase in reactivity of these acids with the aromatic groups of the resin, suggesting that the large uptake of acids from the aqueous solution is probably due to this type of acid-base reaction.

It has recently been shown ³ that the theory of specific interactions for concentrated solutions leads to the following relation between activity coefficients $\gamma_{\pm}(r)$ and internal concentration of electrolytes in the resin phase:

$$\log \gamma_{\pm}(r) = \beta_1 m_{J(r)} + \beta_2 m_{X(r)} \quad (3)$$

where β_1 and β_2 represent the sums of coefficients which are independent of the concentrations. If $m_{X(r)}$ is linearly dependent on $m_{J(r)}$, relation (3) becomes:

$$\log \gamma_{\pm}(r) = a + b \cdot m'_{J(r)} \quad (4)$$

The chloride systems were found to vary according to relation (4) at external electrolyte concentrations above about one molal³. Below this concentration negative deviations of linearity occur. The deviations are due to the relatively low values of $\gamma_{\pm}(r)$ at low external electrolyte concentrations which has been attributed to consistent experimental errors and influence of impurities of the resin phase³.

A similar behaviour was observed with the nitrate systems as is illustrated in fig. 1.

The results of applying relations (3) and (4) are given in table II*.

Table II

Electrolyte	m_{NO_3}	$\log \gamma_{\pm}(r)$	m_J range
$LiNO_3$	$6.3 + 1.20 m_{Li(r)}$	$-0.26 + 0.043 m_{Li(r)}$	3-13
HNO_3	$6.3 + 1.22 m_{H(r)}$	$-0.63 + 0.03 m_{H(r)}$	1-3
NH_4NO_3	$6.3 + 1.31 m_{NH_4(r)}$	$-0.52 - 0.009 m_{NH_4(r)}$	1-22

* The small number of determinations of $\gamma_{\pm}(r)$ at low m_J values did not permit the calculation of the corrections according to the methods of Freeman³. It has been however possible to verify that the fractional retention for $LiNO_3$ is less than 0.1.

The results given in table 1 can be used for the investigation of the stability constants of nitrate complexes from anion-exchange data according to the theory of Marcus and Coryell ⁴. These authors considered invasion effects of the resin by the external solution in the thermodynamic interpretation of the absorption of complexes by anion-exchange resins. The distribution coefficients measured as a function of the activity of the external electrolyte $a_J = m_J \gamma_{\pm}$ are corrected from invasion effects by means of a function $F(a)$ defined by:

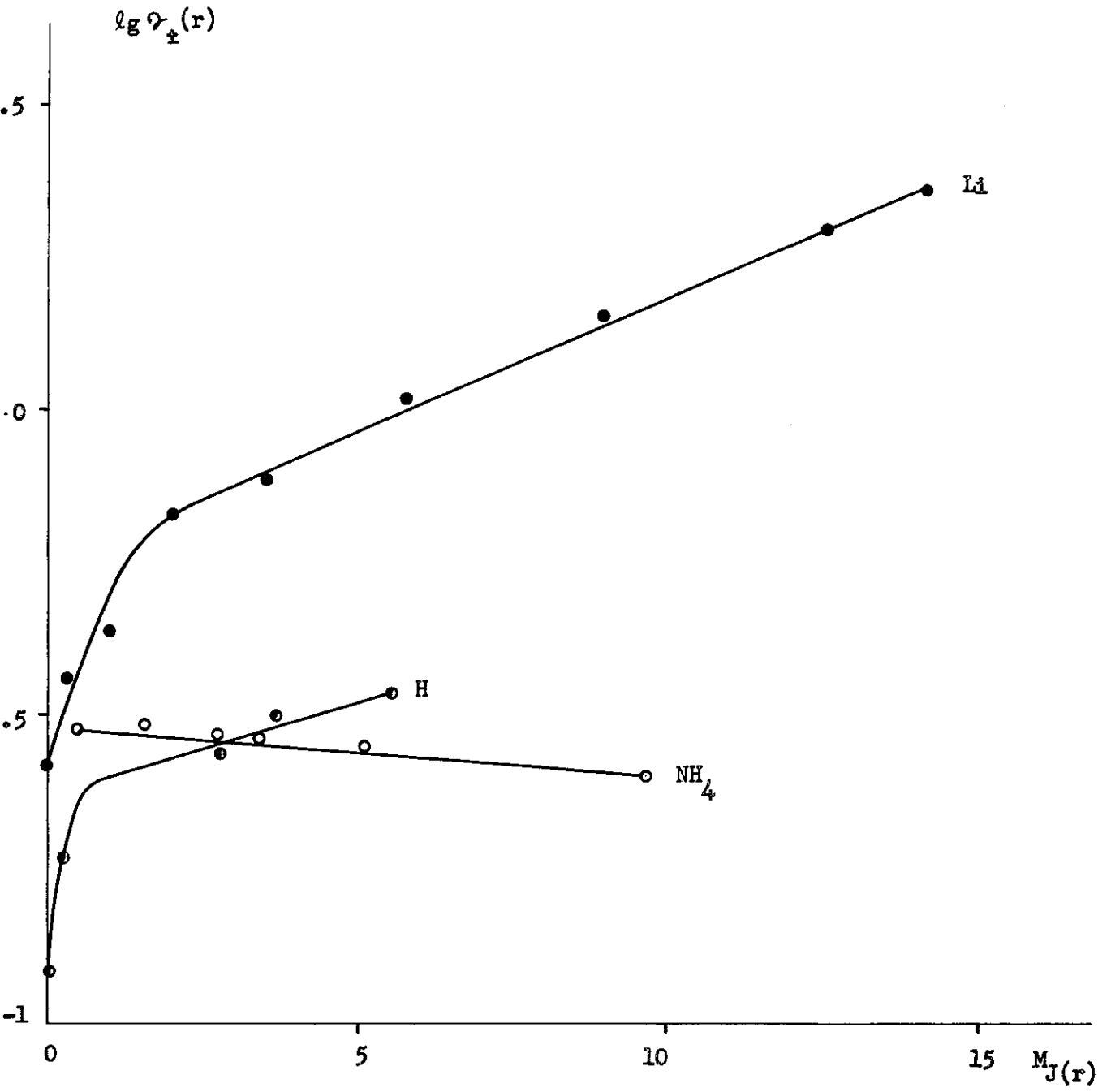
$$F(a) = \log a_{X(r)} - \log a_{X(r)}^{\circ}$$

where $a_{X(r)} = m_{X(r)} \cdot \gamma_{\pm}(r)$ and $a_{X(r)}^{\circ}$ a reference point arbitrarily chosen for the activity of the resin electrolyte. Usually $a_{X(r)}^{\circ}$ is taken as the value of $a_{X(r)}$ at $a_J = 1$.

The values of $F(a)$ as a function of $\log a_J$ for LiNO_3 - Dowex-1, X-8, are given in table III. For this system $a_{J(r)} = 0.48$.

Table III

$\log a_J$	$F(a)$
-1.174	-0.255
-0.270	-0.098
0.071	0.031
0.447	0.285
0.678	0.435
0.951	0.641
1.245	0.904
1.492	1.138
1.608	1.236



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