International Journal of Scientific Research in Science and Technology
Available online at : **www.ijsrst.com**
OPEN ACCESS
Print ISSN: 2395-6011 | Online ISSN: 2395-602X
doi : https://doi.org/10.32628/IJSRST

Quantitative Evaluation of Anion Exchanger Thermax A-127 A Pedagogical Approach

Ajay P. Ganorkar
Department of Chemistry, K.Z.S. Science College, Kalmeshwar Dist. Nagpur, Maharashtra, India

ARTICLEINFO

Article History:
Accepted: 03 March 2024
Published: 13 March 2024

Publication Issue :
Volume 11, Issue 2
March-April-2024
Page Number :
988-992

ABSTRACT

Ion exchange resins can be put to large variety of applications such as ion exchange chromatography, separation of substances and in analytical chemistry (1). The scope of these applications can be widely extended if information of the ion exchange equilibrium is available. In ion exchange reactions, precise determination of equilibrium constant in uni-bivalent ion exchange has been found to be very difficult due to lack of data on activity coefficients of the ions in the ion exchange resin. Helfferich (2) described the unavailability of these important data as a 'missing link' in the ion exchange equilibrium. No doubt various workers (3-6) attempted the determination of such equilibrium constants but they all ignored the activity coefficients. While in electrolytic solutions it has been possible to evaluate the mean activity coefficients of ions, this was not possible for ion exchange resins. Under such difficulties the best that can be done is to evaluate the equilibrium constant from experimental data on some logical basis. In the present study we have evaluated the equilibrium constant for the uni-bivalent ion exchange and mean activity coefficient of the ions in the resin, γ±(R), on the basis of a certain chosen standard state for several ion exchange reactions.

Keywords : Ion Exchange Resins, Ion Exchange Reactions, Exchange Equilibrium

I. INTRODUCTION

Further the enthalpy changes for these reactions have also been determined. As typical cases, the following four reactions have been studied in the strongly basic anion exchanger Thermax A-127.

$$2Cl^{-}_{(R)} + Ma^{2-}_{(aq)} \rightleftharpoons Ma^{2-}_{(R)} + 2Cl^{-}_{(aq)} \quad \ldots\ldots\ldots [1]$$

$$2Cl^{-}_{(R)} + Fm^{2-}_{(aq)} \rightleftharpoons Fm^{2-}_{(R)} + 2Cl^{-}_{(aq)} \quad \ldots\ldots\ldots [2]$$

$$2Br^{-}_{(R)} + Ma^{2-}_{(aq)} \rightleftharpoons Ma^{2-}_{(R)} + 2Br^{-}_{(aq)} \quad \ldots\ldots\ldots [3]$$

$$2Br^{-}_{(R)} + Fm^{2-}_{(aq)} \rightleftharpoons Fm^{2-}_{(R)} + 2Br^{-}_{(aq)} \quad \ldots\ldots\ldots [4]$$

where the subscripts (R), (aq), Ma^{2-} and Fm^{2-} refer to the ion exchange resin, aqueous solution, maleate ion and fumarate ion, respectively.

II. EXPERIMENT

Materials and Procedure

The ion exchange resin supplied by the manufacturer was in chloride form. It was conditioned (7) to remove manufacturing impurities by eluting successively with 1M HCl, water, 1M NaOH and water. The resin was eluted with 5% KCl followed by water to ensure that it was completely in the chloride form. It was air-dried, sieved through standard sieves and particle of 30-40 mesh size was used in these studies.

For the study of system [3] and [4], the resin Thermax A-127 was converted into Bromide form by eluting it with 10% NH_4Br followed by water. It was then air-dried and sieved. The complete conversion was checked by mixing 1.0g of the resin with NH_4Br of known concentration and, after 24 hours, titrating with $AgNO_3$. Only one potentiometric peak was observed for the Bromide, without any decrease of its concentration, and no chloride was detected.

In a typical equilibrium study, 0.5g of the resin was mixed with 30 cm^3 of 0.05 M maleate solution and final volume was made upto 200 cm^3. The mixture was shaken in a thermostat at 25.0°C for three hours and kept for 24 hours. Preliminary trials showed that the equilibrium was reached almost completely within 24 hours. The chloride in solution was estimated by potentiometric titration with $AgNO_3$. From this the amount of maleate exchanged into the resin was estimated, since one mole of maleate replaces two moles of chloride. This was used to calculate the concentration of maleate in the solution at equilibrium. Further, from the known resin capacity and the amount of chloride replaced by the maleate, the amount of chloride remaining in the resin was calculated. From these results, the apparent equilibrium constant, Kapp was calculated as explained in result and discussion.

The various aspects of the equilibrium were studied as follow :

(a) The complete experiment was repeated for various temperatures in the ranging from 0.0045 M to 0.0085 M.

(b) The equilibrium constants were determined at various temperatures in the range from 25.0°C to 40.0°C, and hence enthalpy change for the reaction was calculated.

(c) The determinations of Kapp at various bivalent ion concentrations and of the enthalpy change were carried out for the reactions [1] – [4] with Thermax A-127.

$$K = \frac{[a_{Y^{2-}(R)}] \; . \; [a_{X^-(aq)}]^2}{[a_{X^-(R)}]^2 \; . \; [a_{Y^{2-}(aq)}]} \qquad \text{------------ [5]}$$

where the ‘a’s are the activities of various ionic species, $X^- = Cl^-$ or Br^- and $Y^{2-} = Ma^{2-}$ or Fm^{2-}. Here $a_{X^-(aq)}$ and $a_{Y^{2-}(aq)}$ are obtained from the respective concentration $C_{X^-(aq)}$ and $C_{Y^{2-}(aq)}$ and the mean activity coefficient $\gamma_{\pm(aq)}$ derived from Debye Huckel limiting law (8). The activities of the two ions in resin also have to be obtained as the product of the respective concentrations $C_{Y^{2-}(R)}$ and $C_{X^-(R)}$ and the mean activity coefficient $\gamma_{\pm(R)}$. It is best to express the concentration of the ion in the resin in terms of milliequivalents of the ion in the amount of resin used. Such an expression yielded quite satisfactory results for the equilibrium constants in uni-univalent ion exchange equilibria (9). The equation [5] therefore can be written as

$$K = \frac{[C_{Y^{2-}(R)}\,\gamma_{\pm(R)}]\ .\ [C_{X^{-}(aq)}\,\gamma_{\pm(aq)}]^2}{[C_{X^{-}(R)}\,\gamma_{\pm(R)}]^2\ .\ [C_{Y^{2-}(aq)}\,\gamma_{\pm(R)}]} \quad \text{------ [6]}$$

Here, the concentrations of the ions in the resin are known while their mean activity coefficient is not known. However, it cannot be ignored because in equation [6] it occurs as the whole as $1/\gamma_{\pm(R)}$ and there is little chance of its being unity. The need for this mean activity coefficient is all the more pressing because, as the concentrations of ions in the resin vary, $\gamma_{\pm(R)}$ is likely to vary and hence also $1/\gamma_{\pm(R)}$ varies. This confirmed from the fact that the apparent equilibrium constant calculated from the expression

$$Kapp = \frac{[C_{Y^{2-}(R)}]\ .\ [C_{X^{-}(aq)}\,\gamma_{\pm(aq)}]^2}{[C_{X^{-}(R)}]^2\ .\ [C_{Y^{2-}(aq)}\,\gamma_{\pm(aq)}]} \quad \text{---- [7]}$$

varies with concentrations of the ions in the resin. Under these circumstances it is expedient to determine $\gamma_{\pm(R)}$.

In ionic equilibria, zero concentration is regarded as the standard state when the mean activity coefficient becomes unity. However, such a standard state cannot be chosen for the ions in the resin because the resin will always contain its capacity full of ions, which cannot be decreased to zero. Further, the ions in the resin might be all univalent, all bivalent or partly univalent and partly bivalent. The ionic strengths of the resin in these cases will be much different from one another. Since the mean activity coefficient depends on ionic strength, it will vary according to proportions of univalent and bivalent ion contained in the resin. It is therefore best to choose the resin completely in the univalent anion form as the standard state and refer a resin having any other composition of the uni/bivalent ions to this state. Therefore the Kapp calculated by equation [7] are plotted versus equilibrium concentration of the bivalent ion in the solution. The lower the concentration of this ion in solution, the lower is its concentration in the resin, and in the limiting case of zero concentration in the solution its concentration in the resin is zero. The resin would then be entirely in the univalent anion form and hence in its standard state. Therefore, when extrapolating the above curve to zero equilibrium concentration of the bivalent ion in the solution one obtains the equilibrium constant in standard state, Kstd (see Fig.). One can then obtain $\gamma_{\pm(R)}$ for any finite equilibrium concentration of the bivalent ion in the solution as

$$\gamma_{\pm(R)} = \frac{Kapp}{Kstd} \quad \text{-------- [8]}$$

The results for Cl^{-}-Ma^{2-} exchange at 25.0°C in Thermax A-127, which are typical of those for the several ion exchange reactions, are presented in Table 1. They clearly show that for any equilibrium concentration of the bivalent ion in the solution Kapp differs appreciably from Kstd, and the higher this concentration, the higher is the difference. This emphasizes the need for considering the mean activity coefficient of ions in the resin.

The results for an X^{-}-Y^{2-} exchange in reaction [1]-[4] are presented in Table 2. At higher initial concentration of Y^{2-} in solution, its equilibrium concentration in resin would be higher and more of X^{-} in the resin is exchanged by Y^{2-} ions. This leads to a higher ionic strength of the resin and hence to a lower mean activity coefficient, $\gamma_{\pm(R)}$. This deduction is fully borne out by the experimental results in Table 2.

The equilibrium constant measurements are carried out at various temperatures and the Kstd at these temperatures are evaluated. By plotting log Kstd versus 1/T, one obtains a satisfactorily straight line, from the slope of which the enthalpy change of the ion exchange reaction is determined. The results for reaction [1], as a typical case, are presented in Table 3.

Table 1 : Equilibrium constant for the

$$2Cl^{-}_{(R)} + Ma^{2-}_{(aq)} \rightleftharpoons Ma^{2-}_{(R)} + 2Cl^{-}_{(aq)}$$

in Thermax A-127

Quantity of the ion exchange resin:0.500 g

Volume of the Maleate ion solution:200 cm3

Temperature:25oC

Initial concentration of Ma^{2-} ion in solution / 10^{-3} M	Concentration at equilibrium				$\gamma_{\pm}$ aq	Apparent equilibrium constant Kapp	$\gamma_{\pm R}$ = Kapp / Kstd
	In solution / M		In the resin / meq / 0.5g				
	Cl^{-}/ 10^{-2}M	Ma^{2-} / 10^{-3}M	Cl^{-} / 10^{-1}M	Ma^{2-} / 10^{-4}M			
4.5	0.87	0.15	0.290	0.435	0.798	10.41	0.738
5.5	0.99	0.55	0.230	0.495	0.778	6.48	0.459
6.5	0.97	1.65	0.240	0.485	0.753	1.80	0.127
7.5	1.00	2.50	0.235	0.500	0.734	1.44	0.102
8.5	1.02	3.40	0.215	0.510	0.715	1.20	0.085

Equilibrium constant in standard state K_{std} = 14.1

Table 2 : Comparison of the $\gamma_{\pm}$ (R) in ion exchange resin Thermax A-127

Initial concentration of Ma^{2-} / Fm^{2-} in solution 10^{-3}/m	$\gamma_{\pm (R)}$ for Cl^{-}/Ma^{2-} exchange	$\gamma_{\pm (R)}$ for Cl^{-}/Fm^{2-} exchange	$\gamma_{\pm (R)}$ for Br^{-}/Ma^{2-} exchange	$\gamma_{\pm (R)}$ for Br^{-}/Fm^{2-} exchange
4.5	0.738	0.760	0.777	0.760
5.5	0.459	0.506	0.435	0.242
6.5	0.127	0.157	0.185	0.154
7.5	0.102	0.096	0.167	0.132
8.5	0.085	0.079	0.141	0.126

Table 3 : Variation of Kstd with temperature for the reaction

$$2Cl^-_{(R)} + Ma^{2-}_{(aq)} \rightleftharpoons Ma^{2-}_{(R)} + 2Cl^-_{(aq)}$$

Quantity of the ion exchange resin : 0.500 g

Volume of the Maleate ion solution : 200 cm^3

Temperature / °C	25.0	30.0	35.0	40.0
Kstd	14.1	16.7	19.0	22.3

Slope of the plot of log Kstd versus 1/T = -1254.83

Enthalpy of the ion exchange reaction = 10.43 KJ mole^{-1}

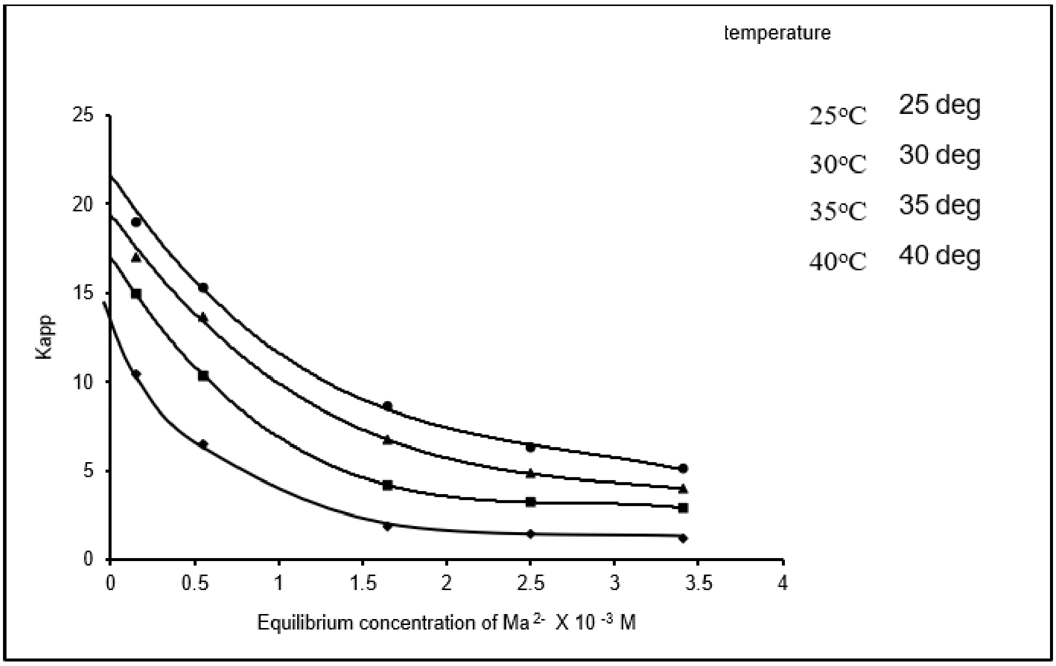

Fig. 1 : Variation of Kapp with equilibrium concentration of $Ma^{2-}_{(aq)}$ in the reaction

$$2Cl^-_{(R)} + Ma^{2-}_{(aq)} \rightleftharpoons Ma^{2-}_{(R)} + 2Cl^-_{(aq)}$$

III. REFERENCES

[1]. Wilson, G.E., Davidson A.W., Argressnger, W.J. J.Chem. Soc. 1954, 76, 3824.

[2]. Helfferich, F. In Ion Exchange, McGraw-Hill Book Company, Inc. 1962 p.171.

[3]. Nelson, F., Kraus, K.A. J.Am. Chem. Soc. 1958, 80, 4154.

[4]. Nikolaev, A.V., Sokolova, N.P., Bochkareva, O.N., Bogatyrev, V.L., Neorg. Inoobman. Mater. 1974, 1, 31.

[5]. Ruvarac, Aleksander, Trfanj, Millan, J. Inorg. Nucle. Chem., 1972, 34, 3893.

[6]. Djurfeldt, R., San)., Acta. Chem.. Scand. 1957, 11, 1209.

[7]. Reiman, W; Wa '. In Ion Exchange in Analytical Chen 'ergamon Press 1970, p.64.

[8]. Glasstone, S.; In An Introduction to Electrochemistry, 3rd East West Reprint, New Delhi : Affiliated East-West Press Pvt. Ltd., 1971 p.144.

[9]. Patil Dilip B., Ganorkar Ajay P., Orien. J. Chem., 2005, 21(2), 251.

25°C
30°C
35°C
40°C