BKR 2010227/23103

Assessment of the exchange parameters of Amberlite IR-45 (OH) resin from its elution with saturated Na_2SO_4

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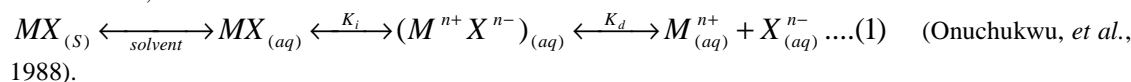[2]Department of Chemistry, Kano State University of Science and Technology, Wudil

ABSTRACT: Simple quantitative technique has been developed for assessing the exchange parameters of Amberlite IR – 45 (OH) using column chromatographic techniques from the displacement of exchangeable hydroxyl ions of the resin by sulphate ions. The results obtained showed retention time of 33min, retention volume of $56.5cm^3$, void volume of $18cm^3$, and exchange capacity of 41mmole/g and exchange site density of 2.4682×10^{22} sites /g.

Key Words: Resin; Solubility; Ion exchange; Column chromatography; Elution; Amberlite.

Introduction

The term solubility simply refers to the amount of solute needed to form a saturated solution in a given amount of solvent at a given temperature (James, 1990). Upon a critical look of the dissolution process of the solute, a number of dynamic equilibria are involved, which for a generalized electrolyte MX can be outlined thus;

$$MX_{(S)} \xleftrightarrow[solvent]{} MX_{(aq)} \xleftrightarrow{K_i} (M^{n+}X^{n-})_{(aq)} \xleftrightarrow{K_d} M^{n+}_{(aq)} + X^{n-}_{(aq)} \text{ ....(1)}$$ (Onuchukwu, *et al.*, 1988).

In ion exchange chromatography (IEC), the free exchangeable ion of the synthetic exchanger (resin) is exchanged with the dissociated ions of the mobile phase in a reversible manner. For a resin having OH^- as the exchangeable ion and a stationary polymeric backbone **P**, on elution with a mobile phase having anion X^{n-}, the following exchange takes place:

$$P-OH^- + X^{n-}_{(aq)} \leftrightarrow P-X^{n-} + nOH^-_{(aq)} \dots\dots\dots\dots(2)$$
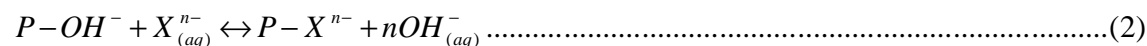
Further estimation of the amount of $nOH^-_{(aq)}$ serves as a measure of the amount of $X^{n-}_{(aq)}$ exchanged by the resin and by extension to the concentration of $X^{n-}_{(aq)}$ dissolved in the mobile phase. In this study

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exchange parameters like; exchange capacity, exchange (active) site density, retention time (t_R), retention volume, (V_R) and void volume (V_m), were assessed for the resin under investigation.

The exchange capacity of the resin, which is dependent on the total number of the ion-active groups per unit weight of the resin expressed in milliequivalents per gram of dry resin or milliequivalents per cm^3 of wet resin as reported by Fritz *et al.,* (1979), and by Rendle *et al.,* (1974), is expressed by the relation:

$$Exchange\ Capacity = \frac{M_{titrant} \times V_{titrant}}{Weight\ of\ Adsorbent} \quad \text{..(3)}$$

where $M_{titrant}$ and $V_{titrant}$ are the molarity and volume of the titrant, respectively.

On the other hand, the exchange (active) site density, assuming all the exchangeable sites of the resin are available to the ions in the mobile phase for exchange, is defined by the relation:

$$Exchange\ (Active)\ Site\ Density = Exchange\ Capacity \times L\ g^{-1} \text{..(4)}$$

where L is Avogadro's number.

Robert (1983) defined the retention time (t_R) as the time required for the mobile phase to sweep a sample component off the stationary phase, and the retention volume (V_R) as the volume of the mobile phase needed to elute a sample component from the column, and is related to the retention time by:

$V_R = F_o t_R$ ……………………………………………………………………. (5) with F_o representing the flow rate of the mobile phase expressed in units of volume per time.

The void volume is expressed either from,

$V_m = F_o t_m$ …………………………………………………………………...…(6) where t_m is the time for average mobile phase molecule to flow from one end of the stationary phase to the other, or using the relationship adopted by McCormick *et al.,* (1980) as:

$$V_m^{\max} = \frac{M_{CCl_4} - M_{meOH}}{\rho_{CCl_4} - \rho_{meOH}} \text{...(7)}$$

where $M\ and\ \rho$ are the masses and densities of the column equilibrated with CCl_4 and methanol, respectively.

Materials and Methods

Prior to usage, the resin was regenerated by washing severally with 2M NaOH and HCl alternately and was allowed to stand in 2M NaOH solution for 30mins (DES, 2001) and was finally washed with distilled water until the washings were neutral to phenolphthalein (Wilson, 1968). The resin was air dried, and in an oven at 60ºC for 1 hour (Sigma, 1991) and stored in container for use as required.

Procedure

a.   Elution

A 10g weight of the regenerated resin was packed as slurry in a sintered chromatographic column (1 x 25cm in dimension). This was achieved by preparing the slurry in $30cm^3$ distilled water in a $100cm^3$ beaker (Ibrahim, 2004).
The column was eluted with a saturated solution of Na_2SO_4 at a flow rate of $2cm^3$/min.
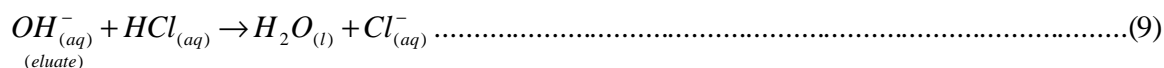
b.   Titration

Combined eluate fractions collected after every 3min were titrated using micro burettes against 0.1M HCl to phenolphthalein end point.
Both elution and titration steps were repeated several times and average of the results are recorded as in the Table.

Results and Discussion

The expected exchange during the elution process between the stationary phase, Amberlite IR – 45(OH), and the mobile aqueous Na_2SO_4 phase (from equation (2)), can be expressed as:

$$2P-OH^- + SO_{4(aq)}^{2-} \leftrightarrow P_2 - SO_4^{2-} + 2OH_{(aq)}^- \text{...(8)}$$
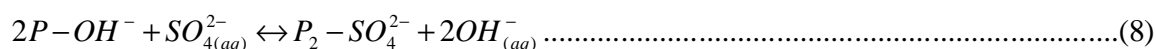
Thus, the quantitative amount of SO_4^{2-} ions adsorbed by the resin can be estimated by titrating the eluate (2OH⁻) with an acid.

$$OH_{(aq)}^- + HCl_{(aq)} \rightarrow H_2O_{(l)} + Cl_{(aq)}^- \text{...(9)}$$
$$(eluate)$$

From the mole ratio of equation (9) above, 0.15cm³ of 0.1M HCl consumed during the titration is equivalent to 1.5 x 10⁻⁵moles of OH⁻ ions exchanged. Therefore, a total of 4.1cm³ of 0.1M HCl consumed represents an equivalence of 41.0 x 10⁻⁵moles of OH⁻ ions exchanged, which by extension from equation (8) is equivalent to 20.5 x 10⁻⁵moles or 19.68mg of $SO_{4(aq)}^{2-}$ adsorbed by the resin. This value compares well with the range of values reported by Tjaart *et al.* (1983) for separating gallium of 1.5mg to 20mg using 3.0g to 10g of AG50W-X4 resin.

The void volume of the exchanger (equation (6)) was deduced from the fact that t_m in the equation corresponds to the total time taken before OH⁻ is detected in the eluate which is 9min. Thus, with a flow rate of 2cm³/min, V_m equals 18cm³. The retention time from the table is equivalent to 33min, whereas an **average** retention volume (V_R) from equation (5) is equivalent to 56.5cm³. The use of the word **average** in referring to the retention volume V_R, of the resin became necessary as after elution the flow rate decreased due to swelling of the resin on prolonged usage.

The exchange capacity and exchange site density were computed from equations (3) and (4) to be 41mmole/g and 2.4682 x 10²²sites/g, respectively.

Conclusion

Comparing the values of the exchange capacity and exchange site density obtained in this study with those reported by Ibrahim and Ekanem, 2001 depicts a difference in the order of about 10³ sites/g of the synthetic Amberlite exchanger in relation to those of modified (activated) charcoal and maize cob peat. This shows that large amount of the exchangeable ions in solution can easily be removed by the resin.

Table: Average volume of titrant consumed and moles of OH⁻ ions exchanged by the resin.

Time(min)	Volume of titrant(ml)	Moles of OH⁻ ($\times 10^{-5}$)
3	0.00	0.00
6	0.00	0.00
9	0.00	0.00
12	0.15	1.50
15	0.50	5.00
18	0.85	8.50
21	1.15	11.50
24	0.70	7.00
27	0.35	3.50
30	0.20	2.00
33	0.20	2.00
Total	**4.10ml**	**41.0 $\times 10^{-5}$moles**

References

D.E.S: Department of Environmental Services (2001), New Hampshire, Ion Exchange Treatment of Drinking Water, p3. http://www.des.state.nh.us/factsheets/ws/ws-2-12.htm

Fritz, J. Z. and Schenk, G. H. (1979). Quantitative Analytical Chemistry, 4th edn., Allyn and Bacon Inc., Boston, p413.

Ibrahim, M. B. (2004). Separation of the Anionic Components of Trona by Ion Exchange Chromatography. Journal of Chemical Society of Nigeria, 29(2), p.167-169.

Ibrahim, M. B. and Ekanem, E. J. (2001). Comparative Analysis of Modified Charcoal and Maize Cob Peat in Desalting Textile Wastewaters. African Journal of Material and Natural Sciences, 1(3), p.116-119.

James, E. B. (1990). General Chemistry, Principles and Structure, 5th edn., John Wiley & Sons, New York, p.118.

Medina, J. L. and Dave, S. (1983): How to Pack a High Efficiency Column. Am. Lab., 15(1), p.83.

Onuchukwu, A. I. and Waziri, M. K. (1988). Determination of Thermodynamic Dissociation Constant, K_d^T, by Conductivity Measurements. Journal of Chemical Education, 65(6), p546-547.

Rendle, P., Vokins, M. and Davis, P. (1974). Experimental Chemistry, A Laboratory Manual, 2nd edn., Edward Arnold, London, p.109.

Sigma Chemical Catalog (1991), p.1530.

Tjaart, N. van der Walt and Franz, W. E. Strelow (1983). Quantitative Separation of Gallium from other Elements by Cation – Exchange Chromatography. Anal. Chem., 55, p.212 – 216.

Wilson, C. L. and Wilson, D. W. (1968). Comprehensive Analytical Chemistry, Vol. IIB, Physical Separation Methods, Elsevier Publishing Co., Amsterdam, p.227.