ACTA CHEMICA SCANDINAVICA 12 (1958) 182—187

On Ion Exchange Equilibria

V. An Approximate Method for Calculating the Partial Molar Volumes of the Species in Ion Exchangers *

ERIK HÖGFELDT**

Brookhaven National Laboratory, Upton, L.I., N.Y., U.S.A.

By formally regarding an ion exchange system as a binary mixture of the two resin forms, partial molar volumes can be determined using the intercept method of Roozeboom. This method has been applied to the potassium-tetramethylammonium exchange on resins with DVB content 2, 10 and 26 %, reported by Gregor, Gutoff and Bregman. It is surprising to find that, to a first approximation all three systems have an ideal volume of mixing over the large range of variation, 1.3 to 18, in total molality of the resin.

Boyd *et al.*[1,2] have recently calculated equilibrium quotients for ion exchange equilibria using rigorous thermodynamics. In these calculations there is need for evaluation of a term $p(Z_B\overline{V}_A—Z_A\overline{V}_B)$ where p is the swelling pressure. $\overline{V}_A$ and $\overline{V}_B$ are the partial molar volumes of the two ionic resin forms, and Z_A, Z_B are their respective charges. Methods for calculating the swelling pressure have been described[3,4]. A method for obtaining the partial molar volume *difference* using cross differentiation relationships has recently been given by Myers and Boyd[1].

It is the aim of this paper to show how the partial molar volumes themselves can be obtained, by using the approximation that the partial molar volume of water is a constant.

The volume, V, of a resin (in this case a cation exchanger exchanging monovalent ions) is made up of three components:

$$\overline{V} = N_{AR}\overline{V}_{AR} + N_{BR}\overline{V}_{BR} + N_{WR}\overline{V}_{WR} \tag{1}$$

---

* Research performed under the auspices of the U.S. Atomic Energy Commission.

** On leave of absence from the Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm, Sweden.

where N_{AR}, N_{BR} and N_{WR} are the number of moles of the three components A^+R^-, B^+R^- and water and $\overline{V}_{AR}$, $\overline{V}_{BR}$, $\overline{V}_{WR}$ their partial molar volumes. By dividing all terms with the capacity of the resin (S_o) (1) is transformed to:

$$V_e = \frac{V}{S_o} = X_{AR}\overline{V}_{AR} + X_{BR}\overline{V}_{BR} + X_{WR}\overline{V}_{WR} \qquad (2)$$

where V_e = the equivalental volume
X_{AR}, X_{BR} are the mole fractions of the resin forms A^+R^- and B^+R^-
X_{WR} = the number of moles of water per equivalent of resin; no water is assumed to belong to the ions as water of hydration.

Now, Gregor *et al.*[5] as well as Boyd *et al.*[1,2] have shown that the partial molar volume of water is constant for each ionic form provided the water content of the resin is not too small. According to Boyd *et al.* $\overline{V}_{WR}$ remains constant down to $X_{WR} = 4$. Water contents as low as $X_{WR} = 4$ are never encountered when one deals with moderately cross-linked ion exchange resins in equilibrium with a water phase. Even a 26% DVB resin[6] contains more than 6 moles of water per equivalent of resin, so that on the basis of these results the constancy of $\overline{V}_{WR}$ is a good approximation even for this rather extreme case. Thus in view of the fact that the partial molar volume of water is practically the same for several different ions[5], it is reasonable to assume that the partial molar volume of water is constant. Using this assumption eqn. (2) can be rearranged to give:

$$V_e - X_{WR}\overline{V}_{WR} = \Delta V = X_{AR}\overline{V}_{AR} + X_{BR}\overline{V}_{BR} \qquad (3)$$

ΔV can now be calculated using a known value for V_{WR}. According to eqn. (3) we can formally regard the resin as a binary mixture of A^+R^- and B^+R^-. By plotting ΔV against the mole fractions of the resin species, the partial molar volumes can be obtained from the intercepts of the tangent to the curve with the axes $X_{AR} = 1$ and $X_{BR} = 1$[7,8].

In order to illustrate the method, we apply it to the data for the potassium-tetramethylammonium exchange on resins with DVB contents 2, 10 and 26 %, reported by Gregor, Gutoff and Bregman[6]. For V_{WR} we adopt the value 17.20, the mean of the two values, 17.15 for tetramethylammonium resin and 17.25 for potassium resin, reported by Gregor, Sundheim, Held and Waxman[5]. The resins used by the latter were not the same as those used by Gregor, Gutoff and Bregman. However, the resins were of the same type, being polystyrene sulfonic acid resins, and the assumption that the partial molar volume of water is the same for both sets of resins is a reasonable one. It is also assumed that the partial molar volume of water is independent of swelling pressure, which is a good approximation, since the difference between the partial molar volumes of water at 100 and 1 000 atmospheres is only 4 %[4].

In Figs. 1—3 V_e and ΔV are plotted against X_{KR} for the three different crosslinkings. It is interesting to note that straight lines are obtained in the ΔV-plots. This behavior implies, that to a first approximation all three systems behave ideally over a range between ~1.3 and ~18 in total molality of the resins.

The values obtained of the partial molar volumes obtained from the ΔV *vs* X plots are given in Table 1.

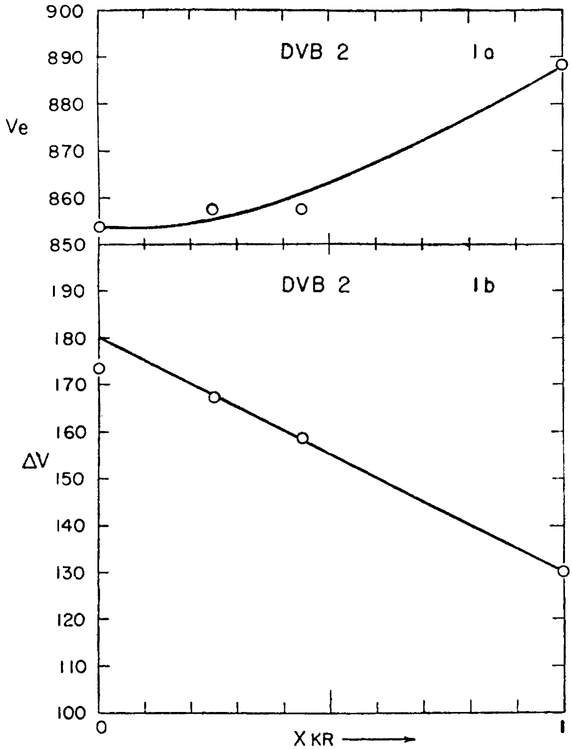


Fig. 1a. The equivalental volume, V_e, plotted against the mole fraction of potassium, X_{KR}, in the DVB 2 resin.
Fig. 1b. The function ΔV plotted against mole fraction of potassium, X_{KR}, in the DVB 2 resin.

Table 1. Partial molar volumes of potassium and tetramethylammonium forms in different resins; ml/equiv. of resin.

Method of evaluation	DVB 2		DVB 10		DV
	$\overline{V}_{KR}$	$\overline{V}_{(CH_3)_4NR}$	$\overline{V}_{KR}$	$\overline{V}_{(CH_3)_4NR}$	$\overline{V}_{KR}$
Extrapolation	130	180	114	154	140
Direct measurement	151	—	—	—	—

These values should be compared with directly determined volumes of pure moisture-free resinates. The measured value in Table 1 is that of Gregor *et al.*[6] who report only the dry volume for potassium saturated DVB 2.

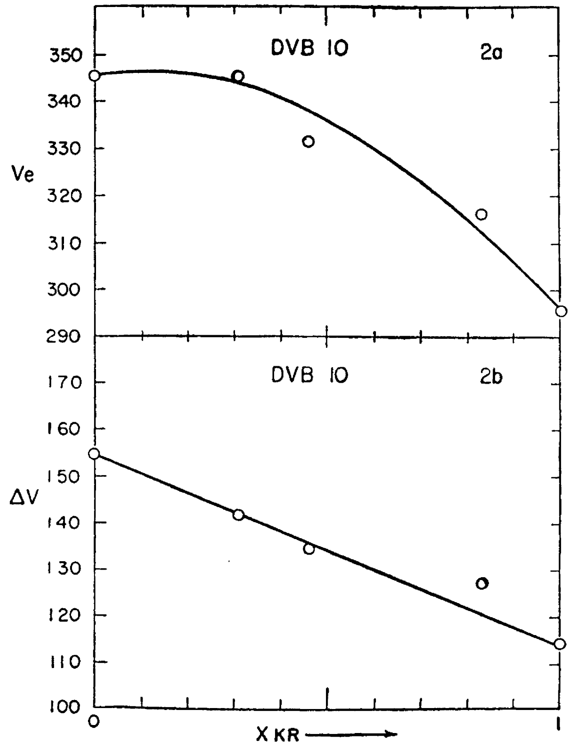
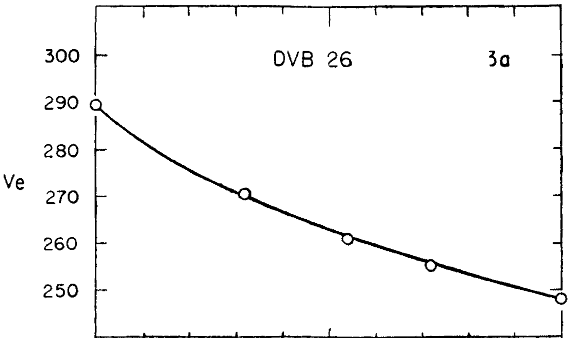


Fig. 2 a. The equivalental volume, V_e, plotted against the mole fraction of potassium, X_{KR}, in the DVB 10 resin.
Fig. 2 b. The function ΔV plotted against mole fraction of potassium, X_{KR}, in the DVB 10 resin.

As is seen from Table 1 the extrapolated volume is smaller than the directly measured volume, an effect previously noted by Gregor *et al.*[5,6] and Boyd and Soldano [4]. The latter authors ascribed it to a contraction in the total volume when the resin is allowed to swell in water. It is also seen from Table 1 that little correlation seems to exist between individual $\overline{V}$-values and degree of crosslinking or water content. However, the difference between the two partial molar volumes decreases with increasing DVB content. In Fig. 4 the partial molar volume difference is plotted against DVB content and average molality ($\overline{m}$) of resin. $\overline{m}$ is equal to the average value of the molalities for the two pure resinates. As is seen from Fig. 4 no straight line is obtained when the difference is plotted against DVB content, but a fairly good straight line is obtained when plotted against the average molality of the resin. The extrapolated value down to $\overline{m} = 0$ is 52 ml/equiv. which has no correlation with the atomic volume difference 76.1 ml/mole, given in Table VII in Ref.[6] No values for the partial molal volume difference at infinite dilution for potassium and



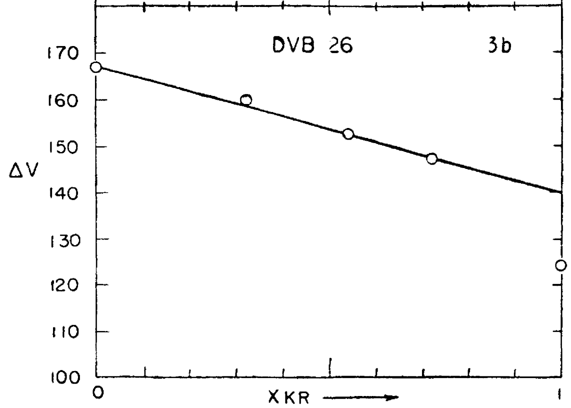


Fig. 3 a. The equivalental volume, V_e, plotted against the mole fraction of potassium, X_{KR} in the DVB 26 resin.

Fig. 3 b. The function ΔV plotted against the mole fraction of potassium, X_{KR}, in the DVB 26 resin.

tetramethylammonium salts with a common anion have been found, so no such comparison can be made. The ideal volume behavior of the potassium-tetramethylammonium system shows that the interaction between water and resin is independent of ionic composition.

If we make another choice of components such as $A^+R^- (H_2O)_m$ and $B^+R^- (H_2O)_n$ and water in order to split up the water content in water of hydration belonging to the ions and "free" water, again straight lines are obtained in the ΔV *vs* X_{KR} plots as this only means that we add the constant quantity $(n + m)\overline{V}_{WR}$ to the original ΔV.

More measurements are needed to show how far the concept of ideal volume of mixing is valid for other systems and at what molalities deviations start to occur.

Acknowledgments. The author is indebted to Dr. William Rubinson for valuable discussions and for correcting the English text.

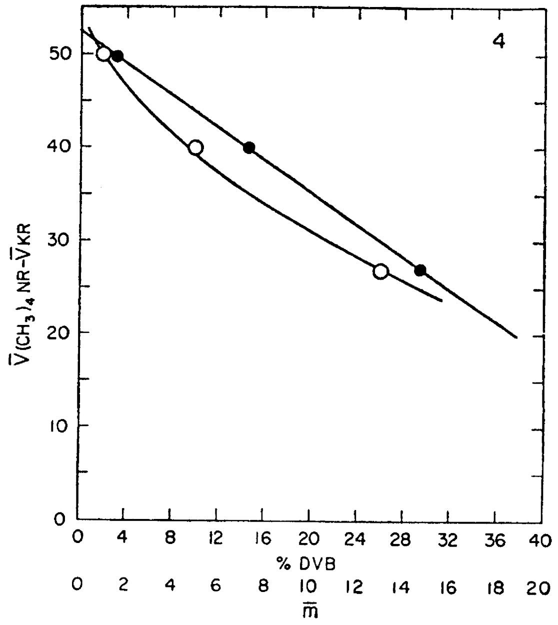


Fig. 4. The partial molar volume difference, $\bar{V}_{(CH_3)_4NR} - \bar{V}_{KR}$ plotted against: (a) DVB content of resins, ○, (b) Average molality of resins, ●.

REFERENCES

1. Myers, G. E. and Boyd, G. E. *J. Phys. Chem.* **60** (1956) 521.
2. Boyd, G. E., Myers, G. E. and Lindenbaum, S. *ORNL-2159* (1956) 43; Boyd, G. E. *132nd Meeting, Am. Chem. Soc.* September 1957.
3. Glueckauf, E. *Proc. Roy. Soc. London* **A214** (1952) 207.
4. Boyd, G. E. and Soldano, B. A. *Z. Elektrochem.* **57** (1953) 162.
5. Gregor, H. P., Sundheim, B. R., Held, K. M. and Waxman, M. H. *J. Colloid Sci.* **7** (1952) 511.
6. Gregor, H. P., Gutoff, F. and Bregman, J. I. *J. Colloid Sci.* **6** (1951) 245.
7. Roozeboom, H. B. *Die heterogenen Gleichgewichte,* II—1, Braunschweig 1904, p. 288.
8. Lewis, G. N. and Randall, M. *Thermodynamics and the free energy of chemical substances,* McGraw-Hill Book Co., New York 1923, p. 38.

Received October 14, 1957.