

ION EXCHANGE CHROMATOGRAPHY
OF RARE EARTHS IN AQUEOUS ORGANIC MEDIA. VIII.*
THE DISTRIBUTION OF SOLVENTS
IN THE ION EXCHANGER PHASE IN MIXED MEDIA SYSTEM**

J.ALEXA

*Institute of Nuclear Research,
Czechoslovak Academy of Sciences, Prague-Řež*

Received December 5th, 1969

In our previous papers¹⁻⁴, we were interested in the study of the influence of mixed media, *i.e.* of water organic mixtures, on the elution chromatography. For interpretation of experimental results obtained, namely for explanation of the existence of maximum on curves representing the dependence of the separation factor on the relative permittivity of the system, it was found as advantageous to consider the existence of three types of solution in the system². We named them the extra-solution which is identical with the aqueous phase, the inter-solution *i.e.* the solution bound in the solid phase by capillary forces and the intra-solution, surrounding the active groups of the resin. The intra-solution is supposed to exhibit higher water content than the extra solution. It is probably formed by molecules solvating active groups, ions and ionic pairs. This conception is in agreement with that of other authors^{5,6}. Previously², we tried to demonstrate indirectly the existence of the intra-solution. In this paper we present the method and results of the determination of its probable composition.

EXPERIMENTAL

The strongly acidic polystyrene cation exchange resin with 8% divinylbenzene Katex S in pearl form (20—30 mesh) was used. All other reagents were A. R. grade.

1 g of the air dried resin in hydrogen form was equilibrated 21 days with 5 ml of solutions containing different concentrations of ethanol. Then, after centrifugation on sintered glass filter for 45 min at 2500 r.p.m. the resin was weighed before and after drying at 105°C and the composition of the extra-solution was determined refractometrically.

RESULTS AND DISCUSSION

The composition of the solution inside of the resin particle *i.e.* the average concentration of water in the inter and intra solutions can be calculated in a simple way based on the ethanol balance in the system. The dependence of this concentration on the equilibrium concentration of water in the extra solution both in % (w/w) of water is presented on Fig. 1. Similar curves were published by many other authors⁷. The higher water content in the solid phase is evident. Let us suppose now that the inter-solution is of the same composition as the extra one and that there is the concentration $x\%$ of alcohol in the intra solution in all systems studied. Then, if G is the weight of the internal solution (sum of the inter and intra solutions), g the weight of the intra-solution, a and A the ethanol concentrations %, w/w) in the internal and extra solutions, it can be derived that

$$a = [(G - g) A + gx]/G \quad (1)$$

* Part VII: This Journal 35, 1921 (1970).

** Paper presented on the 5th Radiochemical Conference, Zvíkov 1969.

and

$$g = (aG - AG)/(x - A). \quad (2)$$

The alcohol content in the intra-solution can theoretically reach the values from 0 to a . It can be supposed that the enrichment of the internal solution of the resin by water is caused only by the higher water concentration in the intra-solution. The concentration of ethanol in the intra solution x is therefore expected to be lower than its concentration in the internal solution of the resin. It can be shown also if we calculate g from Eq. (2) for $x = a$. The extrapolation of the curve representing the dependence of G on g obtained as given above to pure water system results in the higher value of G than determined experimentally. To compute the most probable values of x and g we suppose that the weight of the liquid in the resin is proportional to its weight in the intra-solution. This weight was 0.765 g per 1 g of dried resin in the water system, and 0.195 g per 1 g of dried resin in the alcohol system, *e.g.* 25.5% of the value determined in water. Let us suppose, therefore, that the alcohol concentration in the intra-solution is 25.5% of its concentration in the extra-solution. According to Eq. (2) and to this assumption the values of g and the number of water molecules per one active group n were calculated. For the plot of n versus (w/w) of water in the extra solution see Fig. 2, curve 1. The number of water molecules per one active group in the water system can be obtained by extrapolation of the curve 1 (Fig. 2) to the pure water point (black point). The number of 5.4 water molecules per one active group in the intra-solution system was found for the pure water system.

The assumption of $x = 0.255 A$ in all mixed media systems studied was only a tool which aimed in the determination of the number of water molecules in the intra-solution in the aqueous system. The determination of more probable composition of the intra-solution was based on the

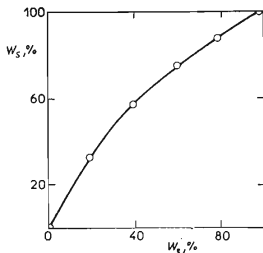


FIG. 1

Dependence of Water Percentage in the Internal-Solution on Water Percentage in the Extra-Solution

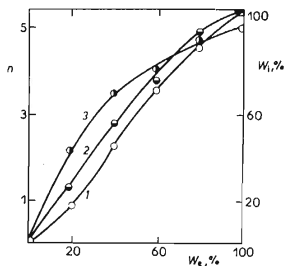


FIG. 2

Dependence of Water Molecules Number and Water Percentage in the Intra-Solution on Water Percentage in the Extra-Solution

1 Number of water molecules according to Eq. (2) (○ extrapolated); 2 number of water molecules and 3 water percentage in the intra-solution according to Eq. (3).

following consideration. The stepwise exchange of one ethanol molecule for one water molecule with increasing concentration of ethanol in the extra solution is not probable because it would result in higher G values than obtained. The exchange of some volume of water for an equal volume of ethanol with increasing concentration of ethanol in the system can be supposed as more probable. It means that sterical influences in the resin matrix play a role. It is therefore possible to compute the composition of the intra-solution if we suppose that its volume is equal to the volume of 5.4 water molecules per one active group corrected for the decreased swelling of the resin in mixed media systems.

The condition of the constant volume of the intra-solution can be expressed by the equation

$$gx/d + g(100 - x)/d' = CMnf/d', \quad (3)$$

where d is the density of ethanol, d' the density of water, C the capacity of the resin, M molecular weight of water, n number of water molecules in the intra-solution per one active group in the aqueous system and f the ratio of swelling of the resin in the due system and in water. The solving of last equations (2) and (3) results in the determination of the weight and composition of the intra-solution in mixed media systems. The results of such a computation are presented on Fig. 2 (curve 2 and 3). The enhanced concentration of water in the intra-solution in comparison with the water concentration in the extra-solution is evident.

Let us try to find connexion between the composition of the intra-solution and the separation efficiency of mixed systems. To be able to explain the existence of maximum on the curve representing the dependence of the separation factor on the concentration of water in the system we have to find such a quantity, the dependence of which is similar. According to our previous interpretation^{2,4} such a quantity could be the difference of the relative permittivities of the intra and extra solution. The dependence of this difference ($\Delta\epsilon$) on the water percentage in the extra solution can be seen on Fig. 3 (curve 1). For comparison see curve 2 representing the similar junction of the separation factor of europium-yttrium mixture obtained as a result of elution chromatography using α -hydroxyisobutyric acid in different ethanol-water mixtures as eluting solution.

The composition of the intra-solution is very complicated. High ionic strength, different kinds of ions, associates and reactions must be considered. The value of the relative permittivity

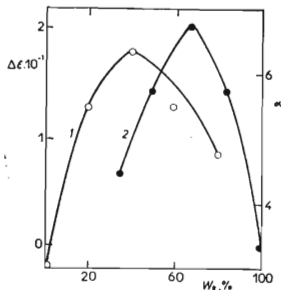


FIG. 3
Dependence of the Difference of the Relative Permittivity in the Intra- and Extra-Solution and of the Separation Factor of the Europium-Yttrium Mixture on Water Percentage in the Extra-Solution
1 Differences in relative permittivity $\Delta\epsilon$, 2 separation factor α .

of the extra solution influences the complexation reaction of ions to be separated with the eluting agent, the relative permittivity of the intra-solution affects the association of these ions with the active group. It can be supposed that equilibrium constants of these reactions differ considerably. The non-identical position of maxima on both curves is therefore not surprising. Nevertheless, the qualitative agreement of both curves seems to show out that the composition of the intra solution plays some role in the enhanced separation efficiency of mixed media and that the existence of three types of solutions in the system ion-exchanger, liquid phase can be accepted as probable.

The author wishes to express his thanks Mrs M. Veselá for carrying out experiments and measurements.

REFERENCES

1. Alexa J.: This Journal 30, 2344 (1965).
2. Alexa J.: This Journal 30, 2351 (1965).
3. Alexa J.: This Journal 30, 2361 (1965).
4. Alexa J.: This Journal 30, 2368 (1965).
5. Alexander W. A., Markson A. M., McAuley A.: J. Chem. Soc. 1965, 4330.
6. Shigehiko Kurosaki: J. Phys. Chem. 58, 320 (1954).
7. Gable R. W., Strobel A. H.: J. Phys. Chem. 60, 513 (1956).

Translated by the author.

ON THE DETERMINATION OF STRONTIUM IN SILICATES, CARBONATES AND SULPHATES BY ATOMIC ABSORPTION SPECTROSCOPY

B. MOLDAN and M. MIKŠOVSKÝ

Geological Survey of Czechoslovakia, Prague 7

Received October 22nd, 1969

Strontium is one of the elements that are frequently determined by atomic absorption spectroscopy. The sensitivity of the determination for 0.0044 Å in the conventional conditions of the air — acetylene flame is 0.2 p.p.m. Like the other alkaline earths strontium is not completely dissociated in this flame; the bulk of strontium is present in the form of its oxide. At the temperature of the air — acetylene flame about 11% of the total of strontium are free atoms¹. The incompleteness of dissociation of the oxide interferes with the determination of strontium by the formation of only slightly volatile compounds. These compounds are formed in the presence of aluminium, titanium, silicates, phosphates, sulphates and some other cations and anions. This interfering effect of the condensed phase is common to all alkaline earths and has been the subject of many papers; an excellent review has been published by Dean and Rains². In analysis of a geological