## Velocity of Intersolvate Exchange Reactions

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As a result of their exchange experiments, using radioactive halogens as indicators, Roginsky and co-workers[1,2] have reported the startling result that solvated halide ions, initially present in two separate, miscible solvents, maintain their original solvate envelopes for an appreciable time after the solutions are mixed. The exchange was complete only after a period of several hours at room temperature.

Because this result is so foreign to our ideas of solutions, an attempt has been made to check it. The observed exchange in our experiments was rapid, in contradiction to the results of Roginsky and co-workers. The following experimental procedure is patterned closely after that of the abovementioned authors.

(1) An aqueous bromide or iodide solution was prepared containing, respectively, either radioactive $Br^{82}$ (34 hours half-life)[3] or $I^{131}$ (8 days half-life)[4] as tracers. This solution was mixed with a solution of the corresponding inactive halide in an organic solvent miscible with water, and the mixed solution allowed to stand for a definite length of time.

(2) Three or four equal portions of a silver nitrate solution, the sum of which was equivalent to the total halide content of the mixed solution, were used in a series of successive precipitations of the silver halide, the precipitates being either quickly filtered or centrifuged depending on the state of the precipitate.

(3) The precipitates were washed, dried, and covered with collodion layer and their activity determined with a Geiger–Müller counter.

Using this type of procedure Roginsky and co-workers found a difference in the *specific* activity of their precipitates, the first precipitate having the greater activity. To explain this result they state that the following conditions must exist: (1) the interchange between the hydrated halide ions and the halide ions solvated with the organic solvent is slow; (2) silver ion preferentially precipitates hydrated halide ion; (3) the heterogeneous exchange between solid silver halide and solvated halide ion is slow. They found this unequal distribution of the activity in the successive precipitates using alkali chlorides, bromides, and iodides as solutes, silver and mercurous ions as the precipitants, and water–ethanol, water–methanol, water–acetone, water–glycerol, and glycerol–acetone as the mixed solvents.

In attempting to check the above results we used bromides and iodides (as alkali salts), at concentrations ranging from 0.15 to 2.0 $M$, and precipitated them with silver nitrate from water–ethanol, water–acetone, and water–glycerol solutions. The time of standing of the mixed solutions was varied from one to ten minutes, and the temperature from $\sim -30°$ to room temperature. However, no unequal distribution in the activity of the precipitates was observed. The heterogeneous exchange between the precipitate and the halide ions was found to be sufficiently slow in water–ethanol solutions so that it would not have concealed the effect.

In a later publication[5] Roginsky and Afanasiev describe a somewhat different procedure which they used in a study of the kinetics of the exchange in water–acetone mixtures using sodium bromide as solute. The procedure was to mix 10 ml. of acetone solution with 10 ml. of water solution, each containing 0.024 g. of bromide ion (the radiobromine being in the water), and then to precipitate one third of the total bromide with silver nitrate while stirring vigorously. Knowing the specific activity of the water solution and allowing the mixed solutions to stand for different lengths of time, they found the half-life of the exchange at 0, 16, and 30° to be 11 minutes, 7 minutes, and 4 minutes, respectively.

Using the above procedure at room temperature and the same concentration of bromide ion (from lithium bromide) as Roginsky and Afanasiev reported they used, we found complete exchange in less than two minutes, which was the time required to mix the solutions and precipitate and filter the silver bromide.

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[1] N. Breshneva, S. Roginsky and A. Schilinsky, *J. Phys. Chem. U. R. S. S.*, **9**, 296 (1937); *Acta Physicochim. U. R. S. S.*, **6**, 473 (1937).

[2] S. Z. Roginsky and V. E. Tartakovskoja, *Compt. rend. acad. sci. U. R. S. S.*, **24**, 709 (1939).

[3] B. Kurtchatow, I. Kurtchatow, L. Myssowsky and L. Roussinow, *Compt. rend.*, **200**, 1201 (1935).

[4] J. J. Livingood and G. T. Seaborg, *Phys. Rev.*, **54**, 775 (1938).

[5] S. Z. Roginsky and P. B. Afanasiev, *Compt. rend. acad. sci. U. R. S. S.*, **26**, 376 (1940).