

- <sup>10</sup> Fields, P. R., Stein, L., and Zirin, M. H., *J. Amer. Chem. Soc.*, **84**, 4164 (1962).
- <sup>11</sup> Chernick, C. L., *et al.*, *Science*, **138**, 136 (1962).
- <sup>12</sup> Grosse, A. V., Kirshenbaum, A. D., Streng, A. G., and Streng, L. V., *Science*, **139**, 1047 (1963).
- <sup>13</sup> Pomeroy, J. H., in *Noble Gas Compounds* (edit. by Hyman, H. H.), 123 (University of Chicago Press, Chicago, 1963).
- <sup>14</sup> Slivnik, J., in *Proc. of Symp. on Treatment of Airborne Radioactive Wastes*, 315 (Int. At. Energy Agency, Vienna, 1968).
- <sup>15</sup> Stein, L., *Science*, **175**, 1463 (1972).
- <sup>16</sup> Stein, L., *J. Inorg. Nucl. Chem.*, **35**, 39 (1973).
- <sup>17</sup> Shamir, J., and Binenboym, J., *Inorg. Chim. Acta*, **2**, 37 (1968).
- <sup>18</sup> Edwards, A. J., Holloway, J. H., and Peacock, R. D., *Proc. Chem. Soc.*, 275 (1963).
- <sup>19</sup> Sladky, F. O., Bulliner, P. A., and Bartlett, N., *J. Chem. Soc. (A)*, 2179 (1969).
- <sup>20</sup> Baranov, G. S., Egorov, N. P., Sopikov, A. N., and Chaivanov, B. B., *Zh. Fiz. Khim.*, **46**, 18 (1972).
- <sup>21</sup> Selig, H., and Peacock, R. D., *J. Amer. Chem. Soc.*, **86**, 3895 (1964).
- <sup>22</sup> Selig, H., in *Halogen Chemistry* (edit. by Gutman, V.), **1**, 403 (Academic Press, London and New York, 1967).

## Inverse Mass Dependence in Liquid Diffusion of Heavy Ions

AFTER the failure of early attempts to find isotope effects in liquid diffusion it was assumed<sup>1</sup> that these effects would be destroyed by two mutually antagonistic mechanisms. Firstly, a first approximation gas model resulted in higher speed for

than in gases. Recently<sup>5</sup> liquid diffusion cascades have been used in the search for isotope effects in liquid diffusion. A normal gas-like isotope effect was found for the Li isotopes in polyethylene glycol (PEG) solution but the inverse effect occurred for the U isotopes. Only one experiment has shown the same mass dependence: Cini-Castagnoli *et al.*<sup>6,7</sup> investigated the diffusion of argon in liquid nitrogen and found slower diffusion for <sup>37</sup>A than for <sup>40</sup>A. The difference was up to 10% but it was not emphasized and was apparently considered to be within the range of experimental error.

Here I report further confirmation of this inverse mass dependence for diffusion of uranyl ions in aqueous solution and in agar gel. A prismatic cascade<sup>8</sup> 60 cm high, with a cross section 10 by 60 cm at the top, containing 59 barriers of nylon gauze, was filled with distilled water. Uranyl nitrate solution with density 1.194 was introduced at the top. A layer of glass powder on the top barrier prevented convection of this concentrated solution. After 21 days a sample was drawn from the bottom which showed a depletion of <sup>235</sup>U against the blank. The result is given in Table 1. The simple process factor  $\epsilon$ , which may be deduced from these results, has the same order of magnitude as previously<sup>5</sup>. Hydration of the uranyl ion does not suppress appreciably the isotope effect.

It was possible to improve the efficiency of the barriers by using cylinders of sintered polystyrene beads impregnated with agar gel or solid agar cylinders supported by stainless steel gauze. The diffusion proceeded in radial direction towards a central channel. Details of this method will be published elsewhere. Again a depletion of <sup>235</sup>U occurred as shown in Table 1.

**Table 1** Depletion of <sup>235</sup>U in Solution after Passage through Barriers

System	Stage No.	Type	Cascades	Diffusion time	<sup>235</sup> U/ <sup>238</sup> U
			Material of barrier		
Uranyl nitrate in water	59	Prismatic	Nylon gauze	21 days	Sample: 0.007191 ± 0.000013* Blank: 0.007418 ± 0.000015*
Uranyl nitrate in agar gel	2	Cylinders 47 mm diameter	Agar gel in polystyrene matrix	3 days per stage	Sample: 0.007132 ± 0.000019* Blank: 0.007369 ± 0.000029*
Uranyl nitrate in agar gel	1	Cylinder 125 mm diameter	Agar gel	4 days	Sample: 0.007208 ± 0.000022 Blank: 0.007285 ± 0.000018

\* Arithmetical mean from 2 runs.

the lighter isotopes; secondly, however, in liquids the lighter isotopes would meet with an increased backscatter and would have less persistence than the heavier isotopes. Thus the preference of the mass independent Stokes-Einstein equation appeared justified for a first approach to liquid diffusion coefficients. The slower diffusion of the lighter alkali and alkaline earth ions was attributed wholly to the larger diameters caused by hydration and not to mass effects. The contribution of hydration will be indeed substantial for the lighter ions such as Li and Na but this influence has never been proved quantitatively especially for the heavier ions such as Sr and Ba.

The hydrodynamic model has been questioned by Lindemann<sup>2</sup>. He suggested a kinetic model and explained the slow motion and the high solvent transfer of the Li ion by momentum transfer.

The kinetic approach of Arnold<sup>3</sup>, however, did not take into account the persistence correction. Without this correction by Jeans<sup>4</sup> the Stefan-Maxwell equation could not explain the weak composition dependence of the diffusion coefficients in gas mixtures. In the case of a few heavy molecules diffusing in an excess of light molecules the persistence correction results in a substantial increase in the diffusion coefficient against the uncorrected value.

Because of the higher collision number in liquids the effect of persistence should play a still more important role in liquids

I conclude that the mechanism of persistence and backscatter plays an even more prominent role in the diffusion of heavy solutes in light solvents than was assumed by Hevesy and Paneth<sup>1</sup>. This mechanism not only compensates but overcompensates the features of the gas model and results in inverse mass dependence.

I thank Dr N. C. Fenner for carrying out the mass spectrometric analysis.

L. MILLER

National Chemical Research Laboratory,  
PO Box 395,  
Pretoria

Received January 16, 1973.

<sup>1</sup> Von Hevesy, G., and Paneth, F., *A Manual of Radioactivity* (English edition), 195 (1938).

<sup>2</sup> Lindemann, F. A., *Z. Phys. Chem.*, **110**, 394 (1924).

<sup>3</sup> Arnold, J. H., *J. Amer. Chem. Soc.*, **52**, 3937 (1930).

<sup>4</sup> Jeans, J. H., *The Dynamical Theory of Gases* (Cambridge University Press, London, 1925).

<sup>5</sup> Miller, L., *Ber. Bunsen Ges. Phys. Chem.*, **75**, 206 (1971).

<sup>6</sup> Cini-Castagnoli, G., Pizzella, G. P., and Ricci, F. P., *Nuovo Cimento*, **10**, 300 (1958).

<sup>7</sup> Cini-Castagnoli, G., Dupré, F., and Ricci, F. P., *Nuovo Cimento*, **13**, 464 (1959).