The anchored fractions p found in the present experiments are considerably higher than the fraction of anchored segments postulated by the theory of Simha, Frisch and Eirich.[3] A later theoretical treatment[4] for the case of appreciable adsorption energies shows much better agreement with our experimental results. The order of magnitude of the adsorption energy ϵ_0 can be estimated roughly by analogy with corresponding monomeric substances, at least for the case of un-ionized polymers near the electrocapillary maximum. The estimated ϵ_0 per methacrylic acid residue is 4–5 kT and per lysine residue is about 8–10 kT. The effective range of the forces R under these conditions is narrow and the approximate solution of eq. 14 in reference 4 which gives $\langle p \rangle =$ const. $\times$ $(1 - \theta)\alpha/R$ seems only of limited validity. Here α is the probability of a successful contact between segment and surface, and θ is the fraction of the surface covered. Close to the adsorption potentials, ϵ_0 is of the order of kT. $\langle p \rangle$, as postulated in reference 4 for this case, is $2\alpha(1 - \theta)(1 + \epsilon_0/kT)/(\pi fZ)^{1/2}$. The p's found in our experiments under these conditions are considerably higher and they depend very little on the molecular weight.

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(3) R. Simha, H. L. Frisch and E. R. Eirich, *J. Phys. Chem.*, **57**, 584 (1953).

(4) H. L. Frisch, *ibid.*, **59**, 633 (1955).

SELF-DIFFUSION IN MOLTEN PbCl₂

Sir:

We have had occasion recently to repeat an earlier measurement of the self-diffusion coefficients of Pb^{210} and Cl^{36} in molten $PbCl_2$. The original paper[1] reported anomalous results for these quantities. The present results, although generally similar, are more nearly what might be expected for this system in the light of corresponding data for other systems. The experimental procedure employed in this work is described in detail in an earlier paper.[2] Since this procedure uses doubly

(1) G. Perkins, Jr., R. B. Escue, J. F. Lamb and T. H. Tidwell, THIS JOURNAL, **64**, 495 (1960).

(2) G. Perkins, Jr., R. B. Escue, J. F. Lamb, T. H. Tidwell and J. W. Wimberley, THIS JOURNAL, to be published.

labeled $PbCl_2$ as tracer, the two ions experience identical environments during the experiment and the measurement should be ideal for comparing the coefficients of the two species. This fact, together with the generally improved accuracy, leads us to prefer the present results, which are presented in Table I.

TABLE I

THE DIFFUSION COEFFICIENTS OF Pb^{210} AND Cl^{36} IN MOLTEN $PbCl_2$

Temp., °C.	$D_{Pb} \times 10^5$ cm.² sec.⁻¹	$D_{Cl} \times 10^5$ cm.² sec.⁻¹
510	0.997 ± 0.02	1.80 ± 0.05
518	1.05 ± 0.004	1.90 ± 0.03
533	1.12 ± 0.07	1.92 ± 0.07
546	1.13 ± 0.01	2.09 ± 0.07
556	1.26 ± 0.03	2.26 ± 0.03
566	1.37 ± 0.02	2.34 ± 0.03

It will be seen that a plot of log D vs $1/T$ for these data does not give the apparent discontinuity found in the earlier work.[1] These data fit very well a relationship of the form

$$D = A \exp(-\Delta H^*/RT), \text{ with}$$

$$D_{Pb} = 7.73 \times 10^{-4} \exp(-6777 \pm 643/RT)$$

and

$$D_{Cl} = 8.95 \times 10^{-4} \exp(-6099 \pm 483/RT)$$

ΔH is the energy of activation for diffusion, which shows no significant difference for the two ions within experimental error. This corresponds to the results reported for other systems.[3] However, there is no immediately apparent correlation between the diffusion coefficient and either the ionic radius or the ionic weight, as has been reported variously for other systems. As was the earlier experience, and as is usual in molten salts, neither the Nernst–Einstein nor Stokes–Einstein relations hold for this system. We are, at present, investigating the influence of a variety of factors on the diffusion coefficient and this work will be published within the coming year. We gratefully acknowledge the continuing financial support given this work by the Robert A. Welch Foundation.

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                                   J. WAYNE WIMBERLEY
              RECEIVED AUGUST 26, 1960

(3) A. S. Dworkin, R. B. Escue and E. R. VanArtsdalen, THIS JOURNAL, **64**, 872 (1960).