

## Tracer Diffusion Coefficients of Naphthalene, Biphenyl, and Anthracene

Sir:

A previous study reported the utility of tracer diffusion coefficients of aromatic molecules in solutions of interest to organic electrochemists.<sup>1</sup> Herein we report the tracer diffusion coefficients ( $D_{tr}$ ) of naphthalene, biphenyl, and anthracene in the solvent systems: 75% dioxane–25% water (D–W), dimethylformamide (DMF), and acetonitrile (MeCN). All solvents contained 0.1 *M* tetraethylammonium perchlorate supporting electrolyte. The organic molecules and solvents were chosen to provide maximum correlation with electrochemically determined  $D$  values in the literature. Secondly, these solvent systems provide a good test of the constancy of the product of  $D$  times viscosity ( $D\eta$ ).

The experimental techniques were identical with those described previously.<sup>1</sup> The organic molecules were labeled generally by the method of Yavorsky and Gorin.<sup>2</sup> The viscosities of the solvents with supporting electrolyte and electroactive species present were measured at 25° with an Ostwald viscometer.

### Results and Discussion

Table I summarizes the measurements. As the next to the last column shows, the product of  $D_{tr}$  times viscosity ( $D\eta$ )<sub>tr</sub> for each of the three molecules is clearly

a given compound by a factor of two or more with only one value (anthracene in MeCN) within the experimental deviation of the tracer data. These figures first attest to the reliability of the  $D_{tr}$  values (the product  $D\eta$  should be constant) and, secondly, indicate that almost all of the electrochemically determined  $D$  values for these compounds are surely incorrect. The  $D_{el}$  values determined in the present study were obtained from the appropriate diffusion current constants using the Ilkovic equation for a dropping mercury electrode. To evaluate the diffusion constant, the diffusion current ( $i_d$ ) was taken as the difference between the observed  $i_d$  and the residual current. The value of  $m^{3/2}t^{1/6}$  was determined at the applied potential at which  $i_d$  was measured. All values of  $D_{el}$  from the literature were calculated directly from stated diffusion constants or from listed  $i_d$  values combined with  $m^{3/2}t^{1/6}$  data measured at the applied potential as mentioned above.

The large errors in  $D_{el}$  arise, of course, in the false assumption that one can assign with certainty the value  $n_T$ , the total number of electrons transferred in the electrochemical reaction. In DMF and MeCN it is normally assumed  $n_T = 1$  and for dioxane–water  $n_T = 2$ . While electron paramagnetic resonance studies indicate without question that the anion radicals of naphthalene, biphenyl, and anthracene are the predominant products during reduction in DMF and MeCN, the polarographic currents do not correspond

Table I. Comparison of Tracer and Electrochemical Diffusion Coefficients<sup>a</sup>

Compound	Solvent	$D_{tr} \times 10^5$ , cm. <sup>2</sup> /sec.	$D_{el} \times 10^5$ , cm. <sup>2</sup> /sec.	Viscosity, mp.	$D\eta \times 10^5$	
					( $D\eta$ ) <sub>tr</sub>	( $D\eta$ ) <sub>el</sub> <sup>b</sup>
Naphthalene	D–W	0.56	0.62 (3) 0.62 (6)	18.80	10.5	11.7 11.7
	DMF	1.27	2.5 2.9 (9)	8.55	10.8	21.4 24.8
	MeCN	2.74	6.9	3.88	10.6	26.8
Biphenyl	D–W	0.57	1.26 (3)	18.80	10.7	23.8
	DMF	1.20	1.41	8.66	10.4	12.2
	MeCN	2.48	9.4	3.92	9.7	36.8
Anthracene	D–W	0.52	0.39 (3) 0.31 (4)	18.80	9.8	7.3 5.8
	DMF	1.19	1.32 (9) 0.78 (7) <sup>c</sup>	8.55	10.2	11.3 6.7
	MeCN	2.55	2.65 (5)	3.92	10.0	10.4
			6.6 (8) <sup>d</sup>			25.8

<sup>a</sup> The number in parentheses to the right of  $D_{el}$  refers to the literature source of the diffusion current constant from which  $D_{el}$  was calculated, assuming  $n_T = 1$  for DMF and MeCN and  $n_T = 2$  for D–W.  $D_{el}$  values without reference numbers were determined in this study. <sup>b</sup> The ( $D\eta$ )<sub>tr</sub> values were calculated from the viscosity measured in this study and given in column 5. There is a small error involved since some of the  $D_{el}$  values were measured with different supporting electrolytes and have viscosities slightly different from those of the literature electrochemical studies. <sup>c</sup> Measured by alternating current polarography. <sup>d</sup> Measured by anodic oxidation at a platinum electrode via chronopotentiometry.

a constant within experimental error. On the other hand, using electrochemical  $D$  values determined in this study and from the literature,<sup>3–9</sup> ( $D\eta$ )<sub>el</sub> varies for

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(4) G. J. Hoijtink, J. van Schooten, E. de Boer, and W. I. Aalbersberg, *Rec. trav. chim.*, **73**, 355 (1954).

(5) S. Wawzonek, E. W. Blaha, R. Berkey, and M. E. Runner, *J. Electrochem. Soc.*, **102**, 235 (1955).

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(7) A. C. Aten, Thesis, University of Amsterdam, 1959.

to integral one-electron transfers. These measured currents are the sum of the one-electron process plus contributions from the presence of proton donors in these solvents and background processes. It is noteworthy that biphenyl and naphthalene, which are more difficult to reduce than anthracene (and whose polarographic waves are therefore closer to background reduction), show serious differences in  $D_{el}$  and  $D_{tr}$ .

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(9) A. C. Aten, C. Büthker, and G. J. Hoijtink, *Trans. Faraday Soc.*, **55**, 324 (1959).

