

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

## Dependence of Conductance on Field Strength. II. Tetrabutylammonium Bromide in Diphenyl Ether at 50°

BY DARWIN J. MEAD WITH RAYMOND M. FUOSS

## I. Introduction

In the first paper of this series,<sup>1</sup> we showed that the Wien effect for tetrabutylammonium picrate in diphenyl ether at 60 cycles was in agreement with Onsager's theory.<sup>2</sup> A dependence of the Wien coefficient on concentration and frequency also was observed. In this paper, further work on the frequency effect is reported. We find that the Wien coefficient decreases with frequency at concentrations where the product of the Langevin time of relaxation into frequency is of the order unity. This time is defined by the equation<sup>2</sup>

$$\tau_L = \frac{1}{8\pi^9} \frac{\epsilon'}{10^{11} \kappa} \quad (1)$$

where  $\epsilon'$  is the dielectric constant and  $\kappa$  is the specific conductance (in mho/cm. cube) of the solution. It is a measure of the time required for establishment of equilibrium between charge distribution and external electrical field. For diphenyl ether,  $\epsilon' = 3.53$  at 50°, so (1) becomes for this solvent

$$\tau_L = 15.6 \times 10^{-14} / \kappa \text{ sec.} \quad (2)$$

(The solutions to be considered are so dilute that the dielectric constant is not appreciably increased.) At  $10^{-4} N$ , tetrabutylammonium bromide in diphenyl ether at 50° has a conductance of  $3.43 \times 10^{-10}$ , so  $\tau_L = 0.46$  millisecond. Consequently frequencies of the order of kilocycles should show a dispersion of the Wien effect, as found in the data presented here.

## II. Materials, Apparatus and Procedure

Diphenyl ether was purified as before.<sup>1</sup> Tetrabutylammonium bromide was that used in the low voltage work in chlorobenzene.<sup>3</sup> Cells, bridges, and general procedure were the same as in the preceding work.<sup>1</sup>

For frequencies above 60 cycles, a variable speed alternator (480–1920 cycles at 450–1800 r. p. m., 55–220 volts output) was used. For low voltages, the machine fed the bridge circuit directly. For the higher voltages, a 1-KVA transformer was used: it had 4480 turns in the secondary, and primary taps at 100, 150 and 300 turns, giving output to input ratios of 15, 30 and 45. In order to get a good sine wave output from the generator-transformer circuit,  $8\mu f$  (Pyranol condensers) were connected

across the primary and a load of 50,000  $\Omega$  ("blue sticks") across the secondary. One side each of primary and secondary were grounded. With this circuit, the output gave a very nearly circular Lissajou figure when fed into the vertical plates of an oscilloscope whose horizontal plates were connected to the output of a General Radio beat frequency oscillator set at the same frequency. During the voltage runs on the solutions, the frequency was determined by beating against the above oscillator, which was in turn checked against the fundamental and harmonics of a 1000-cycle fork.

Voltages were read on an electrostatic voltmeter, 0–5 KV range. The usual high series resistance protection in the meter was replaced by 75,000  $\Omega$  in order to make the readings independent of frequency in our working range; the capacity of the meter was 20  $\mu f$ . The calibration was checked by measuring the current through our 100,000  $\Omega$  high voltage standard.<sup>4</sup> In calibration the whole range of frequencies and voltages were covered; a typical calibration point is as follows:  $f = 2000$  cps,  $i = 28.9$  milliamperes,  $iR = 2.89 \times 10^3$ , E. S. voltmeter = 2.93 KV,  $iR/E = 0.986$ .

## III. Experimental Results

The low voltage data used to establish the conductance–concentration curve are given in Table I. These were determined in some cases at 1000 cycles on the parallel bridge and in others on the resistance or Schering bridges at 60 cycles. In contrast to tetrabutylammonium picrate, the solutions of the bromide gave low voltage conductances independent of frequency. For example, for a  $8.27 \times 10^{-4} N$  solution,  $\kappa$  (60  $\sim$ ) =  $3.822 \times 10^{-9}$ ,  $\kappa$  (500  $\sim$ ) =  $3.815 \times 10^{-9}$  and  $\kappa$  (2000  $\sim$ ) =  $3.818 \times 10^{-9}$ .

The conductances at both high and low voltages were independent of cell geometry when reduced to a field strength basis, so designation of the cells used is omitted in the tables. Typical voltage curves at three frequencies, 60, 600, and 1000 cycles, are given in Table II. Field strength,  $E$ , is given in *average kilovolts per centimeter*; it is determined from the root mean square voltage  $V_r$  read on the electrostatic voltmeter by the relationship<sup>1</sup>

$$E = 2\sqrt{2} V_r / \pi(r_2 - r_1) \quad (3)$$

where  $r_1$  and  $r_2$  are the radii of the electrodes. The conductances are given as ratios to the low voltage conductance  $\kappa_0$ , which, by definition, is a

(1) (a) Mead and Fuoss, *THIS JOURNAL*, **61**, 2047 (1939); (b) correction, *ibid.*, **61**, 3589 (1939).

(2) Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

(3) McIntosh, Mead and Fuoss, *THIS JOURNAL*, **62**, 506 (1940).

(4) Fuoss, *ibid.*, **60**, 451 (1938).

voltage so low that doubling it makes no detectable change in conductance.

TABLE I

CONDUCTANCE OF TETRABUTYLAMMONIUM BROMIDE IN DIPHENYL ETHER AT 50° AND LOW VOLTAGE

$c \times 10^4$	$\Lambda \times 10^3$	$c \times 10^4$	$\Lambda \times 10^3$
8.270	4.62	1.504 <sup>a</sup>	3.48
7.840	4.57	1.002 <sup>a</sup>	3.43
7.180	4.45	0.887	3.52
5.009 <sup>a</sup>	4.06	.865	3.53
4.051	3.94	.785	3.58
4.001 <sup>a</sup>	3.94	.448	3.76
3.587 <sup>a</sup>	3.88	.2867	4.20
3.009 <sup>a</sup>	3.70	.1925	4.56
2.558	3.68	.0964	5.78
1.999 <sup>a</sup>	3.54	.0479	7.93
1.782	3.59	.0240	11.28

<sup>a</sup> Voltage-frequency runs made on these solutions. Their low voltage values are shown as solid circles in Fig. 1.

TABLE II

WIEN EFFECT FOR TETRABUTYLAMMONIUM BROMIDE IN DIPHENYL ETHER AT 50° AND VARIABLE FREQUENCY

$E$	$\kappa(60)/\kappa_0$	$E$	$\kappa(600)/\kappa_0$	$E$	$\kappa(1000)/\kappa_0$
$c = 5.009 \times 10^{-4}$					
0.74	1.002	0.37	1.002	0.64	1.003
1.86	1.011	2.78	1.023	5.64	1.057
3.71	1.036	3.79	1.037	7.54	1.082
5.57	1.061	5.61	1.061	9.28	1.112
7.43	1.102	7.43	1.088	11.14	1.161
9.25	1.130	9.36	1.125	13.11	1.200
10.84	1.164	11.14	1.157	14.85	1.215
12.70	1.220	13.07	1.196	16.71	1.251
15.41	1.261				
16.63	1.292	14.85	1.246		
18.00	1.289	16.71	1.288		
$c = 4.001 \times 10^{-4}$					
0.92	1.004	0.24	1.001	0.36	1.001
1.37	1.007	1.36	1.008	2.42	1.018
1.83	1.014	1.83	1.013	2.75	1.021
2.75	1.026	2.75	1.023	3.66	1.031
3.87	1.043	3.74	1.035	4.58	1.045
4.47	1.051	4.58	1.047	5.50	1.057
5.57	1.071	5.50	1.063	6.60	1.069
6.74	1.087	6.32	1.073	7.38	1.082
7.48	1.100	7.31	1.091	8.24	1.096
8.15	1.114	8.24	1.108	9.20	1.113
8.98	1.128	9.16	1.124		
$c = 3.009 \times 10^{-4}$					
0.74	1.003	0.48	1.003	0.74	1.003
1.86	1.015	3.79	1.039	5.68	1.060
3.71	1.043	5.57	1.063	7.50	1.085
5.50	1.064	7.43	1.089	9.28	1.103
7.43	1.102	9.28	1.112	11.18	1.128
9.25	1.125	11.14	1.141	13.03	1.159
11.03	1.172	13.07	1.170	15.11	1.196
13.11	1.214			16.71	1.222
14.74	1.243				
16.71	1.298				
18.08	1.322				

$c = 1.999 \times 10^{-4}$

5.57	1.079	0.48	1.002	0.87	1.002
7.28	1.098	3.71	1.038	5.57	1.059
9.28	1.138	5.57	1.062	7.43	1.082
11.00	1.168	7.43	1.087	9.36	1.114
12.96	1.216	9.32	1.116	11.25	1.133
14.85	1.246	11.21	1.140	13.26	1.166
16.50	1.275	12.96	1.172	14.85	1.197
18.38	1.310	14.96	1.208	16.86	1.219
		16.71	1.234	18.49	1.237

$c = 1.504 \times 10^{-4}$

1.86	1.018	5.61	1.060	5.57	1.053
3.71	1.048	7.54	1.088	7.46	1.081
5.57	1.076	9.36	1.108	9.36	1.105
7.46	1.111	11.25	1.136	11.14	1.130
9.36	1.141	13.03	1.168	12.85	1.148
10.84	1.175	14.93	1.183	15.04	1.183
13.00	1.210	16.79	1.227	16.89	1.204
14.85	1.249	18.27	1.257		

$c = 1.002 \times 10^{-4}$

0.92	1.007	1.37	1.011	2.38	1.017
1.83	1.021	1.83	1.015	2.77	1.024
2.75	1.037	2.75	1.026	3.68	1.035
3.66	1.053	3.65	1.038	4.58	1.046
4.58	1.065	4.62	1.050	5.50	1.059
5.50	1.081	5.48	1.061	6.45	1.073
6.41	1.100	6.41	1.075	7.29	1.086
7.33	1.114	7.31	1.088	8.24	1.098
8.28	1.133	8.21	1.101	9.16	1.109
9.09	1.147	9.16	1.114		

$c = 0.601 \times 10^{-4}$

1.86	1.019	2.78	1.021	5.64	1.062
3.71	1.049	3.71	1.034	7.50	1.086
5.57	1.080	5.68	1.060	9.32	1.110
7.43	1.108	7.50	1.082	11.21	1.138
9.25	1.138	9.32	1.106	13.03	1.165
11.14	1.172	11.25	1.132	14.63	1.185
13.00	1.206	13.03	1.158	16.93	1.218
14.85	1.243	14.96	1.189		
16.71	1.268	16.78	1.202		
		18.38	1.242		

IV. Discussion

The conductance-concentration curve (Fig. 1) is typical for electrolytes in solvents of low dielectric constant: it comprises a linear section with slope  $(-1/2)$  at low concentrations on a  $\log \Lambda - \log c$  plot, followed by a minimum at  $10^{-4} N$ . Assuming  $\Lambda_0 \eta = 0.484$ , we estimate  $\Lambda_0 = 23.1$ . From a plot<sup>5</sup> of  $\Lambda \sqrt{c} g(c)$  against  $c$ , we find

(5) Fuoss and Kraus, THIS JOURNAL, 55, 1019 (1933). An approximation for  $g(c)$  was used here, which is much simpler to handle than the original formula. It is

$$\log_{10} g(c) \approx -0.4343 \sqrt{1000} \left( \frac{2.303 \Lambda_0 \beta - \alpha}{\Lambda_0^{3/2}} \right) \sqrt{\kappa}$$

where  $\beta$  is the Debye-Hückel coefficient for activity,  $\alpha$  is the Onsager coefficient for conductance and  $\kappa$  is the specific conductance. For diphenyl ether at 50°,  $\log g(c) = -78.3 \sqrt{\kappa}$ .

from the slope and intercept of the resulting straight line

$$K = 4.68 \times 10^{-13}$$

$$k = 5.85 \times 10^{-5}$$

for the ion pair and triple ion equilibrium constants. From the former, an average ion size  $a = 4.60 \times 10^{-8}$  cm. is obtained.<sup>6</sup>

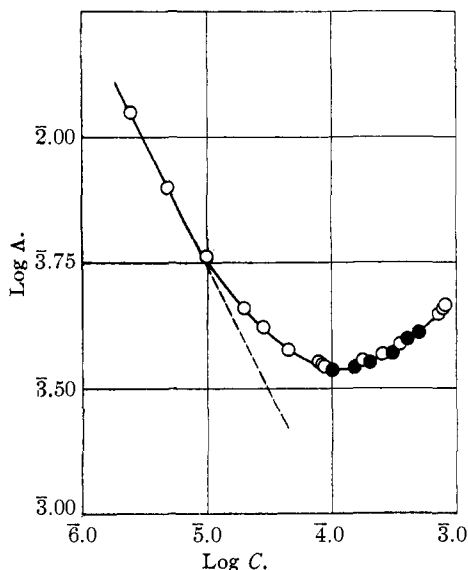


Fig. 1.—Conductance of tetrabutylammonium bromide in diphenyl ether at 50°.

An example of the Wien effect is shown in Fig. 2, where the open circles are 60-cycle data and the solid ones 1000-cycle. At low field strengths, the conductances are the same, which indicates absent or negligible polarization for this system in the range of concentration studied. The slopes of the conductance-field strength curves are

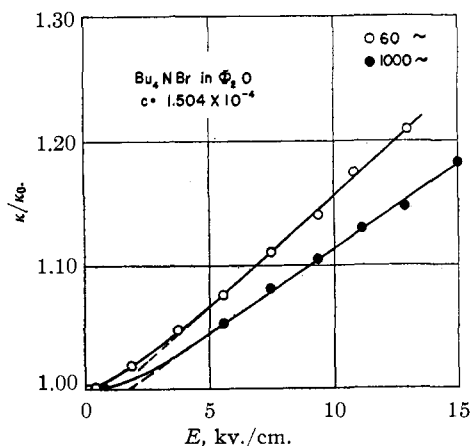


Fig. 2.—Wien effect at 60 and 1000 cycles.

(6) Fuoss, *Chem. Rev.*, **17**, 27 (1935).

summarized in Fig. 3 for the seven concentrations studied,  $0.6$  to  $5.0 \times 10^{-4} N$  as given on the right in the figure. The ordinate is  $\kappa/\kappa_0$ , where  $\kappa$  is conductance at frequency  $f$  and field strength  $E$ , and  $\kappa_0$  is the low voltage conductance at the same frequency. In order to simplify the figure, the ordinate scale is shifted vertically for each concentration, which is given in multiples of  $10^{-4} N$  on the figure.

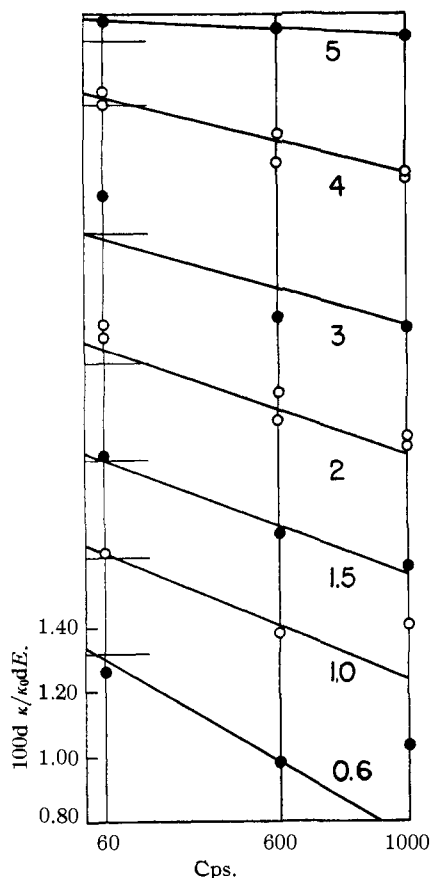


Fig. 3.—Dispersion of the Wien effect.

According to Onsager's theory, we have

$$\kappa/\kappa_0 = 1 + (\epsilon^3/4 Dk^2T^2) \bar{X} \quad (4)$$

which for our case becomes

$$\kappa/\kappa_0 = 1 + 0.0132 E \quad (5)$$

where  $E$  is field strength in kilovolts per centimeter. To allow for the harmonic analysis made by our filter and amplifier,<sup>1b</sup> we multiply the slopes or the  $\kappa - E$  plots obtained from the data of Table II by  $3/4$  in order to obtain the points of Fig. 3. The theoretical value, 1.32%/KV, is shown for each concentration by the horizontal line at the left. It is seen that for low frequencies the experimental slope is in excellent agreement

with the theoretical. In contrast to tetrabutylammonium picrate, no concentration dependence of the 60-cycle slope is visible, but there is a systematic decrease of the Wien coefficient with increasing frequency, which becomes more pronounced with decreasing concentration.

As stated in the introduction, the Langevin time constant is of the order of milliseconds for these solutions: at  $c = 5 \times 10^{-4}$ ,  $\tau_L = 0.077 \times 10^{-3}$  sec., and at  $c = 1 \times 10^{-4}$ ,  $\tau_L = 0.455 \times 10^{-3}$  sec. With decreasing concentration,  $\tau_L$  increases, almost hyperbolically in the region of the minimum in equivalent conductance. For the higher concentrations and low frequency the ionic distribution has time to adjust itself to the field and we find the normal Wien effect. But when the frequency becomes high and the concentration low, the field-sensitive reaction Ion pair  $\rightarrow$  Free ions becomes increasingly less able to follow the field. Consequently the Wien coefficient decreases.

The Langevin time constant also depends on field strength, as Onsager pointed out; for our case, this dependence is a second order effect, because the fields used were far below those corresponding to saturation.

### Summary

1. The conductance of tetrabutylammonium bromide in diphenyl ether at  $50^\circ$  has been measured at low voltage over the approximate concentration range  $10^{-6}$ – $10^{-3}$  normal.

2. Conductances at 60, 600 and 1000 cycles at field strengths up to 20 KV/cm. were measured in the concentration range  $0.5$ – $5.0 \times 10^{-4}$  N.

3. For low frequencies, the Wien effect is in agreement with Onsager's theory; when the Langevin time of relaxation becomes comparable to the period of the impressed field, a dispersion of the Wien effect appears.

SCHENECTADY, N. Y.

RECEIVED APRIL 20, 1940

[CONTRIBUTION FROM THE BUREAU OF AGRICULTURAL CHEMISTRY AND ENGINEERING AND GEORGE WASHINGTON UNIVERSITY]

## On a Theory of the van der Waals Adsorption of Gases\*

BY STEPHEN BRUNAUER, LOLA S. DEMING, W. EDWARDS DEMING AND EDWARD TELLER

A search of the literature on the van der Waals adsorption of gases reveals that there exist five different types of isotherms. To give an example of each type we may mention the adsorption of oxygen on charcoal at  $-183^\circ$  (Type I),<sup>1</sup> nitrogen on iron catalysts at  $-195^\circ$  (Type II),<sup>2</sup> bromine on silica gel at  $79^\circ$  (Type III),<sup>3</sup> benzene on ferric oxide gel at  $50^\circ$  (Type IV),<sup>4</sup> and water vapor on charcoal at  $100^\circ$  (Type V).<sup>5</sup> The five isotherms in Fig. 1 illustrate these five types; they are imaginary, not real isotherms. Type I is the well-known Langmuir adsorption isotherm, Type II is the S-shaped or sigmoid isotherm, but no names have been attached so far to the three other types. Types II and III are closely related to Types IV and V, only in the former cases the adsorption increases as the vapor pressure  $p_0$  of the adsorbed gas is approached, whereas in the latter cases the maximum adsorption is attained, or almost attained, at some pressure lower than the vapor pressure of the gas.

(\* Not subject to copyright.

(1) Brunauer and Emmett, *THIS JOURNAL*, **59**, 2682 (1937).

(2) Emmett and Brunauer, *ibid.*, **59**, 1553 (1937).

(3) Reyerson and Cameron, *J. Phys. Chem.*, **39**, 181 (1936).

(4) Lambert and Clark, *Proc. Roy. Soc.*, **A122**, 497 (1929).

(5) Coolidge, *THIS JOURNAL*, **49**, 708 (1927).

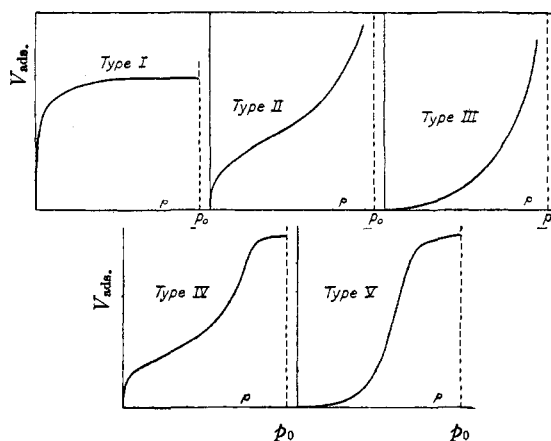


Fig. 1.—The five types of van der Waals adsorption isotherms.

An interpretation of the Type I isotherm was given by Langmuir who in 1915 derived his celebrated isotherm equation for adsorption in a unimolecular layer.<sup>6</sup> Brunauer, Emmett and Teller<sup>7</sup> derived an isotherm equation for the multimolecular adsorption of gases that includes both the Langmuir isotherm and the S-shaped isotherm as

(6) Langmuir, *ibid.*, **37**, 1139 (1915).

(7) Brunauer, Emmett and Teller, *ibid.*, **60**, 309 (1938). This paper henceforth will be referred to as paper I.