Dielectric Investigation on Coals. V. Microwave Dielectric Constant

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Dielectric methods have been applied to the study of coals during these several years[1-4]. In the laboratory of the present writers[1,2] measurements were made directly on polished coal plates as well as on mixtures of coal powder and paraffin-wax, and a frequency range from 300 c./sec. to 50 Mc./sec. was employed. In contrast to the work by Groenewege et al.[3,4], special attention was paid to the frequency dependence of dielectric constants and losses of coals. In the present paper new and more complete information will be given which was obtained by use of a wider frequency range including a microwave measurement at 4.28 cm. wavelength. Representative coals were kindly selected and provided for this measurement by Dr. H. Honda, Resources Research Institute of Japan.

Experimental Apparatus and Method

The dielectric measurement at the microwave frequency of 7000 Mc./sec. was made by use of the transmission method developed by von Hippel and others[5,6]. The block diagram of the apparatus is shown in Fig. 1.

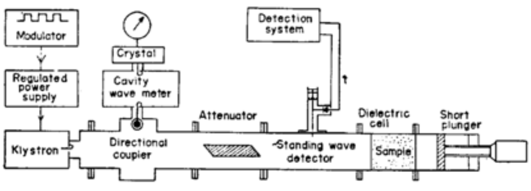

Fig. 1. Block diagram of the apparatus for measuring dielectric constant and loss at 7000 Mc./sec.

1) a) I. Miyasita, R. Miura and K. Higasi, This Bulletin, **28**, 148 (1955); b) I. Miyasita and K. Higasi, ibid., **30**, 513 (1957); c) K. Higasi, I. Miyasita and Y. Ozawa, ibid., **30**, 546 (1957), d) I. Miyasita, K. Higasi and M. Kugo, ibid., **30**, 550 (1957); e) K. Higasi, Y. Higasi and I. Miyasita, ibid., **30**, 556 (1957); f) K. Higasi, *Kagaku*, **27**, 148 (1957); g. K. Higasi and Y. Higasi, ibid., **27**, 630 (1957).

2) a) I. Miyasita, *Bull. Res. Inst. Appl. Elec. Hokkaido Univ.*, (*Oyodenki Kenkyujo Iho*), **5**, 123 (1953); b) I. Miyasita, ibid., **6**, 117 (1954); c) I. Miyasita, ibid., **7**, 17 (1955); d) I. Miyasita, ibid., **9**, 122 (1957).

3) M. P. Groenewege, J. Schuyer and D. W. van Krevelen, *Fuel*, **34**, 339 (1955).

4) D. W. van Krevelen and J. Schuyer, "Coal Science", Elsevier Publ. Co., Amsterdam (1957).

5) S. Roberts and A. R. von Hippel, *J. Appl. Phys.*, **17**, 610 (1946).

6) A. R. von Hippel, "Dielectrics and Waves", John Wiley and Sons, New York, N. Y., (1954); A. R. von Hippel, "Dielectric Materials and Applications", John Wiley and Sons, New York, N. Y., (1954).

The complex dielectric constant $\varepsilon^* = \varepsilon' - j\varepsilon''$ is given by

$$\varepsilon' - j\varepsilon'' = \frac{(1/\lambda_c)^2 - (\gamma_2 d/2\pi d)^2}{(1/\lambda_c)^2 + (1/\lambda_g)^2} \tag{1}$$

where λ_c and λ_g are the cut-off wavelength and the wavelength in the air-filled guide, respectively. γ_2 is the complex propagation factor of the coal sample and d is the thickness of the sample. For determining $\gamma_2 d$ of the sample, the standing wave ratio $E_{min.}/E_{max.}$ and the distance from the sample

TABLE I. MICROWAVE DIELECTRIC CONSTANT OF COAL MIXTURE ESTIMATED BY THE METHOD OF DAKIN AND WORKS[7]

No.	Specimen	Thickness cm.	Dielectric constant (Short)	(Open)	(Values taken)
1	Taihei	0.41	2.845	2.840	
		1.40	2.87	2.85	2.86
2	Tempoku	0.40	3.15	2.85	
		1.40	2.946	2.84	2.89
3	Nakago-kaso	0.415	2.757	2.85	
		1.415	2.908	2.802	2.86
4	Nakago	0.410	2.837	2.789	
		0.310	2.884	2.854	2.81
5	Kasima	0.415	2.620	2.688	
		0.910	2.726	2.692	
		1.305	2.692	2.653	2.67
6	Pocahontas	0.40	2.926	2.720	
	(USA)	1.40	2.887	2.683	2.79
7	Hutago	0.40	2.908	2.695	
		1.40	2.690	2.670	2.68
8	Yubari	0.40	2.923	2.700	
		0.82	2.763	2.622	
		1.40	2.680	2.365	2.69
9	Hasima	0.405	2.802	2.660	
		0.305	2.940	2.722	2.73
10	Kamati	0.92	2.800	2.765	
		1.40	2.812	2.765	2.79
11	Yatake	0.40	2.930	2.700	
		1.40	2.796	2.738	2.77
12	Onuki	0.405	2.910	2.735	
		1.310	2.854	2.730	2.79
	Paraffin	0.415	2.230	2.285	
		0.320	2.302	2.248	2.26

7) T. W. Dakin and C. N. Works, *J. Appl. Phys.*, **18**, 789 (1947).

TABLE II. CHEMICAL ANALYSIS OF COAL

No.	Specimen	Moisture	Ash	Dry-ash-free basis				
				C%	H	O	N	S
1	Taihei	12.86	5.84	65.10	4.93	28.43	0.93	0.62
2	Tempoku	12.80	1.52	70.37	4.74	23.79	1.10	0
3	Nakago-kaso	11.19	4.75	70.92	4.65	23.59	0.73	0.11
4	Nakago	13.32	3.96	74.33	5.26	19.29	0.95	0.17
5	Kasima	4.11	5.02	77.94	6.07	12.62	0.65	2.72
6	Pocahontas (USA)	2.09	2.59	82.79	6.02	8.86	2.01	0.32
7	Hutago	1.54	2.31	83.16	6.31	8.81	1.56	0.16
8	Yubari	1.13	2.67	84.85	6.16	7.20	1.78	0.01
9	Hasima	1.24	2.09	86.59	5.56	6.48	1.22	0.15
10	Kamati	1.05	2.47	89.47	4.61	3.43	1.84	0.65
11	Yatake	1.11	2.74	89.55	4.86	3.07	1.88	0.64
12	Onuki	1.68	1.80	91.16	3.97	2.56	1.78	0.53

boundary to the position $E_{\min.}$ were measured[6]. The ambiguity in finding $\gamma_2 d$ can be avoided by carrying out both open and short circuit measurements by the standard method. Further, as the samples treated here had low dielectric losses the simplification due to Dakin and Works[7] could be introduced into the calculation. Values of ε' obtained independently in this manner by open and short circuit methods were compared with each other (see Table I). A weighted mean value is taken for each sample.

The sample material which was made of coal powder and paraffin-wax was prepared in the form having the exact dimension required by the size of the wave guide, the possible error being ± 0.05 mm. (see Fig. 1).

The measurement at the frequency range between 1~20 kc./sec. was made by a low frequency bridge (Yokogawa BV-z-103) (see Ref. 2 for further information.). For the frequency range between 1~50 Mc./sec. a Q-meter (Yokogawa CA-102) was used. In order to compare the values of dielectric constants obtained by three different apparatuses, the absolute determination of dielectric constants becomes necessary. For this purpose, standard reference materials of dielectric constants provided by the Government Electrotechnical Laboratory, Tokyo, were measured with the apparatuses described above and compared with the results on coals. The maximum error in the dielectric constant is believed to be 5% and reliability in values of dielectric losses are somewhat lower but the latter are not so important in the interpretation as dielectric constants. All the measurements were carried out at room temperature.

Experimental Materials

All the coal specimens examined in these experiments were kindly provided by Dr. H. Honda, Resources Research Institute, Japan. The chemical analyses of the samples are given in Table II. The paramagnetic susceptibility has been examined by the present writers for the following specimens[8]: No. 4, 0.40; No. 8, 0.28; No. 11, 1.23; No. 12, 3.90 10^{-8} c. g. s. electromagnetic units per gram.

On account of its exceptionally high dielectric constant, water is the greatest cause of error in the dielectric measurement. Great care was taken to eliminate any traces of moisture contained in the samples. The coal samples were reduced into powder form below 200 mesh and strongly dried by heating at 105°C and reduced pressure of 10^{-2} mmHg for 30 hr.

About 26 g. of dried powder of coal thus obtained was mixed with 20 g. of melted paraffin-wax, cooled in a mold and cut carefully into a shape suitable for the measurement. The volume percent of coal in the mixture was estimated for each sample by measuring the densities of coal and paraffin-wax. The properties of solid paraffin-wax used are: density 0.914/24°C, m. p. 58.5~60°C, dielectric constant 2.29/1 Mc., 2.26/7000 Mc. and $\tan\delta$ 0.000/1 kc.~7000 Mc.

Results

Dielectric constants ε' and $\tan\delta$ obtained for the coal mixture are recorded in Table III.

In order to determine the value of the dielectric constant of a coal from that of a mixture, Böttcher's equation[1,9,10] was employed, in which ε', ε_1' and ε_2' are the dielectric constant

$$\frac{\varepsilon'-\varepsilon_1'}{3\varepsilon'}=v_2\frac{\varepsilon_2'-\varepsilon_1'}{\varepsilon_2'+2\varepsilon'} \tag{2}$$

of the mixture, the paraffin-wax and coal particles, respectively and v_2 is the volume fraction of the coal particle in the mixture. The value ε_2' for each specimen of coal thus obtained is shown in parentheses below that for the mixture.

8) H. Honda, K. Chitoku, Y. Yokozawa and K. Higasi, This Bulletin, **31**, 891 (1958).

9) C. J. F. Böttcher, *Rec. trav. chim.*, **64**, 47 (1945); C. J. F. Böttcher, "The Theory of Electric Polarisation", Elsevier, Amsterdam (1952), p. 417.

10) Y. Zyomoto, *J. Fuel Soc. Japan*, (*NenryoKyokaishi*), **37**, 248 (1958).

TABLE III. DIELECTRIC CONSTANTS (ε') AND LOSS TANGENT (UNIT: 10^{-4}) OF COAL MIXTURES MEASURED AT FREQUENCIES 1 kc./sec.~7000 Mc./sec. AND DIELECTRIC CONSTANTS OF COALS ESTIMATED (ε_2')

No. (Specimen)	Vol. % of coal		1 kc.	3 kc.	10 kc.	20 kc.	1 Mc.	3 Mc.	50 Mc.	7000 Mc.
		ε'	3.17	3.17	3.19	3.19	3.06	3.03	3.01	2.86
1	40.1	ε_2'	(4.75)	(4.75)	(4.82)	(4.82)	(4.51)	(4.44)	(4.38)	(3.95)
		$\tan\vartheta$	238	169	113	83	92	101	108	142
		ε'	3.26	3.21	3.21	3.21	3.19	3.18	3.14	2.89
2	49.0	ε_2'	(4.45)	(4.32)	(4.32)	(4.32)	(4.35)	(4.34)	(4.24)	(3.66)
		$\tan\vartheta$	91	67	58	72	72	84	127	158
		ε'	3.21	3.23	3.22	3.22	3.12	3.10	3.08	2.86
3	46.0	ε_2'	(4.48)	(4.53)	(4.51)	(4.51)	(4.33)	(4.29)	(4.24)	(3.69)
		$\tan\vartheta$	64	72	61	49	68	76	95	134
		ε'	3.09	3.10	3.09	3.05	3.10	3.09	3.08	2.81
4	48.0	ε_2'	(4.07)	(4.09)	(4.07)	(3.97)	(4.17)	(4.16)	(4.14)	(3.50)
		$\tan\vartheta$	83	64	50	61	52	53	67	99
		ε'	2.89	2.89	2.89	2.89	2.78	2.78	2.77	2.67
5	47.4	ε_2'	(3.59)	(3.59)	(3.59)	(3.59)	(3.40)	(3.42)	(3.39)	(3.18)
		$\tan\vartheta$	32	58	55	40	39	37	50	92
		ε'	2.87	2.87	2.81	2.81	2.81	2.81	2.79	2.79
6	48.4	ε_2'	(3.52)	(3.52)	(3.38)	(3.38)	(3.45)	(3.46)	(3.41)	(3.44)
		$\tan\vartheta$	229	143	138	97	44	41	48	70
		ε'	2.85	2.79	2.79	2.79	2.79	2.79	2.78	2.68
7	50.4	ε_2'	(3.42)	(3.29)	(3.29)	(3.29)	(3.35)	(3.36)	(3.34)	(3.14)
		$\tan\vartheta$	106	65	43	47	22	25	31	59
		ε'	2.77	2.77	2.77	2.77	2.76	2.76	2.76	2.69
8	49.6	ε_2'	(3.26)	(3.26)	(3.26)	(3.26)	(3.30)	(3.31)	(3.31)	(3.18)
		$\tan\vartheta$	68	10	26	22	17	19	16	51
		ε'	2.84	2.84	2.84	2.84	2.77	2.77	2.77	2.73
9	49.5	ε_2'	(3.42)	(3.42)	(3.42)	(3.42)	(3.32)	(3.34)	(3.34)	(3.27)
		$\tan\vartheta$	66	75	81	65	25	21	33	75
		ε'	2.83	3.87	2.89	2.89	2.81	2.81	2.80	2.79
10	47.2	ε_2'	(3.45)	(3.55)	(3.60)	(3.60)	(3.48)	(3.49)	(3.47)	(3.47)
		$\tan\vartheta$	67	120	46	23	19	21	21	25
		ε'	2.85	2.86	2.86	2.86	2.84	2.83	2.82	2.77
11	45.9	ε_2'	(3.54)	(3.57)	(3.57)	(3.57)	(3.59)	(3.58)	(3.56)	(3.46)
		$\tan\vartheta$	152	68	72	48	21	18	13	26
		ε'	3.19	3.05	3.05	3.05	2.89	2.89	2.87	2.79
12	40.0	ε_2'	(4.83)	(4.37)	(4.37)	(4.37)	(3.98)	(4.00)	(3.94)	(3.73)
		$\tan\vartheta$	886	563	311	192	60	37	21	40
Paraffin[a]		ε_1	2.34	2.34	2.34	2.34	2.29	2.28	2.28	2.26

a) Values of ε_1 used in calculating ε_2 by Eq. 2.

Dielectric Constant and Oxygen Content.—Dielectric constants obtained at 1 kc./sec. and 7000 Mc./sec. are plotted against oxygen content (Fig. 2). Intermediate frequency dielectric constants lie between the two curves.

Dielectric constants decrease sharply at first but increase regularly with increase in oxygen content after reaching a minimum at about 8%. From functional group analysis of coal it has been found that the amounts of hydroxyl groups, carboxyl groups, carbonyl groups and methoxyl groups increase with oxygen content[11]. Among them, the hydroxyl group is regarded as the most important*. From the infrared analysis, the absorption band at 3.0 μ is ascribed to the existence of associated OH and NH bonds[12]. One might infer from these

11) M. Ihnatowicz, *Prace Glownego Inst. Gornictwa* (Katowice) *Komun.*, 125 (1952); L. Blom, L. Edelhausen and D. W. van Krevelen, *Fuel*, 36, 135 (1957) cited by Ref. 3, p. 217.

* According to private communication from Dr. H. Honda, functional analysis gives the following data. No. 2, Tempoku. O, 23.79%; O_{OH}; 10.3%; O_{COOH}, 0.4%. No. 6, Pocahontas: O, 8.86%; O_{OH}, 2.4%; O_{COOH}, 0.5%. No. 8, Yubari: O, 7.20%; O_{OH}, 0%; O_{COOH}, 0.9%. No. 10, Kamati: O, 3.43%; O_{OH}, 0%; O_{COOH}, 0%.

12) C. G. Cannon and G. B. B. Sutherland, *Trans. Faraday Soc.*, 41, 279 (1945) and others, see Ref. 3, p. 185.

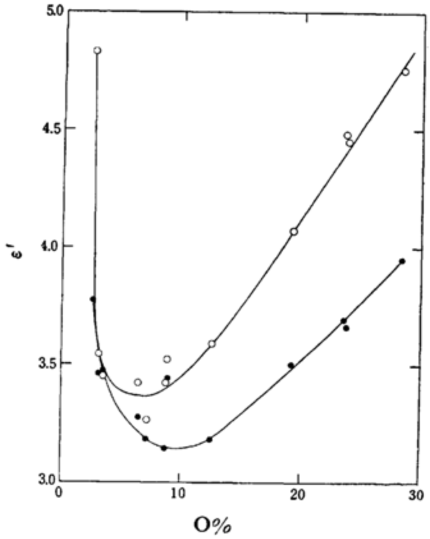

Fig. 2. Dielectric constants of coals (ε_2') at frequencies 1 kc./sec. and 7000 Mc./sec. and oxygen content (dry-ash-free basis).

—○— 1 kc. —●— 7000 Mc.

pieces of evidence that polar groups which are closely associated with the oxygen content are mainly responsible for the dielectric constant of coal containing more than 10% oxygen. This seems parallelled by the fact that dielectric constants of polymers increase with the amount of polar groups contained in them[13,14]. Indeed, coals generally speaking are a sort of high-polymers having some polar groups.

Dielectric Constant and Carbon Content. — Dielectric constants obtained at three frequencies, 1 kc./sec., 1 Mc./sec. and 7000 Mc./sec. are plotted against carbon content (Fig. 3). For the sake of comparison, optical dielectric constants as defined by the refractive index n and the absorption index k for visible light of the wavelength 5460 Å.

$$\varepsilon_\infty = n^2(1-k^2) \tag{3}$$

are plotted as dotted lines in the same graph. The optical measurement is due to Huntjens and van Krevelen[15]. There are available other optical measurements[16], but they are not recorded here in order to prevent the figure from becoming overcrowded with points.

From a glance at Fig. 3, it will be seen that in the region C 85~89% all the dielectric constants, at audio, radio and microwave frequencies converge so that they become almost identical to each other. The plotted curve for

13) R. M. Fuoss, *J. Am. Chem. Soc.*, 63, 369 (1941).
14) C. P. Smyth, "Dielectric Behavior and Structure", McGraw-Hill Book Co., Inc., New York, N. Y., 1955.
15) F. J. Huntjens and D. W. van Krevelen, *Fuel*, 33, 88 (1954).
16) D. G. Murchison, *Brennstoff Chem.*, 39, 47 (1958); S. R. Broadbent and A. J. Shaw, *Fuel*, 34, 385 (1955).

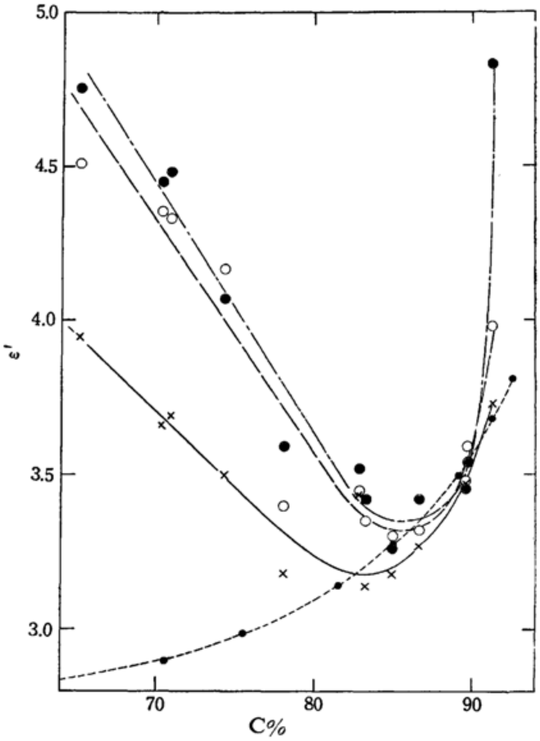

Fig. 3. Dielectric constants of coals (ε_2') at various frequencies and carbon contents of coals.

---⊙--- 1 kc.
——○—— 1 Mc.
——×—— 7000 Mc.
----●---- van Krevelen $n^2(1-k^2)$

optical dielectric constants lies between these three curves. This is probably anomalous, but it must be remembered that optical dielectric constants were obtained for coals of different origins**. It may be reasonable to assume that microwave values in this region are almost identical with the optical dielectric constant.

With the decrease in carbon content (less than 80%) the difference between the optical and the microwave dielectric constants becomes significant. It was unexpected that there should be such a large difference between these values in this region. If this difference is due to the rotation of polar groups, these groups must have a small size[14]. One might infer from this that the perticular polar groups responsible for this phenomenon are hydroxyl groups situated at the periphery of the aromatic system, because the internal rotation of non-associated OH groups around the C–O axis will be least sterically hindered.

Fischer found that diphenyl ether has an anomalously small relaxation time[17]. Recently

** In fact, Broadbent and Shaw[16] gave smaller optical dielectric constants than van Krevelen.
17) E. Fischer, *Z. Elektrochem.*, 53, 16 (1949).

an explanation has been given for this observation as arising from the internal rotation of the two benzene rings around C–O axes[18]. Coal is sometimes considered as built up of aromatic ring complexes linked through oxygen or non-aromatic bridges containing oxygen atoms[19]. Possibly these units might provide certain contributions to the microwave dielectric constant, if a particular type of internal rotation is to occur. But roughly speaking the hydroxyl group will be mainly responsible for this effect.

It would be a matter of speculation to estimate dipole moments for coals. However, if coal may be regarded as a supercooled liquid[3], the Onsager equation for liquids may be used for this purpose[1e,f]. Further, on account of the low dielectric constant, the Debye equation will give practically the same moment values the Onsager equation[13]. It can be shown that the dipole moment μ for the unit having the molecular volume M/d is

$$\mu = A\left[(\varepsilon_2' - \varepsilon_\infty)\frac{M}{d}\right]^{1/2} \tag{4}$$

where A for Debye equation is

$$A^2 = \frac{27kT}{4\pi N(\varepsilon_2'+2)(\varepsilon_\infty+2)}\ , \tag{5}$$

in which k is Boltzman constant, N is Avogadro constant and T is the absolute temperature. Further, at room temperature, $T=298°$C

$$A^2 = \frac{0.147\times10^{-36}}{(\varepsilon_2'+2)(\varepsilon_\infty+2)} \qquad \text{Debye}$$

In similar way it can be shown that

$$A^2 = \frac{0.147\times10^{-36}(2\,\varepsilon_2'+\varepsilon_\infty)}{3\varepsilon_1'(\varepsilon_\infty+2)^2} \qquad \text{Onsager}$$

There exist no reliable data for the molecular weight of coal. According to van Krevelen and Schuyer[3] the average molecular weight is in the vicinity of 2500. We shall assume an arbitrary molecular volume $M/d=2000$ for the purposes of the present calculation. For coal with a density of 1.3, this assumption gives a molecular weight of 2600.

Regarding the static dielectric constant ε_2' in Eq. 1 we shall use values obtained at frequency of 1 kc. Optical dielectric constants ε_∞ are calculated by Eq. 3 using van Krevelen's data, which are supposed to be somewhat higher than those of the coals considered here; the estimated dipole moment is consequently slightly smaller than the actual moment. Further, the A value for the Debye equation will be used in the calculation of the moment. The result is shown in Table IV.

TABLE IV. DIPOLE MOMENTS OF COALS (μ) FOR THE MOLECULAR VOLUME ($M/d=2000$)

No.	Specimen	C%	ε_2'/1 kc.	ε_∞	μ, D
1	Taihei	65.10	4.75	2.85	4.1
2	Tempoku	70.37	4.45	2.90	3.8
3	Nakago-kaso	70.92	4.48	2.91	3.8
4	Nakago	74.33	4.07	2.96	3.3
5	Kasima	77.94	3.59	3.05	2.4
6	Pocahontas (USA)	82.79	3.52	3.20	1.8
7	Hutago	83.16	3.42	3.21	1.5
8	Yubari	84.85	3.26	3.28	0
9	Hasima	86.59	3.42	3.36	~0
10	Kamati	89.47	3.45	3.53	0
11	Yatake	89.55	3.54	3.54	0
12	Onuki	91.16	4.83	3.68	—

As an example we shall consider a dipole moment 3.8 D obtained for specimen No. 2 Tempoku brown coal. If this magnitude of moment arises only from OH groups which have complete freedom of rotation around C–O axis, the number of OH groups in a volume 2000 cc. will be estimated by

$$\mu^2_{\text{obs}} = n\cdot\mu^2_{\text{OH}} \tag{6}$$

where μ_{obs} and μ_{OH} are moments observed and that of the OH group respectively. Putting $\mu_{\text{obs}}=3.8$ D and $\mu_{\text{OH}}=1.56$ D[20] we obtain $n=5.9$; there are about 6 OH groups capable of rotation.

On the other hand, functional analysis reveals that this particular coal specimen has a hydroxyl (phenolic) percentage of 10.3%. In molecular volume $M/d=2000$ ($d=1.41$), this gives 291 g. oxygen, that is 18 OH groups. Therefore, one may conclude that about one-third of the total OH groups can rotate freely. The hydroxyl percentage chemically determined does not represented the amount of OH group actually existing in coal. There is no strong reason for supposing that a certain fraction of OH groups has complete freedom of rotation while another fraction has not and that other polar groups can not make a contribution to dielectric constant. In fact, the estimation of the dipole moment described above and its related discussion has only qualitative significance.

Summary

1. Using the transmission method, resonance method and bridge method, dielectric constants

18) K. Higasi and C. P. Smyth, to be published in *J. Am. Chem. Soc.*

19) S. G. Ward, *J. Inst. Fuel*, 21, 80 (1947); cited in Ref. 3, p. 207.

20) Y. Kurita and M. Kubo, This Bulletin, 27, 364 (1954). This is not the moment of OH group moment itself but the component of the phenolic OH moment perpendicular to the C-O axis.

and losses are measured on paraffin-wax mixtures of twelve specimens of coal ranging from C 65 to 92%.

2. Dielectric constants of coals are estimated for these coals by means of Böttcher's equation.

3. The relation between dielectric constant and oxygen content is discussed and it is shown that polar groups contribute to dielectric constant.

4. From the comparison with optical dielectric constant, the motion of dipoles in coals in the electric field can be discussed. Rough estimates of dipole moments are also given.

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