Dielectric Investigation on Coals. IV. Notes on Dipole Moment

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Introduction

Some years ago it was suggested to one of the present writers that a determination of electric dipole moment should be most desirable for coals. Indeed, the usefulness of dipole moments for attacking problems in structural chemistry has long been appreciated[1]. As was true in the cases of simpler molecules, it was then hoped, they migt become the most effective means among the various physical methods applicable for the study of coal structure.

Now, rather ample data[2,3] on the dielectric properties of coals being available, it was thought worth while to make some trials in this direction. One may say that such a trial is destined to be labour lost, since in the solid state the orientation of polar groups is almost completely restricted by lattice forces. However, coals differ from most of the crystalline solids. According to van Krevelen[4] the main constituent such as vitrain is to be regarded as a supercooled liquid. Perhaps coals are sorts of organic glasses or polymers[4]. If this view be correct, one may use equations for liquids in determining a dipole moment[5]. This affords a basis for the trial and speculations to be described in the present paper.

Equations of Liquids

From among many equations for liquids, the Onsager equation[6] is the only one to have been used extensively in calculating the dipole moment.

$$\mu^2=\frac{9kT}{4\pi N}\frac{M}{d}\frac{(2\varepsilon+\varepsilon_\infty)(\varepsilon+2)}{3\varepsilon(\varepsilon_\infty+2)}\times\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\right) \qquad (1)$$

in which μ is the molecular dipole moment, k is the Boltzmann constant, T is the absolute temperature, N is the Avogadro number, M is the molecular weight and d is the density. In the above equation ε is the ordinary dielectric constant*, while ε_∞ is the optical dielectric constant, or the dielectric constant measured at the frequencies which are so high that the permanent dipoles are unable to exert any influence. In the original form of Eq. (1) the square of refractive index, n^2 is used instead of ε_∞. The above equation is a modification due to Smyth[7] and useful for the present work, where the atom polarization may play a significant role.

The Debye equation is originally an equation for gases and vapours. Its use will be considered on account of the simpler form:

$$\mu^2=\frac{9kT}{4\pi N}\frac{M}{d}\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\right) \qquad (2)$$

The Onsager equation holds mostly for highly polar liquids[8,9]. On the contrary the Debye equation is known to be valid for non-polar liquids and a few groups of polar liquids such as ethers[10], amines[11] and chloroform[12]. There is uncertainty as to the choice of a proper equation for liquids, if other equations excepting the above two are left out of consideration.

The difference in the above equations lies in the factor

$$S=\frac{(2\varepsilon+\varepsilon_\infty)(\varepsilon+2)}{3\varepsilon(\varepsilon_\infty+2)} \qquad (3)$$

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[1] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York (1955); J. W. Smith, "Electric Dipole Moments," Butterworths Sci. Publ., London (1955). K. Higasi, "Foundation of Structural Chemistry—Dipole Moments," Kawade Book Co., Tokyo (1952).

[2] I. Miyasita and K. Higasi, This Bulletin, **30**, 513 (1957)

[3] I. Miyasita, K. Higasi and M. Kugo, This Bulletin, **30**, 550 (1957).

[4] D. W. van Krevelen, *Brennstoff-Chem.*, **34**, 167 (1953).

[5] C. P. Smyth, *op. cit.*, p. 226; J. W. Smith, *op. cit.*, p. 145; K. Higasi, *op. cit.*, p. 14.

[6] L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

* In the present article ε will be used instead of ε'.

[7] C. P. Smyth, *op. cit.*, p. 23.

[8] C. J. F. Böttcher, *Physica*, **6**, 59 (1939).

[9] H. Fröhlich, *Trans. Faraday soc.*, **42A**, 39 (1946).

[10] K. Higasi, *Sci. Pap. Inst. Phys. Chem. Res.*, **24**, 57 (1934).

[11] M. Shirai, This Bulletin, **29**. 518 (1956).

[12] R. J. W. Le Fèvre et al., *J. Chem. Soc.*, 487, 491, 496 (1936).

If $S=1$*, Eq. (1) will become the same with Eq. (2).

In most bituminous coals both values of ε and ε_∞ (as estimated from n) do not much vary with the specimen. On putting some average values, $\varepsilon=4$ and $\varepsilon_\infty=3.24$, in Eq. (3), S will be evaluated as 1.07. Consequently the dipole moment calculated from Eq. (1) slightly differs from that estimated by Eq. (2), the difference being only 3–4 per cent. This result is very encouraging, since an error of less than 5% in moment is insignificant in the present case.

Both Eqs. (1) and (2) can be reduced to a very simple equation

$$\mu=A[(\varepsilon-\varepsilon_\infty)M/d]^{1/2} \tag{4}$$

where A has the values

$$A_1^2=0.147/(\varepsilon+2)(\varepsilon_\infty+2) \quad \text{(Debye)} \tag{5}$$

$$A_2^2=0.147(2\varepsilon+\varepsilon_\infty)/3\varepsilon(\varepsilon_\infty+2)^2 \quad \text{(Onsager)} \tag{6}$$

in which dipole moment μ is expressed in Debye unit (10^{-18}e.s.u.cm.) and the temperature is assumed to be 20°C.

Further, in a rough estimation the coefficient A may be regarded as a constant. Usually for coals of C% 65–90 ε lies between 3.3–5.5 and ε_∞ between 2.8–4.0 (see Tables I and II). The values of A (Debye) are 0.075–0.057 and A (Onsager) 0.078–0.061, respectively.

For $A=0.068$ ($\varepsilon=4$, $\varepsilon_\infty=3.24$) and $M/d=300$ cc Eq. (4) becomes

$$\mu=1.17\sqrt{\varepsilon-\varepsilon_\infty} \tag{7}$$

The above equation is incorrect but convenient for a quick judgement. Moment values calculated from Eq. (7) are shown by curve b in Fig. 1. In this figure two other curves a and c are drawn for the cases with $M/d=400$ and 200, respectively.

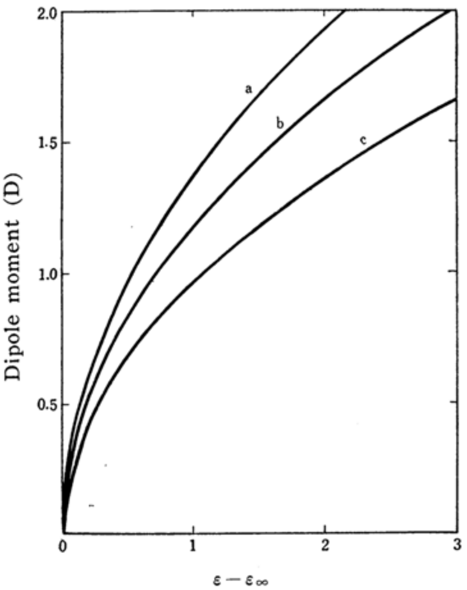

Fig. 1. Dipole moment of coal as a function of the quantity $\varepsilon-\varepsilon_\infty$. Curve a, $M/d=400$; curve b, $M/d=300$; and curve c, $M/d=200$.

Dielectric Constant

Both Eqs. (4) and (7) well illustrate the physical significance of the dielectric constant. The dielectric constant ε of a polar substance has three origins: (a) the orientation effect of the permanent dipole, (b) the displacement effect of the atoms, and (c) the displacement effect of the electrons. As the optical dielectric constant ε_∞ is contributed only from the latter two effects, the difference $\varepsilon-\varepsilon_\infty$ represents the part of dipole orientation.

As the dielectric constant is a function of frequency, a question arises as to the method of choosing a proper ε value for the calculation. In the study of liquids, ε values at frequencies 1–10 Mc/s have been usually employed[13], because the measurement is easiest at these frequencies and also because the obtained values are generally equal to static dielectric constants. As the relaxation time is expected to be different from liquids, a more cautious attitude is demanded in treating coals. Before being able to choose a proper value of ε one must examine the dependence of the dielectric constant upon frequency.

There are found in coals at least three types of frequency dependences. In one of them (A type) there is apparently little dispersion: that is, both the dielectric constant and loss factor have values almost indepedent of frequency in the range of 300 c/s—50 Mc/s. See curves (A) in Figs. 2 and 3. Examples: most of the Japanese bituminous coals. In the second type (B type), dispersion appears to exist in the high frequency region. Examples: Tempoku brown coal (specimen VI) and probably two other low rank coals (E1 and E2). The third type (C type) is charac-

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* If ε is equal to ε_∞, S will become unity. See further Böttcher, "The Theory of Electric Polarisation," Elsevier Publ. Co., Amsterdam (1952).

[13] C. P. Smyth, *op. cit.*, p. 209; J. W. Smith, *op. cit.*, p. 30; Y. Morino and I. Miyagawa, *Kagaku-no-Ryoiki*, Spec. no., **8**, 1 (1953).

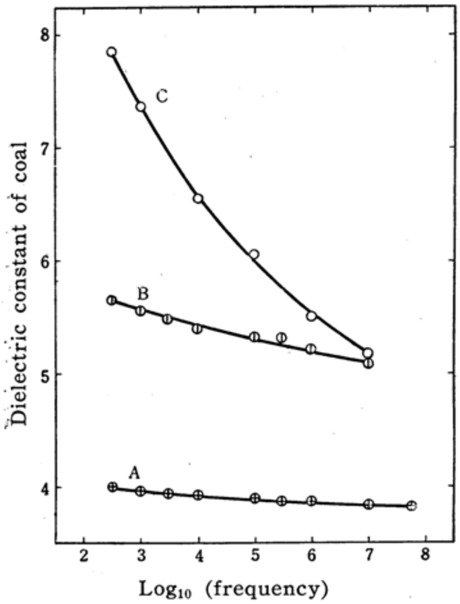

Fig. 2. Frequency dependence of dielectric constant of coal. ⊕, Moziri bituminous coal; ⦶, Tempoku brown coal; and ○, British coal (Durham). Data for the British coal were obtained from powdered mixture.

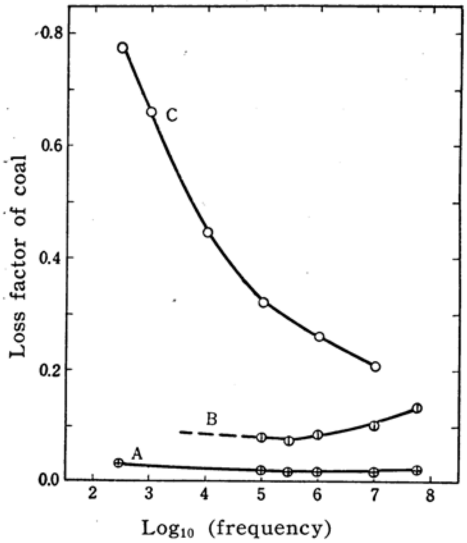

Fig. 3. Frequency dependence of loss factor of coal. ⊕, ⦶, and ○, the same with Fig. 2.

-terized by high loss factor and high dielectric constant at the low frequency region. Examples: European and American high rank coals (F1-5).

In view of the above facts the following assumptions will be taken as a basis for some considerations.

1) For A type coals, 1 Mc/s values are preferred. The Q meter gives most reliable values when measured at this frequency.

2) For B type coals, 1 kc/s values are taken. Lower frequency values in general may be preferable. But there is no guarantee that moisture was completely removed. The impedance bridge gives best values at 1 kc/s.

3) For C type coals, 10 Mc/s values are arbitrarily selected. It is questionable whether the dipole rotation at this high frequency is as free as at the static fields. But the high ε values at low frequencies may not be attributable to the usual dipole effect.

Opitical Dielectric Constant and Atom Polarization

The optical dielectric constant ε_∞ is often assumed as equal to the square of refractive index for visible light. But the refraction of visible light is due primarily to the displacement of electrons, while ε_∞ is due to the displacement of both electrons and atoms in the molecule. The small difference between the two determines the magnitude of the atom polarizations. Regarding the latter quantity there exists no general relationship, but sometimes it was assumed for the sake of convenience that the atom polarization amounts to 5% or 10% of the electron polarization[14].

There is available no literature concerning the refractive index of Japanese coals. The only existing data are those on European coals by van Krevelen[4] who found a relation between the refractive index and carbon content (see curve 3 in Fig. 4).

Dielectric constant of Mayazi coal B (C% 85.24) measured at a micro-wave frequency (4000 Mc/s) is 3.35[15]. This ε value is just equal to the square of the same carbon content estimated from the curve ($n_D=1.83$). From this astonishing coincidence, one may imagine that ε at the frequency of 4000 Mc/s is equal to ε_∞, and further that the contribution from atom polarization is insignificant. Yatake coal (C% 89.4) has ε 3.45 at 10 Mc/s which is even smaller than $n_D^2=3.65$. Again this may indicate that the contribution from the atom polarization is not important.

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[14] C. P. Smyth, *op. cit.*, p. 416; J. W. Smith, *op. cit.*, p. 256.

[15] K. Higasi, I. Miyasita and Y. Ozawa, This Bulletin, **30**, 546 (1957).

By reason of the above it will be assumed in the next section that the square of refractive index for D-line approximately represents ε_∞ of the coal of the corresponding carbon content.

There are two points to be considered against this assumption. First, the neglect of atom polarization is not justified by the above argument. To provide an answer for this, two curves 1 and 2 in Fig. 4 are plotted. As in usual treatments of atom polarization the following equation is considered.

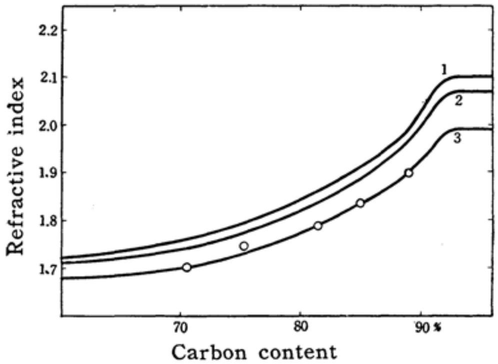

Fig. 4. Variation of refractive index with carbon content. Curve 1, given by the assumption $P_A=7\%\ P_E$; curve 2, given by the assumption $P_A=5\%\ P_E$ and curve 3, observed by van Krevelen[4] on European coals.

$$\frac{n'^2-1}{n'^2+2}=(1+\delta)\frac{n^2-1}{n^2+2} \tag{8}$$

The values of modified refractive indices n' which have been obtained from Eq. (8) are plotted in the graph*. (Curve 2: n' for $\delta=0.05$; curve 1: n' for $\delta=0.07$). By using the values n'^2 for ε_∞, check on the effect of atom polarization will be made.

Second, there is no reason why carbon content should be the determining factor of the refractive index. Further, one is not certain whether or not van Krevelen's relation obtained for European coals is applicable to all the Japanese coals. Under these circumstances any discussion on ε_∞ has ambiguity to be cleared up in the future.

Molecular Volume and Dipole moment

Difficulties in measuring the molecular weight of coal are well-known. It is not right to speak of a molecual dipole moment for a substance with unknown molecular weight. But this situation may be saved by considering the fact that a molecular dipole in coal may not rotate as a whole. Actually some rotatable groups in a molecular unit will orient with the direction of an externally applied field. Therefore the "molecular weight" for the present study need not to be a definite quantity.

In the present work a molecular volume 300 cc will be somewhat arbitrarily chosen without regard to the actual weight of coal. Dipole moments of coals are all to be calculated with reference to this volume. If the density of the coal is 1.4, the apparent molecular weight will amount to 420. Dipole moments thus calculated from Eq. (2) are summarized in Tables I and II. Values in Table II are obtained

TABLE I

DIPOLE MOMENTS OF COALS

Coal	C %	ε/freq.	ε_∞	μ
VI Tempoku (brown coal)	66.62	5.56/1 kc (5.20/1 Mc)	2.87	1.78 (1.69)
Vb Mitui-bibai	78.40	4.19/1 Mc	3.07	1.24
Va ,,	80.12	4.10/1 Mc	3.14	1.15
V ,,	80.47	3.61/1 Mc	3.15	0.83
Vc ,,	80.62	(4.70/1 kc)	3.16	(1.39)
IV Akabira	80.76	3.66/1 Mc	3.16	0.86
II Moziri	81.71	3.92/1 Mc (4.37/1 kc)	3.20	1.01 (1.23)
IIIa ,,	82.07	3.69/1 Mc	3.21	0.84
III ,,	82.98	3.88/1 Mc	3.26	0.93
I ,,	85.25	4.47/1 Mc	3.35	1.18

Values without parentheses are preferred.

TABLE II

DIPOLE MOMENTS OF COALS

(ε is estimated from powdered mixture)

Coal	C %	ε/freq.	ε_∞	μ
E1 Taihei (lignite)	65.1	4.78/1 kc (4.45/1 Mc)	2.86	1.58 (1.48)
E2 Tempoku (brown coal)	70.2	4.58/1 kc (4.38/1 Mc)	2.90	1.50 (1.43)
C7 Sunagawa	81.84	3.98/1 Mc	3.20	1.04
C3 ,,	82.09	3.56/1 Mc	3.21	0.72
B Mayazi	85.24	4.02/1 Mc	3.35	0.95
F4 Pocahontas (U.S.A.)	87.99	4.83/10 Mc (5.16/1 Mc)	3.53	1.22 (1.33)
F1 India	88.03	4.71/10 Mc (5.00/1 Mc)	3.54	1.17 (1.27)
F5 Durham (England)	89.31	5.18/10 Mc (5.51/1 Mc)	3.63	1.29 (1.39)
D1 Yatake	89.4	3.45/1 Mc	3.65	0

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* The choice of $\delta=0.05$ for the correction of the atom polarization is a practice due to Groves et al. (*J. Chem. Soc.*, 971 (1935); 1779 (1937)). The reason for choosing $\delta=0.07$ is as follows. Suppose that coal is composed of two parts: for the major part (70%), P_A is taken as 3.4% P_E from the data of benzene, toluene and ethylene, and for the remaining part (30%), $P_A=15\%\ P_E$ is assumed from the data for alcohols, ethers and ketones (J. W. Smith, op, cit., Table 39, p. 261). Atom polarization of coal will then have the value of 7% of P_E, viz., $\delta=0.07$.

from powdered mixtures, so that they are less accurate*.

Groenewege, Schuyer and van Krevelen[16] gave a dipole moment 0.5 D for a certain coal. No particulars were reported except that they employed Eq. (2) and that the molecular weight for the coal was taken as 420.

Discussion

Polar groups which might exist in coals[17] will be assumed to have the following magnitudes of dipole moments. O–H 1.51; C–O 0.74; C=O 2.3; N–H 1.31 D[18]. Some of these groups must interact upon each other**, and some others must be in a state of complete non-rotation on account of the strong field of lattice forces. Suppose as an extreme case in spite of the above, that all these groups can rotate independently. Then the resultant moment μ will be given by

$$\mu^2 = 1.51^2 n_{\mathrm{O-H}} + 0.74^2 n_{\mathrm{C-O}} + 2.3^2 n_{\mathrm{C=O}} + 1.31^2 n_{\mathrm{N-H}} \qquad (9)$$

where $n_{\mathrm{O-H}}$, $n_{\mathrm{C-O}}$, etc. represent the number of O—H groups, etc. in a molecule —or more exactly in a molecular unit defined by $M/d=300$. In a special case in which none of the others except the O—H group are important so that they can be neglected,

$$n_{\mathrm{OH}} = \mu^2/2.28 \qquad (10)$$

The numbers of O—H groups will then be calculated. The polarity of brown coals corresponds approximately to one rotatable O—H group, while others to some small fractions in the molecular unit.

For three specimens of Moziri coals a comparison is made between calculated values and the results of chemical analyses.

TABLE III

A COMPARISON WITH CHEMICAL COMPOSITION

	Coal	C %	O %	d	M	N_{oxy}	$n_{\mathrm{O\text{-}H}}$
I	Moziri No. 4	85.25	6.91	1.357	407	7.00	0.61
II	,, No. 3	81.71	9.78	1.340	402	8.04	0.45
III	,, No. 9	82.98	9.07	1.304	391	7.39	0.39

Table III shows the values of the molecular weights as calculated from specific gravities and $M/d=300$. From M and C%, the number of oxygen atoms, N_{oxy}, in this molecular unit is obtained. The ratio $n_{\mathrm{O-H}}/N_{\mathrm{oxy}}$ is 0.05–0.09. Reliablility of such estimation is certainly low, but it suggests that the rotatable part is only a small fraction of the total oxygen.

It is evident from Table II that Yatake coal (D1) is non-polar. Besides the fact that no moment is detected, there is also no anomalous dispersion in the wide range of frequencies. (See curves in Figs. 3 and 4 in the preceding paper[3].)

For some coals (IIIa, IV and C3) small moments below 0.9D are observed. Regarding these small moments there is uncertainty whether they are real or not. To make this point clearer a little examination on errors will be necessary. First, error in measuring ε amounts to 5–10%. If the deviation in ε is 0.2–0.4, a small moment below 0.5–0.7D will not be distinguishable from zero. See curve b in Fig. 1. Second, there exists an error concerning the estimation of atom polarization, even if van Krevelen's relation be actually valid. An inspection of curves in Fig. 4 will reveal that a small moment less than 0.6 D is unreliable. Under these circumstances it may not be wise to enter into any serious discussion on small moments observed.

Besides the comparatively small polarities found for bituminous coals there is another phenomenon which seems to suggest that these coals are nearly nonpolar. That is, there has been observed scarcely any distinct dispersion* in the frequency range of this experiment. See curves A for a Moziri coal in Figs. 2 and 3.

There is one important fact in this connection that Mayazi coal, which has a moment value 0.95 D, shows a remarkable change in ε between 4000 Mc/s and 10 Mc/s[15]. This strongly suggests that anomalous dispersion due to dipole rotation exists in this region and therefore that the magnitude 0.9 D is real. This is encouraging, but it may not be very convinicing. In view of the fact that the above offers just one example and further that the microwave measurement of the desired accuracy is still lacking, it is premature to speak, with confidence at least, of the polarity of these bituminous coals.

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* Maximum errors in ε are ± 5% in Table I and ± 10% in Table II.

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

[17] See for instance, R. A. Friedel and J. A. Queiser, *Anal. Chem.*, **28**, 22 (1956).

[18] C. P. Smyth, *op. cit.*, p. 244.

** Regarding the interaction between polar groups see for example S. Mizushima, Y. Morino und K. Higasi, *Physik. Z.*, **35**, 905 (1934); S. Mizushima, "Structure of Molecures and Internal Rotation," Academic Press, New York (1954), p. 7.

* Excepting those in the low frequency region which may be due to other causes.

Summary

If coal be regarded as a supercooled liquid, a basis will be provided for determining the dipole moment of coals. Further uncertainty as to choosing a proper equation for liquids is dispelled by the fact that the Onsager equation gives for coal almost the same magnitude of dipole moment as obtained by the Debye equation.

After discussion focussed on the values of the ordinary and optical dielectric constants, dipole moments are evaluated for 19 coal specimens including four samples of foreign origin.

Brown coals are found to have a moment near to that of one O—H group. The polarity of bituminous coal is in general too small to be distinguishable from zero. These results are consistent with the observations on the frequency dependence of dielectric constant and loss factor of these coals.

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