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Anomalous Viscosity of Bitumen Solutions and the Agglomeration of "Molecules"

Katsuya INOUYE,[*] Junichi TATSUTA[*1] and Tsutomu SAKABE[**]

[*] *Department of Chemistry, Faculty of Science, Chiba University, Chiba*
[**] *Resources Research Institute, Kawaguchi*

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The flow property of catechol and phenol solutions of 14 bitumen fractions was examined by means of a horizontal viscometer to compare with the molecular weight values of the fractions determined in each solvent. The catechol solutions showed Newtonian flow which corresponds to the homogeneous solutions containing molecules of a limited value of molecular weight. The molecular weight from phenol solutions varies with the fractions, and all fractions showed non-Newtonian (structural) viscosity. The experimental results indicated that bitumens in phenol agglomerate to different extent particular to each fraction. It was presumed that the stress destroys the agglomerated state to a monodisperse state, which is gradually recovered to the original state on standing. It was noted however that the unit particle (or molecule) composing each fraction is not identical in the apparent size in phenol, but varies with fractions.

It has been well recognized that the apparent molecular weight of bitumen fractions extracted from coals or hydrogenated coals showed values within the limited range of 200 to 350, when determined cryoscopically in catechol.[1,2] The fact has consequently led to the concept that the coal or bitumen as coal component is composed of "molecules" of molecular weight of approximately 300. The apparent molecular weight determined by use of other solvents, however, gives different values with fractions. For example, the molecular weight obtained by Weiler *et al.*,[1] determined from the boiling-point elevation of benzene solutions and the freezing-point depression of diphenyl solutions vary considerably with the fractions.

The problem has not been solved if the coal "molecules" of an identical size exist, which may form, in particular situations, their aggregated clusters, or if the varying molecular weights indicate continuously differing dimensions of coal constituting substances.

The present work intends to ascertain the existence of the aggregated state of bitumen "molecules" in the specific solvent by determining the viscosity behavior of the solution. The Newtonian viscosity would be observed, if the "molecules" of the same size or covalently bonded particles of different sizes are dissolved in a solvent, while an anomalous (non-Newtonian) viscosity would appear due to the breaking-down of apparent aggregates with the shear stress in the course of the viscosity measurement.

Experimental

a) Materials. The preparation of fractions has been described in a preceding paper.[3] A Japanese bituminous coal (Yubari) of 83% carbon was ground under 60 Tyler meshes and extracted with benzene

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[*1] Present address: Nihon Tenkazai Kogyo Co., Ltd., Itabashi, Tokyo.

1) J. F. Weiler, J. J. Ward and H. C. Howard, *J. Am. Chem. Soc.*, **64**, 734 (1942).

2) I. G. C. Dryden, *Fuel*, **31**, 176 (1952).

3) T. Sakabe, K. Inouye, K. Ouchi and H. Honda, *J. Fuel Soc. Japan*, **32**, 610 (1953).

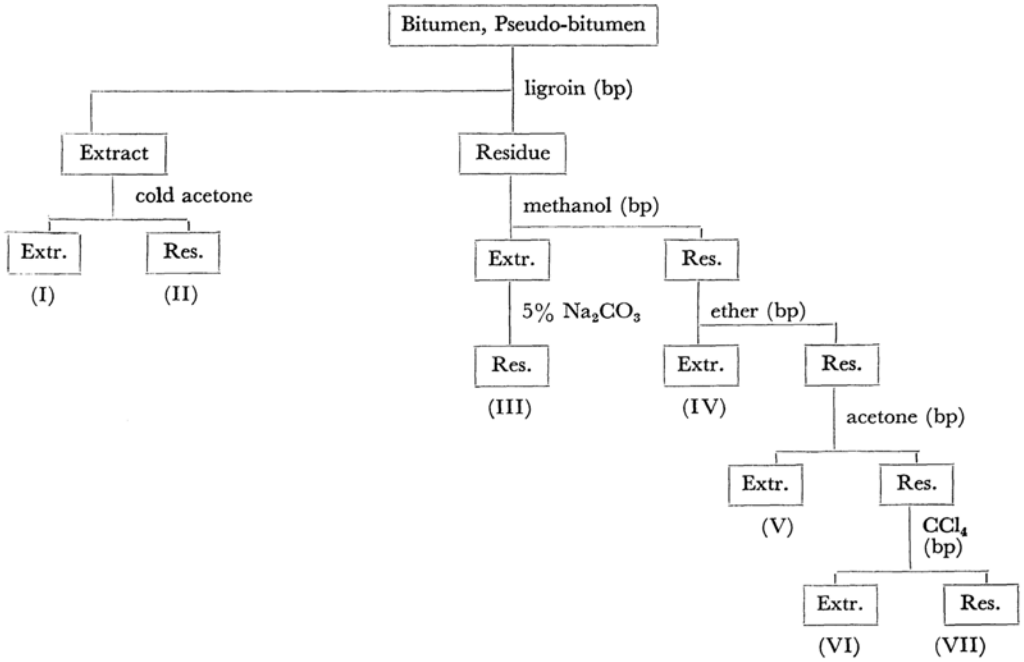

Fig. 1. Fractionation of bitumen and pseudo-bitumen.

at 220—260°C for 15 hr in total in a rotating autoclave. The solid bitumen from the extract, washed repeatedly with petroleum ether, was 7.0% of the original coal (dry-ash-free basis).

The residue of the above extraction was then subjected to catalytic hydrogenation in the autoclave with decalin in the presence of Adkins Ba-Cu-Cr oxide catalyst at 350°C for 6 hr and the initial hydrogen pressure of 100 atm. The product was extracted with benzene at 260°C for 9 hr in total, followed by the separation from the solvent. The pseudo-bitumen obtained was 50.7% of the original coal.

The bitumen and pseudo-bitumen thus obtained were fractionated successively by use of ligroin, methanol, ether, acetone and carbon tetrachloride to give the fractions shown in Fig. 1. Each of the seven fractions from bitumen and pseudo-bitumen is denoted respectively as B-I, -II, -III, -IV, -V, -VI and -VII and PB-I, -II, -III, -IV, -V, -VI and -VII.

Various properties (melting point, ultimate analysis, iodine value, true density, ultraviolet absorption, X-ray diffraction and diamagnetic susceptibility) of the similar fractions have been reported elsewhere.[3)]

b) Molecular Weight. The cryoscopic molecular weight in phenol solvent was determined for 4 to 5 solutions of different bitumen concentrations in the range of 0.5 to 2.0%, with much care of avoiding moisture. The melting-point depression value at the zero concentration was obtained by the least-square method. In the case of catechol solvent, the method by Smith and Howard[4)] was employed. The molecular depression of 59 was used for the molecular weight calculation.

c) Viscosity Measurement. The viscometer used in this work is a slightly modified Tsuda horizontal viscometer,[5)] shown in Fig. 2, with a capillary of 0.5 mm inner diameter and 20 cm length. Apart from the original Tsuda viscometer, the moisture absorption into sample solutions was carefully avoided by connecting it with a drying vessel containing P_2O_5.

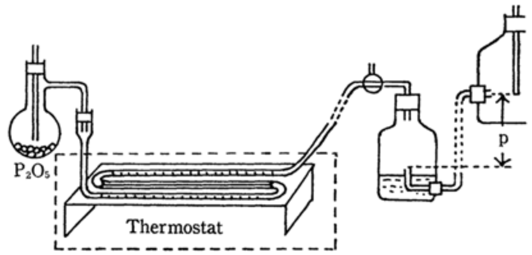

Fig. 2. Horizontal viscosimeter.

The absolute viscosity determined by the present viscometer of phenol and catechol was 4.949×10^{-2} poise at 41.0 ± 0.5°C and 3.11×10^{-2} poise at 105 ± 0.5°C, respectively. In case of the determination using catechol solvent, the viscometer was submerged in a liquid-paraffin thermostat.

The time (t) required for 1 cc sample solution to flow through the capillary was measured at various pressure differences (p) supplied from two large water containers, as also schematically illustrated in Fig. 2.

For Newtonian liquids the following relationship is applied:

$$tp = \text{constant.} \tag{1}$$

The product tp is, therefore, independent of p. According

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4) R. C. Smith and H. C. Howard, *J. Am. Chem. Soc.*, **57**, 512 (1935).

5) S. Tsuda, *Kolloid-Z.*, **45**, 325 (1928).

to Ostwald,[6] the non-Newtonian "structural" viscosity is well expressed by

$$tp^n = \text{constant } (k), \qquad (2)$$

where the tp value decreases with the increase of p in characteristic manner to the state of secondary "structure" of colloidal particles in the solution. The relationship between $\log t$ and $\log p$, which is to be linear, gives the values of n and the constant k in Eq. (2).

Results and Discussion

a) Viscosity of Bitumen Solutions in Catechol. The pt-p relationships of catechol solutions in each case gave an identical result that the product pt is independent of p and consequently that bitumen solutions in catechol show the Newtonian flow.

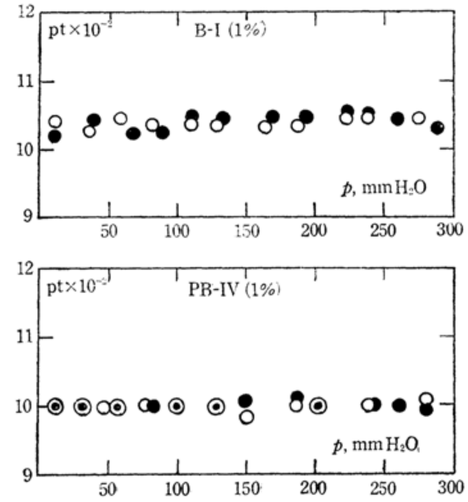

Fig. 3. The pt-p relationships of catechol solutions.

Figure 3 shows those of 1.0% solutions of B-I and PB-IV fractions determined at 105±0.5°C. The measurement was performed, at first, in increasing pressure (○), followed then by decreasing pressure (●); no departures were observed between values in the elevating and reversed pressure changes. The results also would indicate the absence of any agglomerates in the solutions.

TABLE 1. ABSOLUTE VISCOSITY AND MOLECULAR WEIGHT OF CATECHOL SOLUTION (1%)

Sample	Absolute viscosity (η), poise	Molecular weight
B-I	3.29×10^{-2}	330
B-VII	3.38×10^{-2}	280
PB-I	3.23×10^{-2}	320
PB-IV	3.23×10^{-2}	360
PB-VII	3.38×10^{-2}	300

Table 1 gives the absolute viscosity calculated from pt values at $p=0$ for the solutions of some fractions with respect to the molecular weight determined cryoscopically in catechol solvent. The molecular weight in catechol solvent appears to represent, as discussed by Dryden[2] and Sakabe *et al.*,[3] a more or less degradated state, although the elucidation has not fully been given on the reason why a value of around 300 is usually found.

b) Viscosity of Bitumen Solutions in Phenol. The pt-p curves given by the phenol solutions determined at 41±0.5°C, were those of typically non-Newtonian structural viscosity for each solution. There are, however, three types of curves (A, B and C) as illustrated in Fig. 4 as examples. In Type A, the change of pt with increasing pressure (○) is almost exactly similar to that with decreasing pressure (●). For the samples of Types B and C, curves of reversed directions do not coincide, but the pt values in pressure change of decreasing direction are more or less lower than those in increasing direction. Particularly in Type C, the above mentioned discrepancy is quite apparent so as to indicate that the "structure" in the solution is completely destroyed by the foregoing application of the shearing stress.

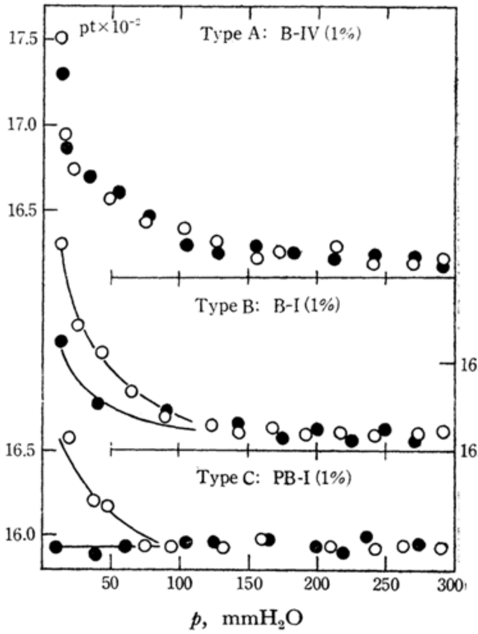

Fig. 4. The pt-p relationships of phenol solutions.

If the solutions of Types B and C are subjected to stand at the same temperature after the end of measurement, in other words, after supposed breaking of the secondary structure, the pt value increases gradually with the standing time up to the original high value in 24 hr, suggesting that

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[6] Wo. Ostwald, *Kolloid-Z.*, **36**, 99 (1925).

the once destroyed structure is ultimately recovered, but in a rather slow process.

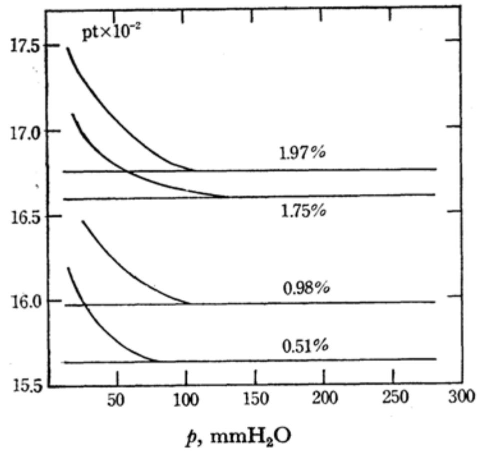

Fig. 5. The variations of *pt-p* relations with concentrations of phenol solutions; sample: PB-I.

TABLE 2. ABSOLUTE VISCOSITY, n, k AND MOLECULAR WEIGHT OF PHENOL SOLUTIONS (1%)

Sample	Absolute viscosity (η), poise	n	k	Molecular weight
B-I	5.19×10^{-2}	1.01	3.23	347
B-II	5.28×10^{-2}	—	—	350
B-III	5.23×10^{-2}	1.04	3.25	406
B-IV	5.22×10^{-2}	1.05	3.28	522
B-V	5.22×10^{-2}	1.04	3.26	638
B-VI	5.31×10^{-2}	1.08	3.31	1085
B-VII	5.34×10^{-2}	1.08	3.33	1359
PB-I	5.12×10^{-2}	1.03	3.24	396
PB-II	5.21×10^{-2}	1.03	3.25	590
PB-III	5.20×10^{-2}	—	—	392
PB-IV	5.25×10^{-2}	1.04	3.26	539
PB-V	5.34×10^{-2}	1.03	3.26	623
PB-VI	5.32×10^{-2}	1.06	3.30	1085
PB-VII	5.32×10^{-2}	1.09	3.35	1139

Figure 5 gives the influence of concentration on the viscosity behavior (*pt-p* relation) in the case of PB-I fraction. It is suggested that the shape of *pt-p* curve is identical and that the viscosity calculated from *pt* at the non-structural state increases with the concentration.

The values of absolute viscosity (η), n and k in Eq. (2) are tabulated in Table 2 with respect to the molecular weight. Values given were obtained from measurements for the 1% solutions. Values of n are nearly equal to unity, but both the values n and k tend to increase with the molecular weight. It appears that the molecular weight approaches to a value around 300, when n approaches to unity. This result would be plausible, if one assumes that the molecular weight is measured at a state in which agglomerates are incompletely destroyed by the stirring during the course of cryoscopic measurement.

The absolute viscosity, increasing with the molecular weight, is also characterized by the following results. Table 3 gives the η values at different concentrations for some selected fractions as well as the intrinsic viscosity $[\eta]$. Once again, the increase of $[\eta]$ with molecular weight is observed. The linear relationship between $[\eta]$ and the molecular weight, accepted generally for chain polymers, can not however be applied in the present case.

The results shown in Table 3 are also expressed in a different manner. From concentration and pycnometric true density measured at 25.0°C in methanol, the volume fraction (ϕ) occupied by the bitumen was calculated and inserted in the following Einstein equation[7]:

$$\eta=\eta_0(1+\alpha\phi). \tag{3}$$

The value of α obtained from the inclination of linear relationships between η and ϕ, is also

TABLE 3. VARIATION OF ABSOLUTE VISCOSITY WITH CONCENTRATION OF PHENOL SOLUTIONS, INTRINSIC VISCOSITY ($[\eta]$) AND EINSTEIN CONSTANT (α)

Sample	Molecular weight	Concentration, %	Absolute viscosity (η), poise	Intrinsic viscosity ($[\eta]$), poise	Einstein constant (α)
PB-I	396	0.51	5.02×10^{-2}	3.0×10^{-2}	2.5×10^{-3}
		0.98	5.12×10^{-2}		
		1.75	5.32×10^{-2}		
		1.99	5.37×10^{-2}		
PB-IV	539	0.50	5.07×10^{-2}	5.2×10^{-2}	4.1×10^{-3}
		1.02	5.25×10^{-2}		
		1.52	5.39×10^{-2}		
		2.01	5.54×10^{-2}		
PB-VII	1139	0.50	5.18×10^{-2}	6.8×10^{-2}	5.2×10^{-3}
		1.00	5.32×10^{-2}		
		1.51	5.50×10^{-2}		
		1.99	5.71×10^{-2}		

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[7] *Cf.* M. Reiner, "Deformation and Flow," H. K. Lewis and Co., London (1949), Chapt. 4.

given in Table 3. The η_0 observed graphically from the similar linear relations at $\phi=0$ was 4.90×10^{-2} poise, which is coincident with the viscosity of pure phenol (4.949×10^{-2} poise).

All these results described above strongly suggest that bitumens in phenol, contrary to the cases of catechol solutions, agglomerate to different extent particular to each fraction. It is generally recognized that the application of shearing stress by the flow dissociates the agglomerated state easily into a monodisperse state, which may be recovered to the original state on standing.

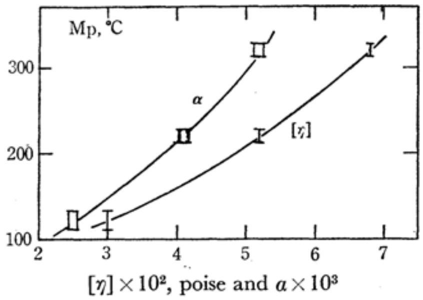

Fig. 6. The increase of melting temperature with intrinsic viscosity and Einstein constant.

However, it is noteworthy that there is no constancy in the values of n and k in Table 2 as well as more apparently of α in Table 3 for different fractions. The fact that these constants show in each case the same tendency to increase with the increase of molecular weight seems to indicate that the unit particle composing each fraction is not identical in the apparent size, but varies from a fraction to another. The increasing tendency described above would mean that the apparent particle size is larger for the fraction which gives larger molecular weight. Also referring to the previously published data,[3] the softening (melting) temperature is almost linearly related with $[\eta]$ and α, as shown in Fig. 6.

It is concluded therefore that the variation of molecular weight obtained by use of phenol solvent is caused partly by the agglomeration of unit particles and partly by the variation of dimension of unit particle. It seems apparent that the dimension of unit particle is larger for the fractions showing larger molecular weights in phenol, and therefore that the molecular weight by phenol is more relevant to the ultimate state of bitumens.