Solvent Extraction of Coal—Relation between the Yield of Extract and the Solubility Parameter of the Solvent*

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In spite of the obvious variations in the yield of extract found with different solvents, only a few workers have attempted to study systematically the solvent effect of extraction for coal. The most extensive work on the extraction of coal has been done by Dryden(1–3). Dryden developed an interesting classification of suitable coal solvents from his results, and observed that the yield of extract obtained from a given coal varies largely with the type of solvent employed and that the better solvents for coals, such as ethylene diamine, have structures containing a nitrogen or oxygen atom possessing an available unshared pair of electrons. Recently Halleux and Tschamler have, from a study of coal extraction with a series of closely related pyridine bases(4), expanded the hypothesis put forward by Dryden. These investigators indicate that the acid-base interaction is important in explaining the relative solvation power of pyridine bases for coal.

The most important studies made of the relation between the physical or chemical nature of solvents and the yield of extract are those by Kiebler(5,6). A statistical analysis was done from the values of the yield of extract and from the various physical properties of the solvent. The physical properties considered were internal pressure, surface tension, dipole moment, dielectric constant, refractive index, and so on. Of these properties, the internal pressure had the most significant relationship to the yield of extract as shown by correlation coefficients. Kiebler showed that the relation between the yield of extract and the internal pressure of solvent at a given temperature is approximately linear, and that deviations from the resulting regression line could not be related to any physical properties(5,6). There are, however, several reasons why Kiebler's conclusions are not wholly acceptable(2): (i) Kiebler rejected a number of solvents on the suspicion of chemical effects; therefore, his experiments were based on a selected range of liquids; (ii) he excluded water and glycol, because their dissolving power against coal is poor in spite of their high internal pressures; (iii) his extraction method was not based on the Soxhlet principle; therefore, it is doubtful whether the completeness of extraction by all solvents is of the same order.

According to the regular solution theory, on the other hand, cohesive energy density (CED)** is an important factor in determining the action of a solvent on a solute(7). It is also well known that the solvation of a polymer by various organic liquids correlates to a large extent with the CED of the solvent and the polymer(8,9). Consequently, one may expect some relationship between the CED of the solvent and the yield of extract obtained from coal.

Experimental

The coal specimen was pulverized enough to pass through a 30-, and to stand on a 60-, Tyler mesh sieve. The lighter fraction, with a specific gravity of less than 1.30, was isolated by the float-or-sink method, using a mixture of benzene and carbon

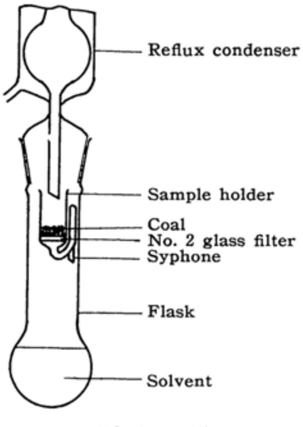

Fig. 1. Modified soxhlet extractor.

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[*] Presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

1) I. G. C. Dryden, *Nature*, **162**, 959 (1948); **163**, 141 (1949); **166**, 561, 606 (1950).

2) I. G. C. Dryden, *Fuel*. **29**, 197, 221 (1950).

3) I. G. C. Dryden, ibid., **30**, 39, 145, 217 (1951); **31**, 176 (1952).

4) A. Halleux and H. Tschamler, ibid., **38**, 291 (1959).

5) M. W. Kiebler, *Ind. Eng. Chem.*, **32**, 1389 (1940).

6) H. H. Lowry, ed., "Chemistry of Coal Utilization", Vol. I, John Wiley & Sons, Inc., New York (1947), p. 736.

[**] CED and internal pressure are of the same meaning.

7) J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes", Reinhold Publishing Corp., New York (1950).

8) G. Gee, *Quart. Revs.* (*London*)., **1**, 288 (1947).

9) E. E. Walker, *J. Appl. Chem.*, **2**, 470 (1952).

TABLE I. CHARACTERISTICS OF SAMPLES USED

Source	Proximate analysis, %				Ultimate analysis d. a. f., %		
	Moisture	Ash	Volatile matter	Fixed carbon	C	H	O+N+S
Yūbari	1.7	2.4	42.0	53.9	85.2	6.3	8.5
Ashibetsu	3.0	4.1	42.9	50.0	81.1	5.5	13.4

tetrachloride. These fractions have ash contents of less than 3% and are estimated to be almost vitrain. The characteristics of the various vitrains are listed in Table I. All solvents were commercial reagents (grade: guaranteed reagent or extra pure) and were used without further purification.

Instead of the customary method of Sexhlet extraction, a modified Soxhlet method at the boiling temperature of the solvent was used. The apparatus is shown in Fig. 1. The extraction was done exactly at the boiling temperature of the solvent. Vitrain samples (dried in vacuo at 110°C) were extracted under the standard conditions, namely, a coal to solvent ratio of 150 mg. to 30 ml. and under dry air for 48 hr. The extraction residue was dried in vacuo at 110～180°C for 7 hr. The extraction residues by the higher boiling solvents were washed with acetone before drying. The extraction yield was determined by direct weighing of the residue. The absorption effect of the solvent on the residue was not considered, because examination of ethyene diamine, one of the more powerful solvents, showed only a small difference (about 2% or so between the yield obtained by the direct weighing method and that obtained by calibrating the nitrogen in increase in the residue.

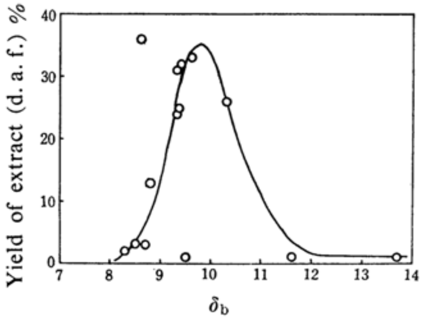

Fig. 2. Relation between yield of extract and solubility parameter of solvent at b. p. (Yūbari vitrain).

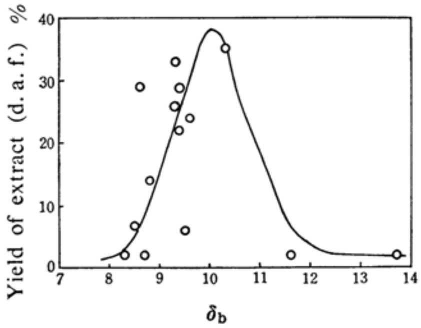

Fig. 3. Relation between yield of extract and solubility parameter of solvent at b. p. (Ashibetsu vitrain).

Experimental Results

The CED of the solvent, e_{ss} (cal./cc.), was calculated from the following relationship:

$$e_{ss}=(L_b-\mu \boldsymbol{R}T)/V_b \qquad (1)$$

where L_b is the latent heat of vaporization at the boiling point in cal./mol., V_b is the molecular volume at a normal boiling point in cc./mol., $\boldsymbol{R}$ is the gas constant, T is the boiling temperature in °K, and μ is the correction term in $\mu=PV/\boldsymbol{R}T$. (For substances boiling above 50°C, and, therefore, for all solvents used, the μ correction can be neglected.) The V_b value was calculated by the additive method using LeBas's volume increments[10]. The average error for the compound tested was 4.7%. The value of L_b was available in the references[11-13].

TABLE II. YIELD OF EXTRACT AT BOILING TEMPERATURE TOGETHER WITH CERTAIN PHYSICAL DATA FOR THE SOLVENTS USED

Solvent	t_b, °C	δ_b	Yield of extract d. a. f., %	
			Yūbari	Ashibetsu
Chloroform	61	8.7	2.6	2.3
Methanol	64	13.7	0.9	1.5
Ethanol	78	11.6	0.6	1.8
Ethyl methyl ketone	80	8.5	3.4	7.0
Benzene	80	8.3	1.8	1.6
Pyridine	116	9.6	33.2	23.8
Ethylene diamine	117	10.3	26.2	34.9
Butanol	118	9.5	0.8	5.0
Dimethyl formamide	153	9.3	24.0	25.6
Cyclohexanone	156	9.4	25.0	29.1
Cyclohexanol	161	8.8	13.0	13.5
Phenol	182	9.4	32.0	21.9
Cresol	185～193	9.3	30.7	32.6
Acetophenone	202	8.6	35.6	29.1

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[10] R. C. Rein and T. K. Sherwood, "The Properties of Gases and Liquids", McGraw-Hill, New York (1958), p. 51.

[11] T. Kuwata "Yōzai", Maruzen, Tokyo (1940).

[12] A. Weissberger, ed., "Organic Solvents", Interscience Pub., New York (1955).

[13] The Chem. Soc. of Japan, "Chemical Handbook" ("Kagaku Binran"), Maruzen, Tokyo (1958).

If L_b was unknown, the estimation was made by the Watson-Negishi method according to the following equation[14]:

$$L_b = 2.48\ (t_b + 273)^2/(A + 0.11t_b) \tag{2}$$

where A is the constant within a given homologus series, and t_b is the boiling point in °C. Therefore, the solubility parameter, δ_b, at the boiling point is deduced from the CED as follows:

$$\delta_b = \sqrt{e_{ss}} \tag{3}$$

The yields of extract for Yūbari coal and for Ashibetsu coal by various solvents are presented in Table II, together with the t_b and δ_b values of various solvents. Figures 2 and 3 show the relation between the yield of extract and the value of δ_b for Yūbari coal and for Ashibetsu coal respectively. The yield of extract increases with the increase of δ_b, reaches a maximum at about 10 of δ_b, and then decreases with the increase of δ_b.

Discussion

Several attempts to find a correlation between the yield of extract and some physical properties of the solvents have been proposed[5,6,15-17]. These methods can, however, be successful in only a limited number of case, for example, in a series of chemically related solvents[4].

In spite of the fact that the solvents we used included various chemically different types, including alcohols (though they were excluded by Kiebler), and have a wide range of boiling temperatures from 61 to 202°C, a good relationship between the yield of extract and the δ_b value of the solvents has been found, as is shown in Figs. 2 and 3, with the exception of acetophenone and butanol.

The poor dissolving power of alcohol and water against coal, in spite of their high CED values, may be explained by the following reasons. Alcohol and water are strongly hydrogen-bonded substances and have high CED values, owing to their hydroxyl associations. These liquids are all substances which form 'solvent-solvent' contacts (hydrogen bonds) with the evolution of a large amount of energy. It seems that they form 'solvent-coal' contacts less readily and that the energy gained in forming these contacts does not balance the energy lost in breaking the 'solvent-solvent' and 'coal-coal' contacts.

From these results, it appears that the CED value is one of the most important factors determining the solvent action of liquids on coal. Moreover, our conclusions, based on the Soxhlet principle and resulting from the employment of solvents having CED values over a wide range, should be borne in mind.

It is possible to propose the following explanations for the deviations from the resulting correlation curves. The solvents include various chemically different types and have a wide range of boiling temperatures. The various polar groups in solvents, therefore, may have some specific influences on coal. Coal is a mixture of complex compounds, and the CED value of coal varies with the temperature. Moreover, the estimation error of the CED value at the boilng temperature may contribute to the deviation.

Further strict experiments on the action of solvents on coal have been made; these results will be reported later[18].

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[14] K. Satō, "Bussei Zyōsū Suisanho", Maruzen, Tokyo (1957), p. 240.

[15] W. Ostwald and H. Ortlov, *Kolloid Z*, **59**, 25 (1932).

[16] D. J. W. Kreulen, *Brennstoff-Chem.*, **16**, 165 (1935); *Fuel (London)*, **25**, 99, 104 (1946).

[17] G. Agde and R. Hubertus, *Brennstoff-Chem.*, **17**, 149 (1936); *Braunkohlenarchiv*, **No. 46**, 3 (1936).

[18] Y. Sanada and H. Honda, in preparation.