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Liquid Chromatographic Analysis of Coal Surface Properties

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Quarterly Progress Report For the Period July - September 1992

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I. ABSTRACT

Experiments on equilibrium adsorption of various alcohols on 60 - 200 mesh Illinois #6 coal (DECS-2; Randolph county) were performed during the July - September period. The alcohols include ethanol, methanol, isobutanol, t-butanol, 1-heptanol, 1-octanol, 1-hexadecanol, 4-methyl-2-pentanol, and 2-methyl-1-pentanol. Amounts of Equilibrium adsorption of alcohols (ALCO) on 60 - 200 mesh Illinois #6 coal are $1 - 230 \times 10^{-6}$ mg-ALCO/g-coal, whereas equilibrium concentrations of alcohols are 3 - 40 ppm. Relationships between equilibrium loadings of alcohols on the coal and equilibrium concentrations of alcohols in aqueous solutions are shown to be linear.

II. INTRODUCTION

The main objectives of this proposed research are to refine further the inverse liquid chromatography technique for the study of surface properties of raw coals, treated coals and coal minerals in water, to evaluate relatively surface properties of raw coals, treated coals and coal minerals by inverse liquid chromatography, and to evaluate floatability of various treated coals in conjunction with surface properties of coals.

Coals such as Pittsburgh seam coal, Illinois #6 coal, Wyodak coal are chosen as representatives of high-rank bituminous coal, high volatile bituminous coal and subbituminous coal, respectively. Coal minerals such as pyrite and dolomite are chosen as representative coal minerals.

Alcohols such as methanol, ethanol, isopropanol, isobutanol, tert-butanol, heptanol, 1-hexadecanol, 2-methyl-1-pentanol,

4-methyl-2-pentanol (methyloisobutyl carbinol), n-octanol, s-octanol, and cyclohexanol as probe compounds are utilized to evaluate hydrophilicity of coals and coal minerals.

N-alkanes such as hexane, heptane and octane, and stearic acid are employed as probe compounds to evaluate hydrophobicity of coals and coal minerals. Aromatic compounds such as benzene and toluene as probe compounds are used to examine aromaticity of coal surface. Aromatic acids such as o-cresol, m-cresol, p-cresol, phenol and β -naphthol are used to detect aromatic acidic sites of coal surface.

Hydrophilicity, hydrophobicity and aromaticity of surfaces for either raw coals or treated coals in water are relatively determined by evaluating both equilibrium physical/chemical adsorption and dynamic adsorption of probe compounds on various raw coals and treated coals to compare affinities of coals for water.

III. PROJECT STATUS

1. Experiments

Experiments on equilibrium adsorption of various alcohols on Illinois #6 coal were performed in aqueous solutions at 25°C. Illinois #6 coal (DECS-2; Randolph county) were pulverized and sieved to obtain 60-200 mesh coal particles. Sieved 60-200 mesh Illinois #6 coal particles were washed with distilled water (DW) to get rid of any water-soluble organic compounds on the surfaces of the coal particles. Coal particles were submerged under water overnight, and then filtered next day to remove organic-

dissolved water from surfaces of coal particles. These washing processes continued for 3 weeks. Washed coal particles were dried at 110°C for 4 hours.

Dry 2.5-g coal particles were introduced into a 4.6-mm-ID 250-mm-long empty column. The coal particles packed in the column were washed with DW for 10 hours to eliminate any water-soluble contaminants introduced in the coal-packed column during the process of packing dry coal particles into the column.

The alcohols include ethanol (ETHL), methanol, isobutanol (ISB), t-butanol (TBL), 1-heptanol, 1-octanol, 1-hexadecanol, 4-methyl-2-pentanol (4M2P), and 2-methyl-1-pentanol (2M1P). Stock solutions with the 1000-ppm concentration were prepared for each compound by dissolving alcohols into distilled water. Concentrations of alcohols in aqueous solutions were 3-40 ppm for equilibrium experiments. Equilibrium concentrations of alcohols were analyzed with the HP-1047A Reflux Index detector and the HP-1050 high pressure pump. The standard column was prepared by packing 2.5-g Teflon into an empty column. Equilibrium data of adsorption of alcohols on the coal were obtained by calculating peak areas of the coal column and the standard column. A computer program was developed to determine a peak area with the trapezoidal numerical integration method.

Experiments on equilibrium adsorption of methanol on the coal was aborted. RI index of water as a carrier solvent is slightly different from that of methanol. It is difficult to detect peaks of methanol in aqueous solutions with the RI

detector.

Experiments on equilibrium adsorption of 1-hexadecanol and 1-octanol on the coal were aborted. Solubilities of these compounds in water were very low. Stock solutions (1000 ppm) of these compounds could not be prepared at 25°C.

Experiments on equilibrium adsorption of 1-heptanol on the coal were also aborted. Adsorption of 1-heptanol on the coal was very low. Error ranges of experiments masked accuracies of adsorption data.

Mr. Ricardo Rigby, Ms. Katanya M. Bolling and Ms. Natasha A. Bostic, senior chemical engineering students, worked as research assistants for this project during the July - September period.

2. Experimental Results

Experimental data on equilibrium adsorption of alcohols (ALCO) on coal were shown in Tables 1 and 2, and Figures 1 through 5. Amounts of Equilibrium adsorption of alcohols on 60 - 200 mesh Illinois #6 coal are $1 - 230 \times 10^{-6}$ mg-ALCO/g-coal, whereas equilibrium concentrations of alcohols are 3 - 40 ppm. Relationships between equilibrium loadings of alcohols on the coal and equilibrium concentrations of alcohols in aqueous solutions are shown to be linear.

Equilibrium loadings of ethanol on the coal are $3 - 20 \times 10^{-6}$ mg/g-coal with its 10 - 40 ppm equilibrium concentrations. Equilibrium loadings of ISP on the coal are $3 - 40 \times 10^{-6}$ mg/g-coal with its 1 - 40 ppm equilibrium concentrations.

Equilibrium loadings of ISP on the coal is higher than those of ethanol.

Equilibrium loadings of isobutanol (ISB) on the coal are $3 - 60 \times 10^{-6}$ mg/g-coal with its 5 - 40 ppm equilibrium concentrations, whereas equilibrium loadings of t-butanol (TBL) on the coal are $2 - 8 \times 10^{-6}$ mg/g-coal with its 10 - 40 ppm equilibrium concentrations. Equilibrium loadings of ISB on the coal are much higher than that those of TBL.

Equilibrium loadings of 2-methyl-1-pentanol on the coal are $5 - 240 \times 10^{-6}$ mg/g-coal with its 5 - 40 ppm equilibrium concentrations, whereas equilibrium loadings of 4-methyl-2-pentanol on the coal are $10 - 90 \times 10^{-6}$ mg/g-coal with its 3 - 30 ppm equilibrium concentrations. Equilibrium loadings of 2M1P on the coal are much higher than those of 4M2P.

IV. FUTURE EXPERIMENTAL PLANS

Experiments on equilibrium adsorption of various aromatic acids and aromatic compounds on Illinois #6 coal will be conducted to investigate surface properties of this coal in the presence of water. Experiments on dynamic adsorption of selected compounds on Illinois #6 coal will be conducted.

V. PRESENTATIONS

A research paper, entitled "Adsorption of Various Alcohols on Illinois #6 Coal in Aqueous Solutions", were presented to the Miami AIChE annual meeting in November 1992. A research paper, entitled "Analysis of Surface Properties of Coal by Inverse Liquid Chromatography", was accepted for presentation at the 18th

International Technical Conference on Coal Utilization & Fuel
Systems, Clearwater, Florida, April 26-29, 1993.

Table 1. Equilibrium adsorption of t-butanol, ethanol, isopropanol and isobutanol on 60-200 mesh Illinois #6 coal, and their equilibrium concentrations in aqueous solutions at 25°C.

Run #	Alcohols	Equilibrium Concentrations Alcohols, ppm	Equilibrium Adsorption on Coal, 10^{-6} mg/g-coal
62	t-butanol	10.00	4.16
70	t-butanol	19.97	3.59
69	t-butanol	29.89	1.74
68	t-butanol	39.72	8.08
58	ethanol	10.00	5.63
43	ethanol	9.97	7.85
50	ethanol	14.99	3.98
53	ethanol	14.99	4.08
53	ethanol	14.99	9.05
49	ethanol	20.02	9.04
47	ethanol	29.96	9.92
60	ethanol	29.96	16.01
55	ethanol	40.17	19.77
1	isopropanol	3.00	1.36
2	isopropanol	5.01	4.41
3	isopropanol	7.02	6.17
4	isopropanol	10.16	4.36
404	isopropanol	10.16	8.82
5	isopropanol	16.01	13.38
6	isopropanol	20.33	17.20
1001	isopropanol	40.02	37.98
20	isobutanol	4.88	2.57
8	isobutanol	5.02	3.10
63	isobutanol	4.99	4.45
14	isobutanol	10.01	9.86
57	isobutanol	10.01	12.32
56	isobutanol	19.99	19.21
61	isobutanol	19.99	22.97
65	isobutanol	29.94	42.09
101	isobutanol	40.02	52.16
64	isobutanol	39.97	55.44

Table 2. Equilibrium adsorption of 4-methyl-2-pentanol and 2-methyl-1-pentanol on 60-200 mesh Illinois #6 coal, and their equilibrium concentrations in aqueous solutions at 25°C.

Run #	Alcohols	Equilibrium Concentrations Alcohols, ppm	Equilibrium Adsorption on Coal, 10^{-6} mg/g-coal
21021	4-methyl-2-pentanol	3.01	12.17
21021	4-methyl-2-pentanol	3.01	16.48
27	4-methyl-2-pentanol	4.99	18.27
26	4-methyl-2-pentanol	9.99	27.40
26	4-methyl-2-pentanol	9.98	44.54
19019	4-methyl-2-pentanol	15.00	44.36
20020	4-methyl-2-pentanol	29.98	83.38
29	2-methyl-1-pentanol	5.00	6.64
36	2-methyl-1-pentanol	5.00	27.32
39	2-methyl-1-pentanol	5.00	27.38
41	2-methyl-1-pentanol	10.00	31.75
34	2-methyl-1-pentanol	10.00	39.02
30	2-methyl-1-pentanol	10.00	42.05
35	2-methyl-1-pentanol	14.99	93.93
31	2-methyl-1-pentanol	14.99	97.83
45	2-methyl-1-pentanol	15.00	109.22
33	2-methyl-1-pentanol	29.96	129.03
32	2-methyl-1-pentanol	29.96	127.96
44	2-methyl-1-pentanol	30.03	183.38
42	2-methyl-1-pentanol	40.00	228.63
46	2-methyl-1-pentanol	40.00	232.96

Figure 1. Equilibrium concentration of ethanol (ETHL) and adsorption of ethanol on 2.5-g 60-200 mesh Illinois #6 coal in aqueous solutions at 25°C.

Figure 2. Equilibrium concentration of isopropanol (ISP) and adsorption of ISP on 2.5-g 60-200 mesh Illinois #6 coal in aqueous solutions at 25°C.

Figure 3. Equilibrium concentrations of isobutanol (ISB) and t-butanol (TBL), and their adsorption on 60-200 mesh Illinois #6 coal in aqueous solutions at 25°C.

Figure 4. Equilibrium concentration of 2-methyl-1-pentanol (2M1P) and 4-methyl-2-pentanol (4M2P), and their adsorption on 2.5-g 60-200 mesh Illinois #6 coal in aqueous solutions at 25°C.

Figure 5. Equilibrium concentration of alcohols (ALCO) and adsorption of alcohols on 2.5-g 60-200 mesh Illinois #6 coal in aqueous solutions at 25°C.

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