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SOLVENT EXTRACTIONS OF ILLINOIS NO. 6 COAL

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This paper summarizes several early experiments to find the best solvent for Illinois No. 6 coal and a recent investigation of some solvent mixtures.

EXPERIMENTAL

The coal was beneficiated Illinois No. 6 obtained from Pennsylvania State University as PSOC-26. The coal was ground to pass 60 mesh Tyler screening and kept under nitrogen. It contained 76.8% C, 5.0% H, 1.57% N, 2.13% S, 2.2% ash and 12.3% O by difference.

Most experiments were carried out in Pyrex bulbs with 1 g of coal and 50 g of solvent. The mixtures were cooled to -78°C , evacuated, sealed off, and heated with shaking for 1 hour at 100°C . The resulting mixture was separated by centrifuging; the bulb was rinsed with an additional 10 mL of solvent, also used to wash the insoluble coal. This mixture was again separated by centrifuging. Solutions from experiments with phenol, n-butylamine (BuNH_2), and benzylamine (BnNH_2), and nearly all with dimethyl sulfoxide (DMSO) and ethylenediamine (EDA) were checked for colloidal material by filtration through a $0.5\text{ }\mu\text{m}$ Millipore filter; the residue on the filter was no more than 0.5%. The main, compact, wet precipitate was weighed and solvent was removed from precipitate and solution by distillation or evaporation at reduced pressure. Both were finally dried in a Abderhalden drier containing concentrated sulfuric acid at 0.13 Pa (0.001 torr) at 76°C . After drying, the first DMSO-EDA

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extract was redissolved in this solvent mixture. After centrifuging at 39,000 g, >96% was still soluble.

Less volatile solvents were sometimes removed by extraction with methanol. Amine solvents could not be completely removed even on drying at 140°C; they were therefore washed out with 1 M HCl, which was then removed with water and, as noted, with aqueous ammonia. The resulting residues were first dried over CaCl_2 at room temperature and reduced pressure to avoid loss of dust on further drying. Some amines were retained even after acid washing. Most products of amine extractions were analyzed for nitrogen and N contents >1.6% and material balances >100% are assumed to be due to retained solvents. However, after acid washing and correction for excess nitrogen, material balances are around 95%; the missing material is thought to be mostly volatile and water-soluble coal products. Sulfur analyses showed that DMSO was also bound to the coal.

The swelling ratios in Table 1 are the ratios of the weights of the wet, swollen, centrifuged precipitates (usually fairly firm) to the weights of the final dried precipitates; they measure the abilities of the solvents to swell the insoluble coal network. The ratio for hexane, 1.64, represents mostly mechanical retention of solvent between hard coal particles, but larger numbers represent mostly, or entirely, absorption of solvent and swelling of soft particles.

RESULTS AND DISCUSSION

The results in Table 1 are arranged in order of increasing solubility in single solvents, interspersed with results with solvent mixtures. (This order may not apply in other coals.^{1,2}) The solubilities range

from 1 to 52%, with a parallel increase in swelling ratio of the undissolved coal from 1 - 1.6 to 9.6 or more. In our opinion, pyridine is the best inert solvent for coal at 100°C. We attribute higher solubilities in the presence of amines to their chemical action on crosslinks in the coal, probably by cleaving ester groups:

and, with long heating with EDA, also ether groups. The evidence, partly discussed elsewhere, includes saponification of coal fractions by alcoholic KOH, the binding of amines in the products, relations between solvent power and swelling of undissolved coal, and increases in solubility and swelling with longer reaction times and higher temperatures.

The usual abilities of amine solvents, especially EDA, were recognized many years ago.^{3,4} Some recent work has dealt with solvents mixtures.⁵ What we think is new is the idea that amines have a chemical as well as a physical action and the finding that DMSO assists the action of EDA, at least partly because it increases the swelling of the coal. The EDA + DMSO combination is more effective than the EDA + pyridine combination.

The results with solvent combinations in Table 1 bring out the separate physical and chemical effects of solvents and the effects of longer reaction time and higher temperature when chemical reaction is involved. The data of Lahaye and Decroocq³ are best interpreted on this basis. Some effects of individual solvents suggest that steric hindrance and base strength are involved in the chemistry. The primary amines are the best solvents,^{3,4} the smallest and strong base, EDA, being best. Benzylamine and 2-phenethylamine are next best among those tested, with

solvent properties closely proportional to their nitrogen contents. The weak base, aniline, is not as good as pyridine. Pyrrolidine, a secondary amine with a tight 5-membered ring, is about as good as benzylamine, but piperidine, with a loose 6-membered ring, is distinctly inferior. From previous work,^{1,2,3} secondary and tertiary amines are poor solvents.

The third pyrrolidine experiment shows how easily coal reacts with this amine and oxygen at room temperature. The overall result was that 19.8 mg-atoms of C in the original coal apparently took up 2.93 mmoles pyrrolidine and up to 10 mg-atoms of oxygen, and lost 1.3 mg-atoms of C.

Without unusual precautions to exclude air during 1 to 18-hour extractions at 100°C, the EDA/DMSO combination extracted more material than EDA alone. However, in longer extractions with more effort to exclude air, the extract yields increase and the difference between the solvents tends to disappear. We ascribe the higher rate of extraction by the mixed solvent to the greater swelling of the insoluble material. The difference is not due to oxidation by DMSO. Increasing the temperature and duration of extraction with DMSO alone does not increase by much the amount of coal dissolved and the advantage of DMSO added to EDA decreases with longer reaction times.

That 50% of Illinois No. 6 coal can now be dissolved at 100°C to give a solute mostly soluble in pyridine and an extracted coal with much less crosslinking (higher swelling ratio) than pyridine-extracted coal provides a new and exceptional opportunity to investigate the structure of coal that has never been heated above 100°C since it was mined.

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Table 1

EXTRACTIONS OF ILLINOIS NO. 6 COAL

Solvent ^a	Time ^b , hr	Temp., °C ^b	Soluble, %	Insoluble, %	Total Recovery ^c , %	Swelling Ratio ^d
Hexane	--	--	0.86	96.2	97.0	1.64
Toluene	--	--	4.1	96.8	100.9	2.64
10/1, toluene/ pyrrolidine	1.2	--	8.1	97.3	105.5	2.85
Tetrahydrofuran	--	--	8.0	95.3	103.3	2.80
Hexamethyl- phosphoramidate ^e	--	125	10.4 ^f	-- ^f	--	--
Aniline ^e	--	--	11.7 ^f	79.6 ^f	91.3	4.59
Phenol ^e	--	182	11.8 ^f	-- ^f	--	3.42
Dimethyl sulfoxide	--	--	14.6 ^f	86.9 ^f	101.5	5.5
	20.4(5) ^g	--	16.4 ^{f,i}	77.7 ^{f,i}	94.1	4.0
N-Dimethyl- formamide ^e	--	--	14.9	--	>90	<6.2
Pyridine ^e	--	--	16.0	86.3	102.3	3.71
5/1 pyridine/ acetic anhydride	--	--	20.8	86.2	107.6	5.14
42/1 by wt. pyridine/NH ₃	--	--	14.8 ^{f,h}	78.1 ^{f,h}	92.8	5.05
10/1 pyridine/ pyrrolidine	{ 12	--	20.2 ^{f,h}	73.6 ^{f,h}	93.8	5.49
		--	20.7 ^{f,h}	72.1 ^{f,h}	92.8	5.53
Piperidine	-	--	18.0	94.4	112.4	2.98
N-Methyl-2- pyrrolidinone	--	--	21.6 ^{f,h}	70.1 ^{f,h}	91.7	5.73
n-Butylamine	--	--	22.1	87.0	109.1	3.75
2/1 molar, BuNH ₂ / dimethyl sulfoxide	--	--	38.0 ^f	64.0 ^f	102.0	7.4
2-Pyrrolidinone	--	--	26.9 ^f	70.4 ^f	97.3	6.36
2-Phenethylamine	--	--	27.7 ^{f,h}	72.7 ^{f,h}	100.4	6.41
	{ 4	20-25	22.5 ^{f,h}	75.4 ^{f,h}	97.9	6.07
Benzylamine	{ --	--	32.8 ^{f,h}	66.1 ^{f,h}	98.9	7.07
	{ 12	--	35.8 ^{f,h}	60.1 ^{f,h}	95.9	7.35
	{ 264	20-25	>22.2 ^{f,h}	>62.0 ^{f,h}	>84.2	4.68
Pyrrolidine	{ --	--	27.9 ^h	84.4 ^h	112.3	4.45
	{ 248 ^j	20-25	82.9	109.8	192.7	4.29
			43.4 ^{f,i}	50.0 ^{f,i}	93.4	
	{ 72	20-25	35.1 ^{f,h}	79.7 ^{f,h}	114.8	3.81
	{ --	--	32.9 ^{f,h}	62.0 ^{f,h}	96.9	5.02
Ethylenediamine	{ 18	--	44.3 ⁱ	68.4 ⁱ	112.7	4.26
	{ 203(7)	--	55.1 ⁱ	61.3 ⁱ	116.4	5.01
			47.4 ^f	49.7 ^f	97.1	
	{ 147(6) ^g	--	51.5 ⁱ	57.3 ⁱ	108.6	4.63
			44.5 ^f	53.3 ^f	97.8	
30/70 EDA/pyridine	--	--	32.1 ^{f,h}	69.1 ^{f,h}	101.2	
{ 32/68	--	--	44.1 ^{f,h}	62.5 ^{f,h}	106.6	7.17
{ v/v			43.7 ⁱ	54.3 ⁱ	98.0	
	{ 16	--	48.3 ⁱ	61.2 ⁱ	109.5	9.61
EDA/ DMSO	{ 160(10) ^e	--	50.4 ^{f,i}	40.5 ^{f,i}	91.0	
{ 1/2 in molec	{ 135(6) ^{e,g,k}	--	47.6 ⁱ	58.6 ^f	106.2	18.7
			41.1 ^f	53.5 ^f	94.6	
			49.7 ^k	43.9 ^k	93.6	

Notes to Table 1

- a 1.00 g beneficiated coal + 50 mL solvent in sealed, evacuated tube; ratios in mixtures are by volume, } except as noted.
- b 1.0 hour at 100°; numbers of extraction steps are in parentheses, }
- c Relative to initial weight of coal,
- d Weight of wet, centrifuged, insoluble fraction divided by its dry weight.
- e Results of large-scale extraction.
- f After correcting for bound solvent, as measured by excess N or S content.
- g Containers were flushed with N₂ before and after each transfer.
- h,i After washing with 1 M HCl,^h and then with 3 M NH₃.ⁱ
- j Run with 0.3103 g of coal in very slow stream of air, with 13 successive 2-mL portions of pyrrolidine, with separations of undissolved coal and replacement of solvent after each step.
- k Started with pyridine-extracted coal; last results corrected for 16% extract and 2% loss in pyridine extraction.