

Compound Type Separation and Classification of Petroleum by Titration, Ion Exchange, and Adsorption

An Index of the Acidity, Basicity, and Adsorptivity on Alumina of Various Petroleum Compound Types

L. R. SNYDER and B. E. BUELL

Union Oil Co. of California, Union Research Center, Brea, Calif.

A comprehensive tabulation has been assembled of the acid and base dissociation constants and relative adsorptivities on alumina of various compound types which may be present in petroleum and related materials. These data form a basis for the separation and/or classification of petroleum nonhydrocarbons by compound type, using titration, ion exchange, or adsorption chromatography.

THE present paper provides a comprehensive classification or index of various petroleum compound types with respect to their relative acidity, basicity, and adsorptivity in standard systems of immediate interest to petroleum analysis. Previous data of this type are either nonexistent or scattered widely through the literature. This over-all classification scheme provides a rational basis for the design of petroleum separations prior to analysis, and is also useful in the qualitative analysis of petroleum fractions by titration, ion exchange, or adsorption procedures *per se*. The value of the present index will be obvious to those engaged in the analysis of petroleum and related materials, and will be further illustrated in subsequent communications dealing with the separation and/or qualitative analysis of petroleum by ion exchange, titration, and adsorption chromatographic procedures.

EXPERIMENTAL

Extrapolated pK_a values (relative to water) were obtained by potentiometric titration of acids in pyridine and bases in acetic anhydride (7, 48) using the calculation procedure of Streuli (45). This involves plotting the half-neutralization potential (HNP) values (in millivolts) *vs.* water pK_a values. These data are summarized in Tables I and II, and yield the correlational Equations 1 and 1a:

Table I. Titration of Acids in Pyridine (7)

Acid	HNP ^a	pK_a		Ref.
		Lit.	Calcd. ^b	
Thiophenol	800	6.5	6.9	(1)
Acetylacetone	920	8.2	8.9	(1)
Benzotriazole	880	8.6	8.2	(16)
2-Naphthol	1000	9.9	10.2	(1)
Nitromethane	1100	10.2	11.8	(1)
4-Hydroxypyridine	860	11.1	7.9	(16)
2-Quinolinol	1050	11.7	11.0	(16)
Dextrose	1140	12.2	12.4	(4)
Di- <i>tert</i> -butyl- <i>p</i> -cresol	1110	12.2	12.0	(5)
Anthrone	870	...	8.1	
1,2-Benzcarbazole	1100	...	11.8	
1,2-Benzcarbazole	1110	...	11.9	
Carbazole	1120	...	12.1	

^a Half-neutralization potential in millivolts. ^b pK_a equal to 0.0167 (HNP - 380).

$$\text{(Acids in pyridine) } pK_a = 0.0167 \text{ (HNP - 380)} \quad (1)$$

and

$$\text{(Bases in acetic anhydride) } pK_a = 0.0054 \text{ (480 - HNP)} \quad (1a)$$

Values of pK_a calculated from the data of Tables I and II and Equations 1 and 1a agree with literature pK_a values for water within a standard deviation of ± 1 pK_a unit.

Adsorptivity data (on 3.8% $H_2O-Al_2O_3$) were acquired and generalized to other compound types as previously (25, 29-31, 33-39). These new experimental data are summarized below according to compound type. For details on the measurement and interpretation of these data see (31) and Equation 2 of the present paper.

Alkyl Sulfoxides. R^o for dimethyl sulfoxide was 11 ml. per gram with 10 volume % acetonitrile-methylene chloride as eluent ($\alpha\epsilon^o = 0.332$).

Alkyl Thiols. R^o values for butane-1-thiol, butane-2-thiol, and 2-methylpropane-2-thiol eluted by pentane were 1.10, 0.96, and 0.87 ml. per gram, respectively. Butane-1-thiol gave R^o equal to 0.62 ml. per gram for elution by 3.5 volume % methylene chloride-pentane ($\alpha\epsilon^o = 0.055$). Values of Q^o , the adsorption energy of the thiol group, are 2.8, 2.78, and 2.72, respectively. A_s (the relative area) for butane-1-thiol was calculated equal to 4.2.

Hydroxypyridine Derivatives. 4-Hydroxypyridine was not eluted by 9 ml. per gram of 20%v. 2-propanol-pentane ($\alpha\epsilon^o = 0.461$)—i.e., this solute is strongly adsorbed. 2-Quinolinol eluted by 10, 20, and 35 volume % 2-propanol-pentane solutions ($\alpha\epsilon^o = 0.431, 0.461, 0.484$, respectively) gave R^o values of 7.3, 4.4, and 2.7 ml. per gram, respectively. 2-Mercapto-quinoline eluted by 10 volume %, 2-propanol-pentane gave R^o equal to 7.0.

Other Amide Types. Table III presents retention volume data and derived S^o values for the amides *N*-propionyl indole and benzanilide.

Azapyrrole Derivatives. 1-Azaindole and 2-azacarbazole eluted by 1.7% 2-propanol-pentane ($\alpha\epsilon^o = 0.342$) gave R^o values of 3.6 and 2.5 ml. per gram, respectively. Imidazole eluted by 2- and 35-volume %, 2-propanol-pentane gave R^o values of 2.35 and 1.38 ml. per gram, respectively. The adsorption parameters for these compounds in Table IX were then calculated in the usual manner: S^o equal to 8.0, 8.3, and 9.1, respectively. For each of these three compounds, S^o could be calculated with a precision of 0.1 unit by assuming that Q^o for the nitrogen atoms equals 0.8 times the normal value for monoazaaromatics. This

Table II. Titration of Bases in Acetic Anhydride (48)

Base	HNP ^a	pK _a		Ref.
		Lit.	Calcd. ^b	
Pyridine	280	5.2	5.4	(16)
<i>N,N</i> -Dimethylaniline	300	5.1	4.9	(1)
8-Hydroxyquinoline	300	5.1	4.9	(16)
Quinoline	300	4.9	4.9	(16)
3,4-Benzacridine	340	4.7	3.8	(3)
Phenanthridine	300	4.5	4.9	(16)
7,8-Benzoquinoline	380	4.3	2.7	(3)
Phthalazine	400	3.5	2.2	(16)
4-Hydroxypyridine	410	3.3	1.9	(16)
3-Bromopyridine	360	2.8	3.2	(16)
3-Chloropyridine	380	2.8	2.7	(16)
Thiazole	380	2.5	2.7	(2)
3,4-Benzocinnoline	390	2.2	2.4	(16)
Benzotriazole	440	1.6	1.1	(2)
Phenazine	430	1.3	1.3	(2)
Benzothiazole	420	1.2	1.6	(2)
Dimethylsulfoxide	430	1.0	1.4	(45)
2-Chloropyridine	465	0.7	0.4	(2)
Urea	440	0.1, 0.5	1.1	(11, 18)
Phenyl urea	490	-0.3	-0.3	(11)
Acetamide	510	-0.5, 0.1	-0.8	(11, 18)
Acetanilide	540	-2.9 to 0.4	-1.6	(11, 18, 45, 49)
2-Hydroxyquinoline	470	-0.4	0.5	(16)
<i>N</i> -Methyl-2-hydroxyquinoline	460	-0.7	0.6	(16)
Benzamide	550	est -1.0	-1.8	(11)
2-Quinolineshiol	450	-1.4	0.8	(16)
Benzanilide	~560		~-2	
Benoxazole	500		-0.5	
1,4-Dimethyl-2-hydroxyquinoline	450		0.8	
2-methyl-4-hydroxyquinoline	360		3.2	
1-Azacarbazole	350		3.5	
1-Azapyrene	320		4.3	
<i>n</i> -Benzylideneaniline	390		2.4	
11-Ethyl-1,2,3,4-tetrahydrocarbazolidene	325		4.2	

^a Half-neutralization potential in millivolts. ^b pK_a = 0.0054 (480 - HNP).

Table III. LEAC Separability of Various Solutes; 3.8% H₂O-Al₂O₃

Porphyrim	(αε ^o)	Log \bar{R}^o					S ^o	A _s
		27%v. CH ₂ Cl ₂	42%v. CH ₂ Cl ₂	65%v. CH ₂ Cl ₂	CH ₂ Cl ₂	3.2% Acetonitrile CH ₂ Cl ₂ (0.307)		
Etioporphyrin I	(αε ^o)	(0.188)	(0.222)	(0.241)	(0.269)	(0.307)		
Etioporphyrin I, vanadium complex			1.12	0.37	-0.43		14.7	30.0
Mesoporphyrin IX, dimethyl ester		1.67	0.71	-0.28			13.6	30.0
Mesoporphyrin IX, dimethyl ester vanadium				1.63	0.94	-0.16	19.4	(36) ^a
				1.53	0.53		18.9	(36) ^a
Other solutes	(αε ^o)	Log \bar{R}^o (for different %v. CH ₂ Cl ₂ -pentane)						
		18.5	31.5	52	100			
<i>N</i> -Propionyl indole	(αε ^o)	(0.154)	(0.192)	(0.230)	(0.269)			
Benzanilide		0.73	0.30				6.32	10.0 ^a
Thiazole				0.97	0.18		8.59	12.5 ^a
Benzothiazole				0.63	0.21		5.80	6.0 ^a
Benoxazole				0.34			6.22	8.0 ^a
1,2,3,4-Tetrahydro, 11-ethyl carbazolidene				0.34	-0.09		5.94	7.5 ^a
				0.62	0.08		7.65	11.0 ^a

^a Calculated.

empirical relationship was used in estimating S° values for the remaining azapyrrole derivatives of Table IX.

Thiazoles and Oxazoles. R° values and derived adsorption parameters for thiazole, benothiazole, and benzoxazole are given in Table III.

Porphyryns. Table III summarizes R° values and derived adsorption parameters for some porphyryns and their vanadium complexes.

Schiff Bases. R° values and derived adsorption parameters are given for 1,2,3,4-tetrahydro-11-ethyl carbazolidene in Table III.

DISCUSSION

Tables IV to X summarize the acidities, basicities, and adsorptivities (on alumina) of a number of compound

types which are known or suspected to be present in petroleum. Where these compound types have been reported in either petroleum or refined petroleum fractions, reference to that work is made. Tables IV to X are undoubtedly incomplete with respect to possible compound types, but they can be amended and expanded easily as additional information becomes available on the actual composition of petroleum.

The most widely used and reported measure of compound acidity and basicity is the pK_a value in water. The pK_a data of Tables V to X are for the solvent systems of Tables I and II where possible, because these solvents are more useful in petroleum titrations. Compounds with pK_a values in the range -2 to 13 can be titrated. pK_a values were drawn from a number of general references (1-4, 16) and the data of Tables I and II. The effect

Table IV. Index of Hydrocarbon Parameters

Compound Type	Parent Compound ^a	Parent Compound Data ^b			ϵ_1 For Petroleum Fractions, ° F.			Previously Found	
		S°	A_s	ϵ_1	600	800	1000	Petr.	Other ^c
Monoaromatic hydrocarbons	Benzene	1.86	6.0	-0.16	-0.09	-0.07	-0.06	(21)	(27)
Diaromatic hydrocarbons	Naphthalene	3.10	8.0	0.04	0.06	0.06	0.07	(21)	(27)
	Biphenyl	3.41	9.7	0.06	0.07	0.07	0.08		
	ϕ -CH ₂ - ϕ	3.2	11	0.06	0.07	0.07	0.08		
Triaromatic hydrocarbons	ϕ -(CH ₂) ₁₀ - ϕ	3.7	19	0.04	0.04	0.05	0.05		
	Fluorene	4.3	9.5	0.15	0.17	0.16	0.16	(21)	(27)
	Phenanthrene	4.5	10.0	0.17	0.17	0.18	0.18		
Tetraaromatic hydrocarbons	Anthracene	4.6	10.0	0.18	0.18	0.19	0.19		
	3,4-Benzphenanthrene	4.9	12.0	0.17	0.17	0.17	0.19	(21)	(27)
	Pyrene	5.0	11.0	0.20	0.20	0.22	0.20		
	Benzfluorene	5.7	11.5	0.25	0.25	0.25	0.25		
	Triphenylene	5.7	12.0	0.24	0.24	0.22	0.24		
Pentaaromatic hydrocarbons	Benzanthracene, chrysene	5.9	12.0	0.26	0.26	0.24	0.26		
	Naphthacene	7.5	12.0	0.39	0.39	0.38	0.35		
	Benzpyrenes(i)	6.4	13.0	0.28	0.28	0.28	0.29		
	Dibenzfluorenes(i)	7.0	13.5	0.31	0.31	0.31	0.32		
	Dibenzanthracenes(i)	7.2	14.0	0.31	0.31	0.31	0.32		
	Pentacene	10.2	14.0	0.53	0.53	0.53	0.48		

^a ϕ refers to a phenyl ring; (i) includes all unsubstituted isomers. ^b No pK_a data since hydrocarbons are generally nonacidic and nonbasic (see Discussion); for calculation of adsorption data see (30, 35, 37, 38). ^c Cracked gas oils.

Table V. Index of Sulfur Compound Parameters

Compound Type	Parent Compound ^a	Parent Compound Data			ϵ_1 For Petroleum Fractions, ° F.			Previously Found			
		S°	A_s	ϵ_1	pK_a		600	800	1000	Petr.	Other ^b
Thiophene derivatives	Thiophene	1.98	5.0	-0.17			-0.10	-0.08	-0.05	(21)	(43)
	Benzothiophene	3.08	7.0	0.04			0.06	0.06	0.07		
	Dibenzothiophene, naphthothiophenes(i)	4.2	9.0	0.15			0.15	0.15	0.18		
	Naphthobenzothiophenes(i)	5.3	11.0	0.22			0.22	0.20	0.22		
Aliphatic sulfides	Dimethyl sulfide	2.69	4.2	-0.03			0.00	0.00	0.01		
Aromatic sulfides (vicinal)	ϕ -S-CH ₃	3.2	8.5	0.04			0.04	0.04	0.05	(21)	(26)
	$\phi\phi$ -S-CH ₃	4.4	10.5	0.15			0.15	0.13	0.13		
	$\phi\phi\phi$ -S-CH ₃	5.7	12.5	0.20			0.20	0.21	0.21		
Aromatic sulfides (nonvicinal)	ϕ -CH ₂ -S-CH ₃	3.8	9.5	0.10			0.09	0.08	0.08	(26)	(26)
	ϕ -(CH ₂) ₁₀ -S-CH ₃	4.4	17.5	0.09			0.07	0.07	0.08		
	$\phi\phi$ -CH ₂ -S-CH ₃	4.4	11.5	0.14			0.14	0.13	0.12		
Aliphatic disulfides (vicinal)	Dimethyl disulfide	2.7	6.6	-0.02			-0.01	0.00	0.01	(47)	
Aliphatic disulfides (nonvicinal)	CH ₃ -S-CH ₂ -S-CH ₃	4.0	6.0	0.20			0.15	0.12	0.12	(26)	(26)
	CH ₃ -S-(CH ₂) ₁₀ -S-CH ₃	5.0	15.0	0.15			0.10	0.10	0.11		
Aliphatic thiols	Methyl mercaptan	2.8	3.1	0.00	10.5		0.01	0.02	0.03	(47)	
Aromatic thiols	Benzenethiol ^c	8.7	6.0	0.98	6.5		0.65	0.57	0.54		
Aliphatic sulfoxides	Dimethyl sulfoxide	6.7	4.3	0.90		1.4	0.38	0.34	0.33		
Aromatic sulfoxides	ϕ -SO-CH ₃	5.9	8.0	0.39			0.30	0.28	0.27		

^a (i) includes all unsubstituted isomers; ϕ refers to phenyl ring; $\phi\phi$ refers to a naphthalene ring; $\phi\phi\phi$ refers to an anthracene or phenanthrene ring; for calculation of adsorption data see (30, 31, 33-35). ^b Cracked gas oils. ^c Approximate value; same for related petroleum fraction data. ^d Unknown but probably similar to value for aliphatic sulfoxides.

Table VI. Index of Oxygen Compound Parameters

Compound Type	Parent Compound ^a	Parent Compound Data				ϵ_1 For Petroleum Fractions, ° F.			Previously Found	
		S°	A_s	ϵ_1	pK_a acid	600	800	1000	Petr.	Other ^b
Aliphatic ethers	Dimethyl ether	3.5	3.7	0.19		0.07	0.07	0.08		
Aromatic ethers	ϕ -O-CH ₃	3.6	7.8	0.10		0.08	0.08	0.08		
	$\phi\phi$ -O-CH ₃	4.7	9.8	0.19		0.18	0.17	0.17		
	$\phi\phi\phi$ -O-CH ₃	5.8	11.8	0.25		0.25	0.25	0.23		
Furanes	Furane	2.34	4.5	-0.10		-0.03	-0.02	0.00	(50)	(12)
	Benzofuranes	2.78	6.5	0.00		0.03	0.04	0.05		
	Dibenzofuranes	3.7	8.5	0.10		0.10	0.13	0.13		
	Naphthobenzofuranes(i)	5.1	10.5	0.22		0.22	0.23	0.23	(20)	
Aliphatic esters	Methyl acetate	5.0	4.8	0.46		0.25	0.23	0.23		
Aromatic esters	ϕ -CO ₂ CH ₃									
	ϕ -O-CO-CH ₃	5.2	9.0	0.27		0.22	0.21	0.21		
	$\phi\phi$ -CO ₂ -CH ₃	6.0	11.0	0.29		0.28	0.24	0.24		
	$\phi\phi\phi$ -CO ₂ -CH ₃	6.7	13.0	0.30		0.30	0.30	0.27		
	ϕ -CO ₂ - ϕ	5.9	12.0	0.26		0.26	0.21	0.21		
	$\phi\phi$ -CO ₂ - ϕ	6.8	14.0	0.28		0.28	0.25	0.25		
	$\phi\phi$ -CO ₂ - $\phi\phi$	7.7	16.0	0.31		0.31	0.31	0.26		
Aliphatic aldehydes	Acetaldehyde	4.7	3.5	0.54		0.27	0.25	0.24		
Aromatic aldehydes	ϕ -CHO	5.2	7.0	0.34		0.25	0.23	0.23		
	$\phi\phi$ -CHO	6.0	9.0	0.35		0.32	0.27	0.27		
	$\phi\phi\phi$ -CHO	6.8	11.0	0.36		0.36	0.34	0.31		
Aliphatic ketones	Acetone	5.0	4.2	0.52		0.21	0.20	0.20	(19)	
Aromatic ketones	ϕ -CO-CH ₃	5.6	8.0	0.35		0.27	0.25	0.24	(17)	
	$\phi\phi$ -CO-CH ₃	6.3	10.0	0.35		0.3	0.28	0.28		
	$\phi\phi\phi$ -CO-CH ₃	7.0	12.0	0.35		0.35	0.34	0.34		
	Benzophenone	6.2	11.0	0.31		0.29	0.24	0.24		
	Fluorenone	6.6	10.0	0.38		0.36	0.31	0.31		
	Benzfluorenes(i)	7.1	12.0	0.36		0.36	0.35	0.33		
Quinones (nonortho)	1,4-Quinone	5.8	7.0	0.43		0.35	0.29	0.28		
	1,4-Naphthoquinone	8.7	9.0	0.44		0.44	0.35	0.28		
	9,10-Anthraquinone	6.9	11.0	0.37		0.37	0.37	0.32		
	Benz-9,10-anthraquinones(i)	7.8	13.0	0.38		0.38	0.38	0.37		
Quinones (ortho)	1,2-Quinone	7.2	7.0	0.63		0.51	0.42	0.40		
	1,2-Naphthoquinone	7.9	9.0	0.57		0.57	0.45	0.42		
	9,10-Phenanthrenequinone	8.7	11.0	0.54		0.54	0.54	0.44		
	Benz-9,10-phenanthrenequinones(i)	9.7	13.0	0.53		0.53	0.53	0.49		
Aliphatic alcohols	Methanol ^c	6.5	6.0	0.62		0.32	0.31	0.31		
Aromatic alcohols	Benzyl alcohol ^d	6.5	6.0	0.62		0.38	0.37	0.36		
Phenols	ϕ -OH	7.4	6.0	0.77	10-12	0.52	0.45	0.42		
	$\phi\phi$ -OH	7.4	6.0	0.77		0.62	0.47	0.43		
	$\phi\phi\phi$ -OH	7.4	6.0	0.77		0.77	0.57	0.44		
Aliphatic carboxylic acids	Acetic acid			> 1.3	4.8					
Aromatic carboxylic acids	Benzoic acid			> 1.3	4.2		> 1.0			

^a ϕ refers to phenyl ring; $\phi\phi$ refers to naphthalene ring; $\phi\phi\phi$ refers to phenanthrene ring; (i) includes all unsubstituted isomers; for calculation of adsorption data see (31, 33-36) and Experimental section. ^b Cracked gas oils. ^c Anthrone has an acid pK_a of 8.1. ^d Approximate values for these compounds and related petroleum fractions.

of alkyl substitution on pK_a generally is small and has been discussed (3).

The adsorptivity data of Tables IV to X are exclusively for the adsorbent alumina, which has been used widely in petroleum separations (6, 15, 24, 40). Differences in the adsorption properties of various solids have been reviewed (29, 32). A previous treatment (29, 34) has shown that sample separability or compound retention volume R^o in linear elution adsorption chromatography (LEAC) can be related to various adsorbent, eluent, and sample parameters:

$$\log R^o = \log V_a + \alpha(S^\circ - A_s \epsilon^\circ) + \Sigma \Delta_{res} \quad (2)$$

V_a and α are properties of the adsorbent, ϵ° is the eluent strength parameter, A_s is the cross-sectional area of the sample molecule, and S° is the sample adsorption energy in a standard system. The term $\Sigma \Delta_{res}$ can be ignored in the standard adsorption system described below. Values

of V_a , α , ϵ° , and A_s are available or calculable for various systems (25, 29, 33, 42). Values of S° are available or calculable for a wide range of sample types (26, 29-31, 33-39 and Experimental section). S° is the principal contributor to relative sample adsorptivity, but a better index of relative adsorptivity is the derived parameter ϵ_1 , defined as $(\alpha S^\circ + \log V_a)/\alpha A_s$. In addition to values of S° , A_s , and ϵ_1 for individual compounds, Tables IV to X give ϵ_1 values for the aliphatic derivatives of these compounds which occur in various petroleum boiling ranges. A following section describes the calculation of these latter values.

Standard Adsorption Chromatographic System. The ϵ_1 values of Tables IV to X are strictly applicable only to a standard system: 3.8% H₂O-Al₂O₃ (25, 30), with certain eluents (bases, ethers) excluded. Values of ϵ_1 vary with changes in the adsorbent parameters V_a and α , and all ϵ_1 values become progressively larger as alumina water content is reduced. In some cases, decrease in alumina water content

Table VII. Index Of Basic^a Mononitrogen Compound Parameters

Compound Type	Parent Compound ^b	Parent Compound Data				ϵ_1 For Petroleum Fractions, ° F.			Previously Found	
		S°	A_c	ϵ_1	pK_a base	600	800	1000	Petr.	Other ^b
Aliphatic amines	Dimethylamine	6.2	3.9	0.87	9-11	0.31	0.31	0.31	(22)	(22)
Pyridines	Pyridine									
	Type I	6.3	6.0	0.58	5-7	0.52	0.48	0.47	(8, 19)	(8, 15)
	Type II	5.5	6.0	0.46		0.41	0.38	0.38		
	Type III	5.3	6.0	0.42		0.39	0.36	0.36		
	Azanaphthalene									
	Type I	7.0	8.0	0.53		0.54	0.47	0.46		
	Type II	6.2	8.0	0.43	3.5-5.5	0.45	0.39	0.39		
	Type III	6.0	8.0	0.40		0.43	0.37	0.37		
	Type IV	4.8	8.0	0.25		0.27	0.24	0.24		
	Type V	3.8	8.0	0.12		0.14	0.13	0.13		
	Azaphenanthrene, azaanthracene									
	Type I	7.7	10.0	0.49		0.59	0.51	0.46		
	Type II	8.9	10.0	0.41		0.50	0.44	0.40		
	Type III	8.7	10.0	0.39	3-5	0.47	0.42	0.38		
	Type IV	5.8	10.0	0.30		0.35	0.32	0.30		
	Type V	5.0	10.0	0.22		0.24	0.24	0.22		
	Type VI	4.2	10.0	0.14		0.14	0.16	0.15		
	Azachrysenes(i)									
	Type I	8.4	12.0	0.47		0.54	0.43	0.47		
	Type II	7.8	12.0	0.40	3-5	0.46	0.46	0.41		
	Type III	7.4	12.0	0.38		0.44	0.44	0.39		
	Type IV	8.8	12.0	0.33		0.36	0.36	0.33		
	Type V	8.3	12.0	0.29		0.30	0.30	0.29		
	Type VI	5.5	12.0	0.22		0.22	0.22	0.23		
Anilines	Aniline									
	Type I	6.3	7.5	0.46		0.45	0.40	0.40		(23)
	Type II	5.8	7.5	0.39	4-5	0.38	0.33	0.33		
	Type III	4.9	7.5	0.28		0.29	0.26	0.26		
	Aminonaphthalene									
	Type I	6.9	9.5	0.43		0.49	0.41	0.40		
	Type II	6.4	9.5	0.38	4-5	0.43	0.37	0.35		
	Type III	5.7	9.5	0.30		0.36	0.31	0.30		
	Benzalmethylamine	6.3	9.0	0.39		0.32	0.28	0.27		(15)
	Benzylidene aniline	6.0	11.0	0.29	2.4	0.29	0.24	0.22		
	1,2,3,4-Tetrahydro-carbazolidene	7.6	9.5	0.50	4.2	0.50	0.38	0.36		

^a Compounds titrable in glacial acetic acid. ^b (i) Includes all unsubstituted isomers; for calculation of adsorptivity data see (30, 31, 33, 34, 39) and Experimental section. ^c Cracked gas oils.

also results in changes in separation order (35). Basic eluents such as pyridine and diethylamine preferentially retain samples with N—H or O—H groups (33), causing the apparent ϵ_1 values of such compounds to be increased by as much as 0.2 unit. Ethers as eluents preferably retain hydrocarbons relative to more polar samples. The ϵ_1 data of Tables IV to X apply to linear isotherm systems only, but relative separation order should be the same in nonlinear separations.

Contribution of Alkyl Substitution to Compound Type Adsorptivity. Aliphatic substitution on the parent compounds of Tables IV to X, to give petroleum components of differing boiling range, significantly affects ϵ_1 . The magnitude of this effect was evaluated in an adsorption chromatographic study of narrow compound type fractions from petroleum samples of varying boiling range. The results of this study are summarized in Figures 1 and 2, as changes in sample A_s (ΔA_s) or S° (ΔS°) values vs. total aliphatic substitution (carbon number). The results are generally consistent with pure compound studies (30, 43). The solid curve of Figure 1 is that calculated for a single n -alkyl substituent (43), and fits the data for aromatic compounds well. Decrease in adsorbent water content (solid data of Figure 1) causes an increase in ΔA_s , and, relative to this increased value ΔA_s , for the aliphatic sulfides is higher yet by about 2.5

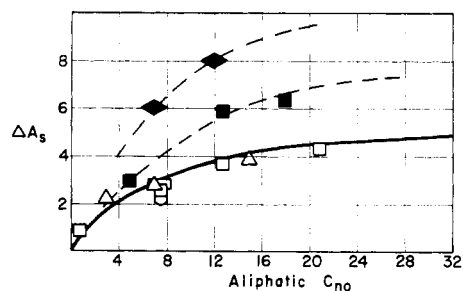


Figure 1. Dependence of experimental ΔA_s values on aliphatic substitution (C_{no})

1.6-2.1% 3.8%
 $H_2O-Al_2O_3$ $H_2O-Al_2O_3$

Diaromatic hydrocarbons^a ■ □
 Triaromatic hydrocarbons^a ▲ △
 Tetraaromatic hydrocarbons^a ◻ ◻
 Aliphatic monosulfides^a ◆ ◆
 Carbazoles ◊ ◊

^a See Table IV for parent compound types.

Table VIII. Index of Weakly Basic^a Mononitrogen Compound Parameters

Compound Type	Parent Compound ^b	Parent Compound Data			ϵ_1 For Petroleum Fractions, ° F.			Previously Found		
		S^0	A_s	ϵ_1	pK _a		600	800	1000	Petr.
Thiazoles	Thiazole	5.8	6.0	0.50		2.7	0.44	0.41	0.41	(10)
	Benzothiazole	6.2	8.0	0.43		1.6	0.45	0.39	0.39	
	Dibenzothiazole	6.9	10.0	0.41			0.50	0.44	0.40	
Oxazoles	Oxazole	5.2	5.5	0.44			0.37	0.34	0.34	(40)
	Benzoxazole	5.9	7.5	0.42		-0.5	0.44	0.38	0.38	
Pyrroles	Pyrrole	5.9	8.0	0.39		-0.3	0.28	0.25	0.24	(40)
	Indole	6.8	10.0	0.40		-2.4	0.33	0.28	0.27	
N-Alkyl pyrroles	N-methyl pyrrole	2.7	6.5	0.02		-1.8	0.12	0.11	0.12	
	N-methyl carbazole ^d					> -2.5				
Amides Anilides	Acetanilide	8.2	9.5	0.57		-1.6	0.52	0.42	0.40	
	Benzacetanilide(i)	8.9	11.5	0.53			0.52	0.42	0.40	
	Dibenzacetanilides(i)	9.6	13.5	0.50			0.50	0.50	0.41	
	Benzanilide	8.6	12.5	0.46		~ -2	0.46	0.41	0.36	
Amides N-Acetylpyrroles	Benzo-benzanilide(i)	9.3	14.5	0.45			0.45	0.45	0.37	
	N-Acetylpyrrole	5.6	7.5	0.37		> -2	0.27	0.25	0.26	
	N-Acetylindole	6.3	9.5	0.37			0.34	0.29	0.31	
	N-Acetylcarbazole ^d	7.0	11.5	0.36			0.36	0.34	0.31	
Amides Benzamides	Benzamide	9.4	8.0	0.83		-1.8	0.71	0.58	0.55	
	Naphthamide(i)	10.1	10.0	0.73			0.73	0.60	0.54	
	Benznaphthamides(i)	10.8	12.0	0.67			0.67	0.67	0.55	
Amides, Aliphatic Amides	Acetamide	8.0	4.2	1.23	15	-0.8	0.68	0.56	0.54	(9)
	Hydroxypyridines	2-Hydroxypyridine	9.2	6.5	0.98	11	0.7	0.71	0.61	
4-Hydroxypyridine		> 9.1		> 0.97			> 0.70	> 0.60	> 0.57	
2-Hydroxyquinoline		9.9	8.5	0.83	12	0.5	0.78	0.61	0.57	
Benzo-2-hydroxyquinoline(i)		10.6	10.5	0.74			0.74	0.68	0.57	
Amides N-Alkylhydroxypyridines	N-Methyl-2-pyridone	7.9	8.0	0.64			0.52	0.44	0.43	
	N-Methyl-2-quinolone	8.6	10.0	0.58		0.6	0.58	0.46	0.43	
	N-Methyl-benzo-2-quinolone(i)	9.3	12.0	0.54			0.54	0.52	0.45	
Amides Mercaptopyridines	2-Mercaptopyridine	9.2	6.5	0.98			0.71	0.61	0.58	(6)
	4-Mercaptopyridine	> 9.1					> 0.70	> 0.60	> 0.57	
	2-Mercaptoquinoline	9.9	8.5	0.83	10	0.8	0.78	0.61	0.57	
	Benzo-2-mercaptoquinoline(i)	10.6	10.5	0.74			0.74	0.68	0.57	

^a Titrable in acetic anhydride. ^b (i) Includes all unsubstituted isomers; for calculation of adsorptivity data see (34, 36, 39) and Experimental section. ^c Cracked gasolines. ^d Nonbasic.

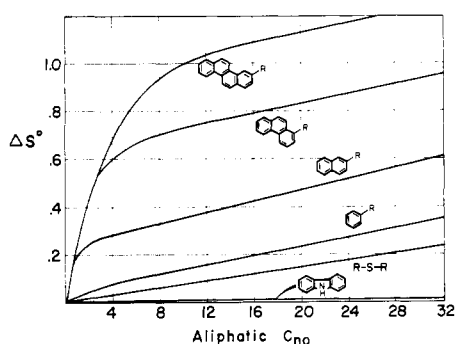


Figure 2. Dependence on experimental ΔS° values of aliphatic substitution n . Smoothed data

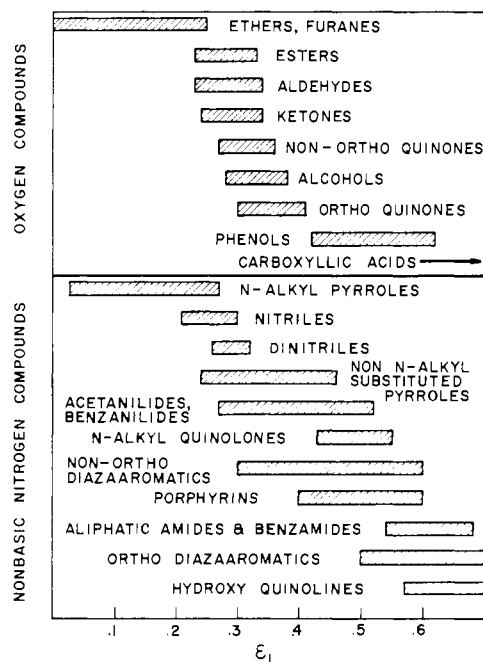


Figure 3. Grouping of different oxygen and nitrogen compound types by separation on 3.8 % H₂O-Al₂O₃

Table IX. Index Of Basic^a And Weakly Basic^b Dinitrogen Compound Parameters

Compound Type	Parent Compound ^c	Parent Compound Data					ϵ_1 For Petroleum Fractions, ° F.			Previously Found			
		S°	A_s	ϵ_1	pK _a ^e		600	800	1000	Petr.	Other ^d		
Diazaaromatics ^f (nonortho)	Pyrazine	5.7	6.0	0.48		0.6	0.31	0.30	0.30		(12)		
	Pyrimidine	6.3	6.0	0.58		1.3	0.37	0.35	0.35				
	Diazanaphthalenes(i)		6.0–	8.0	0.40–			0.33–	0.29–	0.29–			
			8.0		0.75			0.60	0.52	0.51			
Diazaaromatics ^f (ortho)	Diazaanthracenes, diazaphenanthrenes(i)	6.3–	10.0	0.35–		1–4	0.35–	0.32–	0.30				
		9.7		0.69			0.69	0.58	0.53				
	Pyridazine	8.0	6.0	0.86		2.3	0.55	0.52	0.50		(15)		
	Benzpyridazines, 1,8-diazanaphthalenes(i)	7.7–	8.0	0.61–		2.2	0.49–	0.43–	0.42				
9.8			0.87			0.69	0.59	0.54					
Azapyrroles	1,10-Phenanthroline	10.3	10.0	0.75		4.3	0.75	0.63	0.57				
		8.3–	10.0	0.55–			0.55–	0.47–	0.44–				
	Dibenzpyridazines(i)	9.9		0.71			0.75	0.60	0.55				
		Imidazole											
N-Alkyl azapyrroles	Type I	8.0	6.5	0.80	14	3.7	0.61	0.51	0.49		(15)		
	Type II	7.6	6.5	0.73			0.56	0.46	0.45				
	Type III	7.4	6.5	0.71			0.55	0.45	0.44				
	Azaindoles(i)	Type I	8.9	8.5	0.72			0.72	0.55	0.51			
		Type II	8.3	8.5	0.65	14	1.2	0.65	0.50	0.46			
		Type III	8.1	8.5	0.62			0.62	0.48	0.44			
	Azacarbazoles(i)	Type I	9.6	10.5	0.65			0.65	0.61	0.51			
		Type II	9.0	10.5	0.59		3.5	0.59	0.56	0.47			
		Type III	8.8	10.5	0.57			0.57	0.50	0.45			
		Type IV	7.8	10.5	0.48			0.48	0.46	0.39			
	Azabenzcarbazoles(i)	Type I	10.5	12.5	0.61			0.61	0.61	0.55			
		Type II	9.9	12.5	0.56			0.56	0.56	0.51			
		Type III	9.0	12.5	0.49			0.49	0.49	0.45			
		Type IV	8.0	12.5	0.41			0.41	0.41	0.39			
		Type V	7.4	12.5	0.36			0.36	0.36	0.35			
	N-Methylimidazole	Type I	6.8	6.5	0.61			0.53	0.49	0.49			
		Type II	6.0	6.5	0.49			0.43	0.40	0.40			
		Type III	5.8	6.5	0.46			0.41	0.38	0.38			
		N-Methylazaindoles(i)	Type I	7.5	8.5	0.55			0.56	0.49	0.48		
			Type II	6.7	8.5	0.46			0.46	0.41	0.40		
			Type III	6.5	8.5	0.43			0.45	0.40	0.39		
		N-Methylazacarbazoles(i)	Type I	8.2	10.5	0.51			0.51	0.53	0.48		
			Type II	7.4	10.5	0.44			0.44	0.45	0.41		
			Type III	7.2	10.5	0.44			0.42	0.44	0.40		
			Type IV	6.4	10.5	0.34			0.34	0.36	0.33		
		N-Methylazabenzcarbazoles(i)	Type I	8.8	12.5	0.48			0.48	0.48	0.47		
			Type II	8.0	12.5	0.42			0.42	0.42	0.42		
	Type III		7.8	12.5	0.40			0.40	0.40	0.41			
Type IV	7.4		12.5	0.37			0.37	0.37	0.37				
Type V	7.1		12.5	0.34			0.34	0.34	0.33				

^a Titrable in glacial acetic acid. ^b Titrable in acetic anhydride. ^c (i) Includes all unsubstituted isomers; for calculation of absorption data see (34) and Experimental section. ^d Cracked gas oils. ^e Base pK_a refers to first break; in acetic anhydride some of the diazaaromatics (e.g., *m*-phenanthroline) give a second break corresponding to the titration of the second nitrogen. ^f For more detailed information on the adsorptivities of individual diazaaromatics see Table II of (34).

units. Similarly, ΔA_s for an aliphatic ester fraction was 3.5 units higher than the solid curve of Figure 1, for elution from 3.8% H₂-Al₂O₃. ΔA_s values used in the calculation of the petroleum fraction data of Tables IV to X were obtained from the solid curve of Figure 1 for aromatic compound types, and were assumed 3 units higher for aliphatic compounds. Values of ΔS° for the various compound types of Tables IV to X were estimated as follows: ΔS°

for aromatic molecules (other than derivatives of pyridine, aniline, or acidic compounds) from the various curves of Figure 2 for the aromatic hydrocarbons of similar aromatic ring number, aliphatic derivatives from curve of Figure 2 for aliphatic sulfides; acidic compounds, assume ΔS° equal to zero. The pyridine and aniline derivatives show extreme contributions to S° by aliphatic substituents (34, 39). Steric effects are sufficiently important to require subdivision of

Table X. Index of Nonbasic^a Nitrogen Compound Parameters

Compound Type	Parent Compound ^b	Parent Compound Data				ϵ_1 For Petroleum Fractions, ° F.			Previously Found	
		S^0	A_s	ϵ_1	pK_a acid	600	800	1000	Petr.	Other ^c
Aliphatic nitriles	Acetonitrile	5.0	3.1	0.71		0.29	0.27	0.27		(13)
Aromatic nitriles	ϕ -CN	5.1	8.0	0.29		0.22	0.21	0.21		(13)
	$\phi\phi$ -CN	5.6	10.0	0.28		0.27	0.23	0.23		
	$\phi\phi\phi$ -CN	6.1	12.0	0.28		0.28	0.28	0.25		
Aromatic dinitriles	ϕ -(CN) ₂	6.4	10.0	0.36		0.31	0.27	0.26		(13)
	$\phi\phi$ -(CN) ₂	6.9	12.0	0.34		0.34	0.28	0.27		
	$\phi\phi\phi$ -(CN) ₂	7.4	14.0	0.33		0.33	0.33	0.30		
	Carbazole	Carbazole	7.7	12.0	0.41	12.1	0.41	0.34	0.30	(46)
Carbazoles	Benzcarbazoles(<i>i</i>)	8.8	14.0	0.43	11.9	0.41	0.41	0.32		
	<i>N</i> -Alkyl carbazoles	<i>N</i> -Methylcarbazole	5.1	10.5	0.22		0.22	0.22	0.21	
<i>N</i> -Alkyl carbazoles	<i>N</i> -Methylbenzcarbazoles(<i>i</i>)	6.3	12.5	0.28		0.28	0.28	0.27		
	Porphyrins	Porphyrin	14.7	20.4	0.58					(46)
Porphyrin vanadium complexes	Etioporphyrins(<i>i</i>)	14.7	30.0	0.40						
	Mesoporphyrin dimethyl esters(<i>i</i>)	19.4	36.0	0.46						
	Rhodoporphyrin dimethyl esters(<i>i</i>)	19.0	34.7	0.47						
	Pyrroporphyrin methyl esters(<i>i</i>)	17.2	31.7	0.44						
	Phylloporphyrin methyl esters(<i>i</i>)	17.2	32.7	0.43						
	V-porphyn	13.8	20.4	0.53						
	V-etiochlorophylls(<i>i</i>)	13.0	30.0	0.36						
	V-mesoporphyrin dimethyl esters(<i>i</i>)	18.9	30.0	0.45						
	V-rhodoporphyrin dimethyl esters(<i>i</i>)	18.3	34.7	0.45						
	V-pyrroporphyrin dimethyl esters	10.5	31.7	0.42						
V-phylloporphyrin methyl esters(<i>i</i>)	10.5	32.7	0.42							

^a Nontitrable in acetic anhydride. ^b (*i*) Includes all unsubstituted isomers; ϕ refers to phenyl ring; $\phi\phi$ refers to naphthalene ring; $\phi\phi\phi$ refers to phenanthrene or anthracene ring; for calculation of absorption data see (31, 39) and Experimental section. ^c Cracked or hydro-treated gas oils.

Table XI. Classification of Nitrogen Geometry in Pyridine and Aniline Derivatives

Type	Structure	Examples
I		Pyridine, 3- and 4-alkyl pyridines, isoquinoline, aniline
II		Quinoline, 2-alkyl pyridines, 2-alkyl anilines
III		Acridine, 2-methyl quinoline, 2,6-dialkyl pyridines, 2,6-dialkyl anilines
IV		8-Methyl quinoline, 7,8-benzoquinoline, 1-amino, 8-alkyl naphthalenes
V		3,4-Benzacridine, 4-methyl acridine
VI		3,4-5,6-Dibenzacridine, 4,5-dimethyl acridine

these compound types according to the relative crowding of the nitrogen atom, as in the classification scheme of Table XI. Similarly, nonortho alkyl substitution increases S° for these compounds much more than in the case of the aromatic hydrocarbons of similar ring number, and pure compound data (39) were used to estimate the additional contribution to ΔS° in excess of that given by Figure 2.

Given values of ΔA , and of ΔS° for the effect of aliphatic substitution on the original S° and A , values of a parent molecule, it may be shown that

$$\epsilon_1 = [(A_s/A_s + \Delta A_s)](\epsilon_1)^\circ + \Delta S^\circ / (A_s + \Delta A_s)$$

ϵ_1 refers to the value for the aliphatic substituted derivative—i.e., petroleum component—and $(\epsilon_1)^\circ$ is the value of ϵ_1 for the original parent compound.

With the exception of basic nitrogen compounds, compounds of the same type fall into reasonably narrow adsorptivity ranges, as illustrated in Figure 3.

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Thermodynamic Functions of Cyanogen Bromide

JOHN S. GORDON

Astrosystems International, Inc., Fairfield, N.J.

THERMODYNAMIC DATA for BrCN are required in the analysis of combustion of high density oxygen deficient systems with various amine fuels.

As a result of recent higher resolution infrared studies, Maki and Gott (7) have determined the rotation-vibration interaction term, α_3 , and the doubling coefficient, g_{22} . Maki (6) has determined the anharmonic terms, x_{22} , x_{23} , and

($\nu_1 + x_{13}$). Burrus and Gordy (1) determined the rotational constant, B_0 and the rotational stretch constant, D_0 . Townes, Holden, and Merritt (9) have determined the α_2 value. Freitag and Nixon (4) have determined the observed fundamentals, σ_i ; their older values of x_{22} , x_{23} , and g_{22} when used in a comparison calculation led to less satisfactory values of the thermodynamic functions. Maki