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The Activity Coefficients of Indicators in Sulfuric Acid Solutions. The Relationships between Indicator Acidity Functions

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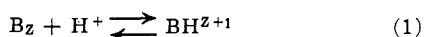
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The variation of activity coefficient with acid concentration in aqueous sulfuric acid solutions has been measured for a number of indicators appropriate to the H_0 , H_R and H_- indicator acidity functions. All ionic indicator activity coefficients have been referred to a common standard ion, the tetraethylammonium ion. The variations of activity coefficients with acid concentration are discussed and the differences between the above acidity functions interpreted in terms of these variations. It is found that from any one of the acidity functions and activity coefficient data the other two may be calculated over a considerable range of concentration. Protonation equilibrium data for some H_0 indicators are also reported.

Introduction

The acidity function approach to the study of concentrated acids since its introduction by Hammett and Deyrup over thirty years ago¹ has proved to be very useful.²⁻⁵ The basic method of using indicators as a means of measuring the protonating ability of acids is simple and direct. However, the interpretation of acidity functions has been the subject of much discussion since the inception of the concept.

The general acidity function, H_Z , based on the equilibrium



is defined by

$$H_Z \equiv pK_B - \log \frac{C_{BH^{Z+1}}}{C_{B_Z}} \quad (2)$$

from which

$$H_Z = -\log a_{H^+} + \log \frac{f_{BH^{Z+1}}}{f_{B_Z}} \quad (3)$$

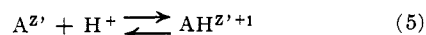
$$= -\log C_{H^+} + \log \frac{f_{BH^{Z+1}}}{f_H f_{B_Z}} \quad (4)$$

where C refers to concentration, f is an activity coefficient and a_{H^+} is the hydrogen ion activity.

Equation 3 demonstrates that H_Z is a measure of the hydrogen ion activity, but when regarded so, involves at least one single ion activity coefficient. These latter two quantities, of course, are not in principle measurable separately. Equation 4 shows explicitly that H_Z actually involves combinations of activity coefficients that are determinable in principle.

The use of a function such as H_Z in a given medium is complicated by two types of difficulties. First, there

is the question of the invariance of the ratio $f_{BH^{Z+1}}/f_{B_Z}$ to indicator structure among the class of indicators used to establish the acidity function. This point can be tested to some extent by the measurements used to establish H_Z .⁵ Second, H_Z is often applied as a measure of hydrogen ion activity in equilibria (or rates^{6,7}) other than of the type used to establish H_Z . When this is done the ratio $f_{BH^{Z+1}}/f_{B_Z}$ always appears relative to another such ratio appropriate to the new equilibrium (or rate). As an illustration, the equilibrium constant for the reaction



can be expressed in terms of H_Z . Thus

$$-pK_A = \log a_{H^+} + \log \frac{C_{A^{Z'}}}{C_{AH^{Z'+1}}} + \log \frac{f_{A^{Z'}}}{f_{AH^{Z'+1}}} \quad (6)$$

and substituting for $\log a_{H^+}$ from eq. 3

$$-pK_A = -H_Z + \log \frac{C_{A^{Z'}}}{C_{AH^{Z'+1}}} + \log \left(\frac{f_{A^{Z'}} f_{BH^{Z+1}}}{f_{AH^{Z'+1}} f_{B_Z}} \right) \quad (7)$$

Thus it is apparent that, although $(f_{BH^{Z+1}}/f_{B_Z})$ involves one or more single ion activity coefficients, its appearance in eq. 7 along with the ratio appropriate to the new equilibrium $(f_{A^{Z'}}/f_{AH^{Z'+1}})$ always involves combinations of activity coefficients which are, in principle, determinable. However, there is, at present, almost no experimental information regarding the actual values of these determinable combinations. In fact, when $Z = Z'$ the last term in eq. 7 is often taken to be zero for lack of better information.

Clearly, a more satisfactory, yet economical, procedure would be to measure the activity coefficients of the charged species appropriate to H_Z relative to a standard ion. Similar measurements of ionic activity coefficients appropriate to any new equilibrium (or rate) relative to the same standard ion would allow the activity coefficient combination in eq. 7 to be constructed. Thus any acidity function, H_Z , could be used in principle to represent the hydrogen ion activity in any other equilibrium or rate. Of course, there may well be experimental difficulties in carrying

(1) L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932).

(2) Nearly every textbook on physical organic chemistry contains a section on acidity functions. See, for instance, J. E. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956; E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959.

(3) For the inorganic-analytical point of view see H. A. Laitinen, "Chemical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(4) For the biochemical point of view see E. Kosower, "Molecular Biology," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

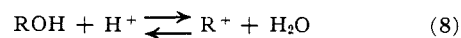
(5) A comprehensive general review is given by M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(6) F. A. Long and M. A. Paul, *ibid.*, **57**, 935 (1957).

(7) H. Zollinger, *Ann. Rev. Phys. Chem.*, **13**, 391 (1962).

out measurements of activity coefficients truly representative of the molecular classes involved.

It is the purpose of the present paper to report measurements in aqueous sulfuric acid (up to ~70% concentration) of the dependence on acid concentration of the activity coefficients of indicator molecules appropriate to three acidity functions. These are, first, the original H_0 function of Hammett based primarily on the protonation of substituted anilines. Second is the H_R function based on the dehydration of triarylcarbinols to carbonium ions.⁸ In this case, eq. 1-4 require some modification,



$$H_R \equiv pK_{\text{ROH}} - \log(C_{\text{R}^+}/C_{\text{ROH}}) \quad (9)$$

$$= -\log a_{\text{H}^+} + \log \frac{f_{\text{R}^+} a_{\text{H}_2\text{O}}}{f_{\text{ROH}}} \quad (10)$$

where $a_{\text{H}_2\text{O}}$ is the activity of water. The third function is H_- which is based on the dissociation of cyanocarbon acids.^{9,10}

Experimental Methods and Results

Activity coefficients were measured *via* solubility of the indicators in the acid solutions. Thus

$$f = f'(C'/C) \quad (11)$$

where f is the activity coefficient of the indicator and C is its concentration in a given acid solution in equilibrium with solid indicator. The primes refer to a solution of different acid concentration. The reference state ($f = 1$) is taken to be a dilute solution of indicator in pure water, so that

$$f = (C_0/C) \quad (12)$$

where C_0 is the solubility in pure water. For a 1-1 salt, $f = f_i = \sqrt{f_i f_-}$.

An experimental limitation on the activity coefficient measurement is imposed by the interference of the protonation equilibrium. Molecules should be chosen which are representative of the class involved. Further, these models must remain protonated or unprotonated (depending on which type of activity coefficient is being measured) over the entire acid concentration range. In the case of the neutral molecules considerable protonation can be tolerated providing only the neutral species in solution is measured.

The solutions were equilibrated by mechanically shaking a considerable excess of finely divided solid indicator in 7-10 ml. of acid solution for several hours to overnight. The equilibration flasks were thermostated at $25.00 \pm 0.02^\circ$ in a water-bath. Samples for analysis were removed by means of a 2-ml. pipet fitted with a fritted glass filter tube over the tip. Dilution was often necessary to obtain convenient optical densities. The concentrations were then measured spectroscopically in either a Cary model 15 recording spectrophotometer or Beckman model DU spectrophotometer.

The charge types of the ionic indicator activity coefficients appropriate to the H_0 and H_R function are positive (f_{BH^+} or f_{R^+}) and must, of course, be measured in combination with an anion ($f_{\text{BH}^+ f_{\text{A}^-}}$ or $f_{\text{R}^+ f_{\text{A}^-}}$). The 1,1,2,3,3-pentacyanopropenide (PCP^-) anion was chosen for this purpose as it is not protonated in the aqueous sulfuric acid solutions used.^{9,10} $f_{\text{BH}^+ f_{\text{A}^-}}$ or $f_{\text{R}^+ f_{\text{A}^-}}$ may be measured as f_{\pm}^2 of a dilute solution of the salt $\text{BH}^+ \text{A}^-$ or $\text{R}^+ \text{A}^-$ in the acid solution. The present work was greatly aided by the availability of a suitable anion for combination in salts with indicator cations.

Salts of Hammett indicators were prepared by mixing warm equimolar solutions of the substituted aniline, in sufficient acid to ensure protonation, with sodium pentacyanopropenide in water. The salt precipitated on cooling to the ice point. It sometimes precipitated partially as an oil in which crystallization was easily induced by scratching. All of the anilines were purchased commercially.

In the case of the weaker bases (*p*-nitroaniline, for example) measurements in the most dilute acid solutions were not made due to the dissociation of the cation. Extrapolated values were arrived at by assuming the variation of the activity coefficient in the less concentrated solutions is the same as for salts of the stronger bases (aniline, for example).

The pentacyanopropenide anion spectral absorption (λ_{max} 410 $\text{m}\mu$) was used as the measure of concentration.

(8) N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

(9) R. H. Boyd, *ibid.*, **83**, 4288 (1961).

(10) R. H. Boyd, *J. Phys. Chem.*, **67**, 737 (1963).

Salts of Triarylcarbonium Ions.—Tri(*p*-methoxyphenyl)-carbonium pentacyanopropenide was the only salt studied. This carbonium ion was selected because it remains ionized in relatively dilute acid.⁸ It was prepared in a manner similar to that of Deno, *et al.*,⁸ except that the product was not isolated as such. The final reaction mixture was extracted with 20% sulfuric acid. The desired salt was precipitated from the aqueous acid by adding an exactly equimolar amount of sodium pentacyanopropenide. Care was required in preparing an exactly stoichiometric salt. Due to the extreme insolubility of the salt a slight adsorbed excess of one of the ions can cause a serious error in the solubility determination through the common ion effect. The prepared salt was washed several times by equilibrating with 20% sulfuric acid and filtering. Measurement of the extinction of both the cation and anion peaks of the equilibrated solutions was used as the criterion of the stoichiometry. These were found to be in the proper ratio^{8,10} and the ratio was independent of the solubility in different acid concentrations.

Cyanocarbon Salts.—The pentacyanopropenide anion as explained above was used in combination with the cations of the H_0 and H_R indicators. Tetraalkylammonium salts (other than the tetramethylammonium) of pentacyanopropene were made by mixing equimolar aqueous solutions of tetraalkylammonium bromides or chlorides (Eastman Organic Chemicals Co.) and sodium pentacyanopropenide. The latter was prepared *via* the free acid from the tetramethylammonium salt¹¹ by ion exchange¹² in hot water followed by potentiometric titration with sodium hydroxide. Tetraalkylammonium salts (other than the tetraethylammonium) of bis-(tricyanovinyl)-amine (*i.e.*, 1,1,2,4,5,5-hexacyano-3-azapenta-1,4-diene) were prepared in a similar manner to the above from the tetraethylammonium salt.¹¹

Neutral Indicators.—The neutral Hammett indicators were purchased commercially (Eastman Organic Chemicals Co., K and K Laboratories, Inc.) with the exception of 2,4-dichloro-6-nitroaniline which was prepared as a custom synthesis by Aldrich Chemical Co. These indicators were appreciably protonated at the higher acid concentrations. They were thus measured either undiluted or diluted with acid of the same concentration so that the protonation did not interfere until the neutral base absorption became small relative to the protonated cation. Triphenylcarbinol (Matheson, Coleman and Bell, Inc.) was recrystallized several times from hydrocarbon solvent (Skellysolve B). Deno and Perrizzolo's procedure¹³ of converting the alcohol in the equilibrated solution to carbonium ion (prior to spectroscopic analysis) by dilution with concentrated sulfuric acid was adopted. Protonation in the equilibrated solution at the highest acid concentration was corrected for by measuring the solution diluted with both concentrated acid and acid of the same concentration and taking the difference.

Ethyl cyanoacetate (Eastman Organic Chemicals Co.) was a special case since it is liquid at room temperature and has no appreciable ultraviolet-visible absorption above 200 $\text{m}\mu$. Its solubility was determined by observing the volume required to titrate the acid solution to cloudiness. This was checked by Kjeldahl nitrogen determination on the acid solution and gave good agreement. The effect of mutual solubility on the activity coefficient obtained from eq. 12 is unknown. *p*-Chloro-*N*-tricyanovinylaniline was prepared according to McKusick, *et al.*¹⁴ This compound is a weak acid which remains undissociated in acid above 0.01 molar.

The solubility data are presented in Table I.

Protonation Studies.—In order to provide additional information on activity coefficients, the protonation ratios $C_{\text{BH}^+}/C_{\text{B}}$ of three Hammett indicators were measured. These were 2,6-dichloro-4-nitroaniline, 2,4-dichloro-6-nitroaniline and 2,4-dinitroaniline. The first of these apparently has not been measured before and the previous data¹ on the others are from visual colorimetry without close temperature control. All measurements were made in 10-cm. cells that had been thermostated at $25.00 \pm 0.02^\circ$ and immediately measured after removal from the thermostat. The data are presented in Table II.

Discussion

1. **Dependence of Activity Coefficients on Indicator Concentration.**—To be useful, the ionic activity coefficients should be independent of indicator concentration and $f(C^+, A^-) = \sqrt{f_C f_{A^-}}$, where f_+ is independent of the indicator anion and *vice-versa*. The indicators used here are rather insoluble and the resulting solutions, low in concentration in indicator, should satisfy the above

(11) C. L. Dickinson, D. W. Wiley and B. C. McKusick, *J. Am. Chem. Soc.*, **82**, 6132 (1960).

(12) W. J. Middleton, E. I. Little, D. D. Coffman and V. A. Englehardt, *ibid.*, **80**, 2795 (1958).

(13) N. Deno and C. Perrizzolo, *ibid.*, **79**, 1345 (1957).

(14) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *ibid.*, **80**, 2806 (1958).

conditions. This point was tested experimentally with tetramethylammonium (TMA⁺) and tetraethylammonium (TEA⁺) salts of pentacyanopropene

(PCP⁻) and bis-(tricyanovinyl)-amine (bis(TCV)A⁻). The activity coefficient ratio $f_{\text{TEA}^+}/f_{\text{TMA}^+}$ is the same nearly to within experimental error when calculated

TABLE I
SOLUBILITIES^a AND ACTIVITY COEFFICIENTS^b OF INDICATORS IN SULFURIC ACID SOLUTIONS, 25°

Wt. % H ₂ SO ₄	TMA ⁺ PCP ⁻ (λ _{max} 410 mμ)		TEA ⁺ PCP ⁻ (λ _{max} 410 mμ)		TBA ⁺ PCP ⁻ (λ _{max} 410 mμ)		TMA ⁺ Bis-(tricyanovinyl)-amine (λ _{max} 467 mμ)	
	D	log f	D	log f	D	log f	D	log f
0	2.01 × 10 ²		0.500 × 10 ²		3.77		0.817 × 10 ²	
4.82	3.06	-0.183	.725	-0.161	4.72	-0.098		
9.62	3.51	-.243	.810	-.210	4.55	-.082	1.320	-0.208
19.03	3.86	-.284	.905	-.258	4.37	-.064		
29.1	4.73	-.372	1.11	-.346	5.14	-.135	1.876	-0.361
40.0	7.45	-.569	2.39	-.680	10.65	-.451		
50.5	15.3	-.883	5.87	-1.070	33.10	-.943	6.38	-0.892
60.2	37.9	-1.277	7.64	-1.528	122.0	-1.510		
70.0			10.31	-2.063	661	-2.244	27.35	-1.72 ^c
Wt. % H ₂ SO ₄	TEA ⁺ bis-(tricyanovinyl)-amine (λ _{max} 467 mμ)		Anilinium ⁺ PCP ⁻ (λ _{max} 410 mμ)		p-Chloroanilinium ⁺ PCP ⁻ (λ _{max} 410 mμ)		Triphenylcarbinol (λ _{max} 430 mμ)	
	D	log f	D	log f	D	log f	D	log f
0	0.260 × 10 ²						0.212	
0.48			3.31 × 10 ³ (-0.12) ^d		7.53 × 10 ²			
4.82	0.360	-0.142	3.81	-.18	8.76	-0.18 ^e	0.150	0.15
9.62	.380	-.165	3.50	-.14	8.41	-.16	.098	.34
19.03	.453	-.241	2.79	-.04	6.35	-.04	.090	.37
29.1	.605	-.367	2.03	.10	4.75	.08	.040	.73
40.0	1.183	-.658	1.85	.14	4.15	.14	.031	.83
50.5	3.01	-1.064	2.55	.00	5.00	.06	.040	.73
60.2	7.77	-1.49 ^c	4.98	-.29	7.50	-.11		
70.0	17.50	-2.03 ^c			15.50	-.42		
Wt. % H ₂ SO ₄	m-Nitroanilinium ⁺ PCP ⁻ (λ _{max} 410 mμ)		p-Nitroanilinium ⁺ PCP ⁻ (λ _{max} 410 mμ)		N-Ethylanilinium ⁺ PCP ⁻ (λ _{max} 410 mμ)		N,N-Dimethylanilinium ⁺ PCP ⁻ (λ _{max} 410 mμ)	
	D	log f	D	log f	D	log f	D	log f
0					2.07 × 10 ²		1.388 × 10 ²	
4.82	1.89 × 10 ³	(-0.18) ^e			2.70	-0.116	1.98	-0.153
9.62	1.94	-.19	6.21 × 10 ² (-0.14) ^e		2.68	-.113	2.13	-.172
19.03	1.90	-.18	3.57	.10	2.39	-.063	1.95	-.147
29.1	1.64	-.12	2.52	.25	2.26	-.038	1.99	-.157
40.0	2.43	-.29	2.66	.22	2.89	-.145	2.63	-.277
50.5	3.88	-.49	3.07	.16	5.55	-.428	4.65	-.525
60.2	6.20	-.70	4.71	-.02	16.35	-.897	10.10	-.862
70.0			12.4	-.44	38.0	-1.265	38.8	-1.446
Wt. % H ₂ SO ₄	Phenyltrimethylammonium ⁺ PCP ⁻ (λ _{max} 410 mμ)		Tri-(p-methoxyphenyl)- carbonium ⁺ PCP ⁻ (λ _{max} 480 mμ)		p-Chloro-N-tricyanovinyl- aniline (λ _{max} 358 mμ)		Ethyl cyanoacetate	
	D	log f	D	log f	D	log f	D	log f
0	0.825 × 10 ²						1.38 ^h	
0.48					4.00 ^p			
4.82	1.200	-0.162			3.50	0.058	1.26	0.041
9.62	1.325	-.205	0.875	(-0.20) ^f	3.25	.090	1.20	.062
19.03	1.49	-.256	0.950	-.24	2.91	.138	1.13	.088
29.1	1.85	-.350	1.435	-.41	2.91	.138	1.21	.058
40.0	3.20	-.589	2.075	-.58	3.94	.006	1.84	-.126
50.5	7.63	-.966	9.45	-1.23	6.85	-.234	3.73	-.433
60.2	23.6	-1.456	33.15	-1.78	12.95	-.509		
70.0	41.3	-1.699	240	-2.64	30.6	-.884		
Wt. % H ₂ SO ₄	2,6-Dichloro-4-nitroaniline (λ _{max} 367 mμ)		2,4-Dichloro-6-nitroaniline (λ _{max} 420 mμ)		2,4-Dinitroaniline (λ _{max} 348 mμ)		2,4,6-Trinitroaniline (λ _{max} 412 mμ)	
	D	log f	D	log f	D	log f	D	log f
0	0.395		0.555		5.78		1.350	
4.82	.375	0.022	.518	0.030	5.93	-0.012	1.460	-0.034
9.62	.360	.039	.497	.048	6.35	-.042	1.675	-.094
19.03	.335	.071	.472	.070	7.00	-.084	2.44	-.256
29.1	.360	.039	.541	.011	8.85	-.185	4.50	-.523
40.0	.550	-.143	.870	-.195	14.78	-.408	10.92	-.908
50.5	1.01	-.407	1.74	-.497	32.3	-.748	27.40	-1.307
60.2	2.15	-.735	3.20	-.762	72.5	-1.100	59.1	-1.642
70.0					182.5	-1.500	63.8	-1.926
78.2							210	-2.192
88.5							1500	-3.046

(Footnotes a through h are on following page)

^a All solubilities are expressed as optical density of 1-cm. equilibrated solution without dilution at the wave length indicated (λ_{\max}). Approximate molar concentrations may be calculated from the following extinction coefficients ($C = D/\epsilon$); $\epsilon = 2.3 \times 10^4$ (410 m μ), PCP⁻ (ref. 10); 3.1×10^4 (467 m μ), bis-(tricyanovinyl)-amine (ref. 10); 1.05×10^5 (483 m μ), tri-(*p*-methoxyphenyl)-carbonium ion (ref. 8); 1.5×10^4 (346 m μ), *p*-chloro-*n*-tricyanovinylaniline (ref. 14); 1.07×10^4 (367 m μ), 2,6-dichloro-4-nitroaniline (this work); 4.58×10^3 (420 m μ), 2,4-dichloro-6-nitroaniline (this work); 1.4×10^4 (345 m μ), 2,4-dinitroaniline (M. E. Carsten and H. N. Eisen, *J. Am. Chem. Soc.*, **75**, 4451 (1953)); 8.53×10^3 (414 m μ), 2,4,6-trinitroaniline (this work); 4.0×10^4 (431 m μ), triphenylcarbonium ion (ref. 13); abbreviations: PCP⁻ = pentacyanopropenide, TMA⁺ = tetraethylammonium, TEA⁺ = tetraethylammonium, TBA⁺ = tetrabutylammonium. ^b Activity coefficient, $f = D_0/D$ where D_0 is optical density of solution in pure water. ^c Corrected for protonation by assuming solubility product relation ($K = C_+C_-$) holds and from protonation ratio, $K = C_A^-/C_{HA}$ (ref. 9, 10). $C^0 = (\sqrt{1/R} + 1)C_-$, where C^0 is corrected anion concentration and C_- is measured concentration. ^d Estimated from Debye-Hückel theory. ^e Estimated by comparison with anilinium⁺ PCP⁻. ^f Estimated by comparison with TEA⁺ PCP⁻. ^g Compound ionizes in pure water. ^h Solubility expressed as volume (ml.) added to 25 ml. of acid solution.

TABLE II

PROTONATION EQUILIBRIUM DATA IN SULFURIC ACID AT 25°

2,4-Dichloro-6-nitroaniline (λ_{\max} 420 m μ)			2,6-Dichloro-4-nitroaniline (λ_{\max} 367 m μ)			2,4-Dinitroaniline (λ_{\max} 348 m μ)		
Concn., wt. %	$\log \frac{C_{BH^+}}{C_B}$	$d \log \frac{C_{BH^+}/C_B}{d \%}$	Concn., wt. %	$\log \frac{C_{BH^+}}{C_B}$	$d \log \frac{C_{BH^+}/C_B}{d \%}$	Concn., wt. %	$\log \frac{C_{BH^+}}{C_B}$	$d \log \frac{C_{BH^+}/C_B}{d \%}$
34.6	-0.983	0.071	40.7	-0.552	0.068	51.3	-0.945	0.112
40.7	- .553	.079	46.9	- .132	.091	55.2	- .514	.120
46.9	- .066	.096	49.7	.123	.093	58.9	- .071	.115
52.4	.462	.100	52.4	.372	.108	62.6	.355	.104
57.4	.965	.098	57.4	.914		65.8	.688	.095
62.2	1.43					67.5	.850	
	$pK^a = -3.15$			$pK = -3.24$			$pK = -4.42$	

^a pK values are from comparison (ref. 5) with Bascombe and Bell's value (ref. 19) of -1.02 for 4 chloro-2-nitroaniline.

from either relation below

$$f_{TEA^+}/f_{TMA^+} = \frac{(f_{TEA^+}f_{PCP^-})}{(f_{TMA^+}f_{PCP^-})} = \frac{f_{TEA^+}f_{bis(TCV)A}}{f_{TMA^+}f_{bis(TCV)A}} \quad (13)$$

2. Use of a Standard Ion.—As discussed in the Introduction there is an advantage in measuring the ionic activity coefficients relative to a standard ion. In this work we have chosen the tetraethylammonium ion (TEA⁺) for this purpose. This allows us to discuss the activity coefficient variations as single ion activity coefficient variations. For example, we define

$$f_{BH^+}^* \equiv f_{BH^+}/f_{TEA^+} = \frac{f_{BH^+}f_{PCP^-}}{f_{TEA^+}f_{PCP^-}} = \frac{f_{\pm}^2(BH^+, PCP^-)}{f_{\pm}^2(TEA^+, PCP^-)} \quad (14)$$

or

$$f_{A^-}^* \equiv f_{TEA^+}f_{A^-} = f_{\pm}^2(TEA^+, PCP^-) \quad (15)$$

The right-hand equality in eq. 14 indicates the experimental origin of the data in this particular example. As long as only comparisons of the variation of activity coefficients between different ions are made, the choice of the standard ion is not important. However, it is clearly a convenience to pick one that has no functional groups that would be expected to lead to specific interactions with the solvent. Thus the variation with acid concentration of the activity coefficient of the standard ion would be kept to a minimum. Deno and his co-workers^{15,16} have pointed out the lack of specific solvent interaction with aryl carbonium ions and protonated olefins and argue that the activity coefficients should remain near one over the entire composition range in sulfuric acid solutions. There is, of course, no way or necessity of proving the above, but the tetraalkylammonium cations should enjoy similar advantages of minimum specific interaction effects. In addition, they are readily available and are completely stable over the entire composition range. The tetraethyl derivative gives solubilities in a convenient range with the pentacyanopropenide anion.

It perhaps should be pointed out that there is a minor difference in behavior between f_+^* and f_-^* . Although the standard ion is chosen to minimize specific interactions with the solvent its charge effect is still present. Thus f_+^* is of the type $f_+f_- = f_{\pm}^2$, and

exhibits typical Debye-Hückel behavior in dilute solution (a moderate decrease in $\log f_{\pm}$ as the electrolyte concentration increases). On the other hand, f_+^* is of the type f_+'/f_+ . The charge effect largely cancels and no Debye-Hückel variation is expected. These effects can be clearly seen in our data for f_+^* and f_-^* in Fig. 1 and 3. The interionic effects also introduce some ambiguity in our reference state (eq. 11). This has been taken to be the solution in pure water, but it is not infinitely dilute. In most cases the solutions of ionic indicators in pure water are dilute enough that the difference in activity coefficient between our reference state and infinite dilution could amount to only a few hundredths of a unit in $\log f$. For some of the more soluble ionic indicators it could amount to as much as one-tenth unit.

3. Hammett H_0 Indicators.—The variation of activity coefficients with acid concentration of ionic Hammett indicators is shown in Fig. 1. These are expressed relative to the tetraethylammonium cation as explained above. The variations for neutral Hammett indicators are shown in Fig. 2. There are several conclusions that may be reached regarding these variations. The variation of $\log f_{BH^+}^*$ corresponds to a sizable positive deviation from ideality in all cases. This appears to be due to a specific interaction between the solvent and the $-NH_3^+$ group on the indicator. Taft¹⁷ has suggested such an interaction previously and attributes it to hydrogen bonding between the $-NH_3^+$ group and the solvent. Deno and co-workers¹⁶ have also stressed the probable role of these interactions in H_0 behavior. If a probe is more strongly hydrogen bonded to the anilinium ion than either the bisulfate or hydronium ion (the latter presumably being due to the repulsive charges) such a positive deviation would occur with increasing acid concentration in the region measured. Above 85% acid concentration where there is no longer free water (*i.e.*, not bound directly in the hydronium ion) and neutral H₂SO₄ appears, a different region is to be expected. The curves for $\log f_{BH^+}^*$ show evidence of flattening out as this concentration is approached. The specific participation of the $-NH_3^+$ group is shown by the results in Fig. 3. Successive N-alkyl substitution of the anilinium ion results in $f_{BH^+}^*$ approaching that of the tetraethylammonium cation.

(15) N. Deno, P. Groves, J. Jaruzelski and M. Lugasch, *J. Am. Chem. Soc.*, **82**, 4719 (1960); N. Deno, P. Groves and G. Saines, *ibid.*, **81**, 5790 (1959).

(16) N. Deno and co-workers, private communications (to be published).

(17) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **82**, 2965 (1960).

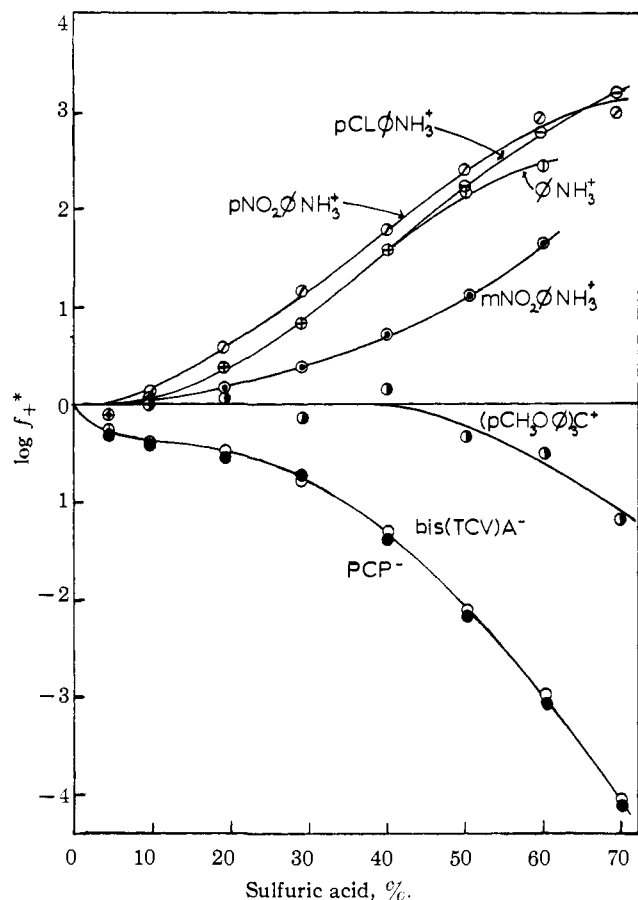


Fig. 1.—Activity coefficient data for ionic indicators, expressed as $f_+^* = f_+/f_{TEA^+}$ or $f_-^* = f_-/f_{TEA^+}$, TEA⁺ is tetraethylammonium ion: ●, pentacyanopropenide anion; ○, bis-(tricyanovinyl)-amine anion; ○, tri-(*p*-methoxyphenyl)-carbonium cation; ○, *m*-nitroanilinium cation; ○, anilinium cation; ○, *p*-chloroanilinium cation; ○, *p*-nitroanilinium cation.

The neutral molecules (Fig. 2) demonstrate the presence of a specific interaction with the nitro group. Increasing the number of nitro groups causes an increasing negative deviation in $\log f_B$. Such an interaction was noticed with nitrobenzene many years ago by Hammett and Chapman.¹⁸

We can now turn to the question of the independence of structure of f_{BH^+}/f_B among the Hammett indicators. It appears that among the indicators consisting of aniline substituted in the ring with one nitro group and halogens, f_{BH^+} and f_B are separately reasonably independent of structure up to ~60% acid concentration. The presence of the halogen appears to have little influence on f_{BH^+} (cf. *p*-chloroanilinium with anilinium, Fig. 1). It would also be expected to have little influence on f_B but we have not demonstrated this experimentally. The presence of a nitro group presents the possibility of specific interaction effects as discussed above. In the neutral molecule its effect is nearly independent of whether it is *ortho* or *para* (cf. 2,6-dichloro-4-nitro- with 2,4-dichloro-6-nitroaniline, Fig. 2). In the protonated forms, BH⁺, the *m* and *p* nitro-substituted anilinium ions appear to have a real difference (Fig. 1). However, measurements with *m*-nitroaniline are restricted to dilute solution^{1,5} where f_{BH^+} is nearly one so that this difference has little practical effect. The *o*- and *p*-nitroanilinium ions appear to have very similar activity coefficients (f_{BH^+}) as evidenced by the protonation behavior. Since the neutral molecule activity coefficients (f_B)

(18) L. P. Hammett and R. P. Chapman, *J. Am. Chem. Soc.*, **56**, 1282 (1934).

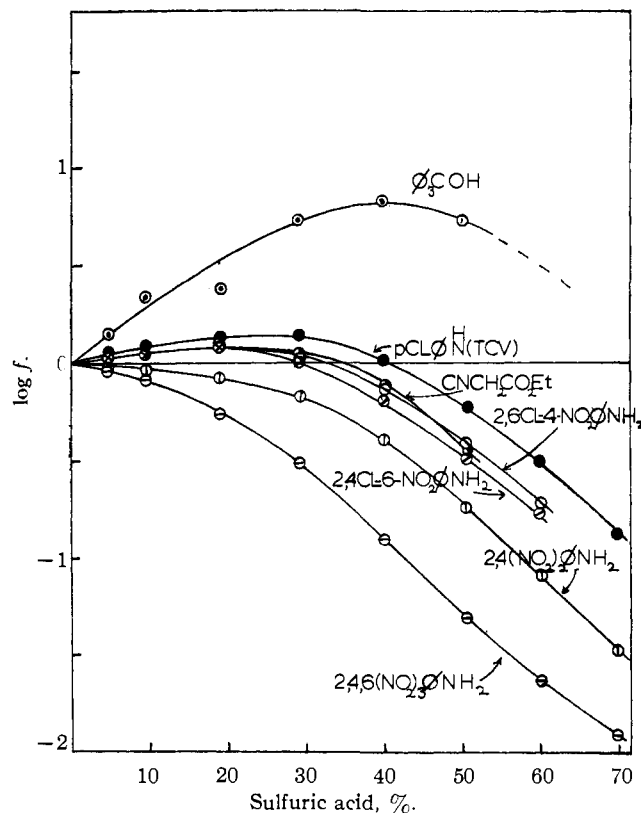


Fig. 2.—Activity coefficient data for neutral indicators: ○, 2,4,6-trinitroaniline; ○, 2,4-dinitroaniline; ○, 2,4-dichloro-6-nitroaniline; ○, 2,6-dichloro-4-nitroaniline; ○, ethyl cyanoacetate; ●, *p*-chloro-*N*-tricyanovinylaniline; ○, triphenylcarbinol.

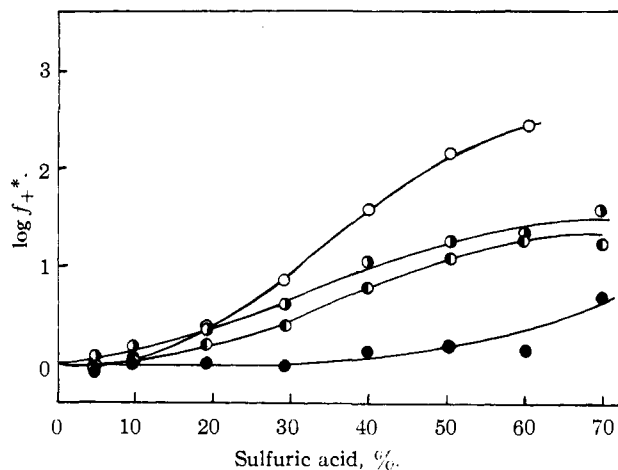


Fig. 3.—Effect of *N*-substitution on anilinium ion activity coefficient: ○, anilinium ion; ●, *N*-ethylanilinium ion; ●, *N,N*-dimethylanilinium ion; ●, trimethylphenylammonium ion.

are nearly identical, differences in f_{BH^+} would show up in the slope of $\log R = \log (C_{BH^+}/C_B)$ ($= pK_B + \log a_{H^+} - \log (f_{BH^+}/f_B)$) vs. concentration plots. Our measurements (Table II and those of Bascombe and Bell¹⁹) show that the plots for 4-chloro-2-nitro-, 2,6-dichloro-4-nitro- and 2,4-dichloro-6-nitroaniline are parallel in the regions of overlap.

Inclusion of two nitro groups to reach higher acid concentrations with H_0 , however, presents some difficulties. The neutral molecule activity coefficient for 2,4-dinitroaniline is parallel to that of the mononitro compounds (cf. Fig. 2) in the region where protonation overlaps (~50–60%). However, it diverges

(19) K. W. Bascombe and R. P. Bell, *J. Chem. Soc.*, part 1, 1096 (1959).

by ~ 0.2 log unit between 0 and 30%. Although this effect is relatively minor, it illustrates that an acidity function scale may not necessarily be perfectly consistent even if the log R plots are parallel. In the present case the log R plots have a significant difference in slope between the dinitro and mononitro indicators (cf. Table II). The higher slope for 2,4-dinitroaniline indicates that f_{BH^+} for this compound has a less positive deviation than for the mononitro compounds. Above $\sim 60\%$ acid concentration, then, an inconsistency of the order of 10–20% in the slope of H_0 is introduced.

The use of 6-bromo-2,4-dinitroaniline to extend the scale to above 90% acid concentration^{1,5} probably does not introduce any further inconsistency. Beyond this point, however, the consistency of H_0 is an open question.

Although, for the indicators discussed above, the independence of indicator structure of f_{BH^+} and f_{B} separately appears to be as good as $f_{\text{BH}^+}/f_{\text{B}}$, there are examples where the ratio is a help. Bascombe and Bell's results¹⁹ for N,N-dimethyl-2,4-dinitroaniline show that log R is parallel to that of the mononitroanilines (region of overlap ~ 24 –37%). This is likely the result of a fortuitous compensation of a decreased positive deviation in log f_{BH^+} from N-substitution by a similar decrease (larger negative deviation) in log f_{B} due to the additional nitro group. In contrast, however, N,N-dimethyl-2,4,6-trinitroaniline shows a considerably greater slope in log R than 2,4-dinitroaniline in the same concentration range^{1,17} (~ 65 –70%). This is probably the result of decreased positive deviation due to N-substitution that is not compensated by a change in log f_{B} . The results in Fig. 2 indicate that, although the N-substituted indicator has an extra nitro group which could result in a considerable difference in log f_{B} , in the region of overlap, the log f_{B} curves may well be nearly parallel. A somewhat smaller difference in slope for log R between *p*-nitrodiphenylamine has also been attributed by Taft¹⁷ to the effect of N-substitution on f_{BH^+} .

4. H_{R} Indicators (Triarylcarbinols).—Since the indicators of this type, for the acid concentrations studied here, are very similar in structure and somewhat difficult to prepare, only one ionic and one neutral model were chosen for study. For tri-(*p*-methoxyphenyl)-carbinol, f_{R^+} shows little variation with acid concentration below $\sim 50\%$. This is consistent with the lack of functional groups capable of strong specific interaction with the solvent. That this should be the case has been pointed out and emphasized by Deno and co-workers, particularly in their studies of hydrocarbon protonation.^{15,16} The nature of the deviation of f_{R^+} above $\sim 50\%$ acid concentration is not known. The fact that log R curves for a large number of these indicators are parallel⁸ suggests it may be a function of the size of the molecule relative to the tetraethylammonium cation. There are some differences among the variations of log f_{R^+} for tetraalkylammonium cations (cf. tetramethyl-, tetraethyl- and tetrabutylammonium pentacyanopropenides in Table I).

The neutral molecule triphenylcarbinol shows a positive deviation which levels out at $\sim 40\%$ acid and may well decrease at higher acid concentrations.²⁰

5. H_{L} (Cyanocarbon) Indicators.—The pentacyanopropenide and bis-(tricyanovinyl)-amine anions were chosen as representative of the cyanocarbon anions and are strong enough acids to remain dissociated over the acid concentration range studied. Their activity

(20) The solubility of this compound has been previously reported by Deno and Perrizzolo (ref. 13) to be nearly invariant with sulfuric acid concentration. We have been unable to confirm this and our data for triphenylcarbinol appear to be more consistent with their data for diphenylcarbinol.

coefficient variations are very similar (Fig. 1) and one is encouraged to believe that f_{A^*} is relatively independent of structure. The deviation in log f_{A^*} is negative and becomes increasingly so over the entire composition range. Thus, we suppose that the anion has a stronger interaction with the hydronium ion than the other solvent species. Since the hydronium ion begins to disappear above 85% acid, variation in log f_{A^*} may well level out above this point. It is interesting to note that although the direct charge effect on the ionic indicators species may be small, the indicator charge may well be important in determining the nature of the ion-solvent interaction. Thus, charge attraction renders hydronium ion interaction favorable with the cyanocarbon anions. Charge repulsion renders it unfavorable with the anilinium ions. The resulting activity coefficient variations are then in opposite directions.

Models for neutral cyanocarbon acids (HA) proved difficult to arrive at. Ethyl cyanoacetate was chosen to represent methyl dicyanoacetate.^{9,10} Up through the protonation region of the dicyano compound (~ 30 –50% acid) the model shows relatively little variation with acid concentration. For its similarity to bis-(tricyanovinyl)-amine, *p*-chloro-N-tricyanovinylaniline was selected. Its behavior is similar to ethyl cyanoacetate, the deviation becoming negative at slightly higher acid concentration.

6. The Relationships between Acidity Functions.—On the basis of the activity coefficients reported here we can discuss the behavior of the acidity functions relative to each other. For convenience in comparison, the three functions studied here may be written

$$-H_0 + \log f_{\text{TEA}^+} = \log a_{\text{H}^+} - \log f_{\text{BH}^+} + \log f_{\text{B}} \quad (16)$$

$$-H_{\text{R}'} + \log f_{\text{TEA}^+} = \log a_{\text{H}^+} - \log f_{\text{R}^+} + \log f_{\text{ROH}} \quad (17)$$

$$\text{where } H_{\text{R}'} = H_{\text{R}} - \log a_{\text{H}_2\text{O}}$$

$$-H_{\text{L}} + \log f_{\text{TEA}^+} = \log a_{\text{H}^+} + \log f_{\text{A}^*} - \log f_{\text{HA}} \quad (18)$$

and where, as usual, f^* is relative to the tetraethylammonium cation. Experimentally, $-H_{\text{R}'}$ is found to rise much more rapidly with acid concentration than $-H_0$ (see Table III). Several factors are responsible for this. First of all, f_{BH^+} has a sizable positive deviation, whereas log f_{R^+} shows relatively little variation. In addition, at lower concentrations ($< 40\%$), the neutral molecule activity coefficients contribute to the divergence of $H_{\text{R}'}$ and H_0 . That is, log f_{ROH} shows a sizable positive deviation, whereas the deviation in log f_{B} is small. Deno and co-workers¹⁶ have emphasized the probable role of log f_{BH^+} in the deviation between $H_{\text{R}'}$ and H_0 .

The functions $-H_0$ and $-H_{\text{L}}$ are very similar experimentally (Table III). This is largely the result of a compensation of the positive deviation in log f_{BH^+} by a negative deviation in log f_{A^*} . At higher concentrations (above 50–60%) where log f_{BH^+} tends to flatten out some, but log f_{A^*} does not, the negative deviations in log f_{B} and in log f_{HA} contribute toward maintaining their similarity.

TABLE III
COMPARISON OF H_0 AND $H_{\text{R}'}$ CALCULATED FROM H_{L} AND MEASURED ACTIVITY COEFFICIENTS WITH EXPERIMENTAL VALUES

% H ₂ SO ₄	$-H_{\text{L}}$ exptl.	$-H_0$		$-H_{\text{R}'}$		log $(a_{\text{H}^+}/f_{\text{TEA}^+})$
		exptl.	calcd.	exptl.	calcd.	
5	-0.44			0.06	0.09	
10	0.09	0.31	0.50	0.70	0.94	0.54
20	0.99	1.01	1.01	1.86	2.16	1.61
30	1.96	1.72	1.63	3.10	3.65	2.86
40	2.93	2.41	2.37	4.55	4.92	4.23
50	3.91	3.38	3.01	6.15	6.81	5.76
60	4.90	4.46	4.01	8.13	8.5	7.39
70	6.21	5.65	5.19	10.18	10.6	9.43

We will now attempt to determine how quantitative these correlations can be made. If the measured activity coefficients of the models chosen represent accurately the true behavior of the indicators, we should be able to calculate the other acidity functions from just one of them and the activity coefficient data. We have chosen to calculate H_O and H_R' from H_- according to the equations

$$H_O = H_- + \log (f_{BH^+} f_{A^-}) - \log f_B - \log f_{HA} \quad (19)$$

$$H_R' = H_- + \log (f_{R^+} f_{A^-}) - \log f_{ROH} - \log f_{HA} \quad (20)$$

For the H_O function calculation, f_{BH^+} was taken to be that for *p*-nitroaniline and f_B to be that for 2,6-dichloro-4-nitroaniline. For the H_R' calculation f_{R^+} is that for tri-(*p*-methoxyphenyl)-carbinol and f_{ROH} for triphenylcarbinol. The latter activity coefficient was estimated at 60 and 70% acid concentration by assuming that its variation is parallel to the others in Fig. 2 in that concentration range. To represent H_- activity coefficients, f_{A^-} was taken to be that for pentacyanopropene, and f_{HA} to be that for *p*-chloro-*N*-tricyanovinylaniline.

The results of the calculation of H_O and H_R' from H_- are shown in Table III. The agreement with the experimental H_O is good and reproduces this function fairly well over the entire acid concentration range studied. The agreement with H_R' is also good, the calculated values being about 0.4 unit higher over most of the concentration range.

Perhaps most closely related to the hydrogen ion activity itself would be the quantity

$$\log (a_{H^+}/f_{TEA^+})$$

which is given by

$$\log a_{H^+} - \log f_{TEA^+} = -H_- - \log f_{A^-} + \log f_{HA} \quad (21)$$

This was also calculated under the above assumptions and is shown in Table III.

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Interaction of Perpendicular π -Electron Systems

BY H. H. JAFFÉ¹ AND O. CHALVET

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The spectra of a series of phenyl-substituted naphthalenes⁴ are interpreted in terms of a resonance interaction of the substantially perpendicular π -electron systems of the naphthalene skeleton and the phenyl groups.

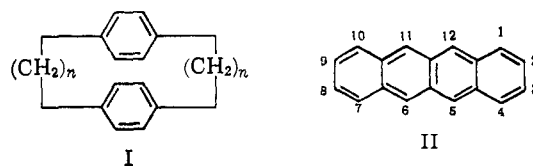
It has long been assumed in the discussion of the chemistry, and particularly of the spectroscopy of conjugated organic systems, particularly hydrocarbons, that two π -electron systems having perpendicular nodal planes do not interact at all with one another, with the possible exception of some minor inductive effect. Thus, for instance, in the calculation of the angle of twist in biphenyl,² the spectrum of the completely twisted model is assumed to be identical to twice that of an isolated benzene; the pure inductive effect of one phenyl on the spectrum of the other is ignored since pure inductive effects are well known to have little importance in the spectra of alternate systems. Any careful test of these assumptions is extremely difficult, because, in general, the two perpendicular π -electron systems are of approximately equal size, and hence their spectra are usually well confounded. Also, it is generally difficult to obtain systems where the nodal planes must really be perpendicular to one another.

The problem seems to have received only very little prior theoretical consideration. The only work³ which appears to consider seriously the effect of one π -electron system on another ascribes all interaction to electron repulsion integrals. Although these undoubtedly make some contribution, the method has not been applied to any system in which experimental verification is available.

A particularly favorable system is that of the various phenyl-substituted naphthalenes, which has recently been carefully investigated.⁴ In this system the naphthalene skeleton has an electronic spectrum in the visible region (400–470 m μ) with a well developed vi-

brational structure, quite far separated from the absorption of the phenyl substituents. In addition, substitution of two phenyl groups in positions *peri* to one another leads to such severe steric strain that any orientation of the phenyl rings other than perpendicular (or virtually so) to the naphthalene skeleton is unthinkable. The presence of two phenyl groups *peri* to one another provides another highly interesting feature: Two such rings will lie substantially parallel to one another, and hence will be subject to similar types of interaction as the *p*-cyclophanes (I).⁵ These interactions are well known to leave the ground state substantially unaffected, but to stabilize considerably the first excited state.⁶

The results in the phenyl naphthalenes are particularly striking, since the longest wave length absorption band, the ${}^1L_a \leftarrow {}^1A$ band in Platt notation, even on substitution of naphthalene (II) by several phenyl groups, retains its characteristic vibrational structure, hence is readily recognized as corresponding to the same electronic excitation, and thus permits the recognition of the effect of phenyl substitution on the naphthalene π -electron system. Substitution of a single phenyl group in either the 1- or 5-position produces a significant batho-



chromic shift, as shown in Table I. This shift might well be interpreted as due to a resonance interaction of the phenyl group with the naphthalene, assuming that

(5) D. J. Cram, *et al.*, *J. Am. Chem. Soc.*, **73**, 569 (1951); **76**, 6132 (1954); **80**, 3115 (1958); **81**, 5963 (1959).

(6) L. L. Ingraham, *J. Chem. Phys.*, **18**, 988 (1950); *cf.* also H. H. Jaffé and M. Orchin, "Theory and Applications of Electronic Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, Ch. 15.

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(4) R. G. Douris, *Ann. Chim.*, **4**, 479 (1959).