

TABLE 2 — CALCULATED VALUES OF ROTATIONAL CONSTANTS ( $\alpha_e$ ), VIBRATIONAL CONSTANTS ( $\omega_e X_e$ ) AND BINDING ENERGIES ( $D_i$ ) OF DIATOMIC HYDRIDES

Hydrides	$\alpha_e(\text{cm}^{-1})$			$\omega_e X_e(\text{cm}^{-1})$			$D_i$ (kJ mol <sup>-1</sup> )		
	Expl.	Calc. Eq. (1)	Error (%)	Expl.	Calc. (Eq. 2)	Error (%)	Expl.	Calc. (Eq. 3)	Error (%)
LiH	0.213	0.1363	-36.01	23.2	18.4	-20.68	677.2	641.9	-5.21
BeH	0.303	0.2622	-13.48	36.3	33.40	-8.01	1015.0	797.9	-21.38
BH	0.412	0.3227	-21.67	49.4	40.4	-18.21	1053.2	874.4	-16.97
CH	0.534	0.4388	-17.8	63.0	54.2	-13.96	1341.7	977.9	-27.11
NH	0.643	0.5459	-15.10	78.3	66.9	-14.56	1633.5	1066.6	-34.70
OH	0.714	0.6563	-8.08	86.4	80.9	-6.37	1660.8	1149.6	-30.79
HF	0.795	0.7655	-3.71	90.1	94.2	4.55	1544.4	1224.9	-20.68
NaH	0.135	0.0995	-26.29	19.7	15.3	-22.34	616.3	564.8	-8.36
MgH	0.167	0.1432	-14.25	32.4	23.0	-29.07	853.3	637.7	-25.26
AlH	0.188	0.1701	-9.52	29.1	27.8	-4.47	779.9	679.4	-12.88
SiH	0.219	0.2254	2.92	35.5	38.5	8.45	1044.3	751.7	-25.15
PH	—	0.2803	—	—	49.8	—	1272.0	815.6	-35.88
SH	0.285	0.3371	18.28	—	61.1	—	1262.6	873.6	-30.81
HCl	0.307	0.3902	27.10 (16.5)	52.8	71.9	36.17 (15.6)	1631.0	925.1	-43.28 (24.2)

Values in parentheses refer to average percentage deviation.

methods, from the experimental values are 15.2, 6.2, and 2.6 respectively as compared to 15.6 obtained in the present work. Similarly the average percentage deviation in binding energy in the present study comes out to be 24.2.

The agreement between the theoretical and experimental values of  $\alpha_e$ ,  $\omega_e X_e$  and  $D_i$  are reasonable considering the approximations involved in the theoretical methods and the uncertainties in the experimental values of molecular parameters used. It is interesting to note that the most of the calculated values of ( $\alpha_e$ ,  $\omega_e X_e$ ) and ( $D_i$ ) are less than the experimental values. This may be due to the fact that diatomic hydrides have less ionicity in comparison to the alkali metal halides. The present model appears more suitable for the alkali halide molecules than to the hydrides. The results of calculation are likely to be improved if we consider charge-dipole interaction, dipole-dipole interaction and dipole-quadrupole terms in the Born-Mayer potential model. Such terms give additional contribution to the interaction energy.

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#### Tautomerism of Some 5-Arylazo-2-thiohydantoin Derivatives as a Criterion of Their Acidity

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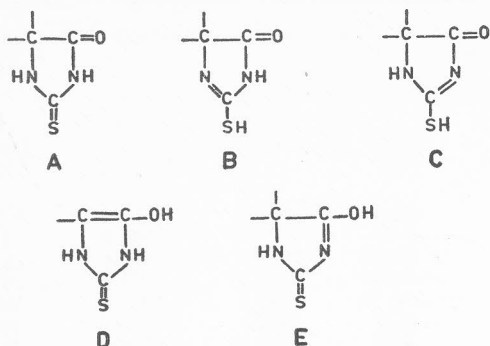
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The apparent  $pK_a$  values of a series of 5-arylazo-2-thiohydantoin derivatives (IIa-e) are reported and discussed in terms of Hammett's correlations and by comparison with related model compounds. The results indicate that the negative charge on the anions is delocalized in a way that prevents direct conjugation with aromatic ring.

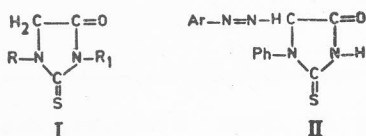
IN literature<sup>1-3</sup> controversy, exists about the reactivity of hydrogens  $C_1$ -H and  $C_2$ -H in 2-thiohydantoin which may have one of the possible tautomeric forms (A-E). The hydrogen atom in the molecule having no substituent at N-3 is labile and reacts in accordance with structure (C).

Tautomeric forms (D) and (E) do not normally react to form enol derivatives but undergo alkylation on nitrogen atoms only. While N-3 alkylation usually proceeds smoothly, substituents at N-1 cannot be introduced<sup>4</sup> into these molecules having no double bond or aryl group at C-5.

Recently, in a programme to develop new synthetic routes<sup>5</sup> and to study the electrochemical behaviour<sup>6</sup> of a series of 5-arylazo-2-thiohydantoin derivatives, we have found that they exhibit predominant acid character in alcoholic buffered media. Thus it seemed worthwhile to determine the ionisation of  $N_3$ -H in compounds (IIa-e)  $pH$ -metrically. Since



thiohydantoin Ia-c represented the heterocyclic portion of our molecules, it was of interest to take them as model compounds for the interpretation of our results.



a,  $R = C_6H_5$ ,  $R_1 = H$

b,  $R = H$ ,  $R_1 = C_6H_5$

c,  $R = R_1 = C_6H_5$

a,  $Ar = C_6H_5$

b,  $Ar = p-CH_3-C_6H_5$

c,  $Ar = p-Br-C_6H_5$

d,  $Ar = p-Cl-C_6H_5$

e,  $Ar = p-NO_2-C_6H_5$

Compounds (Ia-c) were prepared according to reported procedures<sup>7-9</sup>. 5-ArylaZO-2-thiohydantoin derivatives (IIa-e) were prepared as follows: The aromatic amine (0.0034 mol) was dissolved in conc. hydrochloric acid (3 ml) and water (3 ml), cooled to 0°C and then treated with a cold solution of sodium nitrite (0.3 g) in water (3 ml). The diazotised amine was then added gradually to an ice-cold solution of 1-phenyl-2-thiohydantoin (Ia, 0.0034 mol) dissolved in anhydrous pyridine (30 ml). The reaction mixture was left aside in a cold chest for 1 hr, filtered, the solid washed with dil. hydrochloric acid, and recrystallised from glacial acetic acid. Compounds (IIa-e) thus prepared are listed in Table 1. All the compounds were obtained in good yield (70-80%).

**Determination of apparent dissociation constants** — Freshly prepared stock solution ( $10^{-3}M$ ) of IIa-e in absolute ethanol ( $n_D^{25} = 1.359$ ) (25 ml) was diluted to 50 ml with doubly distilled water so that the final concentration of the studied compound was  $5 \times 10^{-4}M$  in 50% (v/v) aq. alcoholic solution. The latter solution was titrated against standard carbonate-free  $10^{-2}M$  aqueous NaOH solution with continuous stirring at  $25^\circ C \pm 2^\circ C$ . The apparent pH values were read on a TS4H Prolabo pH-meter having an accuracy of  $\pm 0.02$  units.  $pK_a$  values were calculated using the Henderson-Hasselbach<sup>10</sup> equation by plotting  $\log ([A^-]/[HA])$  versus pH values.

TABLE 1 — 5-ARYLAZO-2-THIOHYDANTOIN DERIVATIVES (IIa-e)

Compound	m.p. °C	Calc. (%) (Found)*		$pK_a$
		N	S	
a <sup>5</sup>	227	18.91 (18.94)	10.80 (10.77)	8.05
b <sup>5</sup>	276	18.06 (18.00)	10.31 (10.29)	8.00
c	255	14.93 (14.90)	8.53 (8.50)	7.65
d <sup>5</sup>	262	16.93 (16.89)	9.68 (9.70)	7.70
e	265	20.53 (20.50)	9.38 (9.40)	7.40

\*All compounds have correct C, H analyses (within 0.4%)

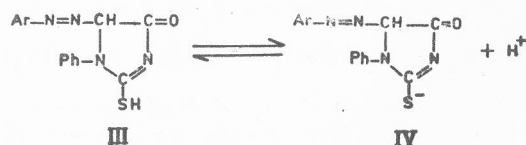
TABLE 2 — STATISTICAL TREATMENT OF THE DATA

	$\sigma$	$\sigma^\circ$	$\sigma^+$
$\rho$	-0.702	-0.678	-0.643
$r$	0.989	0.983	0.901
S.D.	$\pm 0.270$	$\pm 0.255$	$\pm 0.301$

$\rho$  = Slope,  $r$  = correlation coefficient and S.D. = standard deviation.

Compounds (IIa-e) and the model compound (Ia) gave well-defined S-shaped pH-titration curves. However compounds (Ib) and (Ic) did not show any acid character. The obtained  $pK_a$  values are listed in Table 1. These values were correlated against different Hammett's  $\sigma$  sets as tabulated by Ritchie and Sagar<sup>11</sup>. Statistical treatment of the data was made using Jaffe calculations<sup>12</sup> (cf. Table 2). Best correlations were obtained with  $\sigma$  and  $\sigma^\circ$  sets (Table 2). Electron-attracting substituents on the aromatic moiety enhance the ionisation constants of these compounds (Table 1). The higher  $pK_a$  value (8.70) of model compound (Ia) than those of IIa-e can be traced to the greater stabilization of the anions of IIa-e by resonance.

Since Ib and Ic did not show any acid character, structures (D) and (E) can thus be considered most improbable. Therefore tautomeric forms (A) or (C) are the most probable structures favouring the ionisation of the acidic hydrogen atom in these molecules. But form (C) has a greater reactivity presumably due to the favourable location of the hydrogen atom in the N-3 position between the activating carbonyl group as well as the thion group. This fact was realised when 5-benzylidene-1-phenyl-2-thiohydantoin (IIa) underwent condensation with formaldehyde and the appropriate amine under the Mannich reaction to give the expected bases<sup>13</sup>, while 5-benzylidene-3-phenyl-2-thiohydantoin failed



to give the corresponding bases under the above conditions.

Based on the above facts one can conclude that the anions of compounds (IIa-e) have the forms III  $\rightleftharpoons$  IV. These anions can be represented as stabilized anions in which the negative charge is delocalised over the molecule, since the best correlations (cf. Table 2) indicate that the negative charge of the anions is centred such that it is not involved in direct conjugation with the aromatic ring.

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### Solubilization of Anthracene in Ionic Micelles in the Presence of *n*-Alkanols & Salts

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Solubilization of anthracene in anionic and cationic micelles in aqueous medium has been studied spectrophotometrically at 25°C. The standard free energy of solubilization,  $\Delta G_s^\circ$ , decreases linearly with the number of carbon atoms in the alkyl chain of the surfactants.  $\Delta G_s^\circ$  associated per additional  $\text{CH}_2$  group for anionic and cationic surfactants is found to be  $-220$  cal/mol and  $-100$  cal/mol, respectively, and is independent of concentration of added 1-propanol. The chain length of added alcohols has little effect on  $\Delta G_s^\circ$  in cationic micelles and negligible effect in anionic micelles. Counter-ion concentration does not contribute to  $\Delta G_s^\circ$ . The results are discussed in terms of hydrophobic forces, which seem to be the major contributors in the solubilization of nonpolar organic compounds in micelles.

THE solubilization of organic compounds in surfactant solutions occurs according to polar-nonpolar mechanisms, depending upon the chemical structure<sup>1,2</sup>. Solubilization according to a polar mechanism occurs either through the formation of mixed micelles or probably due to adsorption of solubilize molecules on the surface of the surfactant micelles. The solubilization of nonpolar compounds occurs in the hydrocarbon nuclei of the micelles<sup>3,4</sup>. With increasing concentration of the surfactant in aqueous solution, the specific solubilizing ability with respect to non-polar substances increases, while with respect to polar substances it decreases<sup>2,3</sup>.

The process of micellar solubilization of water insoluble compounds has been the subject of many investigations<sup>5,7</sup>. However, the exact mechanism of solubilization in aqueous micellar solution still remains obscure. Recent investigations on the thermodynamics of micellar solubilization of various water insoluble dyes<sup>8,9</sup> have disproved the contention that each micelle solubilizes one dye molecule as described in the earlier mechanisms<sup>5</sup>. We report here the results of our studies on the solubilization of anthracene in ionic micelles in the presence of *n*-alkanols and salts.

Anthracene was E. Merck reagent of high purity (99.9%) and was used as such. Sodium dodecyl sulphate (SDDS) was a BDH reagent of 99% purity. The method for the synthesis of sodium undecyl sulphate (SUDS) and sodium decyl sulphate (SDeS) was exactly similar to that described for SDDS<sup>10</sup>.

Cetyltrimethylammonium bromide (CTAB) was BDH reagent (purity, 99%) and was used as such. Dodecyltrimethylammonium bromide (DTAB) and tetradecyltrimethylammonium bromide (TDTAB) were synthesized by reacting the corresponding halides with trimethyl amine. The precipitates of the corresponding surfactants were recrystallized several times from acetone. The products were then dried in a hot air-oven to constant weight. Distilled water was passed through a millipore filter. All other chemicals used were of AR grade.

For a typical solubilization experiment, excess anthracene (very fine powder) was added to different concentrations of the surfactant in a given solvent. The solutions were then sonicated for 2 hr in an ultrasonic shaker at constant temperature. The solutions were then centrifugated and the absorbance of the clear supernatant liquid was measured at 252 nm (Varian spectrophotometer, model 635), at 25°C.

The equilibrium for the distribution of a solubilize between aqueous and micellar phase can be represented as<sup>8</sup>,



where  $\mu_s^s$ ,  $\mu_s^{aq}$  and  $\mu_s^M$  are chemical potentials of the solubilize in the solid state, aqueous phase and micellar phase, respectively.

The standard free energy change,  $\Delta G_s^\circ$ , associated with the solubilization of a solid solubilize is thus given<sup>8,9</sup> by Eq. 2.