η^{Ex}, which refers to the deviations from a rectilinear dependence of viscosity of the mixture on mole fraction, can be discussed in the light of intermolecular interactions (*6*). The values of η^{Ex} which correspond to $\eta^{Ex} = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]$, in the present case, have been found to be negative for all the systems (see Table II) of C_2Cl_4. For mixtures of C_2Cl_4 with aromatic hydrocarbons at any fixed mole fraction, η^{Ex} has the following sequence:

$$p\text{-xylene} > \text{toluene} > \text{benzene}$$

This béhavior of the values of η^{Ex} gives evidence of the increasing extent of interaction of C_2Cl_4 with the aromatic hydrocarbons having increasing numbers of CH_3 groups substituted in the aromatic ring. The values of η^{Ex} which have been found to be highly negative for C_2Cl_4–cyclohexane can be attributed to the fact that only the dispersion forces are present between the components of this system. The values of η^{Ex} for C_2Cl_4–CCl_4 are, however, much less negative. This, along with the trend in the values of η^{Ex} for the systems of C_2Cl_4 with benzene, toluene, and *p*-xylene, indicates the existence of specific interaction of C_2Cl_4 with CCl_4 and aromatics.

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Registry No. Tetrachloroethylene, 127-18-4; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; carbon tetrachloride, 56-23-5; cyclohexane, 110-82-7.

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Substituent Effects on the Dissociation Constants and the Strength of the Hydrogen Bond in Some Azo Cresol Compounds

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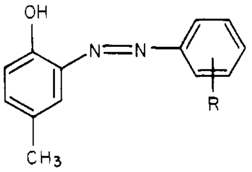
The dissociation constants of some substituted azo cresol compounds were evaluated potentiometrically and the data were explained in terms of the electronic character of the substituents. Electron-donor substituents possess higher p*K* values than the attracting groups. These values are increased by increasing the mole fraction of the dioxane solvent. The thermodynamic parameters (ΔH, ΔF, and ΔS) were evaluated and explained in terms of the strength of the intramolecular hydrogen bond. The cosolvent property was discussed and related to the molecular structure of the molecule. The phenomenon of tautomerism was visualized on the basis of infrared spectral measurements.

The azo compounds occupy an important position especially from an analytical point of view (*1–5*). In this laboratory, the structural chemistry of some azo compounds and their complexes has been determined (*6–13*). In a continuation, of these studies, we aim to focus attention on the strength of the intramolecular hydrogen bond in some substituted azo cresol compounds. The p*K*, ΔH, ΔF, and ΔS values are evaluated and the role of dioxane solvent on the behavior of these compounds is explained.

Experimental Section

The azo compounds were prepared as published elsewhere (*14*). Stock 10^{-2} M solutions of each compound were prepared by dissolving the required weight in dioxane. The exact concentration was determined potentiometrically.



R = H, *p*-NO_2, *p*-NO_2, *p*-CH_3, *p*-OCH_3,
2,4-dichloro, *o*-OCH_3

Stock 5 × 10^{-2} M KOH was prepared in different proportions of dioxane–water media. The dioxane solvent was purified as reported (*14*).

All the titration experiments were done in the following way: 50 mL of 5 × 10^{-3}–3 × 10^{-3} M of the compound containing 0.1 M KNO_3 as a supporting electrolyte thermostated in a cell at different temperatures (25–40 ± 0.5 °C) was titrated against the standard KOH solution in the presence of the desired concentration of dioxane. A stream of purified nitrogen gas was passed through the solution to eliminate CO_2 dissolved in the medium throughout the course of the titrations. A Beckman type 4500 pH meter was used for measurements and calibrated by using two buffer solutions at pH 4.01 and 9.18.

The infrared spectral measurements of a pressed KBr sample were recorded on a Unicam SP 1025.

The dissociation constant of the compound could be estimated from the titration curves where only one inflection point is apparent, indicating that only one proton is titrated. The dissociation of the ligand could be expressed as

$$HL \rightleftharpoons H^+ + L^- \qquad (1)$$

and the dissociation constant is given by the equation

$$K = [H^+][L^-]/[HL] \qquad (2)$$

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Table I. p*K* Values for Some Substituted Azo Cresol Compounds

	p*K*'s in dioxane (±0.07)					
substituent	50%	55%	60%	65%	70%	75%
H	11.13	11.27	11.49	11.92	12.12	12.60
p-NO_2		10.25	10.32	10.65	10.90	11.40
p-Br		10.94	11.17	11.38		12.15
p-CH_3	11.21	11.41	11.67	11.93	12.27	12.74
p-OCH_3	11.26	11.47	11.70	12.00	12.40	12.85
2,4-dichloro			11.32	11.56	11.62	11.94
o-OCH_3			11.90	12.34	12.52	13.08

The material-balance equation throughout the titration course could be expressed as follows:

$$C_{HL}{}^0 = [HL] + [L^-] \tag{3}$$

where $C_{HL}{}^0$ is the initial concentration of the compound and [HL] and $[L^-]$ are the concentrations of the nondissociated compound and the resulting anion existing in equilibrium, respectively.

The electroneutrality of the solution implies that

$$aC_{HL} + [H^+] = [L^-] + [OH^-] \tag{4}$$

where *a* is the neutralization degree of the compound.

From eq 3 and 4, the [HL] and $[L^-]$ could be written as

$$[HL] = (1 - a)C_{HL} + [OH^-] - [H^+] \tag{5}$$

$$[L^-] = aC_{HL} - [OH^-] + [H^+] \tag{6}$$

Fitting these concentrations into eq 2, we get

$$K = [H^+](aC_{HL} - [OH^-] + [H^+])/\{(1 - a)C_{HL} + [OH^-] - [H^+]\} \tag{7}$$

The values of $[H^+]$ in eq 7 were obtained from the pH meter reading and corrected by using the method described by Van Uitert and Harned (*15*, *16*).

The $[OH^-]$ must also be refined by using the values of the ionization constant of water, K_w, determined in dioxane-water (*17*).

In general, the pK_w of water in 50% dioxane-water is 15.83 and has higher values as the concentration increases. The higher values for pK_w make the concentration of OH^- very small compared with the other terms in eq 7 and therefore $[OH^-]$ could be neglected.

Results and Discussion

The azo group is potentially nucleophilic and can act as a proton acceptor in hydrogen bonds. In general, the azo-containing groups may behave as +R as well as -R groups, depending on the electronic requirements of the reaction. The aryl azo group is sufficient in the ortho position where its inherent behavior may be masked by field effects and by direct interaction with the side chain.

To demonstrate such behavior, the evaluation of p*K* values is promising. The data are collected in Table I for different substituents in the presence of different concentrations of the dioxane solvent. The following conclusions can be outlined:

(1) The p*K* values increase linearly with increasing mole fraction of the dioxane solvent (Figure 1).

(2) The plots between p*K* and the nature of the substituents have been paramaterized by using the Hammet constant property (*18*), as a linear function (Figure 2) at all the concentrations of the dioxane solvent.

(3) The electronic character of the substituents plays an important role in controlling the acidity of the compound. The increased p*K* value for the *o*-methoxy compound could be ascribed to the existence of both internal and intramolecular hydrogen bonding. The higher p*K*'s in all these systems neglect the possibility of a zwitterion skeleton. The phenylazo substituent has the potential to behave as a +R group with two competing pathways: (i) the normal one via the azo group and the phenol ring; (ii) the direct one from an azo nitrogen to the phenolic hydrogen.

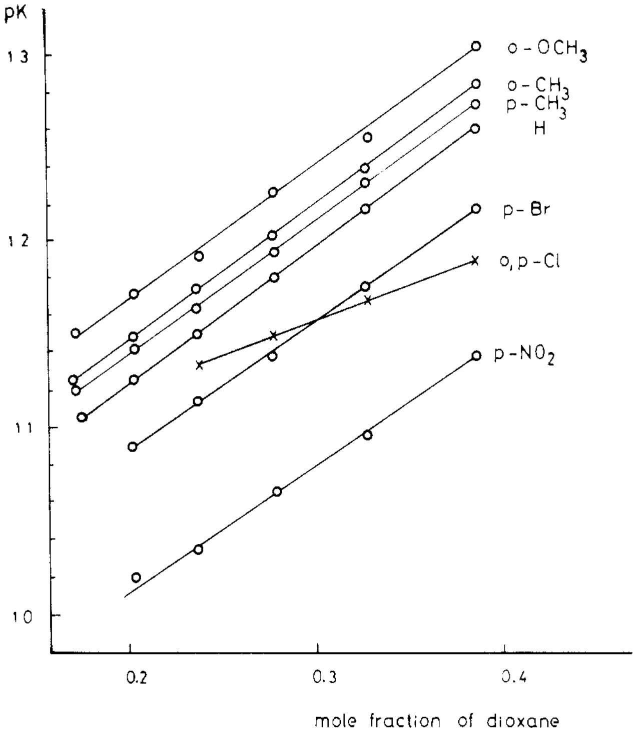

Figure 1. p*K*-mole fraction of dioxane relationships.

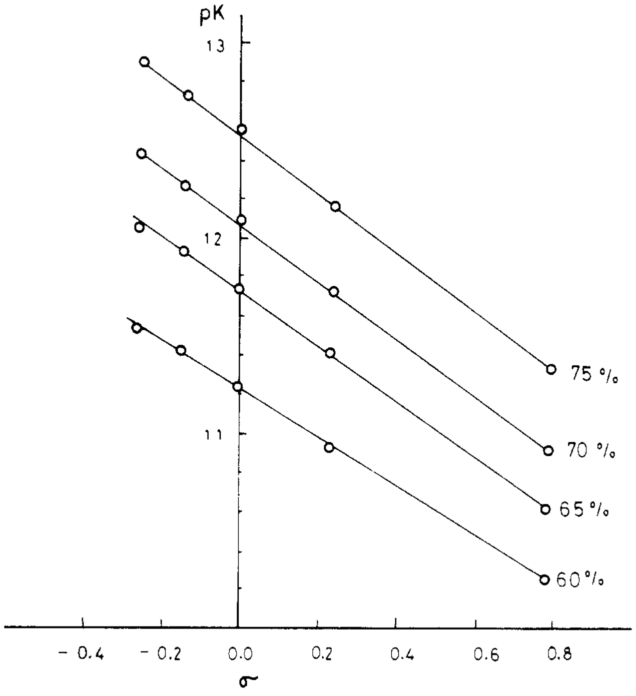

Figure 2. p*K*-σ relationships at different percentages of dioxane (v/v).

The infrared spectra of these compounds gave a broad band in the vicinity of 3400-3450 cm^{-1}, which could be assigned to ν_{OH} in an intramolecular hydrogen bond (*19*). The strong band at 1500 cm^{-1} and those in the frequency range 1630-1590 cm^{-1} are due to $\nu_{N=N}$ and $\nu_{C=C}$, $\nu_{C=N}$, respectively. However,

Table II. Thermodynamic Parameters in 75% Dioxane

substituent	ΔH, kcal/mol	ΔF	$-\Delta S$, eu
p-CH_3	4.60	17.66	43.12
p-OCH_3	7.36	17.82	34.51
o-OCH_3	9.20	18.14	29.49
p-NO_2	11.96	15.81	12.69

those in the frequency ranges of 1380–1315, 1280–1230, 1140–1015, 965–820, and 790–730 could be attributed to δ_{OH}, ν_{C-O}, β_{C-H}, γ_{O-H}, and γ_{C-H}, respectively (*20*). This lets us verify the existence of these compounds in the azo form and excludes the possibility of the hydrazone structure. The hydrogen-bond formation between the phenolic proton donors and the basic azo group plays an important role in stabilizing these compounds leading to conclusive assignment for the azo tautomer rather than the hydrazone structure. The nature of the substituent has no assignable influence on the $\nu_{N=N}$ due to the weak basicity of the azo group. The electron-withdrawing substituents showed either (a) an increase in the OH···N bond strength if they were acting on the OH group or (b) a decrease in the OH···N bond strength as the electron density on the proton-accepting nitrogen atom is depleted, which applies to our systems.

The above-mentioned data for the thermodynamic parameters collected in Table II are promising for interpreting such behavior. Focusing one's attention on the ΔH values, one can say the following: the higher value for the p-OCH_3 compared to the p-CH_3 is due to both higher conjugation and basicity. The still greater increase in the ΔH value for the o-OCH_3 compared to the latter two is related to the ortho effect; i.e., more energy is needed to break up the intramolecular hydrogen bond. However, if we shift our attention to ΔS values, interesting observations can be made. The change in ΔS values for these compounds progressively decreases in the order p-CH_3, p-OCH_3, o-OCH_3, and p-NO_2. However, the sharp decrease in the ΔS value for the p-NO_2 compound (−12.69 eu), i.e., about 2.5–4 times for the electron-donor substituents, and its higher ΔH value (11.96 kcal/mol) indicate that the behavior of this compound is somewhat different. The larger ΔS value for this compound indicates that there should be less ordering of the solvent molecules upon dissociation leading to greater association. This implies more energy for dissociation. The lower solubility for this compound compared to the others supports our view. Again, these data, in general, are due to stabilization of the azo tautomer relative to the hydrazo by the intramolecular hydrogen bond.

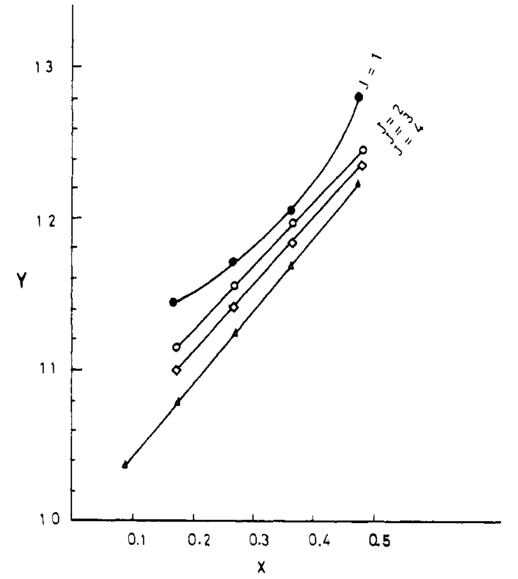

Figure 3. X–Y relationship for p-methylphenylazo-p-cresol.

In the following it is our aim to give a clear picture of the effect of dioxane solvent on the behavior of such compounds. We assume that the J factor, representing a solvent-transfer number characteristic of the tested chemical reaction, can be attributed to the transfer of the solvent. The following relation (*21*, *22*) was tested in our system:

$$J \log [S] + \log K = -\Delta G/(2.303RT) - W \log ([H_2O]/[S] + J \log [H_2O])$$

$$\log [H_2O]_S/[S] = X$$

$$J \log [S] + \log K = Y$$

[S] and ΔG represent the solvent concentration and the free energy, respectively. The data are collected in Tables III–V. Y is plotted vs. X. Trial values of J = 1, 2, 3, ... are used to find values of W for the gradients of Y vs. X. Table VI presents the slopes of the X–Y relation to give the value for water molecules (w). Figure 3 is a representative example, where the

Table III. X–Y Data for Substituted Azo Cresol Compounds[a] in 75% Dioxane

			Y_H			$Y_{o\text{-}OCH_3}$				$Y_{p\text{-}OCH_3}$			
[S], %	−log [S]	$-X$	$J = 1$	$J = 2$	$J = 3$	$J = 1$	$J = 2$	$J = 3$	$J = 4$	$J = 1$	$J = 2$	$J = 3$	$J = 4$
55	0.2596	0.087	11.01	10.75	10.49					11.21	10.95	10.71	10.43
60	0.2218	0.176	11.27	11.05	10.83	11.68	11.46	11.24	11.02	11.48	11.26	11.04	10.82
65	0.187	0.269	11.73	11.56	11.37	12.15	11.97	11.78	11.60	11.81	11.62	11.45	11.26
70	0.155	0.368	11.96	11.67	11.66	12.36	12.21	12.06	11.90	12.25	12.09	11.94	11.78
75	0.125	0.477	12.47	12.35	12.23	12.82	12.69	12.58	12.72	12.72	12.60	12.46	12.35

[a] R = H, o-OCH_3, p-OCH_3.

Table IV. X–Y Data for Substituted Azo Cresol Compounds[a] in 75% Dioxane

			$Y_{p\text{-}CH_3}$				$Y_{p\text{-}Br}$				$Y_{p\text{-}NO_2}$			
[S], %	−log [S]	$-X$	$J = 1$	$J = 2$	$J = 3$	$J = 4$	$J = 1$	$J = 2$	$J = 3$	$J = 4$	$J = 1$	$J = 2$	$J = 3$	$J = 4$
55	0.2596	0.087	11.15	11.15	10.64	10.37	10.68	10.42	10.18	9.90	10.00	9.73	9.49	9.21
60	0.2218	0.176	11.45	11.22	11.00	10.78	10.95	10.73	10.50	10.28	10.01	1.88	9.66	9.43
65	0.187	0.269	11.74	11.56	11.38	11.19	11.19	11.01	10.83	10.64	10.46	10.28	10.10	9.91
70	0.155	0.368	12.11	11.96	11.81	11.65					10.74	10.60	10.44	10.28
75	0.125	0.477	12.61	12.48	12.37	12.24	10.85	11.90	11.78	11.66	11.27	11.15	11.03	10.91

[a] R = p-CH_3, p-Br, p-NO_2.

Table V. X-Y Data for the 2,4-Dichloro Azo Cresol Compound in 75% Dioxane

[S], %	−log [S]	−X	$Y_{2,4\text{-dichloro}}$ $J = 1$	$J = 2$	$J = 3$	$J = 4$
55	0.2596	0.087				
60	0.2218	0.176	11.10	10.88	10.66	10.44
65	0.187	0.269	11.37	11.18	11.01	10.82
70	0.155	0.368	11.46	11.30	11.16	11.00
75	0.125	0.477	11.81	11.68	11.55	11.42

Table VI. Slopes of X-Y Relationship

substituent	slopes $J = 1$	$J = 2$	$J = 3$	$J = 4$
H	3.99	3.99	4.88	
p-CH_3		4.22	4.48	4.80
p-OCH_3		4.18	4.52	4.88
o-OCH_3		4.52	4.80	5.00
p-NO_2				4.52
p-Br	3.00	4.02	4.22	4.52
2,4-dichloro			4.12	

solvation is of minor importance. The obtained straight lines in most cases are the J values between 2 and 4.

Registry No. 2-Phenylazo-*p*-cresol, 952-47-6; 2-(*p*-nitrophenyl)azo-*p*-cresol, 1435-68-3; 2-(*p*-bromophenyl)azo-*p*-cresol, 26029-75-4; 2-(*p*-methylphenyl)azo-*p*-cresol, 17739-97-8; 2-(*p*-methoxyphenyl)azo-*p*-cresol, 15096-05-6; 2-(2,4-dichlorophenyl)azo-*p*-cresol, 19918-08-2; 2-(*o*-methoxyphenyl)azo-*p*-cresol, 15096-06-7.

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Densities of Aqueous NaCl, KCl, $MgCl_2$, and $CaCl_2$ Binary Solutions in the Concentration Range 0.5–6.1 *m* at 25, 30, 35, 40, and 45 °C

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The densities of the binary solutions NaCl–H_2O, KCl–H_2O, $MgCl_2$–H_2O, and $CaCl_2$–H_2O were measured at 1 atm, from 25 to 45 °C and from 0.5 to 6.1 *m*, by using a commercially available oscillating tube-type densitometer. The data sets were described by using least-squares polynomial regression analysis. Statistical evaluation of the experimental data indicates that uncertainties in the concentrations of the solutions due to adsorption of water by the salts during weighing is the major source of error in the density measurements. The magnitude of this error is greater for $MgCl_2$ and $CaCl_2$ solutions because of the hygroscopic nature of these salts. The measured densities of NaCl and KCl solutions have a standard deviation of 5.515×10^{-5} g/cm^3. Standard deviations for $MgCl_2$ and $CaCl_2$ solutions range from 2.329×10^{-4} to 2.334×10^{-4} g/cm^3 and from 2.796×10^{-4} to 2.839×10^{-4} g/cm^3, respectively. The experimental density data compare well with published values.

Introduction

Reliable experimental density data for aqueous binary salt solutions have important applications in geothermal energy and radioactive-waste-disposal research and technologies. The use of such data in fundamental thermodynamic calculations pertaining to the volumetric properties of brines is essential for accurate chemical modeling of complex geothermal brine systems. The Potter and Haas model (*1*) for calculating the density of a brine is one example of a predictive equation which requires precise experimental density data for binary systems. Raw experimental density data are available only for limited concentration ranges and temperature intervals. The diversity of experimental methods and the lack of a common system of units for reporting density data make meaningful comparisons between similar data sets somewhat difficult. This study has been undertaken to improve, as well as extend, the existing data base by providing internally consistent sets of density measurements at 1 atm, from 25 to 45 °C, for aqueous NaCl, KCl, $MgCl_2$, and $CaCl_2$ binary solutions with concentrations ranging from 0.5 to 6.1 *m*.

Experimental Method

We prepared the NaCl, KCl, and $CaCl_2$ solutions by weight using oven-dried (140 °C) reagent-grade chemicals and deionized water distilled with a Corning Mega-Pure automatic still. Because of particulate contamination, all $CaCl_2$ solutions were filtered after preparation. The $MgCl_2$ solutions were made by volumetrically diluting aliquots of a concentrated $MgCl_2$ stock solution. Formula weights used were 58.44, 74.55, 95.22, and 110.99 for NaCl, KCl, $MgCl_2$, and $CaCl_2$, respectively.