

The material was distilled and after a forerun of silylating by-products the trimethylsilyl ether was obtained [113–114° (0.9 mm), 12.9 g, 42%]. Redistillation gave the pure ether, bp 140° (3.5 mm).

Anal. Calcd for $C_{17}H_{23}O_3Si$: C, 71.2; H, 8.5; mol wt, 236. Found: C, 71.0; H, 8.7; mol wt, 243.

Pyrolysis of 2-Acetoxyethyl-4-*tert*-butyl-6-methylphenol.—A small sample (100 mg) of the title compound was heated at 150° for 18 hr under nitrogen. The deep yellow residue was examined by thin layer chromatography (silica gel–benzene–hexane) and was found to consist of recovered phenol, the trimer **2** ($R = \textit{tert}$ -

butyl) and tars. The trimer was identified by comparison with authentic¹ in R_f values and in ir spectrum.

Registry No.—**12**, 25966-85-2; **13**, 25966-86-3; **14**, 25966-87-4; **15**, 25966-88-5; **16**, 25966-89-6; **17**, 25966-90-9; **18**, 25966-91-0; **19**, 25966-92-1; **20**, 25966-93-2; **21**, 25966-94-3; 2,8-dimethyl-2-isopropyl-6-*tert*-butylchroman, 25966-95-4; 2-methyl-4-*tert*-butyl-6-acetoxyethylphenyl trimethylsilyl ether, 25957-28-2.

Selective Solvation of Hydrophobic Ions in Structured Solvents. Azo-Hydrazone Tautomerism of Azo Dyes in Aqueous Organic Solvents

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The azo-hydrazone tautomerism of a series of 4'-substituted 2- and 4-aryloxy-1-naphtholsulfonates was studied spectrophotometrically in a wide range of protic and aprotic polar solvents with dielectric constants varying from 24.3 (ethanol) to 182.4 ($HCONHCH_3$). The effect of solvents on the position of the equilibrium between the tautomers does not correlate with bulk solvent properties but depends upon the solvent structure and the microscopic environment of the dye in the solvent matrix. For solvent-sensitive dyes, the hydrazone form is predominant in those neat solvents capable of forming a three dimensional structure, whereas the azo form is favored by neat solvents that form a two dimensional structure or are unstructured. In binary mixtures of water with methanol, ethanol, and *tert*-butyl alcohol, the shift from hydrazone to azo is most pronounced in the predominantly aqueous compositions, *tert*-butyl alcohol having the greatest effect. At alcohol levels associated with reduction of solvent structure, the shift is gradual and nearly independent of the nature of the alcohol. Pronounced shifts from hydrazone to azo also occur in aqueous compositions of DMF- and DMSO-water mixtures. The results are interpreted in terms of selective solvation of the hydrophobic dyes by the organic cosolvent within the water structure. The tautomerism becomes progressively less exothermic as organic solvent is added to the aqueous binaries.

A number of spectroscopic methods have established that 4-phenylazo-1-naphthols can exist in solution as hydroxy azo or as quinone hydrazone tautomers.¹⁻⁸ The hydrazone is favored by polar solvents^{2a,5,8} and by electron-withdrawing substituents in the phenyl ring.^{2a,5,9} No systematic studies of the tautomerism have been made in structured solvents or in solvents of high dielectric constants, and no quantitative data are available on the effects of solvent dielectric constant or of specific solvation on the tautomeric equilibrium. We have studied the tautomerism of several water-soluble dyes in a number of neat solvents and in binary aqueous organic solvent mixtures and find that the equilibrium is sensitive to specific solvation and to the hydrogen bonded structure of the solvent.

Results

The neat solvents studied and their dielectric constants at 25° are ethanol (24.3), methanol (32.6), *N,N*-dimethylformamide (DMF, 36.7), acetonitrile

(37.5), dimethyl sulfoxide (DMSO, 46.4), propylene carbonate (65.1), water (78.5), formamide (109.5), and *N*-methylformamide (182.4).

Structure **2** dyes ($X = H, OCH_3, Cl, SO_3^-, \text{ and } CF_3$) give more stable hydrazones than the isomeric structure **1** dyes. Whereas the equilibrium concentrations of all the **1** dyes except **1e** can shift with changes in solvent or solvent composition, the **2** dyes exist predominantly as the hydrazones in all solvents studied. The order of stability of the hydrazones of the **1** dyes in a given solvent is **1e** > **1b** \approx **1c** > **1a** > **1d**. The hydrazone of **1e** was the predominant tautomer in all our solvents and solvent mixtures, whereas the azo form of **1d** was preponderant in all solvents. We estimate that aqueous solutions of **1a** contain equal amounts of both tautomers at 25°, with a shift to the azo form in all other solvents. Dyes **1b** and **1c** exist as greater than 95% hydrazone in water at 25° and as pure azo tautomers in ethanol, *tert*-butyl alcohol, and the aprotic dipolar solvents.

The estimation of the predominant tautomer in the neat solvents was qualitative and was based on the relative preponderance of the two absorption bands. The predominance of one tautomer was so great in a given solvent with **1b** and **1c** that a qualitative approach was sufficient for evaluating solvent properties and for separating solvent types. The only neat solvents in which the hydrazones of **1b** and **1c** were predominant were water and formamide. These dyes were present almost exclusively as the azo tautomers in all the other neat solvents, including *N*-methylformamide.

There is no correlation of the position of the equilibrium with the dielectric constant of the neat solvent,

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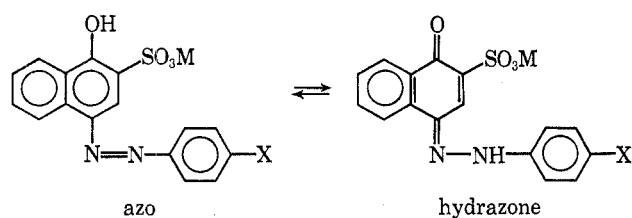
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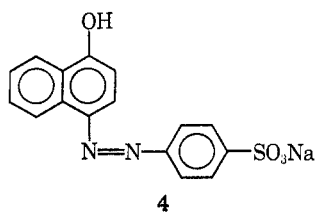
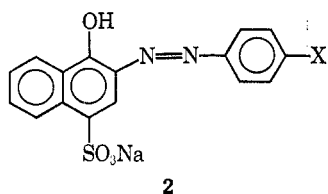
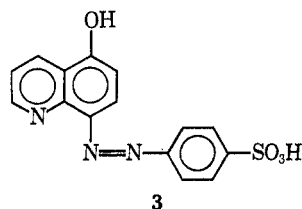
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- 1a, X = H; M = K
 b, X = SO₃Na; M = Na
 c, X = CF₃; M = K
 d, X = OCH₃; M = K
 e, X = NO₂; M = K



with the Kosower "Z" value,¹⁰ or with the fact that a solvent is protic or aprotic. The most important factor seems to be the degree and kind of structuring of the solvent and the manner in which this structuring influences the solvation of the dye. The unique property of water and formamide is the capability of these solvents to form three dimensional hydrogen-bonded regions¹¹⁻¹⁵ with lifetimes in the case of water of the order of 10⁻¹¹ sec.^{13a} There is little agreement at present on how regular or extensive the structured regions are, but it is agreed that in the limit each oxygen atom can be nearly tetrahedrally bonded to four nearest neighbor hydrogens. On the other hand, X-ray studies indicate that the liquid alcohols associate to give linear, two dimensional polymeric structure.^{16,17} *N*-Methylformamide is also believed to exist as linear polymers in the liquid state.¹⁸ Thus, protic solvents with two dimensional structure have the same effect on the equilibrium as aprotic solvents. The stabilization of a given tautomer must be associated with the energetics of forming cavities in the various solvent structures and with the way in which the solvent molecules order them-

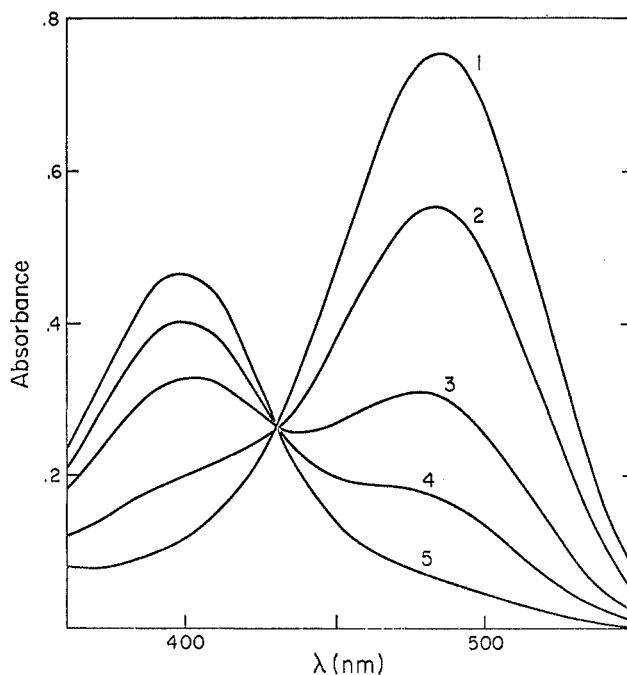


Figure 1.—Spectra of **1b** in ethanol-water at 25°. Curve numbers (1-5) correspond to $x_2 = 0, 0.088, 0.175, 0.320,$ and 0.734 to 1.00, respectively.

selves around the dye for minimum energy of the system.

Figure 1 shows the spectral changes accompanying the shift in the tautomeric equilibrium of **1b** in water-ethanol mixtures. Similar changes occur with **1b** and **1c** in aqueous binaries with DMSO, DMF, methanol, and *tert*-butyl alcohol. The fact that the position of the equilibrium can be shifted between the extreme forms of **1b** and **1c** made these dyes most valuable for studying the effect of solvent on the tautomerism.

Tautomer ratios were determined in mixtures of water with *tert*-butyl alcohol, ethanol, methanol, DMF, DMSO, and *N*-methylformamide, and in formamide-*N*-methylformamide mixtures. The ratios were calculated using eq 1 where the ϵ 's are absorptivities and the

$$K_T = \frac{[\text{hydrazone}]}{[\text{azo}]} = \frac{\epsilon_M - \epsilon_A}{\epsilon_H - \epsilon_M} \quad (1)$$

subscripts refer to pure azo, pure hydrazone, and mixtures of the two. We used the wavelength where the hydrazone absorbs (480-500 nm), because the absorptivity in this region was less subject to small medium effects than was the absorptivity of the azo band. The value of ϵ_A was determined from absorption curves such as curve 5 in Figure 1, after the curve ceased to change with further addition of the organic component.

The absorptivity of the hydrazone bands of **1b** and **1c** in water increased on lowering the temperature from 35 to 10°. These curves were replotted on a frequency scale and folded through the wavelength of maximum absorption to give an isolated symmetric band for each temperature. The integrated areas increased 8 and 4%, respectively, for **1b** and **1c** between 35 and 10° and then became independent of temperature. We took this to mean that the azo form makes negligible contribution to the observed curve at temperatures below 10°, so that ϵ_H could be evaluated. The values are 3.32×10^4 and 3.18×10^4 for **1b** and **1c**, respectively.

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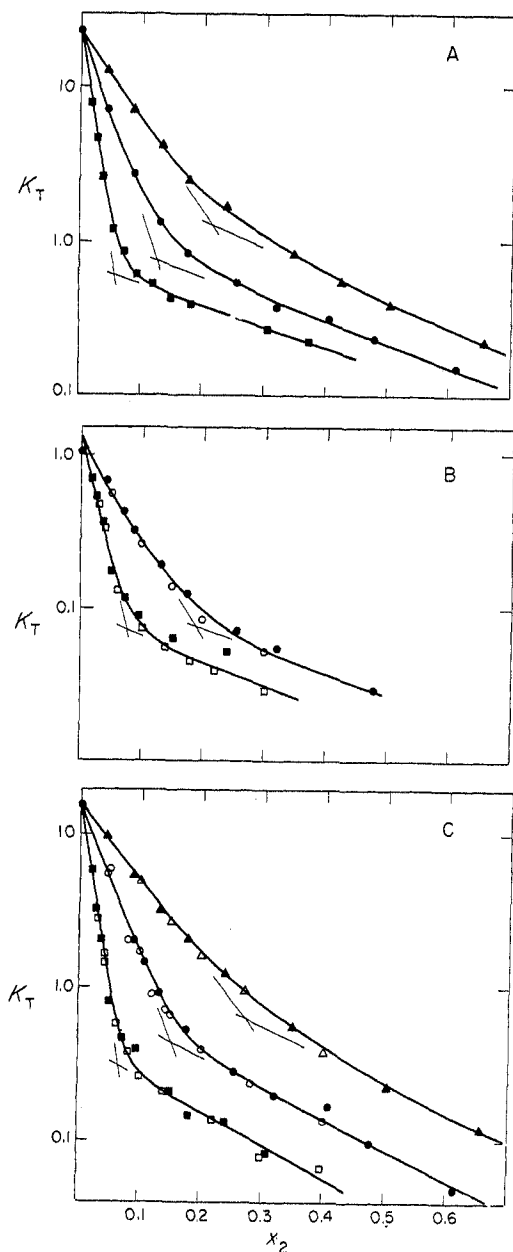


Figure 2.—Semilog plots of K_T at 25° vs. mol fraction of alcohol. Open data points, [dye] = $2.5 \times 10^{-6} M$; closed points, [dye] = $2.5 \times 10^{-5} M$; ■, *tert*-BuOH; ●, EtOH; ▲, MeOH; A, dye 1c; B, dye 1a; C, dye 1b.

We assumed that ϵ_A and ϵ_H were constant in all the aqueous organic binaries. Dye 3 exists as the hydrazone in all water-alcohol mixtures. The values of ϵ_H for this dye deviated from the mean by less than 1.5% over the whole range of ethanol-water compositions. Dye 1d exists as pure azo in ethanol-water at ethanol levels above 0.25 mol fraction. The range of absorptivity values at the hydrazone wavelength was only twice the experimental error in reading absorbances between mol fractions 0.25 and 0.50. Absorptivities may not be as constant in aqueous DMF and DMSO. In these solvent mixtures, there were small changes in band shapes and positions, so that the isosbestic points were more diffuse than with the water-alcohol mixtures. The values of ϵ_A for a given dye were the same in DMF, DMSO, and ethanol.

Because the value of ϵ_H for 1a was experimentally inaccessible, we used the measured value for 1b,

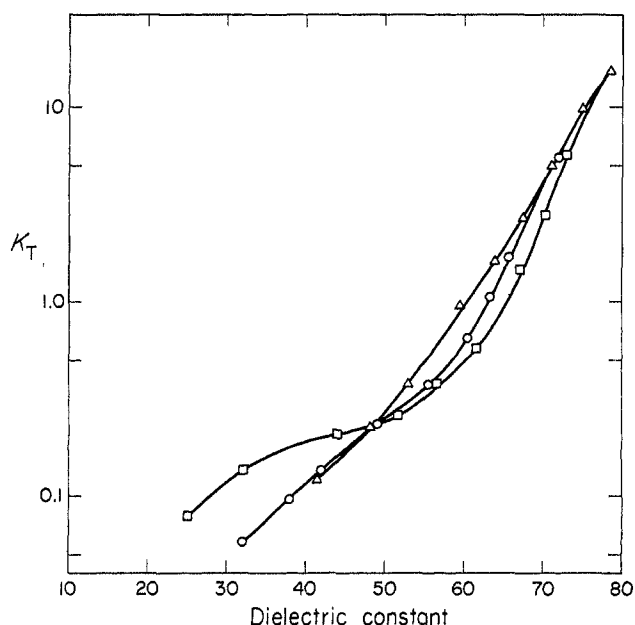


Figure 3.—Semilog plots of K_T for dye 1b vs. solvent dielectric constant at 25° in □, *tert*-BuOH; ○, EtOH; △, MeOH.

assuming the inductive polar effect of the sulfo group did not effect ϵ_H . Neither extreme form could be obtained in the formamide-*N*-methylformamide mixtures. We had to assume that ϵ_H was the same as the value in water at 10°, and that ϵ_A was the same as the value measured in DMF.

Figure 2 shows plots of K_T on a semilog scale vs. solvent composition for two concentrations of 1a-c in aqueous *tert*-butyl alcohol, ethanol, and methanol, where the organic component is regarded as the solute. The plots show that the greatest shift in the tautomeric equilibrium occurs in the predominantly aqueous compositions. The two linear segments of the plots were extended to the points of intersection to obtain the solvent composition corresponding to the break points. The break points occur at $x_2 = 0.06$ – 0.07 , 0.14 – 0.16 , and 0.24 – 0.27 in aqueous *tert*-butyl alcohol, ethanol, and methanol, respectively, and are independent of dye structure or the position of the equilibrium at the break. The plots show that, on the water side of the breaks, the shift in K_T depends on the nature of the added alcohol, but is nearly independent of the alcohol on the alcohol side of the breaks. Plots (not shown) of $\log K_T$ vs. volume fraction of alcohol gave three separate curves falling in the same order as those in Figure 2, although the separation is reduced and the breaks are less sharp. This shows that the three alcohols are specific in their effects on K_T , over and above the differences in molecular volume.

Figure 3 shows a plot of $\log K_T$ for dye 1b vs. solvent dielectric constant at 25° for the aqueous alcohols. The plots not only show the lack of correlation of $\log K_T$ with dielectric constant, but also that each alcohol is rather specific in its effect.

Figure 4 shows plots of K_T vs. x_2 for aqueous DMSO, DMF, and *N*-methylformamide and for *N*-methylformamide in formamide. *N*-Methylformamide is considered the solute in formamide. The binary mixture of amides was chosen to see whether the addition of one amide having two dimensional solvent structure to an

TABLE I
EFFECT OF TEMPERATURE ON K_T VALUES OF DYE 1b

Solvent	x_2	K_T			$-\Delta H^0$, kcal/mol	$-\Delta S^0$ (25°), cal deg ⁻¹ mol ⁻¹
		15°	25°	35°		
EtOH-H ₂ O	0		15.2	6.90	14	40
	0.05	11.0	4.90	2.25	13.7	43.0
	0.10	3.59	1.68	1.01	11.0	35.9
	0.15	0.838	0.642	0.519	4.1	14.4
	0.20	0.413	0.392	0.340	1.8	8.0
	0.40	0.127	0.128	0.123	0	4.0
<i>tert</i> -BuOH-H ₂ O	0.02	5.22	4.59	2.72	5.8	16.4
	0.04	1.83	1.48	1.16	3.9	12.4
	0.06	0.712	0.518	0.474	3.5	13.1
	0.10	0.300	0.294	0.276	0.8	5.0
	0.18	0.192	0.169	0.170	0	3.4
	0.30	0.087	0.092	0.082	0	4.7
DMF-H ₂ O	0.05	2.40	1.68	1.32	5.2	16.4
	0.10	0.800	0.654	0.530	3.5	12.4
	0.20	0.193	0.172	0.148	2.2	10.7

amide possessing three dimensional structure would have the same effect on K_T as the addition of alcohols to water. Figure 4 shows that it does not. The effect of adding DMF and DMSO to aqueous solutions of 1b is similar in magnitude to the effect of added alcohols in the predominantly aqueous mixtures. DMF has nearly the same effect as *tert*-butyl alcohol, and DMSO is similar in effect to ethanol. The main difference between the aqueous solutions of the protic and aprotic cosolvents is the presence or absence of a break in the $\log K_T-x_2$ plots.

Tautomer ratios of 1b were measured at 15, 25, and 35° in various mixtures of water with ethanol, *tert*-butyl alcohol, and DMF. Table I gives the values of K_T and the derived standard enthalpies and entropies for the conversion of the azo tautomer to the hydrazone. The enthalpies were calculated using the Van't Hoff equation. Compositions of the water-alcohol mixtures were chosen to give points on either side of the break points in the $\log K_T-x_2$ profiles. The conversion from azo to hydrazone is exothermic in each case on the water side of the break point, but ΔH^0 becomes less negative as the alcohol content increases. On the alcohol side of the break point, changing temperature did not alter K_T by measurable amounts, *i.e.*, $\Delta H^0 \approx 0$. It is significant that addition of increments of DMF to water also causes the conversion to hydrazone to become progressively less exothermic. Thus, in all respects there appear to be no basic differences between DMF and the alcohols in the effect on K_T except for the shape of the $\log K_T-x_2$ profiles.

Discussion

The significant findings of this work are (1) the most profound shifts in the tautomeric equilibrium occur in the predominantly aqueous compositions and are out of proportion to changes in the bulk solvent properties; (2) the shift is not caused by preferential hydrogen bonding solvation by organic cosolvent to one of the tautomeric pairs, since similar effects are caused by protic and aprotic solvents; (3) there is a high correlation between changes in the three dimensional structure of the solvents and the position of the equilibrium. We believe that the results can be interpreted in terms of selective solvation of the dyes by the organic cosolvents, whereby the solute accumulates around the hydro-

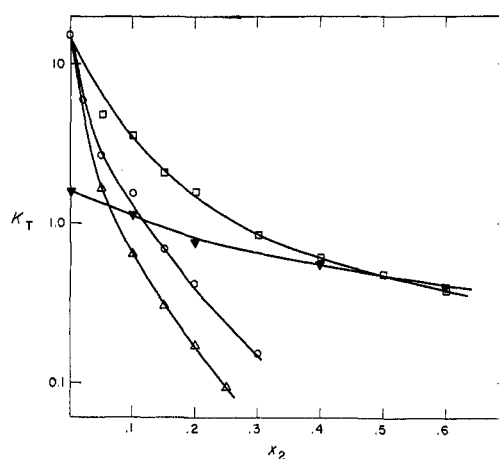


Figure 4.—Semilog plot of K_T for dye 1b at 25° vs. mol fraction of added solvent. Δ , DMF in H₂O; \circ , DMSO in H₂O; \square , *N*-methylformamide in H₂O; ∇ , *N*-methylformamide in formamide.

phobic regions of the dye in microscopic concentrations that are higher than the concentration in the bulk solvent. In our interpretation, the nonpolar moieties of the organic cosolvent are oriented toward the hydrophobic portion of the dye, giving a diffuse interface between dye and bulk solvent with a polarity that is considerably lower than that of the bulk solvent.

In water, the sulfo group is strongly hydrated through hydrogen bonds, giving rise to "positive" hydration.¹⁹ By analogy with the effect of adding small amounts of other hydrophobic solutes to water,²⁰ it is expected that the hydrophobic moiety of the dye would enhance the hydrogen bonded structure of the water in its vicinity relative to that which exists in bulk water. This structure formation, which has been designated as "negative hydration,"¹⁹ is a high energy condition that is partly offset by the positive hydration of the ionic solubilizing group. It has been estimated that the net solvation of the naphthalenesulfonate ion is negative in water.¹⁹ Since the hydrophobic volume of our dyes is even greater, the energy of the systems must be quite high so that the balance between positive and negative hydration is barely sufficient to maintain the dye in

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molecular dispersion. This is reflected in the strong tendency of the dyes to associate into aggregates and to be salted out of aqueous electrolyte solutions.²¹ By our model, the energy at the microscopic dye-water interface is decreased by replacement of water molecules by molecules of organic cosolvents so that there is excess concentration of organic molecules in the interface. Our results show that the hydrazone form is stabilized by the negative solvation characteristic of the hydrogen bonded three dimensional solvent structures, and the azo form by the condition where the adjacent environment consists of nonpolar alkyl groups.

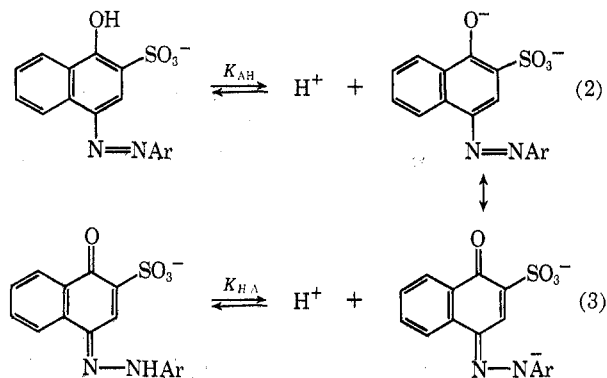
The compositions of the water-alcohol mixtures at which the breaks in the $\log K_T-x_2$ plots occur correspond to the compositions where the three dimensional structure of the solvent is believed to change.^{16,22,23} These compositions are at about 5, 15, and 30 mol % for *tert*-butyl alcohol, ethanol, and methanol, respectively. Thus, the most dramatic shifts in the tautomeric equilibrium occur in the predominantly aqueous compositions where the alcohol is thought to promote hydrogen bonded solvent structure. This is consistent with the view that selective solvation by the organic solute results because of the existence of three dimensional structure around the dye. In these compositions, the OH group of the alcohol may be incorporated into the water structure, with the alkyl group oriented into the dye-solvent interface. On the alcohol side of the breaks, the typical water structure is destroyed. In this region the solvation shell is apparently not altered greatly with increasing alcohol concentration, perhaps because it is already near saturation with respect to alcohol.

The similarities in the $\log K_T$ (ΔF), ΔH , and ΔS changes in the aqueous aprotic solvents and the aqueous alcohols suggest that similar solute-solvent interactions are occurring with changes in solvent composition in all cases. Arnett and McKelvey have shown that the partial molar heat of solution of sodium tetraphenylboron shows an endothermic maximum in water-DMSO mixtures at 15 mol % DMSO which is similar to the maxima found in water-*tert*-butyl alcohol and in water-ethanol.²³ Their finding that aqueous DMSO and aqueous ethanol solutions show similar interactions with a large solute are in agreement with our results. We believe that our results show that aprotic solvents accumulate around the hydrophobic moiety of the dye in the same way as the alcohols. The absence of breaks in the $\log K_T-x_2$ plots may indicate that the aprotic solvents do not cause abrupt changes in the solvent structure.

The chaotic state of our understanding of the structure of water around hydrophobic solutes precludes any description of the hydration shell of our dyes. The decrease in entropy accompanying the conversion of the azo tautomer to the hydrazone in water is consistent with an increased solvent orientation around the hydrazone. Thermodynamics, however, give no clues as to why a structured water environment should stabilize one tautomer. It is possible that the nature of the dye-water interface permits specific hydrogen bonding of a water molecule to a heteroatom in the dye in a way that stabilizes the hydrazone. Replacement of the

water environment with the nonpolar environment of the organic cosolvent apparently destroys this stabilization, even when the bulk solvent is still largely aqueous. The fact that dye 4 also shows the same tautomeric shift in alcohol-water mixtures rules out an intramolecular hydrogen bond between the -OH and -SO₃⁻ groups as an important stabilizing factor.

The fact that K_T is sensitive to the solvation changes implies that the relative acidities of the protons on the OH oxygen and on the NH nitrogen are also sensitive to the same changes. The tautomerization can be written in terms of the two dissociations to a common anion (eq 2 and 3). The effect of adding alcohols,



$$K_T = [\text{HA}]/[\text{AH}] = K_{\text{AH}}/K_{\text{HA}}$$

DMF, or DMSO to water is to decrease K_{AH} relative to K_{HA} and to make the NH proton relatively more acidic.

The type of specific solvation we have discussed here seems general for other types of ionic dyes that are soluble in water and aqueous mixtures of organic solvents. We have found pronounced spectral and kinetic effects from such solvation. It is probable that the phenomenon is general for any large organic ion where most of the volume of the ion is hydrophobic.

Experimental Section

Dyes.—The dyes were prepared in the usual way and were recrystallized as the sodium salts from water or ethanol-water. Dyes 2b-c were samples used in an earlier study.²⁴ Final purification of all the dyes except 1b and 2b was accomplished by chromatography on Sephadex G-25,²⁵ followed by recrystallization as the potassium salts. Dye 1b was chromatographed on polyamide using DMF as eluent. The dihydrate of 1b, and monohydrates of the other dyes were obtained after drying at 120° under water-pump vacuum. Elemental analyses and spectral data are given in Table II.

Solvents.—Commercially available "absolute" ethanol showed no absorption between 240 and 300 nm and was found free of impurities by glpc analysis. This solvent and Eastman Grade methanol were used without further purification. Eastman Grade *tert*-butyl alcohol was fractionated through a Vigreux column and the first and last thirds were discarded. Two separate runs contained 0.29 and 0.31% water by Karl Fischer analysis. Correction for the water content was made in preparing the mixtures with water.

N-Methylformamide and DMF (Eastman Grade) were distilled under vacuum at low temperature and the center third was retained. The solvents were stored over Linde 4A molecular sieves. Eastman Grade formamide was fractionated twice under vacuum through a Vigreux column and a variable take-off still

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TABLE II
 ANALYTICAL AND SPECTRAL DATA FOR DYES

Dye	Calcd, %			Found, %			Solvent	λ_{\max} (nm)	$10^{-4} \epsilon$ ($M^{-1} \text{cm}^{-1}$) ^a
	C	H	N	C	H	N			
1a	50.0	3.4	7.3	50.4	3.4	7.4	H ₂ O	492	1.74
							EtOH	390	1.67
1b	40.8	2.6	6.0	41.0	2.6	6.1	H ₂ O	485	2.96
							EtOH	400	1.85
1c	45.1	2.7	6.2	45.0	2.6	6.1	H ₂ O	479	3.06
							EtOH	406	1.78
1d	51.3	3.8	7.0	b	3.9	6.9	H ₂ O	458, 400	1.22, 1.15
							72% EtOH	400	1.86
1e	44.8	2.8	9.8	b	3.0	9.7	H ₂ O	493	3.07
							80% EtOH	493	2.77
2a	52.2	3.7	7.6	52.4	3.3	7.4	H ₂ O	494	2.10
							EtOH	489	1.62
3	48.8	3.3	11.4	49.0	3.5	11.0	H ₂ O	455	4.25
							EtOH	453	4.30

^a 25°. ^b Replicate analyses from three microanalytical laboratories on the same sample gave divergent values for % C.

head. A sizable forerun and residue were discarded each time. The final distillate was crystallized twice from the melt. All liquid freezing below 2.5° was discarded. The final product froze sharply at 2.5° (lit. 2.45–2.51°).²⁶ Samples of formamide that were not purified rigorously showed variable results and indicated the presence of basic impurities capable of ionizing the OH groups of some dyes.

To 3 kg of DMSO (Matheson Coleman and Bell) was added 500 ml of benzene which had been dried over 4A molecular sieves. The benzene was distilled from the mixture at atmospheric pressure, and the residue was distilled under reduced pressure. A center cut [bp 58° (5 mm)] amounting to half the total volume was distilled directly into a receiver containing 4A molecular sieves.

Eastman Grade acetonitrile containing less than 0.01% water was stored over 4A molecular sieves and was used without further purification. Eastman Practical Grade propylene carbonate was fractionated twice under reduced pressure. Foreruns and residues were discarded.

The binary mixtures of solvents were prepared by mixing weighed amounts of the two solvents. The volume fractions of the alcohols in the mixtures with water at 25° were calculated from the partial molal volumes. We used the density data of Chapas for methanol-water mixtures,²⁷ data from the International Critical Tables for ethanol-water,²⁸ and the data of Nakanishi, Kato, and Maruyama for *tert*-butyl alcohol-water.²⁹

(26) G. R. Leader, *J. Amer. Chem. Soc.*, **73**, 856 (1951).

(27) G. Chapas, *ibid.*, **74**, 6275 (1952).

(28) "International Critical Tables," Vol. III, McGraw-Hill, New York, N. Y., 1928, p 116.

(29) K. Nakanishi, N. Kato, and M. Maruyama, *J. Phys. Chem.*, **71**, 814 (1967).

Spectral Measurements.—Absorption curves were obtained on a Beckman DK-2A recording spectrophotometer at dye concentrations of $2.5 \times 10^{-5} M$ and $2.5 \times 10^{-6} M$. For the higher concentrations, individual weighed samples were dissolved directly into the solvent and the solutions measured in 1-cm cells. The lower concentrations were obtained by adding aliquots of a stock solution in water to an alcohol-water mixture of known composition and density and then correcting for the added water. The more dilute solutions were measured in 10-cm cells. The solutions were thermostated at the desired temperature in a constant temperature bath. A thermostated cell holder was used with the 1-cm cells, and all the temperature variations were made on the more concentrated dye solutions so that the desired temperature could be maintained in the solution while the absorption curve was recorded. The thermostated cell block could not be used with the 10-cm cells. We made all measurements in the very dilute solutions by equilibrating the solutions at 25° and working rapidly after transferring them to the cells.

Registry No.—1a azo, 26156-91-2; 1a hydrazone, 26156-92-3; 1b azo, 26156-93-4; 1b hydrazone, 26156-94-5; 1c azo, 26156-95-6; 1c hydrazone, 26156-96-7; 1d azo, 26156-97-8; 1d hydrazone, 26156-98-9; 1e azo, 26156-99-0; 1e hydrazone, 26157-00-6; 2a azo, 669-05-6; 2a hydrazone, 26157-02-8; 3 azo, 26157-03-9; 3 hydrazone, 26157-04-0.

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