

active centers in the glycerol ethers consist of three separated oxygen atoms instead of a single nitrogen.

A final comparison may be made between ethyl butyl glycerol and ethyl *n*-hexyl oxyethyl glycerol. The water solubility in each solvent is nearly the same and so is the carbon-oxygen ratio in $-OC_4$ and $-OC_2OC_6$. Solvent solubility in water is much less for the compound having the larger alkyl group.

The solubility of a series of propylene glycol ethers is shown in Figure 3. In the series $R(C_3H_5O)_nOH$, the solubility decreases with increasing *n*, while with ethylene glycol ethers the opposite occurs.

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Dipole Moment of Sulfamic Acid and Viscosities of Its Solutions in Selected Nonaqueous Media

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Values of the dipole moment of sulfamic acid have been calculated from dielectric constant, density, and refractive index data for solutions of sulfamic acid in polar solvents using the Onsager and Wyman equations. Variation in the magnitude of the dipole moment with the solvent medium provides evidence of significant solvent effects. The change in viscosity with concentration also has been determined for solutions of sulfamic acid in each of the five nonaqueous media. All experimental data as a function of concentration have been fitted to appropriate equations.

SULFAMIC acid ($H_3N^+-SO_3^-$) in the solid state, like glycine, exists in a dipolar ionic form (8). In water it ionizes upon dissolution to yield an acid with strength comparable to that of nitric or hydrochloric acid. With most organic solvents, it is essentially insoluble or reacts chemically. In *N,N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), and *N*-methyl-2-pyrrolidone (NM2PY), however, sulfamic acid is soluble to the extent of about 2 moles per liter without chemical reaction and yields solutions which are practically nonconducting. The dielectric and nonconducting properties of solutions in these three solvents indicate that the dipolar ionic form of sulfamic acid is retained.

Dielectric constant, density, and refractive index data have been determined for solutions of sulfamic acid in DMSO, DMA, NM2PY, and two DMSO-DMA mixtures in order that the dipole moment of sulfamic acid in each of these nonaqueous media may be evaluated. In addition, viscosities of the sulfamic acid solutions have been investigated to ascertain if a relationship exists between viscosity behavior and electrostriction effects.

EXPERIMENTAL

DMSO was purified by subjecting it to successive fractional freezings until a product with a constant maximum

freezing point of 18.50°C. was obtained. Commercially available DMA and NM2PY were rendered anhydrous by azeotropic distillation with toluene. This was followed by fractional distillation at a pressure of 1 cm. through a 100-cm. column packed with glass helices. In each case the middle 60% of the product was retained. Values for several physical properties of each solvent are included in Table I. Sulfamic acid (purity assay of 99.99% by the G. Frederick Smith Chemical Co.) was stored in a desiccator over Anhydron before use. Solutions in glass-stoppered flasks were prepared on a weight basis. Precautions were taken to minimize atmospheric contamination of the solutions during preparation and transferring.

The impedance bridge assembly, capacitance cells, temperature control, and principal aspects of the procedures for calibrating the cells and calculating the dielectric constants have been described in detail (1, 2, 9). The standard media used in the determination of cell constants were air and water, which have dielectric constants of unity and 78.30 (10), respectively, at 25°C. All capacitance measurements were made at 10 megacycles, after it had been confirmed that capacitance changes were independent of frequency in the 1- to 10-megacycle range.

The procedures for determining viscosities, densities, and refractive indices have been discussed adequately (13, 14).

Table I. Experimental Data for Solutions of Sulfamic Acid in Some Nonaqueous Solvents

100 X ₂	C	ε	d	n _D	η	η _{rel}
DMSO						
0.000	0.0000	46.5	1.0954	1.4764	2.002	1.000
2.135	0.3016	48.9	1.1095	1.4773	2.438	1.218
4.282	0.6098	51.2	1.1244	1.4781	3.041	1.519
6.425	0.9222	53.7	1.1391	1.4792	3.822	1.909
8.365	1.2096	55.9	1.1529	1.4803	4.853	2.424
67 Mole % DMSO in DMA (Mixture 1)						
0.000	0.0000	44.4	1.0336	1.4607	1.499	1.000
2.383	0.3071	47.0	1.0499	1.4622	1.890	1.261
4.685	0.6102	49.7	1.0657	1.4635	2.371	1.582
7.070	0.9307	52.4	1.0822	1.4652	3.104	2.071
9.090	1.2080	54.8	1.0968	1.4671	3.995	2.665
33 Mole % DMSO in DMA (Mixture 2)						
0.000	0.0000	41.8	0.9817	1.4473	1.147	1.000
2.593	0.3067	45.1	0.9987	1.4498	1.453	1.267
5.118	0.6134	48.5	1.0159	1.4522	1.903	1.659
7.640	0.9283	52.0	1.0339	1.4646	2.559	2.231
9.850	1.2105	55.0	1.0493	1.4567	3.449	3.007
DMA						
0.000	0.0000	38.5	0.9365	1.4360	0.906	1.000
2.772	0.3030	43.2	0.9552	1.4389	1.190	1.313
5.584	0.6208	48.3	0.9748	1.4419	1.637	1.807
8.283	0.9360	53.3	0.9938	1.4448	2.268	2.503
10.751	1.2334	58.0	1.0118	1.4478	3.241	3.577
NM2PY						
0.000	0.0000	32.0	1.0279	1.4680	1.666	1.000
2.005	0.2103	34.8	1.0394	1.4695	2.010	1.206
3.918	0.4153	37.5	1.0501	1.4708	2.413	1.448
5.851	0.6273	40.2	1.0615	1.4720	2.977	1.787
7.708	0.8351	43.0	1.0721	1.4736	3.724	2.235
9.776	1.0723	46.2	1.0851	1.4750	4.962	2.978

Appropriate buoyancy corrections were applied prior to the calculation of concentrations and densities.

All measurements were made in duplicate and corresponding values were found to agree consistently within 0.2% for dielectric constants and viscosities and within 0.02% for densities and refractive indices. Mean values are listed in Table I.

RESULTS AND DISCUSSION

The experimental dielectric constant, density, refractive index, and viscosity data for solutions of sulfamic acid in the five nonaqueous media are summarized in Table I. For each system these data may be fitted very well to simple equations of the following types:

$$\epsilon_{12} = \epsilon_1 + \delta C \quad (1)$$

$$d_{12} = d_1 + aC \quad (2)$$

$$n_{12} = n_1 + bC \quad (3)$$

$$\log \eta_{rel} = \log \frac{\eta_{12}}{\eta_1} = \frac{eC}{1 - fC} \quad (4)$$

Other properties of the solute in each system were calculated as follows:

$$\Phi_2 = \frac{M_2 - 1000 a}{d_1} \quad (5)$$

$$R_{D_2} = \frac{n_{D_2}^2 - 1}{n_{D_2}^2 + 2} V_2 \quad (\gamma = 1 \text{ or } 12) \quad (6)$$

$$V_1 = \frac{M_1}{d_1}, \quad V_{12} = \frac{M_1 + (M_2 - M_1) X_2}{d_{12}} \quad (7)$$

$$R_{D_2} = R_{D_1} + \frac{R_{D_{12}} - R_{D_1}}{X_2} \quad (8)$$

$$n_{D_2} = \left[\frac{\Phi_2 + 2 R_{D_2}}{\Phi_2 - R_{D_2}} \right]^{1/2} \quad (9)$$

Values of the constants determined for Equations 1 through 4 and of the properties of sulfamic acid calculated using Equations 5, 8, and 9 are summarized in Table II. The good agreement between the values of the experimental data and those calculated using Equations 1 through 4 is reflected by the per cent deviation data presented in Table III.

The dielectric increment, δ , and the apparent molal volume, Δ_2 , of sulfamic acid in DMA and in DMSO have been investigated by Sears and coworkers (6, 7). The dielectric increment values obtained in this study are 0.2 and 0.3 unit greater; the apparent molal volume data agree within 0.1 cc. per mole with the previous results.

Several equations have been proposed in the literature for calculating the dipole moment of a solute from data for solutions of the solute in a polar solvent having a high dielectric constant. The equations used in this study, and for which the results are compared, are the Onsager and Wyman equations.

The Onsager equation relating the dielectric constant of a solution of a polar solute in a polar medium to the dipole moments of the constituents has the following generalized form (12):

$$\epsilon_{12} = O(n_i^2) + \sum \frac{(n_i^2 + 2)^2}{2} \frac{4\pi}{3} N_i \frac{\mu_{oi}^2}{3kT} \quad (10)$$

If $\epsilon_{12} \gg n_i^2$, the term $O(n_i^2)$ may be considered to be negligible; also, as a reasonable approximation, $n_i^2 = \epsilon_{\infty i} = 1.10 n_D^2$. Incorporating these changes along with letting $N_i = (X_i N) / (V_{12})$, rearrangement of Equation 10 for a binary system gives:

$$\epsilon_{12} V_{12} = \frac{2\pi N}{9kT} \left\{ (\epsilon_{\infty 1} + 2)^2 \mu_{o_1}^2 + \left[(\epsilon_{\infty 2} + 2)^2 \mu_{o_2}^2 - (\epsilon_{\infty 1} + 2)^2 \mu_{o_1}^2 \right] X_2 \right\} \quad (11)$$

(The two solvent mixtures may be treated as pure solvents by using appropriately adjusted molecular weights.)

For a linear plot of $\epsilon_{12} V_{12}$ vs. X_2 ,

$$\mu_{o_2}^2 = \frac{9kT}{2\pi N} \frac{(\text{slope} + \text{intercept})}{(\epsilon_{\infty 2} + 2)^2} \quad (12)$$

Table II. Calculated Values for Constants in Equations 1 through 4 and for Other Related Properties

Solvent	δ	a × 10 ⁴	b × 10 ⁴	e	f	Φ ₂	R _{D₂}	n _{D₂}
DMSO	7.8	475	31	0.2702	0.1280	45.2	14.4	1.55
Mixture 1	8.6	524	51	0.3135	0.0857	43.2	15.2	1.62
Mixture 2	10.9	559	79	0.3216	0.1558	42.0	15.3	1.68
DMA	15.8	612	95	0.3753	0.1316	38.3	14.8	1.70
NM2PY	13.1	533	66	0.3599	0.1698	42.6	15.2	1.63

Table III. Deviations between Experimental and Calculated Values of Properties of Sulfamic Acid Solutions

Solvent	Property	% Deviation × 100	
		Std.	Max.
DMSO	ϵ	5	20
	d	1	2
	n_D	1	2
	η_{rel}	55	66
Mixture 1	ϵ	0	0
	d	2	2
	n_D	2	3
	η_{rel}	62	73
Mixture 2	ϵ	5	19
	d	2	3
	n_D	1	2
	η_{rel}	30	42
DMA	ϵ	5	23
	d	2	3
	n_D	1	2
	η_{rel}	55	78
NM2PY	ϵ	8	27
	d	2	3
	n_D	1	2
	η_{rel}	44	67

and, in view of Onsager's derivation of Equation 10,

$$\mu_2 = \frac{(\epsilon_{\infty 2} + 2)(2\epsilon_{12} + 1)}{3(2\epsilon_{12} + \epsilon_{\infty 2})} \mu_{02} \cong \frac{(\epsilon_{\infty 2} + 2)(2\epsilon_1 + 1)}{3(2\epsilon_1 + \epsilon_{\infty 2})} \mu_{02} \quad (13)$$

The Wyman equation (5, 15) may be written in the form of Equation 14 if the term, $(\epsilon_{\infty 2} + 2)^2/(2)$, is substituted for the empirical constant, 8.5, in the denominator. This alteration has been discussed by Onsager (12), who pointed out that the substitution leads to an approximate equivalence of the Wyman and Onsager treatments of the relationship between dielectric constant and dipole moment.

$$\mu_{02}^2 = \frac{9kT}{2\pi N} \left[\frac{1000\delta + \Phi_2(\epsilon_1 + 1)}{(\epsilon_{\infty 2} + 2)^2} \right] \quad (14)$$

Values of the dipole moment of sulfamic acid in each solvent medium have been calculated using Equations 12, 13, and 14. The resulting dipole moment data are summarized in Table IV. Equations 12 and 14 yield values for μ_{02} , which are in excellent agreement as predicted by Onsager (12).

On the basis of the interatomic distances for the dipolar ionic structures of crystalline sulfamic acid which have been reported by Kanda and King (8), together with assuming a unit positive charge on the nitrogen atom and a unit negative charge to be centered in the plane of the three oxygen atoms, one would predict a charge separation of about 2.4 Å. or a dipole moment of 11.5 debye units, which fits fairly well within the range of μ_2 values obtained in this study.

The dipole moment, μ_{02} , of the addition compound of triethylamine and sulfur trioxide, $(C_2H_5)_3N^+ \cdot SO_3^-$, has been reported by Moede and Curran (11) as 6.84 and 7.3 debye units for benzene and dioxane solutions, respectively. Because of very similar structural features, the dipole moments of triethylamine-sulfur trioxide and sulfamic acid should be of the same magnitude. The corresponding μ_{02} values for sulfamic acid calculated using Equations 12 and 14 range from 6.61 to 7.95 debye units and reflect the expected similarities.

The dipole moment data in Table IV exhibit significant variation with the solvent medium. "Solvent effects" reflect solute-solvent interactions which have been long recognized but not completely understood. The best known example is associated with a dipole moment determined for a substance

Table IV. Calculated Values of Dipole Moment of Sulfamic Acid in Debye Units

Solvent	μ_{02}		μ_2 , Eq. 13
	Eq. 12	Eq. 14	
DMSO	6.70	6.72	10.2
Mixture 1	6.61	6.60	10.6
Mixture 2	6.90	6.91	11.5
DMA	7.94	7.95	13.3
NM2PY	7.66	7.65	12.2

in dioxane solution, frequently being 0.3 to 0.5 debye unit greater than that determined for the same species in benzene solution—for example, triethylamine-sulfur trioxide. Gaumann (3) and Gilkerson and Srivastava (4) have reported that the value for the dipole moment of urea shows considerable dependency upon the solvent medium.

The viscosities of the solutions of sulfamic acid in each medium can be described well within 1% by the relationship constituting Equation 4. At unit molarity, the relative viscosities of NM2PY, DMA, Mixture 2, Mixture 1, and DMSO solutions are 2.713, 2.705, 2.404, 2.202, and 2.041, respectively. The corresponding values for Φ_2 and ϵ_1 may be found in Tables I and II. In view of these data, for a fixed concentration of sulfamic acid in the various solvents, the increase in relative viscosity appears to be a function not only of increasing electrostriction (contraction of volume upon dissolution) but also of decreasing dielectric constant of the medium.

NOMENCLATURE

- ϵ = dielectric constant at low frequency
- ϵ_{∞} = dielectric constant at infinite frequency
- d = density, g./ml. or g./cc.
- n_D = refractive index (D line of sodium)
- n = refractive index including atomic polarization
- δ = molar dielectric increment; constant in Equation 1
- a = constant in Equation 2
- b = constant in Equation 3
- e, f = constants in Equation 4
- Φ = apparent molal volume, cc./mole
- R = molar refraction, cc./mole
- η_{rel} = relative viscosity
- η = absolute viscosity, centipoises
- C = concentration of solute, moles per liter of solution
- X = mole fraction
- M = gram formula weight
- k = Boltzmann constant
- N = Avogadro number
- N_i = number of molecules of a given species per unit volume
- T = temperature, °K.
- μ_1 = dipole moment in vacuo or in gas phase
- μ = actual dipole moment in environment
- V = molar volume, cc./mole

Subscripts

- 1 = designation of property of solvent
- 2 = designation of property of solute
- 12 = designation of property of solution

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Perhaloketones

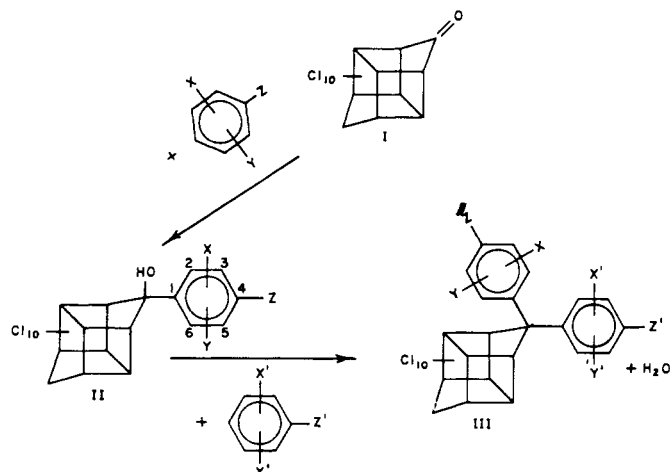
Aromatic Derivatives of a Perchlorinated Caged Ketone

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The perchlorinated cage ketone, decachloropentacyclo [5.3.0.0^{2,6}.0^{4,10}.0^{5,9}] decan-3-one, (I) has been reacted with various aromatic compounds—mainly phenols and hydrocarbons—using several acid catalysts. Tertiary carbinols (II) were prepared from phenols, and "bis" compounds (III) were obtained from phenols and the other aromatic compounds. The carbonyl carbon atom in I is concluded to be less electropositive than that in the fluorinated acetones. A number of secondary derivatives were also prepared from the aromatic condensates of I.

THE electropositive nature of the carbonyl carbon atom in the perchlorinated caged ketone (I), decachlorooctahydro-1, 3, 4-metheno -2*H*-cyclobuta [cd] pentalen-2-one, also known as decachloropentacyclo [5.3.0.0^{2,6}.0^{4,10}.0^{5,9}] decan-3-one, or as Kepone, has already been demonstrated by its ability to form adducts with alcohols or amines, (4) and to undergo uncatalyzed condensation with aliphatic ketones and other compounds containing activated methylene groups (3). The purpose of this study was to determine the ease of reactivity of the carbonyl group of I with various aromatic nuclei, as follows:

The results obtained with three phenols and one phenolic ether are summarized in Table I. Several acid catalysts promote reaction on the nucleus, and good yields of either the 1 to 1 (Type II) or the 1 to 2 (Type III) molar ratio reaction products of I with phenols could be obtained. When toluenesulfonic acid is used as catalyst, temperature appears to be the major variable in determining the reaction ratio when the phenol is applied in large excess. With BF₃, on the other hand, only the Type III product was formed, even at room temperature or at 1 to 1 molar ratio. The Type II product was a mixture of the ortho and para isomers using either of two catalysts (toluenesulfonic acid or AlCl₃) at a 1 to 1 molar ratio of the reagents. (IIa' and IIb' were also prepared in pure form by an alternate unequivocal method comprised of



- IIa: X = Y = H; Z = OH
 IIb: X = H; Y = 2-OH; Z = H
 IIc: X = Y = H; Z = OCH₃
 II d: X = 3-CH₃; Y = 5-CH₃; Z = OH
 IIIa: X = X' = Y = Y' = H; Z = Z' = OH
 IIIb: X = X' = 3-CH₃; Y = Y' = H; Z = Z' = OH
 IIIc: X = X' = Y = H; Y' = 5-CH₃; Z = Z' = OH
 III d: X = X' = Y = Y' = H; Z = Z' = OCH₃
 IIIe: X = X' = 3-CH₃; Y = Y' = 5-CH₃; Z = Z' = OH
 III f: X = X' = Y = Y' = Z = Z' = H
 IIIg: X = X' = Y = Y' = H; Z = Z' = CH₃
 IIIh: X = X' = H; Y = Y' = 3-CH₃; Z = Z' = CH₃
 IIIi: X = X' = Y = Y' = H; Z = Z' = Cl
 IIIj: X = X' = Y = Y' = H; Z = Z' = CH₃CONH

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