

(eq. 7 and 8) can be applied to these data. These

$$\Delta\nu_a = \nu_a - \nu_a^0 = W_0 - W_1 + w_1 \approx 0 \quad (7)$$

$$\Delta\nu_e = \nu_e - \nu_e^0 = W_0 - W_1 - w_0 \approx -800 \text{ cm.}^{-1} \quad (8)$$

equations relate the absorption frequency shift, $\Delta\nu_a$, and the fluorescence frequency shift, $\Delta\nu_e$, to the hydrogen-bond energy in the ground and excited states, W_0 and W_1 , respectively, and to the Franck-Condon energies in the ground and excited states, w_0 and w_1 , respectively. These relations indicate that the hydrogen-bond energy is greater in the excited state than in the ground state. Since all the energies are positive, the maximum difference in energy, $W_1 - W_0$, is about 800 cm.^{-1} or $\approx 2 \text{ kcal./mole}$.

Fluorescence differences were also noted in the condensed phases. The emission maxima for the crystalline phenol hemihydrate and the dilute aqueous solution of phenol were at $295 \text{ m}\mu$, whereas the crystalline phenol and liquid phenol maxima (hemihydrate and pure) were at $297 \text{ m}\mu$. The crystal structures indicate that every phenol is hydrogen bonded to another phenol in the pure crystal and to a water molecule in the case of the hemihydrate.^{20,21} The difference in the wave length of the fluorescence maxima presumably reflects this difference in environment in the two different crystals and the similarity of the environment of the dilute aqueous solution and the crystalline hemihydrate. The observation that the fluorescence maxima of the liquid hemihydrate and the solid phenol occur at the same wave length implies that the local environ-

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ments are similar; *i.e.*, in the liquid hemihydrate the phenol molecules preferentially hydrogen bond to each other rather than to water as in the crystal. The reason that phenol usually crystallizes out of the hemihydrate liquid if cooled slowly below 10° has been explained by this preferential binding.²¹

Excimer emission was not observed for crystalline phenol, phenol hemihydrate, and *p*-ethylphenol. The crystal structures of phenol²⁰ and phenol hemihydrate²¹ indicate that neighboring rings do not overlap. Therefore, the fluorescence results on *p*-ethylphenol may also indicate nonstacking of rings in the crystal.

In a preliminary report of the fluorescence of poly-L-tyrosine¹⁰ the presence of a new fluorescence band near $420 \text{ m}\mu$ was interpreted as being due to excimer emission caused by the interaction of neighboring phenolic side chains. Current work has indicated that this band at $420 \text{ m}\mu$ is due to a new chemical species formed by photoirradiation of the polymer during measurement and also by the chemical treatment during the preparation. This new species has a fluorescence excitation spectrum similar to that of the phenolic chromophores. The present observation, of excimer emission at $345\text{--}350 \text{ m}\mu$ in liquid phenol and *p*-ethylphenol, which are appropriate models for the polymer chromophore, substantiate the current interpretation. Continuing work is in progress and will be reported elsewhere. It is to be noted that the possibility of chromophore interaction in proteins, *i.e.*, excimer formation and phenol-phenol self-quenching, when the side chains are favorably oriented, allows for another mechanism of energy transfer and may offer an explanation for reduced quantum yields commonly observed in proteins.

Dissociation Studies in High Dielectric Solvents. VI. Conductance of Magnesium Sulfate Heptahydrate in Acetone-Formamide Mixtures at 25° ¹

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The conductance of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ has been measured at 25° in 0-50% acetone-formamide mixtures. The dielectric constant, viscosity, and density of each mixed solvent from 0-100% acetone have also been measured at 25° . The conductance data have been analyzed by the Fuoss-Onsager equation for associated electrolytes and reasonable Λ^0 , K_A , and a_j parameters have been obtained. A plot of $\log K_A$ vs. D^{-1} is linear. However, the Walden product decreases and a_j increases with the decrease in the dielectric constant of the mixed solvent.

(1) The work forms part of a thesis for the fulfillment of a Ph.D. degree to be submitted to the University of Gorakhpur, Gorakhpur.

(2) (a) Grateful acknowledgment is made to the University Grants Commission, New Delhi, for a fellowship to G. P. J.; (b) Chemistry Department, University of Maryland, College Park, Md. 20742.

Introduction

In a previous communication of this series, we have shown that magnesium sulfate is essentially unassociated ($K_A \approx 9$) in formamide,³ and the Fuoss-Onsager equation⁴ describes the conductance data fairly satisfactorily. The behavior of this salt was further examined in dioxane-formamide mixtures, where higher pairwise association was forced in.⁵ The results apart from showing the adequacy of the theory in the entire range of dielectric constants (110-21), exhibited an interesting specificity in the hydrodynamic parameter,

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Table I. Physical Properties of Acetone-Formamide Mixtures at 25°

No.	Acetone		D^a	$\rho,^b$ g./ml.	$\eta^c \times 100,$ cp.	$V_{12},^d$ ml.	P_{12}^e	$\delta \times 10^4,^f$
	$W_2,$ wt. %	$X_2,$ mole fraction						
1	0.0	0.0	109.5	1.1296	3.301	39.87	965.8	0.0
2	10	0.0793	97.61 ^g	1.0891	2.783	42.30	912.7	-59.7
3	20	0.1624	85.20	1.0524	2.306	44.81	843.3	-129
4	25	0.2054	79.12	1.0338	2.065	46.13	806.0	-153
5	30	0.2495	73.47	1.0145	1.867	47.61	770.6	-163
6	35	0.2945	67.88	0.9955	1.647	49.10	735.1	-170
7	40	0.3408	62.79	0.9781	1.480	50.59	711.5	-185
8	50	0.4367	53.48	0.9444	1.164	53.72	632.4	-211
9	60	0.5377	44.55	0.9109	0.8835	57.14	559.1	-211
10	70	0.6441	36.97	0.8780	0.6701	60.68	491.6	-189
11	80	0.7562	29.97	0.8475	0.5280	64.78	423.9	-168
12	90	0.8746	24.68	0.8182	0.3761	68.98	370.3	-135
13	100	1.00	20.47	0.7844	0.3040	74.03	327.9	0.0

^a Dielectric constant. ^b Density. ^c Viscosity. ^d Molar volume. ^e Polarizability. ^f Deviation factor. ^g Calculated from $D = D^0 + \delta D$, where $D^0 = 1 + 9(X_1P_1^0 + X_2P_2^0)/2V_{12}(1 - 1/2D)$. P_1^0 and P_2^0 are the molar polarizabilities of formamide and acetone (965.8 and 327.9, respectively). The value of D in the denominator was interpolated from a plot of D against X_2 , and the pertinent δD was obtained from interpolation from the D vs. X_2 plot for the mixtures of measured D .

Λ^0 , of this salt: Λ^0 decreased on initial addition of dioxane to formamide, though the viscosity also decreased. The present study was conducted to satisfy a twofold interest, namely, to temper conclusions derived from our previous studies and to explore in general several new solvent systems which permit a wide range of dielectric constant above that of the conventional aqueous mixtures.

Mixtures of methanol and ethanol with formamide are unstable, as shown by a drastic increase in the specific conductivity with time. Ammonia was also detected in mixtures kept for a few hours. This may be due to the chemical reaction between formamide and alcohol producing conducting products. The acetone-formamide mixture is a sufficiently stable solvent whose conductance does not increase with time.

Experimental Section

The equipment for the measurements of dielectric constant D , density ρ , and viscosity η have already been described earlier.⁵

The dekameter cells used for the measurement of the dielectric constant were calibrated with several more liquids of standard dielectric constant in the close range of the measured dielectric constants (dioxane-water mixtures⁶). The measurements of the dielectric constants are reproducible within 0.05% with this instrument, but the absolute values of the dielectric constants are accurate to 0.5% only.

The viscometers were recalibrated with 10, 20, 30, and 40% glycerol-water mixtures.⁷ However, no appreciable change from the previous calibration was noticed. Kinetic energy correction was negligible. The absolute values of the viscosities obtained were better than 0.1%.

The conductance equipment, cells, and the experimental technique have been described previously.⁸ Each run was repeated twice with a different stock solution and solvent batch (prepared in amounts of 0.4-0.5 kg.). Usual precautions were taken to avoid

changes in the composition of the mixtures due to evaporation of the relatively more volatile acetone. The conductance of the solution was obtained by subtracting the conductance of the solvent of the same batch determined separately in a cell at the same time.

$MgSO_4 \cdot 7H_2O$ was from the previous stock.^{3,5} The anhydrous salt is sparingly soluble in pure formamide and less still in the mixed solvent. Because of this difficulty all the solutions for the conductance measurements were prepared from $MgSO_4 \cdot 7H_2O$. It may be pointed out that conductance data for some anhydrous and hydrated salts in formamide were found very similar.⁸ From the conductance studies of a series of alkaline earth salts and of many multivalent electrolytes, Dawson and his co-workers^{9,10} have reported "anhydrous and hydrated salts show identical behavior within experimental uncertainty. This is interpreted to mean that the water of hydration originally associated with the solute loses its identity as such and becomes a negligible part of the solvent." The difference in D and η resulting from the modification of the solvent structure by introduction of this small amount of water has been disregarded and the solvent properties given in Table I have been used as such. Although the data and the conclusions given here apply to solutions of $MgSO_4 \cdot 7H_2O$, it appears that the results for the anhydrous solutions would not differ appreciably.

Formamide was purified by the procedure described³ earlier.

Acetone (A.R. grade, British Drug House) was shaken with P_2O_5 , filtered, and fractionally distilled twice. With three more distillations through a 100 × 4 cm. glass helices packed column (retaining 60-70% of middle cut), a product of low specific conductance ($< 8 \times 10^{-10}$ mho), density 0.7844 g./ml., b.p. 56.2°, was obtained.

All the measurements were carried out in an oil-filled thermostat at $25 \pm 0.005^\circ$.

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Results

The physical properties of the mixed solvents are summarized in Table I, where W_2 represents the weight per cent of acetone in formamide, X_2 its mole fraction, ρ the density, η the viscosity, and D the dielectric constant of the solvent mixtures. The molar volume V_{12} , polarizability P_{12} , and the deviation factors δ of the solvent mixtures have been calculated from the equations given earlier.⁵

All the three measured properties, D , η , and ρ , are monotonic functions of the mole fraction of acetone, X_2 , and thus of the solvent composition. The

Table II. Conductance-Concentration Data for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ at 25°C^a

$D = 97.61$		$D = 85.20$	
10°C	- Δ	10°C	- Δ
2.1036	28.226	2.2846	29.985
6.6204	26.453	5.5649	28.132
11.913	25.118	8.6804	26.750
18.332	23.866	11.746	25.483
24.085	22.918	15.461	24.366
30.073	22.185	18.543	23.656
40.088	21.161	22.044	22.871
50.761 ^b	20.289	28.356	21.754
59.988 ^b	19.636	34.133	20.894
79.880 ^b	18.473	47.089 ^b	19.489
$D = 79.12$			
10°C	- Δ		
	3.8665	28.809	
	5.9821	27.312	
	8.4355	25.991	
	12.460	24.266	
	16.404	23.002	
	20.596	21.859	
	25.714	20.757	
	32.056	19.649	
	38.706 ^b	18.657	
	54.576 ^b	16.993	
$D = 73.47$		$D = 67.88$	
10°C	- Δ	10°C	- Δ
2.5991	32.114	2.0241	33.526
5.8604	28.338	4.2569	29.629
8.3104	26.385	6.7462	26.841
11.267	24.706	9.5939	24.624
16.192	22.578	12.691	22.902
21.337	20.995	18.577	20.659
25.773	19.912	24.517	19.067
30.935 ^b	18.892	31.509 ^b	17.701
		36.672 ^b	16.917
$D = 62.79$		$D = 53.48$	
10°C	- Δ	10°C	- Δ
2.3991	27.213	1.6898	26.981
3.1355	24.510	2.2811	23.621
4.1352	23.761	2.8992	21.642
5.1761	22.612	3.9998	19.043
6.2111	21.499	4.6211	18.011
7.5611	20.412	5.7610	16.919
9.0032	19.635	6.8594	16.033
10.447	18.860	7.8632	15.295
12.322	18.082		
16.612	16.522	9.9535	14.098
21.068 ^b	15.281	12.331	12.980
25.308 ^b	14.547	15.080	12.089

^a Concentration in moles/l. and Δ in (ohm cm.⁻² equiv.)⁻¹. To avoid the errors in recalculation due to rounding off, the number of figures given is one more than the probable error in measurements would deem significant. ^b Data for which $k_a > 0.2$, theoretically not applicable in calculations.

$d(D,\eta)/d(X_2)$ is notably greater at lower X_2 , suggesting that depolymerization of formamide is more pronounced at lower acetone contents. P_{12} and V_{12} are linear in X_2 , but δ shows that contraction occurs during mixing in the entire range of composition and is maximum at $X_2 \approx 0.5$.

Table II summarizes the equivalent conductance and concentration data for the salt in each mixed solvent. The phoreograms show progressively increasing ion association with the decreasing dielectric constant.

The data were analyzed by the Fuoss-Onsager equation⁴ for associated electrolytes in the form

$$\Lambda = \Lambda^0 - Sc^{1/2}\gamma^{1/2} + Ec\gamma \log c\gamma + Jc\gamma - K_Ac\gamma f_{\pm}^2\Lambda \quad (1)$$

on an IBM 7094 computer using a Fortran program similar to that described by Kay.¹¹ Since Mg^{2+} ion is of the same order of magnitude as the solvent molecules (and even smaller), the Einstein coefficient F was taken as zero and the viscosity term $F\Lambda C$ was, therefore, neglected. The higher terms in $C^{3/2}$ were also neglected.

The results of the analysis are given in Table III, where Λ^0 , K_A , etc., are the parameters defined by the Fuoss equation, and $\sigma\Lambda$ is the standard deviation in $\Delta\Lambda$ unit of the data from the equation, and $\Lambda^0\eta$ is the Walden product.

Table III. Derived Parameters of Fuoss-Onsager Equation for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ at 25°C

W_2	D	Λ^0	K_A	a_j	$\sigma\Lambda$	$\Lambda^0\eta$
0.0	109.5	28.38	9.6	3.0	0.01	0.9373
10.0	97.61	30.16	43.4	2.37	0.01	0.8394
20.0	85.20	32.96	79.7	2.47	0.01	0.7619
25.0	79.12	34.31	263	3.53	0.01	0.7086
30.0	73.47	39.28	693	4.53	0.02	0.7328
35.0	67.88	42.17	1214	6.82	0.04	0.6946
40.0	62.79	44.9	4480	7.91	0.08	0.6645
50.0	53.48	51	31620	8.93	0.12	0.5918

Discussion

As seen from Table III, the contact distance a_j increases with a decrease in the dielectric constant and appears to be slightly in error at the higher D values. Recent theoretical and experimental studies¹² have shown that a_j has little physical significance where only slight association occurs, because K_A in such a case is subject to considerable error. The systematic trend in a_j with the dielectric constant may be due to the still missing linear terms which have been excluded by the approximations made in the theory to derive eq. 1. The viscosity correction has also been ignored which may also be partly responsible. From a plot of a_j , in Table III, against $1/D^4$ an extrapolated value of $a_j = 2.9 \text{ \AA.}$ at infinite dielectric constant was obtained.

The plot of $\log K_A$ vs. $1/D$ (Figure 1) is linear and gives $a_k = 2.93 \text{ \AA.}$, in good agreement with a_j , from the slope. The plot extrapolates to $K_A = 9.2$ in pure formamide and thus is in confirmation of our previous results. From a comparison of the $\log K_A$ vs.

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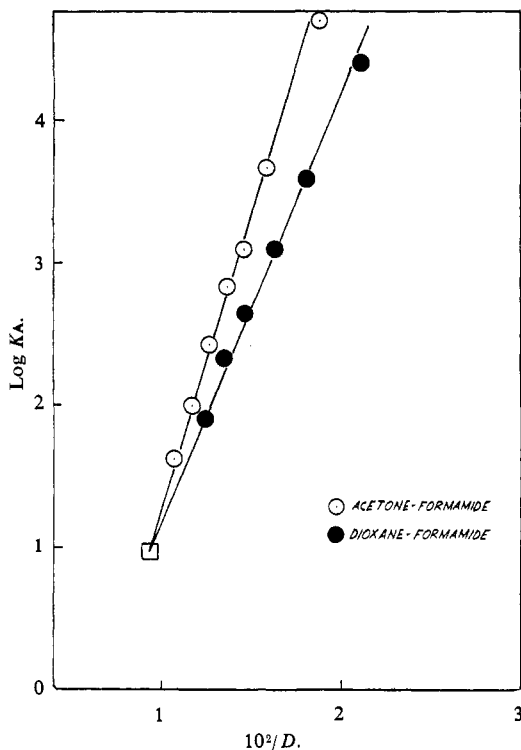


Figure 1. Dependence of association of MgSO_4 on dielectric constant.

$1/D$ plots for the salt in acetone-formamide and in dioxane-formamide⁵ mixed solvents, it appears that the simple Fuoss equation¹³

$$K_A = \frac{4\pi N a_k^3}{3000} \exp(Z_1 Z_2 e^2 / a_k D K T)$$

is unable to describe the dependence of K_A of the salt on the dielectric constant. The lower K_A at the same dielectric constant in dioxane containing mixture appears as a simple thermodynamic analog of the specificity shown in the hydrodynamic behavior.

As seen in Figure 2, the Walden product, $\Delta^0\eta$, decreases monotonically with the decrease in the dielectric constant (the scatter of points near $D \approx 75$ may be due to experimental error). The decrease in $\Delta^0\eta$ may be ascribed to a braking of ions as a result of electrostatic coupling between the fields of moving ions and the solvent dipoles.¹⁴⁻¹⁶ The ion-solvent relaxation drag increases progressively at lower D , and hence the effect is more pronounced at lower D . For a given value of the dielectric constant $\Delta^0\eta$ is less in acetone-formamide than in dioxane-formamide. This may be due to a higher ion-solvent relaxation drag in the former solvent.

A somewhat more detailed consideration of the differences in the hydrodynamic parameter, Δ^0 , in dioxane-formamide⁵ and acetone-formamide mixed solvents will be relevant. The macroscopic viscosity, η , of the solvents decreases monotonically as X_2 , the mole fraction of dioxane or acetone, increases but Δ^0 decreases initially from 28.4 in pure formamide to 24.5 in 20% dioxane-formamide mixture and then

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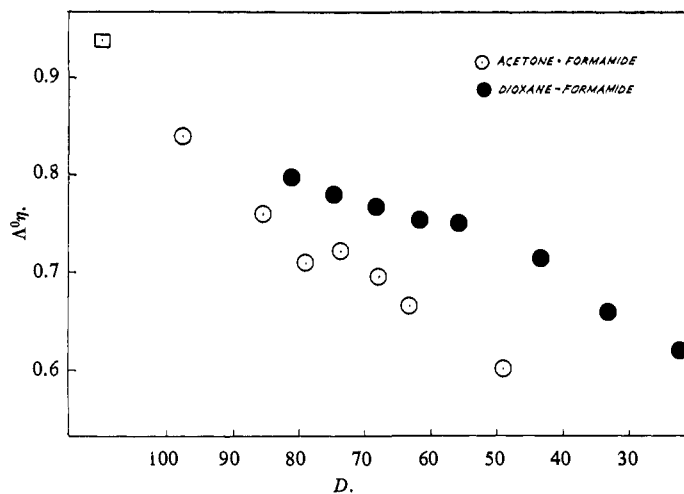


Figure 2. Dependence of Walden product on dielectric constant.

increases very slowly with the increase in the dioxane content of the solvent. While in the case of acetone-formamide mixed solvents, Δ^0 increases steadily with a decrease in η of the solvent as the acetone content of the solvent increases.

This seemingly conflicting hydrodynamic behavior (mobility) in the dioxane-formamide mixture appears to arise owing to a change in the immediate surroundings of Mg^{+2} on the initial addition of dioxane to formamide. Strictly speaking in terms of classical model, this would mean that the size of the hydrodynamically equivalent sphere increases on the addition of dioxane to formamide.

The decrease in $\Delta^0\eta$ for a salt in mixed solvents is usually ascribed to the Fuoss effect.¹⁴ However, an explanation which involves the examination of solvent-solvent interaction may be reasonable to account for the decrease of the ionic mobilities in the dioxane-formamide on the initial addition of dioxane. It also seems attractive to assume that the decrease in Δ^0 on the initial addition of dioxane may be due to an increase in the thickness of the solvate shell (around the ion) as a result of complexation of formamide with dioxane¹⁷ stabilized by strong hydrogen bonding (oxygen in dioxane has exposed ps hybrid). The consideration of solvent-solvent interaction may prove of much value for an understanding of the behavior of a solute in different solvent mixtures. We are extending this study to dioxane mixtures of N -substituted higher homologous amides to see if this behavior turns out as a general one.

In conclusion it seems that acetone-formamide apparently behaves more ideally in terms of the theoretical model than dioxane-formamide mixed solvents; as far as the hydrodynamic ideality is concerned, Fuoss-Onsager theory predicts the conductance data of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in both solvent mixtures satisfactorily.

Acknowledgment. The authors wish to thank Dr. R. P. Rastogi, Head of the Chemistry Department, for providing the necessary facilities and to the research group of Professor G. Atkinson of the University of Maryland, for the computer processing of the data.

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