

The Methanol-Trimethoxyborane Azeotrope as a Solvent^{1a}

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The methanol-trimethoxyborane azeotrope is an easily prepared solvent of strong H-bond donor and weak H-bond acceptor properties. It has a low viscosity and low boiling point, and is completely transparent in the visible and uv at wave lengths above 220 nm. It has a dielectric constant of 9 and ion pair formation constants between 10^3 and 10^4 for simple electrolytes. The glass electrode pH-meter can be used in this solvent, with the ordinary calomel reference electrode. Indicator acidity measurements are somewhat complicated by the formation of H-bonded ion pairs.

The solvent is useful for measuring the relative acidity of strong acids; $\text{CH}_3\text{SO}_2\text{OH}$ and $\text{CF}_3\text{SO}_2\text{OH}$ are readily differentiated. It should be useful for other physico-chemical measurements and also in preparative chemistry.

Trimethoxyborane forms an azeotrope with methanol containing exactly one mole of each constituent². The constituents of this azeotrope are thought to be weakly complexed by the donation of unshared electrons from the alcohol oxygen to the formally empty orbital of boron². Such complexing should promote the proton donor character of the alcohol and reduce its electron pair donor character. This should endow the azeotrope with interesting chemical properties, perhaps similar to those of the polyfluorinated alcohols³. Since the azeotrope is cheap and readily available⁴, it was of interest to investigate its chemical and physico-chemical properties. The present paper deals with its physico-chemical properties, and accompanying papers^{5,6} describe some of its chemical properties.

EXPERIMENTAL

Materials

The azeotrope was prepared by mixing equimolar quantities of methanol and trimethoxyborane and then distilling. It had b. p. 54 °C; lit.⁷ 54.3 °C. The methanol used was obtained from Matheson, Coleman and Bell, and was redistilled before use. It had a residual water content of 0.05%⁸. Trimethoxyborane was a gift of the Ventron Corporation and was distilled before use. It had b. p. 68 °C; lit.⁹ 67.8 °C. Trifluoromethane sulfonic acid was obtained from the 3M Co., and was twice distilled before use: b. p. 160 °C; lit.¹⁰ 162 °C. Methanesulfonic acid was obtained from Aldrich Chemical Co., and sulfuric acid from E. I. du Pont de Nemours, Inc. Both methane sulfonic acid and sulfuric acid were distilled before use under moderate vacuum, but, as the pressure was not measured, the b. p.'s are not significant. 4-Nitroaniline was obtained from Aldrich Chemical Co., and recrystallized from methanol: m. p. 157—158 °C; lit.¹¹ 149 °C. Decyltriethylammonium tetrabutylboride ($\text{N}_{10.2.2.2}\text{B}_{4.4.4.4}$) was a gift of General Mills Chemicals, Inc. It was made by the methods of Ford¹² from lithium tetrabutyl boride and decyltriethylammonium bro-

mide. On analysis the product showed no detectable lithium (less than 2 ppm) but it showed $\sim 2\%$ of bromine. This corresponds to about 8 wt. percent or about 13 mole percent unreacted decyltriethylammonium bromide. This material is an undistillable liquid which would be very difficult to purify, so it was used in this condition. Reagent grade LiBr was obtained from Matheson, Coleman, and Bell (guaranteed minimum assay, 99%). It was dried, but not otherwise purified before use.

Methods

The dielectric constant was measured with a Sargent Oscillometer, Model V. The instrument reading, R , was obtained for six standards of known dielectric constant, ϵ . R increased smoothly with increasing ϵ , while $dR/d\epsilon$ decreased somewhat with increasing ϵ . The value of R for the azeotrope was converted to ϵ by using a graph of R as a function of ϵ , made up from the standards.

Viscosity was measured at 25.0 °C with an Ostwald viscometer¹³, calibrated with methanol and acetone. The known densities¹⁴, d_4^{25} , and viscosities¹⁵, n_{25} , of these liquids, along with the times they required to fall through the viscometer, t , were used to evaluate the constants, B (-2.211) and C (3.273×10^{-3}) of eq. 1.

$$n_{25} = C d_4^{25} t - B d_4^{25}/t \quad (1)$$

Similar measurements were then used to evaluate n_{25} for the methanol-trimethoxyborane mixtures.

Spectrophotometric measurements were made with either a Beckman DU or DK-2 spectrophotometer. The former had a cell compartment in which the temperature was maintained at 25.0 ± 0.1 °C, and was used for quantitative measurements at a small number of wavelengths. The latter was used to obtain spectra.

A Barnstead Conductivity Bridge, Model PM-70CB was used for conductance measurements. The cell constant was obtained by measuring the conductance of aqueous KCl solutions of known concentration and equivalent conductance¹⁶. Solvent corrections were nearly negligible (of the order of 0.3%) for the KCl solutions. The conductance of the nonaqueous solvent varied over a range of $\sim 30\%$ from batch to batch (increasing with an excess of either constituent). The solvent conductance was 2–10% of the solution conductances, depending on the value of the latter. It was subtracted as a correction. These substantial corrections are undoubtedly one source of scatter.

A Corning pH meter, Model 7, and a Corning, No. 476050, combination electrode were used for pH measurements. Aqueous buffers were used for calibration. The electrode was then wiped dry, soaked in the azeotrope for 30 minutes, and used for solutions in the azeotrope. It was convenient to make these readings on the millivolt scale of the meter.

RESULTS AND DISCUSSION

Dielectric Constant

The methanol-trimethoxyborane azeotrope was found to have a dielectric constant of 8.8. The reproducibility of readings for the standards and for the azeotrope suggest that this is uncertain by about 0.3.

Viscosity

The viscosities and densities of the azeotrope and mixtures containing small excesses of methanol and of trimethoxyborane are given in Table I. Each t was measured 7 times and averaged, with average deviations from the mean of about 0.3%, so that the probable error of the t values is about 0.1%. The uncertainties in the densities appear to be no worse than 0.1%. These errors lead to an uncertainty of about 0.2% in the viscosity of the azeotrope. Since the viscosity appears to be only a weak function of the composition in the neighborhood of the azeotrope (Table I), uncertainty in composition does not add to the uncertainty in viscosity.

TABLE I
Viscosities and Densities at 25 °C

Substance	d_4^{25}	η_{25} (cp)
Azeotrope	0.880 ^a	0.424
Azeotrope + 1% CH ₃ OH	0.879 ^b	0.424
Azeotrope + 1% (CH ₃ O) ₃ B	0.881 ^b	0.422

^a T. J. Tully and P. M. Christopher, *J. Phys. Chem.*, **61** (1957) 1578.

^b Calculated using the approximate relation, $d = d_1 d_2 / \{f_2(d_1 - d_2) + d_2\}$.

Conductance and Dissociation Constants

To obtain typical ion association constants K_A , and limiting equivalent conductances, Λ_0 , conductances were measured for various solutions of LiBr and N_{10,2,2,2}B_{4,4,4,4} in the azeotrope. A selection of measured values of Λ is shown in Table II. In a solvent of dielectric constant as low as 9, equivalent conductance Λ , should be describable by eq. 2, which is a modification of the Ostwald dilution law, taking into account only the most important contributions from interionic forces¹⁷. Equation 2 contains, in addition to Λ , K_A , and Λ_0 , the ion activity coefficient

TABLE II
Equivalent Conductances in Methanol-Trimethoxyborane

Substance	Conc. (M)	Λ
LiBr	4.97×10^{-4}	37.79
LiBr	8.28×10^{-5}	52.11
LiBr ^a	8.28×10^{-5}	58.53
LiBr ^b	8.28×10^{-5}	47.88
LiBr	3.31×10^{-5}	62.89
LiBr	1.655×10^{-5}	68.11
N _{10,2,2,2} B _{4,4,4,4}	5.67×10^{-4}	43.98
N _{10,2,2,2} B _{4,4,4,4}	5.67×10^{-4}	49.36
N _{10,2,2,2} B _{4,4,4,4} ^b	5.67×10^{-4}	47.27
N _{10,2,2,2} B _{4,4,4,4}	9.70×10^{-5}	59.95
N _{10,2,2,2} B _{4,4,4,4}	2.27×10^{-5}	63.06
CF ₃ SO ₂ OH	5.57×10^{-4}	49.96
CF ₃ SO ₂ OH	1.39×10^{-4}	70.90
CF ₃ SO ₂ OH	4.05×10^{-5}	90.29
CH ₃ SO ₂ OH	1.070×10^{-2}	3.51
CH ₃ SO ₂ OH	2.14×10^{-3}	6.76
CH ₃ SO ₂ OH	4.28×10^{-4}	13.17

^a One percent excess methanol added to the solvent. ^b One percent excess trimethoxyborane added.

$$F/\Lambda = 1/\Lambda_0 + C \Lambda f^2 K_A/\Lambda_0^2 F \quad (2)$$

f and the quantity, F . The f values were obtained from eq. 3, which is the

$$-\ln f = \beta' C^{1/2} \gamma^{1/2} / (1 + C^{1/2} \gamma^{1/2} \kappa a) \quad (3)$$

Debye-Hückel limiting equation for univalent ions of finite size, adapted for use with conductances. The parameters, β' and κ , are given by theory¹⁸, and have the values 13.58 and 9.18×10^7 respectively in a solvent of dielectric constant 8.8. The sum of the ionic radii, a , was assumed to be 7×10^{-8} cm. The degree of dissociation, γ , is $\Lambda/\Lambda_0 F$. F , which appears both in eq. 2 and in the expression for γ , is a function of Λ and Λ_0 . It has been tabulated by Fuoss¹⁹. A convenient way to obtain K_A and Λ_0 from the data is to plot F/Λ against $C \Lambda f^2/F$. Such a plot has $1/\Lambda_0$ as its intercept and K_A/Λ_0^2 as its slope. To do so, however, requires a value for Λ_0 , in order to evaluate f and F . The problem was solved by assuming a value for Λ_0 , determining the value from the appropriate plot, then making a new plot with the new values of f and F . This was repeated till repetition no longer changed Λ_0 or K_A by as much as 1%. The final plots are shown in Figures 1 and 2. The values of K_A and final values for Λ_0 are shown in Table III.

For $\text{CF}_3\text{SO}_2\text{OH}$ similar measurements yielded similar results, and these are also reported in Table III. As shown by Table II, solutions of LiBr , $\text{N}_{10,2,2,2}\text{B}_{4,4,4,4}$, and $\text{CF}_3\text{SO}_2\text{OH}$ were carried to increasing dilution until Λ values were nearly constant and nearly equal to Λ_0 . For $\text{CH}_3\text{SO}_2\text{OH}$, however, Λ was about one

TABLE III

Limiting Equivalent Conductances and Association Constants for Electrolytes in the Azeotrope

Compound	Λ_0	K_A
LiBr	74.7	5.8×10^3
$\text{N}_{10,2,2,2}\text{B}_{4,4,4,4}$	74.9	2.0×10^3
$\text{CF}_3\text{SO}_2\text{OH}$	119.1	8.4×10^3
$\text{CH}_3\text{SO}_2\text{OH}$	119 ^a	2.1×10^5

^a Assumed

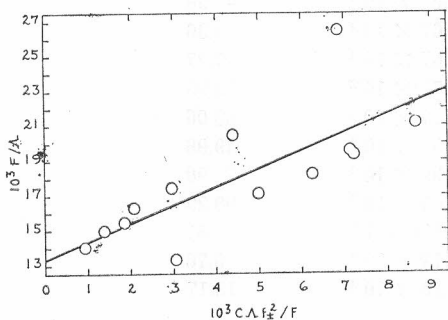


Figure 1. Conductance for LiBr plotted according to eq. 2.

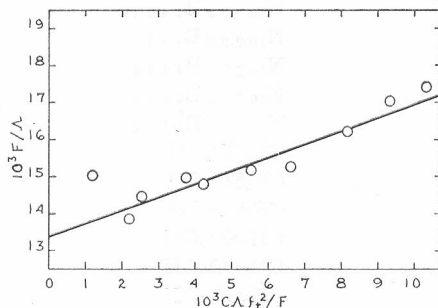


Figure 2. Conductance for $\text{N}_{10,2,2,2}\text{B}_{4,4,4,4}$ plotted according to eq. 2.

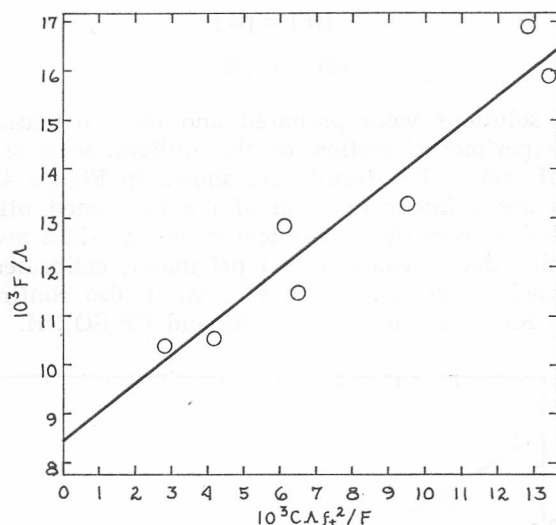


Figure 3. Conductance for $\text{CF}_3\text{SO}_2\text{OH}$ plotted according to eq. 2.

fourth of that for $\text{CF}_3\text{SO}_2\text{OH}$ at the lowest concentrations which produced reliable values and was still rising rapidly with increasing dilution. Such measurements do not easily lend themselves to the accurate experimental determination of Λ_0 using eq. 2. It has, therefore, been assumed that Λ_0 for $\text{CH}_3\text{SO}_2\text{OH}$ is the same as that for the fluorinated analogue. With that assumption, K_A for $\text{CH}_3\text{SO}_2\text{OH}$ is 1.1×10^5 ; larger than that for $\text{CF}_3\text{SO}_2\text{OH}$ by nearly a factor of 20. The difference probably arises from the presence of unionized acid in the $\text{CH}_3\text{SO}_2\text{OH}$. The $\text{CF}_3\text{SO}_2\text{OH}$ is probably completely ionized, or nearly so, even though partly undissociated, since its K_A is comparable to that for LiBr .

Because of the iterative method used to evaluate Λ_0 and K_A , it is difficult to estimate their uncertainty. The statistical uncertainties of the slopes and intercepts are less than 10% but the possible errors in Λ_0 and K_A are larger than this, particularly for Λ_0 because the location of the points themselves depends, circularly, on Λ_0 . In addition, for $\text{N}_{10,2,2,2} \text{B}_{4,4,4,4}$, Λ_0 and K_A are probably both raised by the presence of the bromide as a contaminant, as described in the experimental section. Nevertheless, it seems unlikely that either parameter is in error by more than 20% for any of the four substances. The scatter in the individual points is consistent with the uncertainties introduced by the corrections for the conductance of solvent and errors originating from the solvent composition.

Glass Electrode pH Measurements

From the values of K_A for the two acids, HB, the pH of their solutions can be determined using eqs. 3—6.

$$\frac{1}{K_A} = \frac{f_{\pm}^2 [\text{H}^+] [\text{B}^-]}{[\text{HB}]} \quad (4)$$

$$[H^+] = [B]$$

$$pH = f_+ [H^+] \quad (5)$$

A series of such solutions were prepared and their potential measured, as described in the experimental section, on the millivolt scale of a conventional, glass-electrode, pH meter. The results are shown in Figure 4. The measured millivolt readings are a linear function of the calculated pH values with a slope indistinguishable from the theoretical value of -59.2 mv per pH unit²⁰. This result indicates that a conventional pH meter, calibrated with aqueous buffers, can be used in the azeotropic solvent. It also confirms the general correctness of the K_A values for CH_3SO_2OH and CF_3SO_2OH .

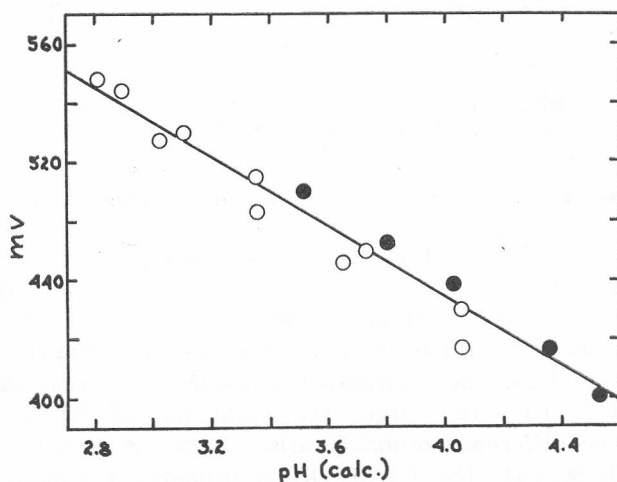


Figure 4. A plot of the glass electrode-calomel electrode potential against calculated pH values for solutions of CF_3SO_2OH (open circles) and CH_3SO_2OH (filled circles) in the methanol-trimethoxyborane azeotrope. The line has the theoretical slope of -59.2 . It is visually indistinguishable from a least-squares line through the points, which would have a slope of -60.4 .

The average deviation of points from the line is about 0.1 pH unit, which is more than would be encountered in aqueous solutions. The excess is probably due, partly, to the lack of buffering in these solutions and, partly, to minor discrepancies in the composition of the solvent, which influences K_A .

Indicator Equilibrium Measurements

The azeotrope is free of absorption in the visible and in the uv above 220 nm. Spectroscopic examination of *p*-nitroaniline in the azeotrope, in the presence and in the absence of 0.09 M CF_3SO_2OH , revealed a λ_{max} at 355 nm for the neutral indicator and at 265 nm for the protonated indicator. There was an isosbestic point at 287 nm. For the neutral indicator (in the absence of acid) it was straight-forwardly determined that ϵ_{355} is 1.404×10^4 and ϵ_{265} is 1.17×10^3 . In the acidic solution the persistence of some absorption at 355 nm suggested incomplete protonation. An increase of the CF_3SO_2OH concentration caused the separation of the azeotrope into two phases. ϵ_{355} for the protonated indicator was, consequently, assumed to be the same as that in

methanol. This permitted the calculation of the residual, unprotonated, indicator concentration, and thereby the true concentration of protonated indicator. From the two concentrations and the known value of ϵ_{265} for the *unprotonated* indicator, ϵ_{265} was calculated for the protonated indicator; it was 6.46×10^3 . From these values the concentrations of protonated and unprotonated indicator were calculated in seventeen solutions with $\text{CF}_3\text{SO}_2\text{OH}$ concentrations ranging from 6×10^{-2} to 1.7×10^{-3} M. The total indicator concentration was constant, 4.7×10^{-5} .

The protonation equilibrium can be formulated in at least three ways, shown by eqs. 7—9 (in which I is *p*-nitroaniline and HA is $\text{CF}_3\text{SO}_2\text{OH}$).



Equilibrium »constants« were calculated for each solution according to each of the equations. A representative sample of the results is shown in Table IV. Only the »constants« calculated according to eq. 8 are free from striking systematic variation with the acid concentration. Even in this formulation there is a drift to lower values at lower acid concentration. This may be due to the incursion of some other species (quadrupoles, as an example) at the higher concentrations, or it may simply be due to the behavior of the activity coefficients. In any event, it is clear that the major species in equilibrium are the unassociated neutral molecules and the hydrogen-bonded ion pairs. The formation constant for the hydrogen-bonded ion pair must be at least a factor of 100 larger than the K_A 's for simple salts, shown in Table III, or substantial dissociation would have occurred, converting eq. 8 to eq. 7. The increased formation constant is probably due to hydrogen bonding.

TABLE IV
Equilibrium »Constants« According to Equations 7—9^a

10^2 ($\text{CF}_3\text{SO}_2\text{OH}$) ^b M	$10^3 K_7$ (dimensionless)	$10^2 K_8$ M	K_9 (dimensionless)
5.10	4.9	1.23	5.9
3.06	4.0	1.12	3.20
1.84	3.3	1.08	1.83
0.87	1.7	0.91	0.69
0.35	0.7	0.79	0.23
0.17	0.3	0.77	0.10

^a The *p*-nitroaniline concentration was 4.7×10^{-5} M throughout. ^b This is the total acid concentration. In calculating K_7 and K_8 (HA) was taken as the *undissociated* acid, and the K_A of Table III was used to evaluate it.

The value of K , obtained by extrapolation to infinite dilution, using all 17 data points, is ~ 73 . Similar results were obtained with methanesulfonic acid, giving an equilibrium constant of ~ 36 . This is in the direction to be expected from the relative values of the dissociation constants (Table III); however, the ratio of dissociation constants is ~ 20 while the ratio of indicator

complexing constants is only about 2. There is no obvious reason for the relative insensitivity to acid strength of the complexing constants.

CONCLUSIONS

The picture that emerges is of a mobile, low boiling, solvent, of moderately low dielectric constant. Ion association constants are substantial, as would be expected for a solvent of this dielectric constant²¹, so that most ionic materials will be present as ion pairs. However, further aggregation does not appear to be important, and activity coefficients of neutral species (even ion pairs) appear to be near unity. Ion activity coefficients in dilute solutions seem to be satisfactorily predicted by Debye-Hückel theory.

In keeping with its expected character as a very weak hydrogen bond acceptor, the azeotrope does not level the strength of acids until very strong acids are reached, so that $\text{CF}_3\text{SO}_2\text{OH}$ is easily identified as a stronger acid than $\text{CH}_3\text{SO}_2\text{OH}$.

The possibility of using a conventional, glass electrode, pH meter greatly simplifies acid-base chemistry in the azeotrope. The absence of visible and uv spectrum facilitates spectroscopic measurements.

In general, it is a solvent similar to glacial acetic acid, but easier to prepare, and much easier to remove from nonvolatile solutes. It should find uses both in physico-chemical measurements and in preparative chemistry.

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SAŽETAK

Azeotropna smjesa metanol-trimetoksiboran kao otapalo

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Azeotropna smjesa metanol-trimetoksiboran otapalo je koje se može lako pripraviti i ima svojstva dobrog H-donora i slabog H-akceptora pri stvaranju vodikovih veza. Ima malu viskoznost, nisko vrelište i ne apsorbira u vidljivom i u v.-spektru iznad 220 nm. Dielektrična konstanta otapala je 9, a konstante brzine stvaranja ionskih parova leže od 10^3 do 10^4 s⁻¹ za jednostavne elektrolite. U tom otapalu se može upotrebljavati pH-metar sa staklenom elektrodom i kalomelovom referentnom elektrodom. Mjerenja kiselosti s pomoću indikatora djelomično su otežana zbog nastajanja ionskih parova povezanih vodikovim vezama.

Otapalo je korisno za mjerenje relativnih kiselosti jakih kiselina: CH₃SO₂OH i CF₃SO₂OH se dobro razlikuju. Moglo bi dobro služiti za druga fizičko-kemijska mjerenja i u preparativnoj kemiji.

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