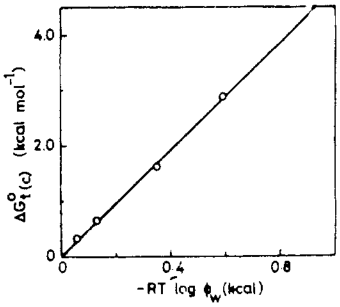

**Figure 3.** Extrapolation of plot of $\Delta G_t{}^\circ{}_c$ against $-RT \log \phi_w$ at 25 °C.

in $\Delta H_t{}^\circ$ around 20 wt % propylene glycol is due to the structure-breaking effect of the acid on the ordered structure in solvent mixtures of low propylene glycol content when the acid is transferred from water to these media. Addition of small amounts of alcohols promotes (*19*) the hydrogen-bonded structure of water and HCl is a better structure breaker in the mixed solvent than in water (*20*).

A plot of the standard molar free energy of transfer, $\Delta G_t{}^\circ{}_c$, against solvent composition in terms of volume fraction of water $\phi_w$ in these solvent mixtures (Figure 3) according to the relation

$$\Delta G_t{}^\circ{}_c = -2.303\, nRT \log \phi_w$$

is linear with $n = 2.0$. This value representing the number of water molecules coordinated to the hydrogen chloride is, however, small compared to the values (*21*) obtained in other media but is almost similar to values reported elsewhere (*22*).

**Registry No.** HCl, 7647-01-0; propylene glycol, 57-55-6; hydronium, 13968-08-6; chloride, 16887-00-6.

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# Solvation Energies and Solvent Transport Numbers of Silver Sulfate in Methanol, Ethanol, and Their Mixtures with Acetonitrile

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**The solvent transport number, Δ, of acetonitrile (AN) and Gibbs solvation energies of $Ag_2SO_4$ in the binary solvent systems methanol + acetonitrile and ethanol + acetonitrile were determined at 30 °C by employing emf and solubility measurements. It was observed that the solubility of the salt increases up to $X_{AN} = 0.4$ in both systems and thereafter decreases with further addition of AN. Further, the Gibbs energy of transfer of silver ion, $\Delta G_t{}^\circ(Ag^+)$, decreases continuously while that of sulfate ion, $\Delta G_t{}^\circ(SO_4{}^{2-})$, increases with the addition of acetonitrile. The solvent transport number, Δ, passes through a maximum at $X_{AN} = 0.55$ and at $X_{AN} = 0.45$ in the case of MeOH-AN and EtOH-AN systems, respectively. These results have been interpreted in terms of a heteroselective solvation of the salt, the silver ion being selectively solvated by acetonitrile and the sulfate ion by the amphiprotic component of the solvent mixtures.**

## Introduction

Selective solvation of ions in mixed solvents profoundly influences solubilities of electrolytes, rates of chemical reactions, redox potentials, etc. (*1*). It also has potential technological value (*1-3*). As part of a program of work dealing with this subject, the selective solvation of silver bromate and iodate in $H_2O$-$Me_2SO$ (*4*), MeOH-$Me_2SO$ (*5*), and $H_2O$-AN (*6*) mixtures was reported earlier. In this paper the solvation behavior of $Ag_2SO_4$ in the binary mixtures of MeOH-AN and EtOH-AN is reported in order to throw light on the ion-solvent interactions in these systems.

## Experimental Section

***Materials.*** Acetonitrile (LR, BDH) was subjected to a preliminary distillation and the middle fraction collected was further purified, after drying over anhydrous potassium carbonate, by a second distillation in the presence of a few added crystals of silver nitrate following the procedure of Jayadevappa (*7*). It had a boiling point of 80 °C (reported (*8*) 80.1 °C) and a density $d^{25} = 0.7766$ g cm$^{-3}$ (reported (*9*) 0.7768 g cm$^{-3}$). Methanol (LR, BDH) was first distilled and dried over heated anydrous sodium sulfate. The second distillation was carried out over magnesium turnings according to the procedure of Kolthoff and Chantooni (*10*) and the middle fraction, "boiling at 64-65 °C", was collected and stored out of contact with air. It had a density $d^{25} = 0.7867$ g cm$^{-3}$ (reported (*11*) bp 64.6 °C and $d^{25}$

= 0.7866). Ethanol was purified by the distillation over magnesium and iodine in accordance with the procedure suggested by Vogel (*12*). Silver sulfate (GR, BDH) dried over $P_2O_5$ under vacuum at 80 °C to constant weight was used. Ferrocene (FoC) (E. Merck, Darmstadt) was purified by sublimation under vacuum and ferricinium picrate (FiC) was prepared according to the method of Kolthoff and Thomas (*13*).

***Methods. Solubility Measurements.*** The various solvent mixtures of the desired composition for solubility measurements were prepared by weight and were accurate to within ±0.02%. Saturated solutions of the salt in the various solvent mixtures were prepared by stirring about 30 mL of the solvent mixture, to which sufficient amount of the salt was added, on a mechanical shaker for over 24 h at room temperature. The mixture was then transferred to a thermostated vessel maintained at 30 ± 0.1 °C and allowed to equilibrate for another 24 h with occasional stirring by means of a magnetic pellet. At the end of this period no detectable change in concentration of the salt was observed and a portion of the mixture was centrifuged. A known weight of the clear supernatant liquid was taken in a beaker at the same temperature and a defined quantity of an excess solution of KI of known strength was added. The excess of KI remaining was back-titrated potentiometrically with a standard solution of silver nitrate by using a Metrohm multidosimat (Type E 415) automatic titrator in conjunction with a Knick pH meter (for recording emf data). The solubility of the salt in the solvent mixtures was calculated from the titration data. All solubility determinations were carried out at least twice and the agreement between them was better than ±1%.

***Determination of $\Delta G_t°(Ag^+)$.*** The Gibbs energy of transfer of silver ion, $\Delta G_t°(Ag^+)$, required for the analysis of the results (as described later) in the various solvent mixtures was determined by emf measurement on cell I using a 0.1 M tetraethylammonium picrate salt bridge in the solvent mixture of the particular composition.

$$\mathrm{Pt}\left|\begin{array}{c}\mathrm{FoC}|\mathrm{FiC^+}(1{:}1)\\ \text{solvent S}\end{array}\right\vdots\begin{array}{c}\mathrm{AgNO_3}\\ \text{solvent S}\end{array}\left|\mathrm{Ag}\right. \qquad (I)$$

The concentrations of ferrocene (FoC) and ferricinium picrate (FiC) were kept constant at 0.005 *m* and the concentration of silver nitrate was varied from 0.002 to 0.008 *m*. The standard potential $E°_s(Ag^+,Ag)$ vs. $FiC^+/FoC$ electrode in various solvent mixtures was obtained by extrapolation of the plot of $E - (2.303RT/F) \log m_{Ag^+}$ against $I$, the ionic strength, to $I = 0$. Such plots were found to be fairly linear in all compositions. The standard error in $E°$'s is about ±1 mV in all the solvent mixtures.

***Determination of Solvent Transference Number, Δ.*** The solvent transference number, Δ, of acetonitrile was determined by employing a galvanic cell with transference of the type

$$\mathrm{Ag}\left|\begin{array}{c}\mathrm{Ag_2SO_4}\text{(saturated)}\\ X'_{\mathrm{AN}} = 1 - X'_{\mathrm{S}}\end{array}\right\vdots\begin{array}{c}\mathrm{Ag_2SO_4}\text{(saturated)}\\ X''_{\mathrm{AN}} = 1 - X''_{\mathrm{S}}\end{array}\left|\mathrm{Ag}\right. \qquad (II)$$

(S = methanol or ethanol)

as suggested by Wagner (*14*) in which the two half-cells contained saturated solutions of silver sulfate in solvent mixtures differing only slightly in solvent composition ($X''_{AN} - X'_{AN} \leq 0.1$). The observed emf of the cell is due to the solvent transport in the two half-cells and can be related to Δ as mentioned subsequently. A U-type cell fitted with ground joints at the top and a G3 frit in the middle to avoid direct contact of the solutions was used in these measurements. The emf measurements associated with the solvent transference and Gibbs energies of transfer of silver ion were performed with a Keithley solid-state electrometer (Model 602) having an input impedence greater than $10^{14}$ Ω.

The dielectric constants, *D*, of ethanol–acetonitrile and methanol–acetonitrile mixtures were measured with a DK meter 60 GK (Franz Küstner Nachf.KG Dresden) at 30 °C by using methanol, ethanol, $Me_2SO$, ethylene glycol, and propylene glycol as standard liquids for calibration. The dielectric constants are accurate to within ±0.2%.

Table I. Solubility, *S*, of $Ag_2SO_4$ and Gibbs Transfer Energies of $Ag_2SO_4$, $Ag^+$, and $SO_4^{2-}$ in MeOH–AN and EtOH–AN Mixtures at 30 °C

| $X_{AN}$[a] | $10^4S$, mol kg$^{-1}$ | $D$[b] | $\Delta G_t°$-($Ag_2SO_4$), kcal mol$^{-1}$ | $\Delta G_t°$-($Ag^+$),[c] kcal mol$^{-1}$ | $\Delta G_t°$-($SO_4^{2-}$), kcal mol$^{-1}$ |
|---|---|---|---|---|---|
| | MeOH–AN System | | | | |
| 0.0 | 0.337 ± 0.003 | 31.8 | 0.0 | 0.00 | 0.00 |
| 0.1 | 3.401 ± 0.004 | 32.3 | −3.88 ± 0.02 | −3.10 | 2.32 |
| 0.2 | 6.815 ± 0.015 | 32.6 | −4.98 ± 0.02 | −4.18 | 3.38 |
| 0.3 | 9.660 ± 0.010 | 33.0 | −5.53 ± 0.02 | −4.70 | 3.87 |
| 0.4 | 10.475 ± 0.005 | 33.3 | −5.66 ± 0.02 | −4.94 | 4.22 |
| 0.5 | 8.990 ± 0.010 | 33.7 | −5.44 ± 0.02 | −5.30 | 5.16 |
| 0.6 | 7.130 ± 0.075 | 34.0 | −5.09 ± 0.04 | −5.65 | 6.21 |
| 0.7 | 4.525 ± 0.045 | 34.3 | −4.38 ± 0.03 | −5.90 | 7.42 |
| 0.8 | 2.575 ± 0.035 | 34.8 | −3.47 ± 0.04 | −6.04 | 8.61 |
| 0.9 | 1.345 ± 0.015 | 35.0 | −2.40 ± 0.04 | −6.30 | 10.20 |
| 1.0 | 0.621 ± 0.003 | 35.5 | −1.09 ± 0.03 | −6.79 | 12.49 |
| | EtOH–AN System | | | | |
| 0.0 | 0.450 ± 0.005 | 23.9 | 0.00 | 0.00 | 0.00 |
| 0.1 | 1.045 ± 0.015 | 25.1 | −1.42 ± 0.05 | −2.57 | 3.72 |
| 0.2 | 1.420 ± 0.020 | 26.2 | −1.94 ± 0.04 | −3.60 | 5.26 |
| 0.3 | 1.650 ± 0.010 | 27.4 | −2.19 ± 0.05 | −4.18 | 6.17 |
| 0.4 | 1.960 ± 0.010 | 28.6 | −2.51 ± 0.03 | −4.55 | 6.59 |
| 0.5 | 1.550 ± 0.010 | 29.6 | −2.15 ± 0.03 | −4.82 | 7.49 |
| 0.6 | 1.375 ± 0.005 | 30.9 | −1.98 ± 0.03 | −5.03 | 8.08 |
| 0.7 | 1.250 ± 0.011 | 32.1 | −1.84 ± 0.04 | −5.26 | 8.68 |
| 0.8 | 1.070 ± 0.001 | 33.3 | −1.59 ± 0.02 | −5.50 | 9.41 |
| 0.9 | 0.874 ± 0.008 | 34.5 | −1.26 ± 0.04 | −5.88 | 10.50 |
| 1.0 | 0.621 ± 0.003 | 35.5 | −0.68 ± 0.03 | −6.19 | 11.70 |

[a] Mole fraction of acetonitrile. [b] Dielectric constant. [c] Accurate to ±0.05 kcal mol$^{-1}$.

## Results and Discussion

Utilizing the solubility data, obtained as described earlier, we calculated the solubility product, $K_{sp}$, of the salt from

$$K_{sp} = 4S^3\gamma_\pm^3 \qquad (1)$$

in the two solvent mixtures. The mean molal activity coefficient $\gamma_\pm$ of the salt required for this purpose was calculated from the extended Debye–Hückel limiting relation with $a$ = 6.5 Å using the dielectric constant data of the solvent mixtures measured earlier. The Gibbs transfer energies of silver ion (on the basis of ferrocene reference method) from methanol and ethanol (reference solvents) to their corresponding mixtures with acetonitrile were calculated from

$$\Delta G_t°(Ag^+) = F(E°_{Ag^+,S} - E°_{Ag^+,S_{ref}}) \qquad (2)$$

where the $E°$'s refer to the standard potentials of the silver, silver ion system against the FoC, $FiC^+$ reference electrode. The Gibbs energies of transfer of silver sulfate, $\Delta G_t°(Ag_2SO_4)$, in the various mixtures were obtained from

$$\Delta G_t°(Ag_2SO_4) = -RT \ln\,[K_{sp}(S)/K_{sp}(\text{MeOH or EtOH})] \qquad (3)$$

The dielectric constants of the solvent mixtures, the solubility, the Gibbs transfer energy of the salt, and the transfer energy of silver ion together with the uncertainties in these values in both methanol–acetonitrile and ethanol–acetonitrile mixtures are recorded in Table I. The Gibbs transfer energies of the sulfate ion, $\Delta G_t°(SO_4^{2-})$, calculated from

$$\Delta G_t°(Ag_2SO_4) = 2\Delta G_t°(Ag^+) + \Delta G_t°(SO_4^{2-}) \qquad (4)$$

in the two mixed solvent systems are also included in Table I.

The solubility of $Ag_2SO_4$ increases (Table I) in both mixed solvent systems up to $X_{AN}$ = 0.4 and then decreases with

Table II. Emf's of Cell II and the Solvent Transport Number, Δ, of AN in $Ag_2SO_4$-MeOH-AN and $Ag_2SO_4$-EtOH-AN Systems at 30 °C

| | MeOH-AN system | | | EtOH-AN system | | |
|---|---|---|---|---|---|---|
| $X_{AN}$ | $-E$, mV | $\partial \ln f_{AN} / \partial \ln X_{AN}$ | Δ | $-E$, mV | $\partial \ln f_{AN} / \partial \ln X_{AN}$[a] | Δ |
| 0.05 | 78 ± 1.0 | −0.110 | 1.60 ± 0.03 | 61 ± 1.0 | −0.216 | 1.42 ± 0.02 |
| 0.15 | 22 ± 1.0 | −0.246 | 1.43 ± 0.07 | 28 ± 1.0 | −0.359 | 2.14 ± 0.08 |
| 0.25 | 21 ± 1.0 | −0.367 | 2.39 ± 0.12 | 16 ± 0.5 | −0.532 | 2.46 ± 0.08 |
| 0.35 | 17 ± 1.0 | −0.486 | 2.88 ± 0.17 | 14 ± 0.5 | −0.604 | 3.08 ± 0.11 |
| 0.45 | 18 ± 1.0 | −0.625 | 4.55 ± 0.25 | 13 ± 1.0 | −0.646 | 3.48 ± 0.27 |
| 0.55 | 17 ± 1.0 | −0.770 | 7.01 ± 0.41 | 11 ± 1.0 | −0.650 | 2.98 ± 0.27 |
| 0.65 | 13 ± 1.0 | −0.792 | 5.45 ± 0.42 | 9 ± 0.5 | −0.525 | 1.65 ± 0.09 |
| 0.75 | 15 ± 1.0 | −0.600 | 2.69 ± 0.18 | 8 ± 1.0 | −0.455 | 1.06 ± 0.13 |
| 0.85 | 16 ± 1.0 | −0.430 | 1.38 ± 0.09 | 9 ± 0.5 | −0.273 | 0.61 ± 0.04 |
| 0.95 | 2 ± 1.0 | −0.260 | 0.05 ± 0.03 | 15 ± 0.5 | −0.125 | 0.31 ± 0.01 |

[a] Mean values were taken from values at 40 (*15*) and 20 (*16*) °C.

further addition of acetonitrile. Thus, $\Delta G_t^\circ(Ag_2SO_4)$ decreases up to $X_{AN} = 0.4$ and thereafter increases. The $\Delta G_t^\circ(Ag^+)$ is negative and continuously decreases with the addition of acetonitrile, indicating that its transfer from the amphiprotic solvent to its mixtures with acetonitrile is favored and hence that it is preferentially solvated by acetonitrile. This can be accounted for on the basis of the specific back-bonding interactions of this cation with the $\pi^*$ orbitals of the nitrile group as pointed out by Parker et al. (*3*). The $\Delta G_t^\circ(SO_4^{2-})$ is positve and increases continuously with the addition of acetonitrile, suggesting that it is preferentially solvated by the amphiprotic component (methanol or ethanol) in these solvent mixtures. A heteroselective solvation of the salt is therefore inferred in these mixed solvent systems.

The solvent transference number, Δ, is defined as the change in the number of moles of a solvent component in the cathode compartment, with the mean molar velocity of the solvent mixture as reference, when 1 faraday of electricity is passed through the cell during electrolysis. The sign and magnitude of Δ provide new ways of obtaining at least qualitative informtion about the composition of ionic solvation shells in mixed solvents.

The Δ of acetonitrile in these mixtures was calculated from the emf data on cell II by using the expression

$$E = -\frac{RT}{F}\left(\frac{X''_{AN} - X'_{AN}}{X_{AN}(1 - X_{AN})}\right)\Delta\left(1 + \frac{\partial \ln f_{AN}}{\partial \ln X_{AN}}\right) \qquad (5)$$

where $X'_{AN}$ and $X''_{AN}$ are the mole fractions of acetonitrile in the two half-cells and $X_{AN} = (X'_{AN} + X''_{AN})/2$. The activity coefficient term in eq 5 accounts for the deviation of the solvent mixtures from ideal behavior and was calculated from the vapor pressure data of ethanol–acetonitrile (*15*, *16*) and methanol–acetonitrile (*17*) mixtures taken from the literature. The measured emf's of cell II, which are accurate to ±1 mV, and the values of the activity coefficient term in eq 5 are recorded in Table II. The significant deviation in emf values, especially at higher compositions of AN, i.e., around $X_{AN} = 0.95$ from the trends noted at lower mole fractions of AN, is presumably due to the effect of the activity coefficient term in eq 5 and also the term $X_{AN}(1 - X_{AN})$ which changes considerably by small changes of $X_{AN}$. The calculated Δ values together with the experimental errors in the data are also given in Table II. The Δ values of acetonitrile are positive throughout and pass through a maximum at $X_{AN} = 0.55$, where $\Delta = 7.0$, in the case of methanol–acetonitrile mixtures and at $X_{AN} = 0.45$, where $\Delta = 3.5$, in the case of ethanol–acetonitrile mixtures. Thus, an increase of 7.0 and 3.5 mol of AN occurs in the case of methanol–acetonitrile and ethanol–acetonitrile mixtures, respectively, per faraday, relative to the mean molar velocity of the solvent mixture as reference (*18*) in the cathode compartment when solutions of the salt are electrolyzed at the given composition of the solvent mixtures. The large positive values of Δ in both systems confirm the heteroselective solvation of $Ag_2SO_4$ in these mixtures as inferred from the transfer energy data earlier. The transport of acetonitrile into the cathode compartment occurs largely through the silver ion while the transport of the amphiprotic component in the opposite direction arises due to the sulfate ion. These two effects add together and thus a heteroselective solvation is characterized by large values of Δ.

**Registry No.** $Ag_2SO_4$, 10294-26-5; AN, 75-05-8; MeOH, 67-56-1; EtOH, 64-17-5; Ag, 7440-22-4; $SO_4^{2-}$, 14808-79-8.

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