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Solvation Energies and Solvent Transport Numbers of Silver(I) Sulfate and Silver(I) Acetate in Acetonitrile, Dimethyl Sulfoxide, and Their Mixtures with Dioxane

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The selective solvation behavior of silver(I) sulfate and silver(I) acetate has been studied in the binary solvent mixtures dioxane + acetonitrile (AN) and dioxane + dimethyl sulfoxide (Me_2SO) at 30 °C by solubility and emf measurements. The solubility of both salts increases continuously with the addition of AN or Me_2SO and these data were used to calculate the Gibbs transfer energies of the salts from dioxane to its mixures with AN and Me_2SO. The transfer energies of the salts were split into their ionic contributions by using the transfer energies of the silver ion in these mixtures determined on the basis of negligible liquid junction potential (nLJP) method. The solvent transport numbers Δ of AN and Me_2SO have been determined by emf measurements using a galvanic cell with transference. The results have been interpreted in terms of a heteroselective solvation of the salts with the silver ion being selectively solvated by AN or Me_2SO and the anions by dioxane.

Introduction

The importance of selective solvation of ions in binary mixed solvents from a fundamental as well as technological aspect is well recognized (*1*–*5*).

In earlier communications from this laboratory, the preferential solvation of some silver halates in the binary protic–dipolar aprotic solvent mixtures of water + Me_2SO (*6*), methanol + Me_2SO (*7*), and water + AN (*8*) has been reported. The present work deals with the selective solvation behavior of silver(I) sulfate and silver(I) acetate in the mixed solvent systems, viz., dioxane + AN and dioxane + Me_2SO in order to elucidate the nature of ion–solvent interactions in these mixtures and further to understand the effect of replacement of the protic component by an aprotic component, viz., dioxane on ion solvation.

Experimental Section

Materials. Dioxane (GR, Merck) was purified following the procedure of Vogel (*9*). It was first kept over fresh KOH pellets for 24 h, decanted, and further refluxed over metallic sodium for 6–12 h until the reaction ceases and the sodium remains bright. A final distillation followed and the middle fraction boiling at 101.5 °C/760 mm was collected and stored over pressed sodium wire. Acetonitrile (LR, BDH) was purified as described earlier (*10*). Me_2SO (LR, Merck) was purified according to the method of Maricle and Hodgson (*11*). Silver sulfate (E. Merck) and silver acetate (E. Merck) were dried over P_2O_5 under vacuum before use. Silver nitrate (AR, BDH) was used without further purification. Silver perchlorate was prepared (*12*) by treating stoichiometric amounts of silver oxide with perchloric acid (70% w/w) and slowly evaporating the solution to crystallization. The resulting product of silver perchlorate was recrystallized thrice from conductivity water and the final sample was thoroughly dried under vacuum at 110 °C (*13*). The purity of the above salts was checked by estimation of the silver content by potentiometry. Tetraethylammonium picrate (TEAP) was prepared as suggested by Rodehüser and Schneider (*14*). Silver electrodes for emf measurements were freshly prepared following the procedure of Carmody (*15*). A Keithley solid-state electrometer (Model 602) having an input impedance greater than 10^{14} Ω was used in all emf measurements. All measurements were carried out at 30 ± 0.05 °C.

Methods. Solubility Measurements. The solubilities of the salts in various solvent mixtures were determined as described earlier (*16*).

Determination of $\Delta G_t°(Ag^+)$. The Gibbs transfer energies of silver ion, $\Delta G_t°(Ag^+)$, from the reference solvent dioxane to the solvent mixtures dioxane + AN and dioxane + Me_2SO were determined by the negligible liquid junction potential (nLJP) method of Parker et al. (*17*) by using cell A, where R is the

$$\underset{\text{AN}}{\mathrm{Ag}|\mathrm{AgClO_4}(0.01\ m)}\|\underset{\text{AN}}{\mathrm{Et_4NPiC}(0.1\ m)}\|\underset{\text{R or S}}{\mathrm{AgClO_4}(0.01\ m)}|\mathrm{Ag} \qquad \text{(A)}$$

reference solvent and S is the solvent mixture. Since the solubility of $AgClO_4$ in pure dioxane is extremely low and hence could not be determined, the reference solvent in the present work has been chosen as the solvent mixture containing dioxane + 0.05 mole fraction of AN or Me_2SO as necessary.

***Determination of Solvent Transport Number*, Δ.** A galvanic cell with transference (cell B, where MX = Ag_2SO_4 or CH_3COOAg and A = AN or Me_2SO) suggested by Wagner (*18*) in

$$\mathrm{Ag}\left|\begin{array}{l:l} \mathrm{MX(satd)} & \mathrm{MX(satd)} \\ X_A' = 1 - X_{\text{dioxane}}' & X_A'' = 1 - X_{\text{dioxane}}'' \end{array}\right|\mathrm{Ag} \qquad \text{(B)}$$

which the two half-cells contained saturated solutions of silver sulfate or silver acetate in solvent mixtures differing only slightly in solvent compositions ($X_A'' - X_A' = 0.1$, maintained throughout) was used for the determination of the solvent transport number, Δ, of AN or Me_2SO in these systems. A U-type cell fitted with ground joints at the top and a G_3 frit in the middle to reduce interdiffusion of the electrolyte was used in these measurements.

Dielectric Constant Measurements. The dielectric constants, *D*, of the various solvent mixtures were determined with a DK meter 60GK (Franz Kustner Nachf. KG Dresden) at 30 °C. The *D* values are accurate to within ±0.2%.

Results and Discussion

The solubilities of Ag_2SO_4 and CH_3COOAg are related to the respective thermodynamic solubility products by

$$K_{SP}(Ag_2SO_4) = 4S^3\gamma_\pm^3 \qquad (1)$$

$$K_{SP}(CH_3COOAg) = S^2\gamma_\pm^2 \qquad (2)$$

where $\gamma_\pm$ is the mean molal activity coefficient of the electrolyte under consideration and it was calculated from the extended Debye–Hückel equation with a = 6.5 Å for silver sulfate and a = 7.0 Å for silver acetate (*19*).

The transfer energies of the salts from the reference solvent R to the solvent mixture S have been calculated by using the expression

$$\Delta G_t°(\text{salt}) = -RT \ln K_{SP(S)}/K_{SP(R)} \qquad (3)$$

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Table I. Solubilities (S) and Solubility Products (K_{SP}) of Ag_2SO_4 and CH_3COOAg in Dioxane + Acetonitrile (AN) Mixtures at 30 °C (Molal Scale)

mole fract of AN (X_{AN})	dielec const (D)	Ag_2SO_4		CH_3COOAg	
		$10^4S^a/(mol\ kg^{-1})$	K_{SP}	$10^4S^a/(mol\ kg^{-1})$	K_{SP}
0.0	2.1	0.115	1.16×10^{-18}	0.560	9.05×10^{-11}
0.05	2.9	0.160	3.24×10^{-17}	0.650	3.94×10^{-10}
0.1	4.2	0.201	5.81×10^{-16}	0.852	1.51×10^{-9}
0.2	6.6	0.355	1.20×10^{-14}	2.54	1.71×10^{-8}
0.3	8.7	0.423	4.28×10^{-14}	3.35	4.09×10^{-8}
0.4	11.4	0.522	1.33×10^{-13}	5.13	1.15×10^{-7}
0.5	14.2	0.608	2.91×10^{-13}	6.19	1.99×10^{-7}
0.6	16.2	0.628	3.85×10^{-13}	7.11	2.85×10^{-7}
0.7	18.5	0.878	1.09×10^{-12}	8.05	3.92×10^{-7}
0.8	21.1	1.01	1.85×10^{-12}	9.03	5.24×10^{-7}
0.9	23.6	1.29	4.01×10^{-12}	10.24	7.08×10^{-7}
1.0	34.1	1.81	3.35×10^{-11}	15.22	1.76×10^{-6}

[a] Values accurate to within ±0.5%.

Table II. Solubilities (S) and Solubility Products (K_{SP}) of Ag_2SO_4 and CH_3COOAg in Dioxane + Me_2SO Mixtures at 30 °C (Molal Scale)

mole fract of Me_2SO (X_{Me_2SO})	dielec const (D)	Ag_2SO_4		CH_3COOAg	
		$10^4S^a/(mol\ kg^{-1})$	K_{SP}	$10^4S^a/(mol\ kg^{-1})$	K_{SP}
0.0	2.1	0.115	1.16×10^{-18}	0.056	9.05×10^{-11}
0.05	4.0	0.301	5.96×10^{-16}	0.100	1.64×10^{-9}
0.1	6.1	0.569	1.70×10^{-14}	0.197	1.03×10^{-8}
0.2	9.4	0.720	1.60×10^{-13}	0.406	6.17×10^{-8}
0.3	12.7	1.07	8.71×10^{-13}	0.705	2.21×10^{-7}
0.4	16.8	1.51	3.59×10^{-12}	1.37	9.10×10^{-7}
0.5	21.2	1.63	6.42×10^{-12}	2.28	2.73×10^{-6}
0.6	25.4	1.73	9.46×10^{-12}	3.56	6.96×10^{-6}
0.7	29.8	1.82	1.28×10^{-11}	5.15	1.52×10^{-5}
0.8	35.4	1.91	1.68×10^{-11}	7.44	3.34×10^{-5}
0.9	40.8	2.29	3.08×10^{-11}	9.95	6.23×10^{-5}
1.0	46.8	4.84	2.71×10^{-10}	13.27	1.15×10^{-4}

[a] Values accurate to within ±0.5%.

Table III. Gibbs Transfer Energies of Ag_2SO_4 and CH_3COOAg and of the Ions Ag^+, SO_4^{2-}, and CH_3COO^- in Dioxane + AN Mixtures at 30 °C (Molal Scale)[a]

mole fraction of AN (X_{AN})	$\Delta G_t°(Ag_2SO_4)$/ (kJ mol^{-1})	$\Delta G_t°(CH_3COOAg)$/ (kJ mol^{-1})	$\Delta G_t°(Ag^+)^b$/ (kJ mol^{-1})	$\Delta G_t°(SO_4^{2-})$/ (kJ mol^{-1})	$\Delta G_t°(CH_3COO^-)$/ (kJ mol^{-1})
0.05	0.0	0.0	0.0	0.0	0.0
0.1	-7.3	-3.4	-10.9	14.5	7.5
0.2	-14.9	-9.5	-21.2	27.5	11.7
0.3	-18.1	-11.7	-26.2	34.3	14.5
0.4	-21.0	-14.3	-29.7	38.4	15.4
0.5	-22.9	-15.7	-33.0	43.1	17.3
0.6	-23.6	-16.6	-34.6	45.6	18.0
0.7	-26.3	-17.4	-37.1	47.9	19.7
0.8	-27.6	-18.1	-38.9	50.2	20.8
0.9	-29.6	-18.9	-41.1	52.6	22.2
1.0	-34.9	-21.2	-43.5	52.1	22.3

[a] Reference solvent: dioxane containing 0.05 mole fraction of AN. [b] Values accurate to within ±0.2 kJ mol^{-1}.

(R = dioxane containing 0.05 mole fraction of AN or Me_2SO).

The transfer energies of silver ion, $\Delta G_t°(Ag^+)$, from reference solvent R (dioxane containing 0.05 mole fraction of AN or Me_2SO) to the solvent mixtures S were calculated from the relation

$$\Delta G_t°(Ag^+) = F(E_S - E_R) - RT \ln a_{Ag^+(S)}/a_{Ag^+(R)} \quad (4)$$

where E_S and E_R represent the emf's of the cell A in the solvent mixture S and the reference solvent R, respectively, and a refers to the activity.

The transfer energies of sulfate and acetate ions were calculated from

$$\Delta G_t°(Ag_2SO_4) = 2\Delta G_t°(Ag^+) + \Delta G_t°(SO_4^{2-}) \quad (5)$$

$$\Delta G_t°(CH_3COOAg) = \Delta G_t°(Ag^+) + \Delta G_t°(CH_3COO^-) \quad (6)$$

The solubilities (S), solubility products (K_{SP}) of Ag_2SO_4 and CH_3COOAg in dioxane + AN and dioxane + Me_2SO, and the dielectric constant values (D) of the above solvent mixtures at 30 °C are given in Tables I and II, respectively. The transfer energies of the salts and of the ions Ag^+, SO_4^{2-}, and CH_3COO^- in dioxane + AN and dioxane + Me_2SO mixtures are given in Tables III and IV, respectively. It may be mentioned that the solubility products and transfer energies of salts given in the tables have not been corrected for ion association in view of the uncertainties associated with such corrections. It is observed (Tables I and II) that the solubilities of silver sulfate and silver acetate increase continuously with the addition of the dipolar aprotic component (AN or Me_2SO) in both the mixed solvent systems. Thus, the transfer energy of the salts decreases continuously (Tables III and IV) with the addition of AN or Me_2SO, indicating that their transfer from dioxane containing 0.05 mole fraction of AN or Me_2SO to dioxane + AN or dioxane + Me_2SO mixtures is favored. The continuous decrease of $\Delta G_t°(Ag^+)$ in both the systems with the addition of AN or Me_2SO suggests that Ag^+ ion is preferentially solvated

Table IV. Gibbs Transfer Energies of Ag_2SO_4 and CH_3COOAg and of the Ions Ag^+, SO_4^{2-}, and CH_3COO^- in Dioxane + Me_2SO Mixtures at 30 °C (Molal Scale)[a]

mole fraction of Me_2SO (X_{Me_2SO})	$\Delta G_t°(Ag_2SO_4)$/ (kJ mol^{-1})	$\Delta G_t°(CH_3COOAg)$/ (kJ mol^{-1})	$\Delta G_t°(Ag^+)^b$/ (kJ mol^{-1})	$\Delta G_t°(SO_4^{2-})$/ (kJ mol^{-1})	$\Delta G_t°(CH_3COO^-)$/ (kJ mol^{-1})
0.05	0.0	0.0	0.0	0.0	0.0
0.1	-8.4	-4.6	-10.9	13.4	6.3
0.2	-14.1	-9.1	-21.6	29.1	12.5
0.3	-18.4	-12.4	-27.3	36.2	14.9
0.4	-21.9	-15.9	-31.8	41.7	15.9
0.5	-23.4	-18.7	-35.6	47.8	16.9
0.6	-24.4	-21.1	-37.5	50.6	16.4
0.7	-25.1	-23.0	-39.2	53.3	16.2
0.8	-25.8	-25.0	-40.8	55.8	15.8
0.9	-27.4	-26.6	-42.3	57.2	15.7
1.0	-32.8	-28.1	-43.3	53.8	15.2

[a] Reference solvent: dioxane containing 0.05 mole fraction of Me_2SO. [b] Values accurate to within ±0.2 kJ mol^{-1}.

Table V. Emf's of Cell B and the Solvent Transport Number, Δ, of Acetonitrile for Ag_2SO_4 and CH_3COOAg in Dioxane + AN Mixtures at 30 °C

mole fraction of AN (X_{AN})	$-\mathrm{d}\ln f_{AN}/\mathrm{d}\ln X_{AN}$	Ag_2SO_4		CH_3COOAg	
		$-E$, mV	Δ	$-E$, mV	Δ
0.05	0.003				
0.15	0.085	14.0 ± 0.5	0.75 ± 0.03	1.0 ± 0.2	0.05 ± 0.01
0.25	0.176	14.5 ± 0.5	1.26 ± 0.05	4.8 ± 0.5	0.42 ± 0.05
0.35	0.169	20.5 ± 1.0	2.15 ± 0.11	15.0 ± 0.5	1.57 ± 0.06
0.45	0.200	22.0 ± 0.5	2.61 ± 0.06	23.5 ± 1.0	2.79 ± 0.12
0.55	0.210	25.0 ± 1.0	3.00 ± 0.12	31.0 ± 1.0	3.72 ± 0.12
0.65	0.192	24.0 ± 1.0	2.59 ± 0.11	29.5 ± 1.0	3.18 ± 0.11
0.75	0.142	22.5 ± 0.5	1.88 ± 0.05	24.0 ± 1.0	2.01 ± 0.08
0.85	0.082	20.0 ± 0.5	1.06 ± 0.03	15.5 ± 0.5	0.82 ± 0.03
0.95	0.040	17.0 ± 1.0	0.32 ± 0.02	4.6 ± 0.5	0.09 ± 0.01

Table VI. Emf's of Cell B and the Solvent Transport Number, Δ, of Dimethyl Sulfoxide for Ag_2SO_4 and CH_3COOAg in Dioxane + Me_2SO Mixtures at 30 °C

mole fraction of Me_2SO (X_{Me_2SO})	$-\mathrm{d}\ln f_{Me_2SO}/\mathrm{d}\ln X_{Me_2SO}$	Ag_2SO_4		CH_3COOAg	
		$-E$, mV	Δ	$-E$, mV	Δ
0.05	0.226				
0.15	0.319	7.0 ± 0.5	0.50 ± 0.04	5.5 ± 0.5	0.39 ± 0.04
0.25	0.370	14.5 ± 0.5	1.65 ± 0.06	11.0 ± 0.5	1.25 ± 0.06
0.35	0.436	29.5 ± 1.0	4.56 ± 0.16	15.5 ± 1.0	2.40 ± 0.16
0.45	0.600	24.5 ± 1.0	5.81 ± 0.24	21.5 ± 1.0	5.10 ± 0.24
0.55	0.253	25.5 ± 1.0	3.24 ± 0.13	29.0 ± 1.0	3.68 ± 0.13
0.65	0.122	20.5 ± 1.0	2.04 ± 0.10	13.5 ± 0.5	1.34 ± 0.05
0.75	0.055	20.0 ± 1.0	1.52 ± 0.08	4.8 ± 0.5	0.36 ± 0.04
0.85	0.032	17.5 ± 1.0	0.88 ± 0.05	4.0 ± 0.5	0.20 ± 0.03
0.95	0.017	9.5 ± 0.5	0.18 ± 0.01	3.5 ± 0.2	0.06 ± 0.01

by AN or Me_2SO in these mixtures. The preferential solvation of Ag^+ by AN or Me_2SO can be explained on the basis of the specific back-bonding interactions of the d^{10} cation with the π^* orbitals of nitrile and sulfoxide group as pointed out by Parker et al (*4*). The transfer energies of the sulfate and acetate ions are seen to be positive and increase continuously with the addition of AN or Me_2SO and suggest that both the sulfate and acetate ions are selectively solvated by dioxane. Although the reference solvent is dioxane containing 0.05 mole fraction of AN or Me_2SO, the conclusions on the selective solvation of ions will be expected to be same even if dioxane is taken as the reference solvent. The selective solvation of the anions by dioxane presumably occurs due to the acidic nature of hydrogen atoms of the $-CH_2$ group adjacent to the ether oxygen linkage, for which there is some evidence (*20*) in the literature. Further, the poor anion solvating capacity of Me_2SO and AN contributes significantly to the observed positive $\Delta G_t°$ values in these mixtures. The large $\Delta G_t°$ values of sulfate ion compared to that of acetate ion reflect the stronger ion–solvent interactions of this doubly charged ion with dioxane than those of the singly charged acetate ion. Thus the transfer of anions from dioxane to its mixtures with AN or Me_2SO is disfavored with increasing mole fraction of the dipolar aprotic component. The heteroselective solvation of the salts is therefore inferred in these mixed solvent systems.

The solvent transport number, Δ, of AN or Me_2SO in these solvent mixtures has been calculated from the emf data of the cell B by using the expression

$$E = -\frac{RT}{F}\left(\frac{X_A'' - X_A'}{X_A(1 - X_A)}\right)\Delta\left(1 + \frac{\mathrm{d}\ln f_A}{\mathrm{d}\ln X_A}\right) \qquad (7)$$

where A = AN or Me_2SO, X_A' and X_A'' are mole fractions of AN or Me_2SO in the two half-cells, and $X_A = (X_A' + X_A'')/2$. The activity coefficient term in eq 7 which accounts for the deviation of the solvent mixtures from ideal behavior was calculated from the vapor pressure data of dioxane + AN (*21*) and dioxane + Me_2SO (*22*) mixtures taken from the literature. The emf's of the cell B, the activity coefficient terms, and the calculated Δ values for silver sulfate and silver acetate in both the mixed solvent systems are recorded in Tables V and VI.

The solvent transport number Δ represents the enrichment of one solvent component in the cathode compartment with the mean molar velocity of the solvent mixture as reference when one faraday of electricity is passed through the cell during a Hittorf experiment. Table V shows that the Δ of acetonitrile for silver sulfate and silver acetate in dioxane + AN mixtures is positive and passes through a maximum at X_{AN} = 0.55 with Δ_{max} = 3.0 for silver sulfate and Δ_{max} = 3.7 for silver acetate. In the case of the dioxane + Me_2SO system, the Δ of Me_2SO

for silver sulfate and silver acetate (Table VI) is positive and passes through a maximum at $X_{Me_2SO} = 0.45$ with $\Delta_{max} = 5.8$ and 5.1, respectively. Thus an increase of 3.0 and 3.7 moles of AN occurs in the case of dioxane + AN mixtures for silver sulfate and silver acetate and an increase of 5.8 and 5.1 moles of Me_2SO occurs in the case of dioxane + Me_2SO for silver sulfate and silver acetate, respectively, per faraday, relative to the mean molar velocity of the solvent mixtures as reference (*23*) in the cathode compartment when the solutions of these salts are electrolyzed at the given composition of the solvent mixtures. The enrichment of AN or Me_2SO in the cathode compartment arises largely through their transport by the silver ion while the anion transports dioxane in the opposite direction, i.e., toward the anode. These two effects add together and thus a heteroselective solvation results in large Δ values. These results support the conclusions based on the transfer energy variation of the ions observed earlier.

Registry No. AN, 75-05-8; Ag_2SO_4, 10294-26-5; CH_3COOAg, 563-63-3; Me_2SO, 67-68-5; SO_4^{2-}, 14808-79-8; CH_3COO^-, 71-50-1; Ag, 7440-22-4; dioxane, 123-91-1.

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Henry's Constants for Phenol over Its Diluted Aqueous Solution

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Henry's constants for phenol over its aqueous solution were measured in the temperature range from -2 to 27 °C. An equation was proposed to correlate these data and those estimated from the literature data at 44-90 °C.

In connection with our study if stripping of phenol from a diluted aqueous phenol solution into air at ambient temperatures, we noticed that little information is available on Henry's constant for phenol at temperatures below about 40 °C. Therefore, we carried out measurements of Henry's constants for phenol in the phenol-water-air system at ambient temperatures.

Judging from the data reported in ref *1-3*, the equilibrium relation is represented by Henry's law when liquid-phase phenol concentrations are less than about 0.1 mol % (about 5200 ppm). At atmospheric pressure, phenol forms an azeotrope with water when the phenol concentration is 1.9 mol % (*1*). This explains the success of Henry's law in this very low concentration range.

Experimental Section

A simple apparatus consisting of four bubbling flasks connected in series was found good enough to produce an equilibrium gas. Each 300-mL flask had about 250 mL of phenol solution in it, and a glass tube with a nozzle at the lower end extended through the solution to the bottom of the flask. Nitrogen gas of a stated purity of 99.999% was introduced at a rate of about 0.3 mL/s onto the bottom of the first flask through the glass tube. Fine nitrogen gas bubbles rose from the nozzle in the solution and the effluent gas went to the bottom of the second flask and so on. Stripping of phenol took place while the bubbles rose in the solutions. The apparatus consisting of the bubbling flasks was placed in a constant temperature chamber.

The aqueous phenol solutions were prepared by dissolving the proper amount of reagent grade phenol (Kanto Chemicals Co., Tokyo) with a stated purity of 99+% in a known amount of deionized water. Phenol concentrations were measured in a Model GC-7A (Shimdadzu Co., Kyoto) gas chromatograph equipped with an FID detector and a 2-m-long column packed with Unisole F-200 50/60 mesh (Nihon Gaschro Co., Tokyo). Liquid analysis was done by withdrawing 5 μL liquid sample by a 10-μL PS (Precision Sampling Corp., LA) syringe and then injecting it into the gas chromatograph. For gas analysis a 5-mL PS syringe was employed to withdraw 2 mL of gas leaving from the fourth flask. The samples were withdrawn slowly and carefully at a rate less than that of nitrogen gas introduced into the first flask. This was done by putting a glass tube for exit gas from the fourth flask into a beaker of water and watching bubble formation at the tube end. The gas was then immediately injected into the gas chromatograph. The operating conditions of the chromatograph were as follows: injection and

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