CROATICA CHEMICA ACTA CCACAA **69** (4) 1537–1544 (1996)

ISSN-0011-1643
CCA–2394

Original Scientific Paper

Solvation of Ions. V. Silver(I) Ion in Water-Dimethyl Sulfoxide Mixtures

Warren L. Reynolds[a,*] *and Steven Davis*[b]

[a]*Department of Chemistry, 207 Pleasant Street SE, University of Minnesota, Minneapolis, MN 55455-0431, USA*

[b]*Department of Applied Mathematics, Cornell University, Ithaca, NY 14853, USA*

Received April 24, 1996; revised July 18, 1996; accepted August 19, 1996

The Gibbs' free energies of transfer of silver(I) ion, $\Delta_t G°$ (Ag^+), from water to water-dimethyl sulfoxide (W/D) binary mixtures have been used to obtain the distribution of solvated ions, $[AgW_jD_k]^+$, present over the mole fraction range from 0.05 to 0.95 for dimethyl sulfoxide. Major species were $[AgW_3D]^+$, $[AgW_{16}D]^+$, $[AgW_3D_2]^+$, $[AgWD_3]^+$, $[AgD_6]^+$, $[AgWD_9]^+$, $[AgD_{14}]^+$. The water-rich solvated ions were present only at small dimethyl sulfoxide concentrations.

INTRODUCTION

Metal ion-solvent molecule interactions are being studied using nuclear magnetic resonance (NMR) methods, molecular dynamic (MD) and Monte Carlo (MC) computer simulations and measurements of Gibbs' free energies of transfer $\Delta_t G°$ from a reference solvent. NMR methods have been successful in mixed solvents but have been used mostly for the first (or innermost) solvation shell.[1,2] Solvent in the solvation shells outside of the first is too labile to produce useful results concerning numbers of solvent molecules located there.

The MD and MC computer simulations have been very successful in obtaining solvent molecule orientation near the ion, solvation numbers and time-dependence of physical processes involving the ion dissolved in a single solvent.[3,4,5] For solvent mixtures the mathematical treatments for the latter

* Author to whom correspondence should be addressed.

two methods quickly become very complicated because of the many parameters involved.

The $\Delta_t G°$ method is restricted to solvent mixtures and yields only solvation numbers, not other structural or rate information, because it measures the change of Gibbs' free energy in an equilibrium process. Although very limited in nature, the $\Delta_t G°$ method can provide some very interesting results on the composition of the main solvated ionic species in a solvent mixture. Previous accounts of this method[6,7,8] have described the mathematical methods used in detail and the results obtained in water (W)-dimethyl sulfoxide (D) mixtures for K^+, $[Co(NH_3)_5Cl]^{2+}$, Cl^-, Br^-, I^-. Some results were particularly interesting. Those for $[Co(NH_3)_5Cl]^{2+}$ (Ref. 7) showed a unique dimethyl sulfoxide molecule in the solvent cage because there was a $[Co(NH_3)_5Cl]^{2+}$. W_0D_1 species present in all solvent mixtures from 0.05 to 0.95 for the bulk mole fraction of dimethyl sulfoxide. Langford *et al.*[9] postulated such a unique dimethyl sulfoxide molecule in the solvent cage of $[Co(NH_3)_5D]^{3+}$ to explain the dependence of the dimethyl sulfoxide self-exchange rate constant on the composition of W+D mixture.

Among the several general results for Cl^-, Br^- and I^- in W+D mixtures it was found that the total solvation number of an ion went through a minimum at a solvent composition near that where the water-dimethyl sulfoxide interaction goes through a maximum. Also, the term 'preferential solvation' is not particularly useful for halide ions because whether the halide ions are preferentially solvated by water or by dimethyl sulfoxide depends on the solvent composition.

The results[7] reported for Cl^- are consistent with those for Cl^- in methanol obtained by MD simulations[10] which found 6 methanol molecules in the first solvation shell of Cl^- with no regularity of structure and without identification of a second solvation shell. The water-dimethyl sulfoxide hydrogen bond is stronger than the water-water hydrogen bond[11] which, in turn, is stronger than the methanol-methanol hydrogen bond (as evidenced by the molecular weights and boiling points of methanol and water). Consequently, Cl^- ion cannot compete as effectively for solvent molecules in water-dimethyl sulfoxide mixtures as it can in methanol and its total solvation number will be less in the former than in the latter as the experimental values for the total solvation number of Cl^- in the two solvent systems have now shown. Also, this lack of preferred solvation by water agrees with the results of Langford and Stengle[12] who studied the chemical shift of ^{35}Cl and concluded that the immediate environment of Cl^- did not show preferential solvation by either component over a large mole fraction range in water-dimethyl sulfoxide mixtures.

Here we report on a study of the main $[AgW_jD_k]^+$ species present in W+D mixtures over the bulk mole fraction range 0.05 to 0.95 for D. It has been shown previously[6] that the distribution of solvated species is very little de-

pendent on whether the ratio $\Delta_t G°$ (Ph_4As^+) / $\Delta_t G°$ (Ph_4B^-) was taken to be unity or 1.08 as recommended by Kim.[13] Errors in the $\Delta G°$ values taken from different sources were more important in affecting the solvated species present than was the ratio of the free energies of transfer of the tetraphenylarsonium and tetraphenylborate ions. Therefore, the $\Delta_t G°$ (Ag^+) values used in this study were those obtained from Cox, Natarajan and Waghorne[14] only for the 1.08 value of the ratio.

RESULTS AND DISCUSSION

The square of the relative error for calculated and experimental Gibbs' free energies of transfer was calculated every 0.02 mole fraction increment in x_D and summed over the range of

$$\chi^2 = \sum_s \left[\frac{\Delta_{ts}G°(\text{expt}) - \Delta_{ts}G°(\text{calc})}{\Delta_{ts}G°(\text{expt})} \right] \tag{1}$$

$0.05 \leq x_D \leq 0.95$ to give the error function χ^2 as given in equation (1). The experimental values of the Gibbs' free energy of transfer of Ag^+, $\Delta_{ts}G°$ (expt), for use in equation (1) were obtained from a fourth degree polynomial fit of x_D to published values.[14] The calculated values, $\Delta_{ts}G°$ (calc), were obtained from equation (2) as explained in detail previously[6,7]

$$\Delta_{ts}G° = -RT \left[\frac{\sum_i \gamma \ln \gamma_i}{\sum_i \gamma_i} + \ln \beta_s + \frac{\sum_{j=0}^{n} \sum_{k=0}^{m} \beta_{jk}\, a_w^j\, a_D^k \ln \beta_{jk}}{\sum_{j=0}^{n} \sum_{k=0}^{m} \beta_{jk}\, a_w^j\, a_D^k} \right] \tag{2}$$

and need not be repeated here. In equation (2), γ_i is the overall formation constant for $[AgW_i]^+$ from the silver ion and water in the pure water phase, β_s is the distribution coefficient for Ag^+ between the pure water phase and the binary solvent phase, β_{jk} is the overall formation constant of $[AgW_jD_k]^+$ from silver ion and water (W) molecules and dimethyl sulfoxide (D) molecules in the binary solvent phase, a_W is the activity of water in the binary solvent, and a_D is the activity of dimethyl sulfoxide in the binary solvent. In the process of minimizing χ^2 it was noted that no solvated species $[AgW_jD_k]^+$ with j or k greater than 20 was found. Consequently 22×22 matrices were used for j and k values in the $0 \leq j \leq 21$, $0 \leq k \leq 21$ ranges. An excellent fit to the experimental data was obtained as shown in Table I for ten mixtures throughout the solvent range.

TABLE I

Gibbs' free energies of transfer of Ag^+ from purely aqueous medium at zero ionic strength to water-dimethyl sulfoxide mixtures at zero ionic strength at 25 °C

x_D[a]	$\Delta_{ts}G°$ (expt)[b]	$\Delta_{ts}G°$ (calc)[b]
0.05	2082	2082
0.15	6591	6591
0.25	10984	10984
0.35	15159	15159
0.45	19029	19029
0.55	22521	22521
0.65	25576	25577
0.75	28149	28148
0.85	30209	30208
0.95	31740	31741

[a] Mole fraction of dimethyl sulfoxide based on solvents only.

[b] In joules mol^{-1}.

The distribution of the solvated $[AgW_jD_k]^+$ ions is shown in Table II. For space reasons only those j values for which solvated Ag^+ ions were found appear in the table. Of course the solvated species found change with the mole fraction x_D of dimethyl sulfoxide present in the solvent mixture. Some major species were found. These were $[AgW_3D]^+$ and $[AgWD_3]^+$ (coordination number, CN = 4), $[AgW_3D_2]^+$ (CN = 5), $[AgD_6]^+$ (CN = 6), $[AgWD_9]^+$ (CN = 10) and $[AgD_{14}]^+$ (CN = 14). Coordination numbers 4, 5, and 6 could possibly be complexes with solvent molecules in the first coordination shell but coordination numbers 10 and 14 probably involve second solvation shells. Many minor species, whose percent mole fraction range down to 0.1% (0.001 mole fraction of total Ag(I) present) and which contributed significantly to fitting the experimental data, were found to be present. Some of these minor species may disappear and be replaced by others when new, somewhat different, experimental data appear but the major species contribute so much to the calculated values of $\Delta_tG°$ (Ag^+) that they will not readily disappear. Many of the »missing« species in the table contribute to the fit of the experimental data but they are present in amounts less than 0.1 mole percent. It is the amounts of these species that would be most subject to change by the introduction of newer experimental data. There are 24 solvated ionic species which appear in Table II in amounts larger than 0.1 mole percent. The natural logarithms of the overall formation constants of these species are given in Table III. Because the existence of a solvated species with 0.1 mole percent, or less, abundance is less certain, the $\ln \beta(j,k)$ values for them have been omitted for space reasons.

TABLE II

Percent mole fraction of solvated Ag(I) ions in water-dimethyl sulfoxide mixtures at 25 °C

x_D[a]	j/k[b]	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
0.05	3		52.7	0.7																	
	4		0.1	0.1																	
	6	0.2																			
	11	0.1																			
	16		45.8																		
	20					0.1															
0.15	1				0.1																
	3		83.3	5.0																	
	4		0.2	0.3																	
	6	0.1																			
	12					0.4															
	16		9.1																		
	17							0.1													
	20					1.1															
0.25	1				1.9																
	2			0.2																	
	3		78.9	15.7	0.1																
	4		0.1	0.7	0.1																
	5			0.1																	
	6				0.1																
	12					0.8															
	16		0.2																		
	17							0.4													
	20					0.3															
0.35	0							0.2													
	1				12.9																
	2			0.4	0.1																
	3		58.3	25.2	0.2																
	4		0.1	0.9	0.1																
	5			0.1	0.1																
	6				0.1																
	9									0.3											
	12					0.3															
	17							0.1													
	18											0.3									

TABLE II, continued.

x_D[a]	j/k[b]	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
0.45	0							4.9													
	1				42.5						0.4										
	2			0.5	0.2			0.2													
	3		27.2	21.2	0.3																
	4			0.5	0.1																
	7															0.1					
	9									0.8											
	11												0.3								
	14																			0.1	
	18											0.1									
0.55	0							25.2								0.1					
	1				50.7							4.5									
	2			0.3	0.1			0.5													
	3		7.5	8.5	0.2																
	4			0.1	0.1																
	7															0.9					
	9									0.3											
	11												0.2								
	14																			0.2	
0.65	0							50.0								1.7					
	1				29.8						13.4	0.1									
	2			0.1	0.1			0.5						0.1							
	3		1.1	1.7														0.1			
	7															0.9					
0.75	0							58.6								9.6					
	1				12.1						17.9	0.1									
	2							0.2					0.1	0.1							
	3		0.1	0.2														0.2			
	7															0.2					
0.85	0							52.7								28.8		0.1			
	1				3.8						13.8	0.1									
	2							0.1						0.1							
	3																	0.2			
0.95	0							39.4								55.1		0.2	0.1	0.1	0.1
	1				0.6						4.2										

[a] x_D is the mole fraction of dimethyl sulfoxide based on the total of the solvents present.
[b] j and k are the number of water and dimethyl sulfoxide molecules, respectively, present in $AgW_jD_k^+$ species.

TABLE III

The natural logarithms for the overall formation constants, β_{jk}, of the solvated species appearing in Table II with an abundance of 0.2 mole percent or greater

k	$\ln \beta(j,k)$		
0	$\ln \beta(6,0) = 11.604439$		
1	$\ln \beta(3,1) = 22.0334$	$\ln \beta(4,1) = 16.1131$	$\ln \beta(16,1) = 22.7831$
2	$\ln \beta(2,2) = 18.0301$	$\ln \beta(3,2) = 22.9313$	$\ln \beta(4,2) = 20.3950$
3	$\ln \beta(1,3) = 22.2924$	$\ln \beta(2,3) = 18.0491$	$\ln \beta(3,3) = 19.8602$
4	$\ln \beta(12,4) = 29.7339$	$\ln \beta(20,4) = 32.7031$	
6	$\ln \beta(0,6) = 22.3340$	$\ln \beta(2,6) = 21.7169$	$\ln \beta(17,6) = 36.5699$
8	$\ln \beta(9,8) = 34.0115$		
9	$\ln \beta(1,9) = 11.8004$		
10	$\ln \beta(18,10) = 45.0911$		
11	$\ln \beta(11,11) = 38.9858$		
14	$\ln \beta(0,14) = 23.0309$	$\ln \beta(7,14) = 36.4448$	
16	$\ln \beta(0,16) = 17.6389$	$\ln \beta(3,16) = 27.4062$	
18	$\ln \beta(14,18) = 49.2298$		

Equation (2) may be rewritten as equation (3). The fit to the data obtained gave $a = -22.496570$, $b = 20.362930$ and $c = -7.557763$ for equation 3 where $g(n,m,s)$ and $f(n,m,s)$ are

$$\Delta_{ts}G^\circ = -RT\left[a + bx_D + cx_D^2 + \frac{g(n,m,s)}{f(n,m,s)}\right] \tag{3}$$

defined by reference to equation (2).

The total solvation number, n_t, the sum of the average number of water molecules and of the average number of dimethyl sulfoxide molecules per Ag^+ in all solvated species, at a given mole fraction of dimethyl sulfoxide went through a minimum value of 4.5 from 0.25 to 0.35 mole fraction where the water + dimethyl sulfoxide interaction is strongest. This number is in agreement with the solvation number of 4.1 ± 0.3 given by Neilson[4] for the neutron diffraction method. But at small or large mole fractions of dimethyl sulfoxide the value of n_t rises to 10 showing the importance of outer shell solvation to the Gibbs' free energy of transfer.

BIBLIOGRAPHY

1. A. Fratiello, V. Kubo-Anderson, S. Azini, E. Marinez, D. Matejka, R. Perrigan, and B. Yao, *J. Solution Chem.* **20** (1991) 893 (and earlier papers referred to therein).
2. S. F. Lincoln, *Coord. Chem. Rev.* **6** (1971) 309.

3. D. Marx, K. Heinzinger, G. Palinkas, and I. Bako, *Z. Naturforsch., Teil A* **46** (1991) 887 (and references therein to previous papers).
4. G. W. Neilson and J. E. Enderby, *Adv. Inorg. Chem.* **34** (1989) 195.
5. G. Palinkas and K. Keinzinger, *ACH – Models in Chem.* **132** (1995) 5.
6. W. L. Reynolds, S. Davis, and M. Glavas, *Trends in Inorg. Chem.* **3** (1993) 257.
7. W. L. Reynolds, S. Davis, and M. Glavas, *Croat. Chem. Acta* **64** (1991) 663.
8. W. L. Reynolds, S. Davis, and M. Glavas, *Croat. Chem. Acta* **64** (1991) 19.
9. C. H. Langford, R. Scharfe, and R. Jackson, *Inorg. Nucl. Chem. Letters* **9** (1973) 1033.
10. Y. Tamura, Y. Watanabe, and K. Heinzinger, *Computer Aided Innovation New Mater. 2, Proc. Int. Conf. Exhib. Comput. Appl. Mater. Mol. Sci. Eng. Part 1*, 1993, p. 275.
11. A. Luzar and D. Chandler, *J. Chem. Phys.* **98** (1993) 8160.
12. C. H. Langford and T. R. Stengle, *J. Amer. Chem. Soc.* **91** (1969) 4014.
13. J. I. Kim, *Bull. Soc. Chim Belg.* **90** (1987) 391.
14. B. G. Cox, R. Natarajan, and W. E. Waghorne, *J. Chem. Soc., Faraday Trans. I.* **75** (1979) 1780.

SAŽETAK

Solvatacija iona. V. Srebrov(I) ion u smjesi voda-dimetilsulfid

Warren L. Reynolds i Steven Davis

Gibbsove slobodne energije prijenosa srebrova(I) iona, $\Delta_t G°$ (Ag^+), iz vode u binarnu smjesu voda-dimetilsulfoksid, upotrijebljene su za određivanje distribucije solvatiranih iona, $AgW_jD_k^+$, prisutnih kod molnog udjela dimetilsulfoksida u rasponu od 0,05 do 0,95. Glavni su oblici iona AgW_3D^+, $AgW_{16}D^+$, $AgW_3D_2^+$, $AgWD_3^+$, AgD_6^+, $AgWD_9^+$, AgD_{14}^+. Vodom bogati solvatizirani ioni prisutni su samo pri niskim koncentracijama dimetilsulfoksida.