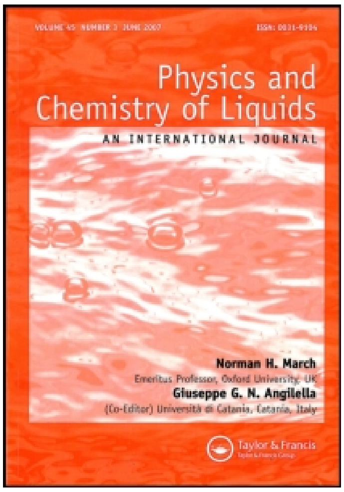

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Raghunath, R. and Kalidas, C.(1995) 'Conductance Behaviour of Silver [Cryptand 2,2,2] Perchlorate Complex in Water-Acetonitrile and Methanol-Acetonitrile Mixtures', Physics and Chemistry of Liquids, 29: 4, 237 — 241
To link to this Article: DOI: 10.1080/00319109508031641
URL: http://dx.doi.org/10.1080/00319109508031641

Phys. Chem. Liq., 1995, Vol. 29, pp. 237–241
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CONDUCTANCE BEHAVIOUR OF SILVER [CRYPTAND 2,2,2] PERCHLORATE COMPLEX IN WATER–ACETONITRILE AND METHANOL–ACETONITRILE MIXTURES

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(Received 24 November 1994)

Conductance studies on silver [Cryptand 2,2,2] perchlorate complex have been made in water–acetonitrile and methanol–acetonitrile mixtures over the complete range of solvent compositions at 30°C. The data were analysed by the Fuoss 1980 three parameter equation and the variation of the Walden products of respective ions with solvent composition was analysed. The considerable decrease of the Walden products of {silver [Cryptand 2,2,2]}$^+$ has been explained in terms of the selective solvation of the ion by acetonitrile in both solvent mixtures.

KEY WORDS: Conductance of silver [Cryptand 2,2,2] perchlorate complex, water–acetonitrile mixtures and methanol–acetonitrile mixtures.

Conductance measurements have often been employed[1-4] to provide information on the preferential solvation of ions in binary mixed solvents. In earlier work from this laboratory, such studies on some silver (I) salts in water–acetonitrile[3] (AN), methanol–acetonitrile (AN) mixtures[3] and copper salts in water–pyridine mixtures[5] have shown that the cations are preferentially solvated by the dipolar aprotic component while the anions are selectively solvated by the protic component. Although cryptands like cryptand 2,2,2 and other similar compounds are known[6] to form strong inclusion complexes with alkali metal and silver ions depending upon size[6], relatively few conductance studies on such complex salts in mixed solvents have been reported[7] to understand their selective solvation characteristics. The present work, involving the conductance behaviour of a complex silver salt viz silver (I) cryptand 2,2,2 perchlorate in water–AN and methanol–AN mixtures, was therefore undertaken to throw light on its preferential solvation vis a vis the solvation of the uncomplexed salt and also to understand the effect of ligand encapsulation of the salt on its conductance. The results will also be compared with the Gibbs transfer energy and solvent transport measurements performed earlier[8] on the complex salt in these mixtures.

MATERIALS AND METHODS

Fresh doubly distilled conductivity water was used throughout and stored out of contact with air. Acetonitrile and methanol [AR grade] were purified as reported earlier[9]. Silver [cryptand 2,2,2] perchlorate complex was prepared following the literature procedure[10].

In view of the sparingly soluble nature of silver [cryptand 2,2,2] perchlorate, the conductance measurements were carried in a concentration range well below the solubility limit of the complex salt in the desired solvent composition.

All conductance measurements were made at 30 ± 0.05 °C using a precision conductance bridge model WBR/TAV (Wissenchaftliche Technische Werkstatten, GmbH, West Germany) using a conductance cell with a cell constant $0.5340\,\mathrm{cm}^{-1}$. The measured resistances are accurate to within ± 0.1%.

RESULTS AND DISCUSSION

The molar conductance data of silver [cryptand 2,2,2] perchlorate in various compositions of water–AN and methanol–AN mixtures at 30 °C were analysed by the Fuoss 1980 three parameter equation given by

$$\Lambda = \gamma[\Lambda_\circ(1 + RXE) + HXV + HY] \ldots\ldots\ldots \quad (1)$$

where $RXE = \Delta X_E/X$ and ΔX_E is the part of relaxation field generated by purely electrostatic interactions between the free ions, $HXV = (\Delta X_v/X)$ the part of the relaxation field term due to the perturbation of that field by the electrophoretic flow $HY = \Delta\Lambda_e + \Delta\Lambda_H$ in which $\Delta\Lambda_e$ is the electrophoretic term and $\Delta\Lambda_H$ is a hydrodynamic— hydrodynamic interaction term. The relevant expressions employed for evaluating these terms are the same as derived by Fuoss[11]. γ in Eq (1) represents the fraction of solute which contributes to the current and the other terms have their usual meaning. All the calculations were performed using the programme of Fuoss and the calculated $\Lambda_\circ$ and the association constants, K_A obtained are given in Table 1. The conductances of the pure solvent mixtures were found to be small and hence neglected in the calculation of molar conductances of the salt. Using the viscosities, $\eta_\circ$ of the various compositions of H_2O–AN[3] and methanol–AN[3] mixtures, the Walden products $\Lambda_\circ\eta_\circ$ of the salt at 30 °C were calculated and are given in Table 2.

Table 1 $\Lambda_\circ$ and Association constants (K_A) of silver (cryptand 2,2,2) perchlorate in water–AN and methanol–AN mixtures

	H_2O–AN			*Methanol–AN*		
Mol % AN	$\Lambda_\circ$ *$ohm^{-1}\,cm^2\,mol^{-1}$*	$\sigma\Lambda$*	K_A *$(mol\,dm^{-3})^{-1}$*	$\Lambda_\circ$ *$ohm^{-1}\,cm^2\,mol^{-1}$*	$\sigma\Lambda$*	K_A *$(mol\,dm^{-3})^{-1}$*
0	148.50 ± 0.46	0.68	7.2	125.35 ± 0.25	0.32	132.4
10	105.98 ± 0.16	0.17	96.4	147.78 ± 0.20	0.29	96.7
30	121.63 ± 0.47	0.35	45.0	173.55 ± 0.33	0.57	73.3
50	156.36 ± 0.22	0.34	51.9	198.15 ± 0.54	0.65	77.4
70	223.80 ± 0.29	0.59	175.0	214.31 ± 0.30	0.60	75.1
90	244.96 ± 0.39	0.96	253.5	199.55 ± 0.46	0.92	48.5
100	192.93 ± 0.84	0.63	54.0	192.93 ± 0.84	0.68	54.0

*Standard deviation of individual points

$\sigma^2 = \Sigma_\circ[\Lambda_{j(calc)} - \Lambda_{i(calc)}]^2/N - 2$; where N = number of data points.

The Λ_o of the complex salt in water–AN mixtures (Table 1) decreases with the addition of AN, passes through a minimum around 10 mole% AN and then increases (except in pure AN). Such minima are also observed for salts like silver bromate[3] in these solvent mixtures. The $\Lambda_o\eta_o$ of the complex salt (Table 2) also decreases rapidly with the addition of AN upto 50 mole%, passes through a minimum around this composition and subsequently increases (except in pure AN).

In methanol–AN mixtures (Table 1), the Λ_o of the salt continuously increases with the addition of AN, passes through a maximum around 70 mole% AN and then decreases. The $\Lambda^\circ\eta^\circ$ values (Table 2) show a gradual increase upto 70 mole% AN and then decrease.

The Λ_o of the salt in the two solvent systems was split into the respective ionic components using the ionic conductance data of perchlorate ion in these mixtures determined earlier[3]. The ionic conductances ($\lambda^\circ \pm$) and ionic walden products of [Ag (cryptand 2,2,2)]$^+$ and ClO_4^- ions in the two solvent systems at 30°C are given in Table 3.

VARIATION OF SINGLE IONIC CONDUCTANCES

In water–AN mixtures (Table 3), the λ°[Ag (cryptand 2,2,2)]$^+$ decreases on the addition of AN, passes through a minimum around 30 mole% AN and then increases with further addition of AN. The maximum in the viscosity of water–AN mixtures around 30 mole% AN gives rise to a minimum in the ionic mobilities around 30 mole% AN as observed. The $\lambda_{ClO_4^-}$ decreases upto 10 mole% AN and then increases.

In methanol–AN mixtures (Table 3) the $\lambda^\circ_{[Ag\,(cryptand\ 2,2,2)]^+}$ passes through a maximum at 70 mole% AN which is presumably due to minimum in the viscosity of these mixtures around 70 mole% AN. The $\lambda^\circ_{ClO_4^-}$ increases rapidly upto 70 mole% AN and subsequently a small increase is observed with further addition of AN.

VARIATION OF IONIC WALDEN PRODUCTS

The large decrease of λ° [Ag (cryptand 2,2,2)]$^+$ η_o with the addition of AN in water–AN (upto 30–50 mole%) and methanol–AN mixtures indicates an increase in the

Table 2 Viscosities (η°) and densities (d°) of the solvent mixtures and Walden products ($\Lambda^\circ\eta^\circ$) of silver [Cryptand 2,2,2] perchlorate in water–AN and methanol–AN mixtures at 30°C

	Water – AN			*Methanol – AN*		
Mol % AN	η° *(poise)*	d° *gm cm*$^{-3}$	$\Lambda^\circ\eta^\circ$ *ohm*$^{-1}$*cm*^{2} *mol*$^{-1}$ *poise*	η° *(poise)*	d° *gm cm*$^{-3}$	$\Lambda^\circ\eta^\circ$ *ohm*$^{-1}$*cm*^{2} *mol*$^{-1}$ *poise*
0	0.00798	1.0004	1.185	0.00517	0.7817	0.648
10	0.00870	0.9600	0.922	0.00460	0.7820	0.680
30	0.00680	0.8850	0.827	0.00388	0.7814	0.673
50	0.00520	0.8400	0.813	0.00352	0.7779	0.697
70	0.00420	0.8100	0.940	0.00334	0.7760	0.716
90	0.00370	0.7750	0.906	0.00334	0.7730	0.666
100	0.00339	0.7720	0.654	0.00339	0.7720	0.654

Table 3 Single ionic conductances λ° (ohm^{-1} cm^2 mol^{-1}) and ionic walden products $\lambda^{\circ}\eta^{\circ}$ (ohm^{-1} cm^2 mol^{-1} poise) at infinite dilution for Ag [Cryptand 2,2,2]$^+$ and Clo_4^- in water-AN and MeOH-AN mixtures

	Water-AN				*MeOH-AN*			
Mol^-_{AN} %	$\lambda^{\circ}_{ClO_4^-}$	$\lambda^{\circ}_{ClO_4^-}\eta^{\circ}$	$\lambda_{\circ}(Ag2,2,2)^+$	$\lambda_{\circ}(Ag2,2,2)^+\eta^{\circ}$	$\lambda^{\circ}_{ClO_4^-}$	$\lambda^{\circ}_{ClO_4^-}\eta^{\circ}$	$\lambda_{\circ}(Ag2,2,2)^+$	$\lambda_{\circ}(Ag2,2,2)^+\eta^{\circ}$
0	64.03	0.510	84.47	0.674	43.20	0.224	82.11	0.424
10	56.00	0.490	49.88	0.434	60.00	0.276	87.78	0.400
30	70.00	0.470	51.53	0.350	78.00	0.303	95.55	0.370
50	83.00	0.430	73.36	0.382	93.00	0.327	105.15	0.370
70	94.00	0.390	129.80	0.545	100.00	0.334	114.30	0.381
90	100.00	0.370	144.96	0.536	100.20	0.335	99.35	0.331
100	100.90	0.340	92.05	0.312	100.90	0.342	92.00	0.312

solvated radius of silver ion due to the entry of the relatively larger AN molecules ($r_{H_2O} = 1.93$ A° $r_{MeOH} = 2.53$ A° and $r_{AN} = 2.76$ A° calculated assuming that the molecules are spherical) into the solvation shell of the complex silver cation. Thus the preferential solvation of Ag (Cryptand 2, 2, 2)]$^+$ ion by AN in both the mixed solvents is inferred from the decrease of the Walden products of [Ag (cryptand 2, 2, 2)]$^+$ with the addition of AN. This is in agreement with the conclusions arrived at earlier[8] on the selective solvation of this ion in these mixtures from various experimental methods such as solvent transport number and Gibbs transfer energy measurements. It may be mentioned that similar results have been obtained for the uncomplexed silver ion in these mixed solvents on the basis of these experiments[3] as well as NMR[12,13], ESR[14] and Raman spectroscopy[15]. It is apparent that despite the encapsulation of the silver ion by the ligand, the specific Ag^+–AN interactions prevail which result in the preferential solvation of the silver cryptand 2, 2, 2 complex ion by AN in both the solvent mixtures. The Walden product of the perchlorate ion increases with the addition of water (considering from the pure water region) and the selective hydration of this ion by water is not observed.

The Walden product of percholrate ion decreases perceptibly in the initial stages in methanol–AN mixtures with the addition of methanol to an infinitely dilute solution of this ion in AN. The decrease is however, significant below 50 mole% AN. This suggests that the percholrate ion is selectively solvated by methanol but other experimental approaches are necessary to confirm this point. These results are in agreement with the results based on the solvent transport number and Gibbs transfer energy measurements obtained earlier[8].

The variation of K_A in water–AN mixtures is quite complex but in methanol–AN mixtures, there is a general decreasing trend of K_A with increasing composition of AN (except pure AN). This presumably arises from the preferential solvation of perchlorate ion by methanol and of the complex cation by acetonitrile, both processes tending to reduce ion pair formation.

References

1. H. Schneider, *Solute-solvent interactions*, vol 2, Edited by J. F. Coetzee and C. D. Ritchie (Marcel Dekker, New York), Chapter II, (1976).
2. S. Janardhanan and C. Kalidas, *Revs Inorg Chem*, **6**, 101 (1984).
3. S. Subramanian and C. Kalidas, *Ind. J. Chem.*, **25 A**, 1018 (1986).
4. C. Kalidas and G. Rajendran, *Bull Soc Chem. Belg.*, **102**, 365 (1993).
5. T. K. Sreekumar, G. Rajendran and C. Kalidas, *Ind. J. Chem.*, **31 A**, 782 (1992).
6. B. G. Cox and H. Schneider, *Co-ordination and transport properties of macrocyclic compounds in solution*, Elsevier, Amsterdam (1992).
7. M. Salomon, *J. Solution Chem.*, **19**, 1225 (1990).
8. C. Kalidas and R. Raghunath, *J. Electroanal Chem* (in press).
9. S. Subramanian and C. Kalidas, *Electrochim, Acta.*, **29**, 753 (1984).
10. B. G. Cox, C. Guminski and H. Schneider, *J. Am Chem. Soc.*, **104**, 3787 (1982).
11. R. M. Fuoss, Proc. Nat. Acad. Sci., U.S.A., **77**, 34 (1980).
12. B. G. Cox, A. J. Parker and W. E. Waghorne, *J. Phys. Chem*, **78**, 1731 (1974).
13. H. Schneider and H. Strehlow, *Z Phys Chem* (Frankfurt), **49**, 44 (1966).
14. C. K. Alesbury and M. C. R. Symon, *J. Chem. Soc Faraday Trans*, **1**, 244 (1980).
15. B. G. Oliver and G. J. Janz, *J. Phys Chem*, **74**, 3819 (1970).