# Influence of Solvent on the Stability of Silver(I)–Olefin Complexes [‡]

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The stability constants of complexes of silver(I) with allyl alcohol, prop-2-en-1-ol, *trans*-but-2-en-1-ol, but-3-en-1-ol, pent-4-en-1-ol, and hex-5-en-1-ol have been determined in a number of solvents. The corresponding enthalpy and entropy changes have been evaluated. The stability constants depend on the solvent in the order propylene carbonate > water > methanol > ethanol ⋙ acetonitrile, which is ascribed to competition between the unsaturated alcohol and the solvent. But-3-en-1-ol shows unexpectedly high stability constants in methanol, ethanol, and propylene carbonate which are ascribed, on the basis of entropy data, to chelate-ring formation; no chelation is observed in water.

THERE have been many studies made of the stability of silver-olefin complexes [1] although relatively few of these have yielded enthalpy and entropy data, most workers being content with free-energy data alone. Very few studies have been made in more than one solvent in spite of the fact that it is clear that solvation effects are very important in determining the overall stability constant. This is particularly well illustrated by the data in Table 1 which show that the stability constant for the formation of the first complex between $Ag^I$ and olefins $RCH=CH_2$ in ethylene glycol solvent decreases steadily as R increases in chain length whereas the opposite trend is found in water. Accordingly we have determined free energies of formation of a series of silver(I)–olefin complexes in four different solvents, namely water, methanol, ethanol, and propylene carbonate. In order to determine the component enthalpy and entropy values from the temperature dependence of the free energies it was essential to obtain data of the highest precision and accordingly a potentiometric method was used since the other available methods all yield significantly less accurate data.[1] In addition, in order to obtain meaningful data it is important to control the activity coefficients of the species present. This necessitated using an inert background electrolyte which limited the choice of solvents. Acetonitrile, which was in other ways excellent, formed too strong a complex with $Ag^I$ to be displaced by olefins. The olefins chosen were a series of unsaturated alcohols which were readily soluble in all the four solvents.

TABLE 1

Influence of chain length on the stability constant *K* for the equilibrium $Ag^+ + RCH{=}CH_2 \overset{K}{\rightleftharpoons} [Ag(RCH{=}CH_2)]^+$

| R | Medium | $\frac{K}{dm^3\,mol^{-1}}$ | $\frac{\theta_c}{°C}$ | Ref. |
|---|---|---|---|---|
| H | Ethylene glycol | 17.5 | 25 | *a* |
| Me | Ethylene glycol | 7.5 | 25 | *a* |
| Et | Ethylene glycol | 8.8 | 25 | *a* |
| $Pr^n$ | Ethylene glycol | 6.7 | 25 | *a* |
| $Bu^n$ | Ethylene glycol | 4.3 | 40 | *b* |
| $n\text{-}C_5H_{11}$ | Ethylene glycol | 3.2 | 40 | *b* |
| $n\text{-}C_6H_{13}$ | Ethylene glycol | 2.6 | 40 | *b* |
| H | Water (1 mol $dm^{-3}$ $K[NO_3]$) | 85.3 | 25 | *c* |
| Me | Water (1 mol $dm^{-3}$ $K[NO_3]$) | 87.2 | 25 | *c* |
| Et | Water (corrected to 0 mol $dm^{-3}$) | 119.4 | 25 | *d* |
| $Bu^n$ | Water (1 mol $dm^{-3}$ $K[NO_3]$) | 860 | 25 | *e* |

[a] R. J. Cvetanović, F. J. Duncan, W. E. Falconer, and R. S. Irwin, *J. Amer. Chem. Soc.*, 1965, **87**, 1827. [b] M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, 1962, **84**, 4697. [c] K. N. Trueblood and H. J. Lucas, *J. Amer. Chem. Soc.*, 1952, **74**, 1338. [d] F. R. Hepner, K. N. Trueblood, and H. J. Lucas, *J. Amer. Chem. Soc.*, 1952, **74**, 1333. [e] S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.*, 1938, **60**, 836.

## EXPERIMENTAL

*Materials.*—Chloride-free sodium perchlorate was obtained by careful selection of Koch–Light analytical reagent-grade sodium perchlorate. The monohydrate was dehydrated by heating at 117 °C *in vacuo* for 6 h. Silver(I) perchlorate (B.D.H.) was dehydrated by placing not more than 6 g over anhydrous $Ca[SO_4]$ in a vacuum desiccator for at least 7 d. Stock solutions (*ca.* 0.2 mol $dm^{-3}$) were prepared by weight and standardised after four-fold dilution with water against an aqueous sodium chloride solution using potassium chromate as indicator (Mohr procedure [2]).

Reagent-grade allyl alcohol was purified by fractional distillation using a 14-in vacuum-jacketted fractionating column; b.p. 96 °C (lit.,[3] 96.6 °C). *trans*-But-2-en-1-ol was prepared by lithium tetrahydridoaluminate reduction of but-2-enal, followed by fractional distillation as before; b.p. 121 °C (lit.,[4] 121.5—122 °C). The purity was checked by g.l.c. and the sample was shown to be the *trans* isomer by comparison of its i.r. spectrum with that in the literature.[5] But-3-en-1-ol, pent-4-en-1-ol, and hex-5-en-1-ol were used as obtained commercially since g.l.c. analysis showed their purity to be better than 99% in all cases. Concentrated stock solutions of the unsaturated alcohols were prepared by weight. G.l.c. analysis was effected using a Perkin-Elmer model 452 gas chromatograph fitted with a flame ionisation detector. A 2-m column packed with diatomite coated with poly(propyleneglycol adipate) (15% w/w) was used.

The solvents were purified as follows. Distilled water was fractionally redistilled under nitrogen after refluxing with potassium permanganate. Analytical reagent-grade methanol and ethanol were dried over magnesium turnings followed by fractional distillation under nitrogen. Propylene carbonate was purified by refluxing over $K[MnO_4]$ (2 g $dm^{-3}$) and sodium carbonate (0.5 g $dm^{-3}$) *in vacuo* for 30 min, followed by vacuum distillation; b.p. 96 °C at 3 mmHg.[§] The purified solvents were all stored under nitrogen. The

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[‡] No reprints available.

[§] Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

[1] F. R. Hartley, *Chem. Rev.*, 1973, **73**, 163.

[2] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1964, p. 259.

[3] T. E. Thorpe, *J. Chem. Soc.*, 1880, **37**, 210.

[4] J. Baudrenghien, *Bull. Soc. chim. belges*, 1922, **31**, 160.

[5] D. Barnes, P. C. Uden, and P. Zuman, *Analyt. Letters*, 1970, **3**, 633.

water contents of all the solvents used were determined by Karl–Fischer titration [6] and found to be less than 0.05%.

All the solutions used in the titrations were made up to 1 mol dm$^{-3}$ in sodium perchlorate, except in ethanol where 0.9 mol dm$^{-3}$ solutions were used (due to solubility limitations). The solutions were prepared at ambient temperatures and their molarities at higher temperatures were obtained by using literature values for the coefficients of thermal expansion of the solvents.[7] The thermal expansion of propylene carbonate was determined using a density bottle and found to be 0.0870% (°C)$^{-1}$ in the range 18—46 °C.

*Silver–Silver Chloride Electrodes.*—The silver–silver chloride electrodes were prepared according to Brown [8] by electroplating silver on to platinum and then chloridising the outer silver layer. The electrodes were aged by storing them in a dilute silver perchlorate solution in the solvent to be used in the potentiometric titration. During storage they were shorted together since it was found that by doing this the electrodes aged within 48 h. Before use the electrodes were checked to ensure (*i*) that their e.m.f.s in a given solution differed by no more than 0.02 mV and (*ii*) that they were reversible over a wide range of silver concentration in the solvent to be studied and at each temperature to be investigated. The gradients of plots of e.m.f. against silver-ion concentration were always close to theoretical, but the experimental value for each electrode was used in the calculation. Typically, the electrodes had a useful working life of 4—6 weeks before showing lack of linearity at low silver-ion concentrations.

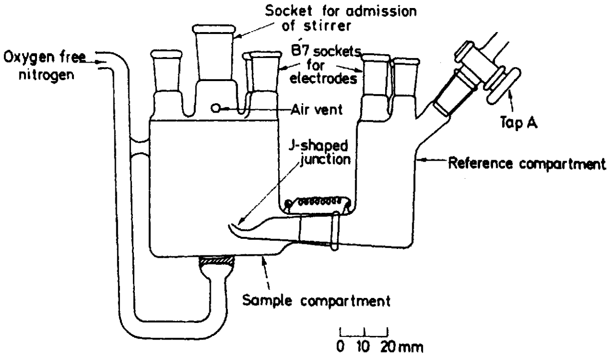

FIGURE 1 Titration vessel

*Potentiometric Titration.*—Because silver–silver chloride electrodes do on occasions fail, the apparatus (see Figure 1) was designed with three reference and three sample electrodes. Since the potentiometric errors are greater than the titration errors, this has the further advantage that one titration yields three sets of data. The reference compartment of the cell, capped at the bottom, was filled with the same silver perchlorate solution as was to be present initially in the sample compartment and was then immersed in the thermostatted bath (Grant Instruments model SBX tank capable of maintaining a given temperature to within ±0.05 °C) for 15 min with tap A open to allow for expansion during thermal equilibration. After closing tap A the reference and sample compartments were joined together before pipetting silver perchlorate solution (50 cm$^3$) into the sample compartment. The sample electrodes were then carefully fitted before allowing the complete cell 30 min to come to thermal equilibrium during which time it was stirred and oxygen-free nitrogen was bubbled in. The oxygen-free nitrogen was presaturated with the solvent by passing it in a fine stream through a wash-bottle containing a 1 mol dm$^{-3}$ solution (0.9 mol dm$^{-3}$ in ethanol) of Na[ClO$_4$] in the solvent under test at the temperature of the titration. This procedure ensured that the initial e.m.f. was constant for *ca.* 15 min before the start of the titration.

The titration was carried out by adding from burettes equal volumes of the solution of the unsaturated alcohol and a silver perchlorate solution of exactly double the concentration of that initially present in the sample compartment. This ensured that the total silver(I) concentration in the sample compartment remained constant and that the measured e.m.f. was solely due to complex formation and did not contain a component due to dilution. The burettes used were 'B' grade (10 cm$^3$) which were provided with glass jackets through which the liquid from the thermostatted tank was circulated. The burettes were calibrated after the glass jackets had been fitted.

The e.m.f.s developed between the three pairs of electrodes were measured using an Advance DPM 300 digital voltmeter which had an input impedance of $>10^8\ \Omega$. This impedance was sufficiently high to ensure that (*i*) a negligible current was drawn from the cell so that the equilibrium present therein was effectively undisturbed and (*ii*) a true measure of the e.m.f. developed was obtained. The digital voltmeter was modified to provide two potential ranges [0—20 ($\pm$0.01) and 20—200 mV ($\pm$0.1 mV)] as well as a switching arrangement to enable the e.m.f. between the pairs of electrodes to be measured conveniently. The digital millivoltmeter was frequently calibrated against a Solatron model 1604/DC (National Physical Laboratory calibrated) digital voltmeter fitted with an internal Weston standard cell. For this purpose a Time Electronics model 404 millivolt source was used. Calibration charts were prepared and used to correct the measured e.m.f.s.

For the water, methanol, and ethanol solutions the e.m.f. was generally established *ca.* 30 s after adding further reagents. To ensure complete equilibrium, however, the e.m.f. readings were taken 3 min after the addition. In the case of the more viscous propylene carbonate the e.m.f. took *ca.* 5 min to settle down and readings were taken 15 min after the addition. The use of three electrodes, in addition to allowing a continuous monitor of electrode performance, also gave an indication of when mixing was complete since at this point the potential difference between all the pairs of electrodes became equal within experimental error.

The titration was performed twice for each ligand at a given silver(I) concentration and all six sets of e.m.f.s were used in the calculation. In addition each titration was performed at two different silver-ion concentrations at 25 °C to check whether polynuclear species were present. Full experimental data are given in Supplementary Publication No. SUP 21966 (21 pp.).*

*Liquid-junction Potential.*—Previously one of us suggested [9] that, since the methods available for the calculation

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[6] I. M. Kolthoff and R. Belcher, 'Volumetric Analysis,' Interscience, New York, 1957, vol. 3, ch. 9.

[7] N. A. Lange, 'Handbook of Chemistry,' 10th edn., McGraw-Hill, New York, 1967, p. 1687.

[8] A. S. Brown, *J. Amer. Chem. Soc.*, 1934, **56**, 646.

[9] F. R. Hartley and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 333.

of liquid-junction potentials are of limited accuracy, they should in cases such as the present be measured by repeating the titration using the corresponding saturated alcohol in place of the unsaturated alcohol. The e.m.f. change observed in such a titration would be due to (*i*) the liquid-junction potential and (*ii*) any complex formation due to co-ordination between the alcoholic oxygen and the $Ag^I$. When such a titration was carried out using propan-1-ol the total e.m.f. change was only 0.2 mV, 1% of the change observed with allyl alcohol. This value is within the experimental error and accordingly the liquid-junction potentials were assumed to be negligible. The rather larger liquid-junction potentials observed previously [9] are thought to have been due to the presence of 0.1 mol $dm^{-3}$ $H^+$ in the background electrolyte.

*Calculation of the Stability Constants.*—Two methods were used for the calculation of the stability constants. The first and simpler was a graphical linear-extrapolation approach based on Leden's method [10] which was very effective when the system could be described by equilibria (1) and (2) (HL = olefin alcohol). However, for more complex

$$Ag^+ + HL \overset{K_1}{\rightleftharpoons} [Ag(HL)]^+ \qquad (1)$$

$$[Ag(HL)]^+ + HL \overset{K_2}{\rightleftharpoons} [Ag(HL)_2]^+ \qquad (2)$$

systems where it was necessary to consider equilibria (3) and (4) as well as (1) and (2) a non-linear least-squares approach was used.

$$[Ag(HL)_2]^+ + HL \overset{K_3}{\rightleftharpoons} [Ag(HL)_3]^+ \qquad (3)$$

$$[Ag(HL)]^+ + Ag^+ \overset{K_4}{\rightleftharpoons} [Ag_2(HL)]^{2+} \qquad (4)$$

(a) *Linear extrapolation.* A function F(HL) is defined as in (5) where the subscripts T and F refer to total and free

$$F(HL) = ([Ag]_T - [Ag]_F)/[Ag]_F[HL]_F \qquad (5)$$

concentrations respectively. It can be shown that equation (6) is applicable, and that in the absence of $[Ag(HL)_2]^+$ and

$$F(HL) = K_1 + K_1K_2[HL]_F + K_1K_2K_3([HL]_F)^2 + \ldots \qquad (6)$$

higher complexes a plot of F(HL) against $[HL]_F$ is a straight line from which $K_1$ and $K_2$ can be evaluated. If $[Ag(HL)_2]^+$ or higher complexes were present a curve would result. If polynuclear species such as $[Ag_2(HL)_2]^+$ were present then the values of $K_1$ and $K_2$ obtained by this method would be dependent on the silver(I) concentration present. In practice only the second possibility arose and when it did the non-linear least-squares approach was used to analyse the data.

In order to obtain the 'best' values of $K_1$ and $K_2$ it is essential to draw the best line through the points on the plot of F(HL) against $[HL]_F$ taking into account that both the ordinates and abscissae contain experimental error. This was effected by determining the distance [$R_i$, given by equation (7)] of the *i*th experimental point from the straight line and noting that the best straight line will be that for

$$R_i = F(HL) - K_1 - K_1K_2[HL]_F \qquad (7)$$

which the sum of the squares of all the residuals [$S_R$, given by equation (8), where $I$ = total number of data points] is a minimum. Analysis of the experimental data revealed

$$S_R = \sum_{i=1}^{I} R_i^2 \qquad (8)$$

that some points clearly lay closer to a straight line than others and accordingly a weighting factor of $1/\sigma_R^2$, where $\sigma_R^2$ is the variance of the residual $R_i$, was introduced into $S_R$ [equation (9)]. The variance of the residual $R_i$ ($\sigma_R^2$) was

$$S_R = \sum_{i=1}^{I} R_i^2/\sigma_R^2 \qquad (9)$$

obtained by evaluating the partial differentials in equation (10) (in which $\sigma_X^2$ is the variance in the experimental quantity $X$ and is considered to be equal to the square of the estimated error in $X$) which is based on error propagation theory [11] and assumes that there are no correlations between the experimental errors in $[Ag]_T$, $[HL]_T$, and e.m.f. ($E$). It

$$\sigma_R^2 = \left(\frac{\partial R}{\partial E}\right)^2 \sigma_E^2 + \left(\frac{\partial R}{\partial [Ag]_T}\right)^2 \sigma_{[Ag]_T}^2 + \left(\frac{\partial R}{\partial [HL]_T}\right)^2 \sigma_{[HL]_T}^2 \qquad (10)$$

should be noted that the Leden approach is an interative one and that it is necessary to evaluate $\sigma_R^2$ for each cycle since the value of $\sigma_R$ is dependent on the assumed concentration of uncomplexed olefin which in turn depends on $K_1$ and $K_2$. Iteration was continued until the change in $S_R$ in consecutive cycles was less than 0.1%, which was normally obtained within three iterations.

The standard deviations of the gradient and intercept ($\equiv K_1$) of the F(HL) against $[HL]_F$ plots were obtained from equations (11) and (12).[11] The standard deviation of $K_2$ was obtained from equation (13).[12a]

$$\sigma(\text{intercept}) = \sigma_{K_1} = \left[\frac{\sum_{i=1}^{n} ([HL]_F)_i^2/\sigma_R^2}{\left\{\sum_{i=1}^{n} \frac{([HL]_F)_i^2}{\sigma_R^2} \cdot \sum_{i=1}^{n} \frac{1}{\sigma_R^2}\right\} - \left\{\sum_{i=1}^{n} \frac{([HL]_F)_i}{\sigma_R^2}\right\}^2}\right]^{\frac{1}{2}} \qquad (11)$$

$$\sigma(\text{gradient}) = \sigma_{K_1K_2} = \left[\frac{\sum_{i=1}^{n} \frac{1}{\sigma_R^2}}{\left\{\sum_{i=1}^{n} \frac{([HL]_F)_i^2}{\sigma_R^2} \cdot \sum_{i=1}^{n} \frac{1}{\sigma_R^2}\right\} - \left\{\sum_{i=1}^{n} \frac{([HL]_F)_i}{\sigma_R^2}\right\}^2}\right]^{\frac{1}{2}} \qquad (12)$$

$$\sigma_{K_2}^2 = K_2^2\{[\sigma_{K_1K_2}^2/(K_1K_2)^2] - (\sigma_{K_1}^2/K_1^2)\} \qquad (13)$$

(b) *Non-linear least-squares approach.* A non-linear least-squares approach to data evaluation was used for two reasons. (*i*) It was used to cope with cases where the linear approach indicated that further equilibria in addition to those in equations (1) and (2) were present. (*ii*) In the remaining cases it was used to check the validity of the linear approach. This was necessary because in using a linear least-squares fitting to find the 'best line' it is assumed that the precision with which the abscissa is measured is much greater than that of the ordinate.[12b] In

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[10] I. Leden, 'Potentiometrisk underskøning av några Kadmiumsalters Komplexitet,' Gleerupska Universitets-Bokhandeln, Lund, 1943; for a description in English see F. J. C. Rossotti and H. Rossotti, 'The Determination of Stability Constants,' McGraw-Hill, New York, 1961, pp. 44—46, 108.

[11] A. A. Clifford, 'Multivariate Error Analysis,' Applied Science, London, 1973.

[12] N. C. Barford, 'Experimental Measurements: Precision, Error and Truth,' Addison-Wesley, London, 1967, (*a*) p. 33, (*b*) p. 57, (*c*) pp. 62—64.

Leden's linear-extrapolation method this is unlikely to be true since the abscissa is the free-ligand concentration and the ordinate is a function of the total metal, free-metal, and free-ligand concentrations, so that it is likely that a similar magnitude of error will be present in both the abscissa and the ordinate.

The non-linear least-squares analysis of the data was achieved using the computer program DALSFEK.[13,14] The equilibria to be considered together with guessed values of the stability constants were the input. The variables were then adjusted simultaneously in order to minimise the variance between the observed and calculated e.m.f.s. Although there is no perfect method for estimating the 'goodness of fit' of a non-linear least-squares treatment, the Hamilton $R$ factor has previously been shown [15] to give a reasonable and statistically acceptable basis for the comparison of several models. A number of models were tested, using this factor, defined in equation (14), to estimate the goodness of fit. The significance limit for $R$ ($R_{\text{limit}}$) is defined according to equation (15) in which $\varepsilon_i$ is

$$R = \left[ \sum_{i=1}^{N} (\text{e.m.f.}_i^{\text{calc.}} - \text{e.m.f.}_i^{\text{obs.}})^2 / \sum_{i=1}^{N} (\text{e.m.f.}_i^{\text{obs.}})^2 \right]^{\frac{1}{2}} \quad (14)$$

the residual in the $i$th equation calculated from pessimistic

$$R_{\text{limit}} = \left[ \sum_{i=1}^{I} \varepsilon_i^2 \Big/ \sum_{i=1}^{I} (\text{e.m.f.}_i^{\text{obs.}})^2 \right]^{\frac{1}{2}} \quad (15)$$

estimates of the errors in all the experimental quantities (e.m.f. readings, ±0.15 mV; total olefin concentration, ±1%; total silver concentration, ±1%) using the normal rules for the propagation of error. When $R < R_{\text{limit}}$ a model can be regarded as a satisfactory fit to the data; furthermore, two models that both yield values of $R$ that are less than $R_{\text{limit}}$ are statistically indistinguishable.

(c) *Comparison of the two calculation procedures*. The results in Table 2 allow a comparison of the two calculation procedures for two cases.

(*i*) Allyl alcohol in water, where the Leden calculation suggested that only equilibria (1) and (2) were present and where the non-linear approach was merely used to confirm the validity of the approximations in the linear extrapolation. It is apparent that addition of equilibrium (4) in the non-linear treatment causes very little difference to the 'goodness of fit' as detected by the Hamilton $R$ factor. In such cases the simplest model should be considered as the most chemically significant. It is apparent that $K_1$ and $K_2$ calculated by the linear-extrapolation approach are, within experimental error, equal to values obtained from the non-linear procedure, indicating that the approximations inherent in the linear approach are valid.

(*ii*) The second case involves pent-4-en-1-ol in water where the linear calculation gave $K_1$ and $K_2$ values that were dependent on the silver-ion concentration indicating the presence of equilibrium (4). In agreement with this, inclusion of equilibrium (4) in the non-linear data treatment led to an improvement in the 'goodness of fit' as detected by the Hamilton $R$ factor. This improvement is not however statistically significant since both $R$ values are below $R_{\text{limit}}$.[15] In view of this, and because the values of $K_1$ and $K_2$ obtained by the linear treatment are within experimental error of those obtained by the non-linear treatment, together with the fact that no other system gave as much evidence for the presence of $[\text{Ag}_2(\text{HL})]^{2+}$ species as pent-4-en-1-ol in water, all the equilibrium constants given in Table 3 and considered subsequently in this paper were obtained by the linear data-treatment approach. The final equilibrium constants in Table 3 were obtained by combining the results from calculations based on the e.m.f.s from each pair of electrodes using equations (16) and (17),[12c] where the subscripts $a$, $b$, and $c$ refer to equilibrium constants from a single pair of electrodes.

$$K_{\text{mean}} = \frac{1}{\sigma_a^{-2} + \sigma_b^{-2} + \sigma_c^{-2} + \ldots} \left( \frac{K_a}{\sigma_a^2} + \frac{K_b}{\sigma_b^2} + \frac{K_c}{\sigma_c^2} + \ldots \right) \quad (16)$$

$$\sigma_{\text{mean}}^{-2} = \sigma_a^{-2} + \sigma_b^{-2} + \sigma_c^{-2} + \ldots \quad (17)$$

*Determination of Enthalpy and Entropy Values*.—Enthalpy and entropy values (Table 4) were obtained by preparing plots of $\log_{10}K_1$ against $1/T$ and determining the best straight line by a least-squares technique. This latter approach was deemed necessary since Edwards [16] has shown that a visual determination of the best straight line can lead to large but mutually compensating errors in $\Delta H$ and $\Delta S$. Since only three points were available for each plot a precise estimate of the error was not possible. The error was estimated by taking the maximum possible value of $\log_{10}K_1$ at 45 °C, as indicated by the estimated error in $K_1$ at 45 °C, and the minimum possible value at 25 °C and recalculating the values of $\Delta H^\ominus$ and $\Delta S^\ominus$.

TABLE 2

Comparison of the linear and non-linear data treatments for allyl alcohol and pent-4-en-1-ol in water at 25 °C

| | | Non-linear data treatment | | | |
|---|---|---|---|---|---|
| Olefin | Equilibria considered | $K(\sigma)$ * | $10^3R$ | $10^3R_{\text{limit}}$ | Linear data treatment, $K(\sigma)$ * |
| Allyl alcohol | (1) and (2) | $K_1$ 17.84 (0.05) | 1.84 | 8.41 | $K_1$ 17.91 (0.19) |
| | | $K_2$ 0.65 (0.06) | | | $K_2$ 0.59 (0.21) |
| | (1), (2), and (4) | $K_1$ 17.82 (1.05) | 1.85 | 8.41 | |
| | | $K_2$ 0.66 (2.9) | | | |
| | | $K_{\frac{1}{2}}$ 0.09 (2.8) | | | |
| Pent-4-en-1-ol | (1) and (2) | $K_1$ 90.54 (0.16) | 2.31 | 6.46 | $K_1$ 91.20 (0.73) |
| | | $K_2$ 2.48 (0.15) | | | $K_2$ 2.30 (0.17) |
| | (1), (2), and (4) | $K_1$ 91.03 (0.18) | 0.99 | 6.46 | |
| | | $K_2$ 2.34 (0.49) | | | |
| | | $K_{\frac{1}{2}}$ 0.42 (0.55) | | | |

* Standard deviations ($\sigma$) are shown in parentheses.

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[13] R. M. Alcock, Ph.D. Thesis, University of Southampton, 1976.

[14] R. M. Alcock, F. R. Hartley, and D. E. Rogers, unpublished work.

[15] A. Vacca, A. Sabatini, and M. A. Gristina, *Co-ordination Chem. Rev.*, 1972, **8**, 45.

[16] J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta*, 1974, **11**, 47.

TABLE 3

Stability constants for the formation of the silver–olefin complexes $[Ag(HL)]^+$ ($K_1$) and $[Ag(HL)_2]^+$ ($K_2$) [a]

| | | | $K_1(\sigma)$ [c]/dm³ mol⁻¹ | | $K_2(\sigma)$ [c]/dm³ mol⁻¹ | |
|---|---|---|---|---|---|---|
| Solvent | Olefin | $\theta_c$ [b]/°C | calculated values [d] | combined value [e] | calculated values [d] | combined value [e] |
| Water | *trans*-but-2-en-1-ol | 25 | 6.59 (0.12)<br>6.46 (0.12) | 6.53 (0.09) | | |
| | | 35 | 5.03 (0.11)<br>4.94 (0.11) | 4.99 (0.08) | | |
| | | 45 | 3.89 (0.11)<br>3.82 (0.11) | 3.86 (0.08) | | |
| | | 25 [f] | 6.44 (0.12)<br>6.46 (0.12) | 6.45 (0.09) | | |
| | prop-2-en-1-ol | 25 | 17.82 (0.20)<br>17.95 (0.20) | 17.89 (0.14) | 0.69 (0.24)<br>0.56 (0.24) | 0.63 (0.17) |
| | | 35 | 14.59 (0.18)<br>14.20 (0.18) | 14.40 (0.13) | 0.75 (0.26)<br>1.22 (0.27) | 0.98 (0.19) |
| | | 45 | 11.12 (0.15)<br>11.18 (0.15) | 11.15 (0.11) | 1.67 (0.31)<br>1.31 (0.30) | 1.49 (0.22) |
| | | 25 [f] | 18.00 (0.19)<br>17.90 (0.19) | 17.95 (0.13) | 0.36 (0.22)<br>0.51 (0.22) | 0.44 (0.16) |
| | but-3-en-1-ol | 25 | 63.09 (0.49)<br>63.47 (0.49) | 63.28 (0.35) | 2.89 (0.20)<br>2.76 (0.20) | 2.83 (0.14) |
| | | 35 | 46.97 (0.38)<br>47.19 (0.38) | 47.08 (0.27) | 2.09 (0.20)<br>2.13 (0.20) | 2.11 (0.14) |
| | | 45 | 34.68 (0.30)<br>34.58 (0.30) | 34.63 (0.21) | 2.02 (0.21)<br>2.18 (0.21) | 2.10 (0.15) |
| | | 25 [f] | 64.46 (0.48)<br>64.41 (0.48) | 64.43 (0.34) | 1.93 (0.18)<br>1.97 (0.18) | 1.95 (0.13) |
| | pent-4-en-1-ol | 25 | 91.54 (0.64)<br>91.58 (0.64) | 91.56 (0.45) | 2.25 (0.19)<br>2.12 (0.19) | 2.19 (0.13) |
| | | 35 | 64.54 (0.48)<br>64.55 (0.48) | 64.55 (0.34) | 2.10 (0.19)<br>2.18 (0.19) | 2.14 (0.13) |
| | | 45 | 47.20 (0.37)<br>46.89 (0.37) | 47.05 (0.26) | 1.78 (0.19)<br>2.00 (0.19) | 1.89 (0.13) |
| | | 25 [f] | 91.91 (0.65)<br>91.91 (0.65) | 91.91 (0.46) | 1.90 (0.17)<br>2.02 (0.17) | 1.96 (0.12) |
| | hex-5-en-1-ol | 25 | 110.6 (1.0)<br>108.8 (1.0) | 109.7 (0.71) | 6.74 (0.82)<br>8.50 (0.84) | 7.62 (0.59) |
| | | 35 | 77.21 (0.77)<br>76.99 (0.77) | 77.10 (0.54) | 5.28 (0.83)<br>5.71 (0.84) | 5.50 (0.59) |
| | | 45 | 53.75 (0.64)<br>54.93 (0.64) | 54.39 (0.45) | 10.24 (0.96)<br>7.89 (0.96) | 9.07 (0.68) |
| | | 25 [f] | 112.6 (0.95)<br>112.6 (0.95) | 112.6 (0.67) | 4.63 (0.63)<br>4.53 (0.63) | 4.58 (0.45) |
| Methanol | *trans*-but-2-en-1-ol | 24.6 | 3.52 (0.09)<br>3.62 (0.09) | 3.57 (0.06) | | |
| | | 35 | 2.91 (0.08)<br>2.85 (0.08) | 2.88 (0.06) | | |
| | | 45 | 2.42 (0.08)<br>2.32 (0.08) | 2.37 (0.06) | | |
| | | 25 [f] | 3.41 (0.08)<br>3.48 (0.08) | 3.45 (0.06) | | |
| | prop-2-en-1-ol | 24.6 | 12.37 (0.14)<br>12.24 (0.14) | 12.31 (0.10) | 0.22 (0.19)<br>0.33 (0.19) | 0.28 (0.13) |
| | | 35 | 9.81 (0.12)<br>9.78 (0.12) | 9.80 (0.08) | 0.21 (0.21)<br>0.32 (0.21) | 0.27 (0.15) |
| | | 45 | 7.87 (0.12)<br>7.72 (0.12) | 7.80 (0.08) | | |
| | | 25 [f] | 11.94 (0.15)<br>12.21 (0.15) | 12.08 (0.10) | 0.32 (0.24)<br>0.07 (0.24) | 0.20 (0.17) |
| | but-3-en-1-ol | 24.6 | 47.08 (0.35)<br>47.52 (0.35) | 47.30 (0.25) | 2.18 (0.15)<br>2.17 (0.15) | 2.18 (0.10) |
| | | 35 | 37.45 (0.28)<br>36.80 (0.28) | 37.18 (0.20) | 1.25 (0.15)<br>1.46 (0.15) | 1.36 (0.10) |
| | | 45 | 29.56 (0.24)<br>29.07 (0.24) | 29.25 (0.17) | 1.13 (0.16)<br>1.23 (0.16) | 1.18 (0.11) |
| | | 25 [f] | 47.75 (0.35)<br>47.89 (0.35) | 47.83 (0.25) | 1.57 (0.14)<br>1.69 (0.14) | 1.63 (0.10) |
| | pent-4-en-1-ol | 24.6 | 29.38 (0.24)<br>30.03 (0.24) | 29.71 (0.17) | 0.96 (0.15)<br>0.72 (0.15) | 0.84 (0.10) |
| | | 35 | 21.88 (0.19)<br>21.88 (0.19) | 21.88 (0.13) | 0.77 (0.16)<br>0.63 (0.16) | 0.70 (0.11) |
| | | 45 | 17.47 (0.16)<br>17.43 (0.16) | 17.45 (0.11) | 0.35 (0.17)<br>0.41 (0.17) | 0.38 (0.12) |
| | | 25 [f] | 29.75 (0.23)<br>29.32 (0.23) | 29.52 (0.16) | 0.33 (0.14)<br>0.35 (0.14) | 0.34 (0.10) |
| | hex-5-en-1-ol | 24.6 | 32.77 (0.25)<br>32.69 (0.25) | 32.73 (0.18) | 0.47 (0.14)<br>0.46 (0.14) | 0.47 (0.10) |
| | | 35 | 24.68 (0.20)<br>24.77 (0.20) | 24.73 (0.14) | 0.39 (0.15)<br>0.33 (0.15) | 0.36 (0.10) |
| | | 45 | 18.86 (0.17)<br>19.12 (0.17) | 18.99 (0.12) | 0.36 (0.16)<br>0.04 (0.16) | 0.20 (0.11) |
| | | 25 [f] | 32.49 (0.25)<br>32.13 (0.25) | 32.31 (0.18) | 0.21 (0.13)<br>0.39 (0.13) | 0.30 (0.09) |

TABLE 3 (*Continued*)

| Solvent | Olefin | $\theta_c$ [b]/°C | $K_1(\sigma)$ [c]/dm³ mol⁻¹ |  | $K_2(\sigma)$ [c]/dm³ mol⁻¹ |  |
|---|---|---|---|---|---|---|
|  |  |  | calculated values [d] | combined value [e] | calculated values [d] | combined value [e] |
| Ethanol | *trans*-but-2-en-1-ol | 25 | 1.21 (0.08)<br>1.22 (0.08) | 1.22 (0.06) |  |  |
|  |  | 35 | 1.00 (0.08)<br>0.97 (0.08) | 0.99 (0.06) |  |  |
|  |  | 45 | 0.75 (0.08)<br>0.73 (0.08) | 0.74 (0.06) |  |  |
|  |  | 25 [f] | 1.17 (0.08)<br>1.16 (0.08) | 1.17 (0.06) |  |  |
|  | prop-2-en-1-ol | 25 | 5.80 (0.10)<br>5.77 (0.10) | 5.79 (0.07) | 0.23 (0.27)<br>0.29 (0.27) | 0.26 (0.19) |
|  |  | 35 | 4.65 (0.09)<br>4.67 (0.09) | 4.66 (0.06) | 0.48 (0.31)<br>0.34 (0.31) | 0.41 (0.22) |
|  |  | 45 | 3.87 (0.09)<br>3.84 (0.09) | 3.86 (0.06) | 0.61 (0.34)<br>0.57 (0.36) | 0.59 (0.25) |
|  |  | 25 [f] | 5.89 (0.10)<br>5.82 (0.10) | 5.86 (0.07) | 0.14 (0.26)<br>0.29 (0.26) | 0.22 (0.18) |
|  | but-3-en-1-ol | 25 | 21.82 (0.20)<br>21.69 (0.20) | 21.76 (0.14) | 1.24 (0.18)<br>1.31 (0.19) | 1.28 (0:13) |
|  |  | 35 | 17.29 (0.17)<br>17.09 (0.17) | 17.19 (0.12) | 1.27 (0.20)<br>1.40 (0.20) | 1.34 (0.14) |
|  |  | 45 | 13.92 (0.15)<br>13.84 (0.15) | 13.88 (0.11) | 1.28 (0.21)<br>1.30 (0.21) | 1.29 (0.15) |
|  |  | 25 [f] | 21.72 (0.20)<br>21.54 (0.20) | 21.63 (0.14) | 1.36 (0.17)<br>1.61 (0.18) | 1.49 (0.13) |
|  | pent-4-en-1-ol | 25 | 11.09 (0.14)<br>11.00 (0.14) | 11.05 (0.10) | 0.19 (0.27)<br>0.34 (0.27) | 0.27 (0.19) |
|  |  | 35 | 8.83 (0.13)<br>8.59 (0.13) | 8.62 (0.09) | 0.39 (0.31)<br>0.39 (0.31) | 0.39 (0.22) |
|  |  | 45 | 6.56 (0.12)<br>6.74 (0.12) | 6.65 (0.08) | 0.31 (0.39)<br>0.39 (0.38) | 0.35 (0.28) |
|  |  | 25 [f] | 10.70 (0.14)<br>10.70 (0.14) | 10.70 (0.11) | 0.24 (0.28)<br>0.34 (0.28) | 0.29 (0.20) |
|  | hex-5-en-1-ol | 25 | 10.96 (0.16)<br>11.17 (0.16) | 11.07 (0.11) | 0.41 (0.36)<br>0.08 (0.35) | 0.25 (0.25) |
|  |  | 35 | 8.45 (0.15)<br>8.40 (0.15) | 8.43 (0.11) | 0.40 (0.42)<br>0.47 (0.42) | 0.44 (0.30) |
|  |  | 45 | 6.67 (0.14)<br>6.77 (0.14) | 6.72 (0.10) | 0.52 (0.49)<br>0.41 (0.48) | 0.47 (0.35) |
|  |  | 25 [f] | 11.14 (0.16)<br>11.13 (0.16) | 11.14 (0.11) | 0.11 (0.34)<br>0.20 (0.34) | 0.16 (0.24) |
| Propylene carbonate | *trans*-but-2-en-1-ol | 25 | 29.62 (0.73)<br>29.58 (0.73) | 29.60 (0.52) | 2.22 (0.91)<br>2.29 (0.91) | 2.26 (0.64) |
|  |  | 35 | 22.14 (0.63)<br>22.18 (0.63) | 22.16 (0.45) | 1.90 (1.02)<br>1.71 (1.02) | 1.81 (0.72) |
|  |  | 45 | 18.88 (0.58)<br>18.85 (0.58) | 18.87 (0.41) | 1.98 (1.09)<br>1.92 (1.09) | 1.95 (0.77) |
|  | prop-2-en-1-ol | 25 | 102.8 (1.4)<br>102.6 (1.4) | 102.7 (1.0) | 5.21 (0.51)<br>5.16 (0.51) | 5.19 (0.36) |
|  |  | 35 | 70.82 (1.02)<br>70.72 (1.02) | 70.77 (0.72) | 3.99 (0.47)<br>3.89 (0.47) | 3.94 (0.33) |
|  |  | 45 | 52.79 (0.82)<br>52.71 (0.83) | 52.75 (0.57) | 3.15 (0.49)<br>3.11 (0.49) | 3.13 (0.35) |
|  | but-3-en-1-ol | 25 | 652.5 (7.9)<br>649.2 (7.9) | 650.9 (5.6) | 58.44 (0.78)<br>58.47 (0.78) | 58.46 (0.55) |
|  |  | 35 | 402.3 (4.9)<br>402.0 (4.9) | 402.2 (3.5) | 39.90 (0.91)<br>39.39 (0.90) | 39.65 (0.64) |
|  |  | 45 | 280.9 (3.5)<br>280.6 (3.5) | 280.8 (2.5) | 29.17 (0.86)<br>29.16 (0.86) | 29.17 (0.61) |
|  | pent-4-en-1-ol | 25 | 210.3 (2.62)<br>211.8 (2.61) | 211.1 (1.9) | 9.88 (0.94)<br>8.81 (0.92) | 9.35 (0.66) |
|  |  | 35 | 141.9 (1.98)<br>141.7 (1.97) | 141.8 (1.40) | 7.38 (0.99)<br>7.04 (0.99) | 7.21 (0.70) |
|  |  | 45 | 104.4 (1.61)<br>104.5 (1.60) | 104.5 (1.14) | 6.33 (1.03)<br>6.04 (1.03) | 6.19 (0.73) |
|  | hex-5-en-1-ol | 25 | 182.5 (2.24)<br>183.0 (2.24) | 182.8 (1.58) | 4.88 (0.82)<br>4.62 (0.82) | 4.75 (0.58) |
|  |  | 35 | 124.0 (1.46)<br>123.8 (1.43) | 123.9 (1.03) | 4.73 (0.22)<br>4.75 (0.22) | 4.74 (0.15) |
|  |  | 45 | 94.69 (1.46)<br>95.18 (1.46) | 94.91 (1.03) | 5.19 (0.93)<br>4.76 (0.93) | 4.98 (0.66) |

[a] $K_1$ and $K_2$ are defined by equations (1) and (2). [b] Silver-ion concentrations were *ca.* 0.01 mol dm⁻³ unless stated otherwise. [c] Standard deviations are given in parentheses. [d] The titration was performed twice for each unsaturated alcohol at each temperature; both values are quoted. [e] The combined stability constants and standard deviations were obtained according to equations (16) and (17). [f] Data refer to a silver-ion concentration of *ca.* 0.005 mol dm⁻³.

## DISCUSSION

The solvent dependence of the stability constants of each of the olefins studied follows the order propylene carbonate > water > methanol > ethanol. This order is that expected on the basis of competition between the olefin and the solvent for co-ordination to $Ag^+$, since the basicity of these solvents decreases in the order[17,18] ethanol > methanol > water > propylene carbonate. No olefin complexes could be detected in acetonitrile, which forms a stronger complex than any of the other solvents with $Ag^I$.

In all the four solvents the introduction of a methyl group on to the double bond of prop-2-en-1-ol led to a significant reduction in the stability constant, as reported previously by several groups.[1] Analysis of the ratio of the stability constants for prop-2-en-1-ol and *trans*-but-2-en-1-ol showed this to be solvent dependent increasing in the order water (2.75) < propylene carbonate (3.44) ~ methanol (3.45) < ethanol (4.75). The increase in this ratio in the hydroxylic solvents with increasing steric bulk of the solvent implies that at least part of the lower stability of the but-2-en-1-ol complex arises from interaction between the methyl group co-ordinated at the double bond and the solvent ligands co-ordinated to the silver(I) ion.

TABLE 4

Thermodynamic quantities (kJ mol⁻¹) determined for $[Ag(HL)]^+$ complexes *

| Solvent | Olefin | $\Delta H_{298}^{\ominus}$ | $T\Delta S_{298}^{\ominus}$ | $\Delta G_{298}^{\ominus}$ |
|---|---|---|---|---|
| Water | *trans*-but-2-en-1-ol | −20.8 (1.2) | −16.1 (1.2) | −4.65 (0.03) |
| | prop-2-en-1-ol | −18.6 (0.7) | −11.4 (1.1) | −7.15 (0.02) |
| | but-3-en-1-ol | −23.8 (0.5) | −13.4 (0.4) | −10.28 (0.02) |
| | pent-4-en-1-ol | −26.3 (0.2) | −15.0 (0.2) | −11.20 (0.01) |
| | hex-5-en-1-ol | −27.7 (0.6) | −16.0 (0.6) | −11.65 (0.01) |
| Methanol | *trans*-but-2-en-1-ol | −15.8 (1.4) | −12.7 (1.5) | −3.16 (0.06) |
| | prop-2-en-1-ol | −17.6 (0.7) | −11.4 (0.7) | −6.22 (0.02) |
| | but-3-en-1-ol | −18.6 (0.5) | −9.0 (0.4) | −9.56 (0.02) |
| | pent-4-en-1-ol | −20.6 (0.5) | −12.2 (0.5) | −8.41 (0.01) |
| | hex-5-en-1-ol | −21.0 (0.4) | −12.4 (0.5) | −8.65 (0.01) |
| Ethanol | *trans*-but-2-en-1-ol | −19.6 (4.6) | −19.0 (4.4) | −0.48 (0.12) |
| | prop-2-en-1-ol | −16.0 (1.1) | −11.6 (1.1) | −4.35 (0.03) |
| | but-3-en-1-ol | −17.7 (0.6) | −10.0 (0.6) | −7.64 (0.01) |
| | pent-4-en-1-ol | −20.0 (0.9) | −14.0 (0.9) | −5.96 (0.02) |
| | hex-5-en-1-ol | −19.7 (1.0) | −13.7 (0.9) | −5.96 (0.03) |
| Propylene carbonate | *trans*-but-2-en-1-ol | −17.8 (1.6) | −9.4 (1.6) | −8.40 (0.04) |
| | prop-2-en-1-ol | −26.3 (0.8) | −14.8 (0.8) | −11.49 (0.02) |
| | but-3-en-1-ol | −33.2 (0.8) | −17.1 (0.8) | −16.06 (0.02) |
| | pent-4-en-1-ol | −27.8 (0.8) | −14.5 (0.8) | −13.27 (0.02) |
| | hex-5-en-1-ol | −25.8 (0.7) | −12.8 (0.7) | −12.90 (0.02) |

* Estimated errors (see text) are given in parentheses.

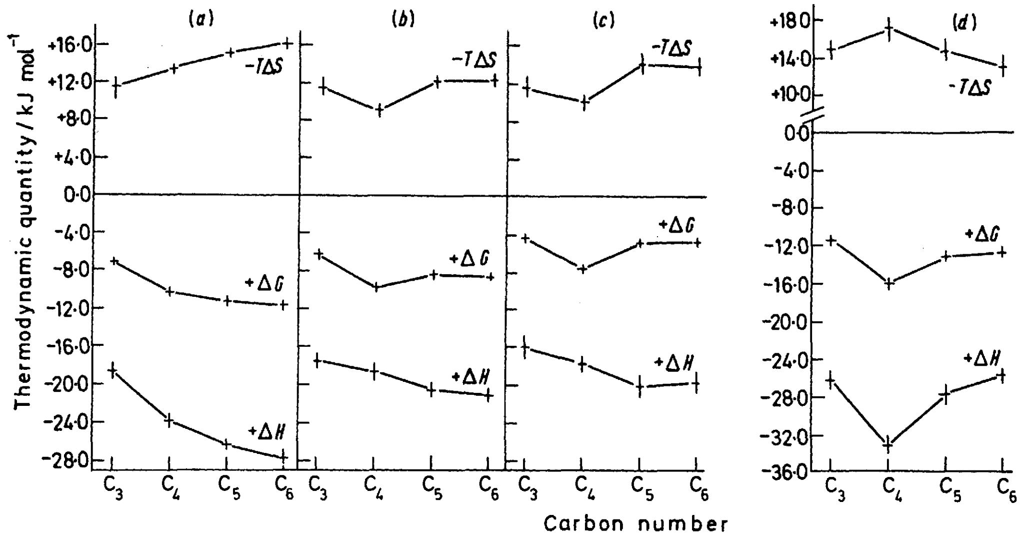

FIGURE 2 Plots of thermodynamic quantities (kJ mol⁻¹) against carbon number for unsaturated alcohols in (*a*) water, (*b*) methanol, (*c*) ethanol, and (*d*) propylene carbonate (note the break in the scale of the vertical axis for propylene carbonate)

Plots of the free-energy, enthalpy, and entropy data for equilibrium (1) against carbon number (Figure 2) show two important features.

(*i*) The free-energy changes in water and propylene carbonate parallel the enthalpy changes, but are opposite to the entropy changes in this solvent. In contrast in

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[17] J. Long and B. Munson, *J. Amer. Chem. Soc.*, 1973, **95**, 2427.

[18] B. Case, 'Reactions of Molecules at Electrodes,' ed. N. S. Hush, Wiley-Interscience, London, 1971, p. 45.

each of the alcoholic solvents the free-energy changes parallel the entropy rather than the enthalpy changes. This behaviour clearly indicates the complexity of factors that influence the solvent dependence of silver(I)–olefin stability constants as reflected in the previous data cited in Table 1.

It is impossible to deduce which factors dominate the observed enthalpy and entropy changes. This is due to the number of factors involved and their mutually conflicting effects. Thus complex formation in any solvent can be considered as involving the steps (18)—(21). The

$$\text{HL}\cdot\text{solvent} \rightleftharpoons \text{HL} + \text{solvent};\ \Delta H_1^{\ominus}, \Delta S_1^{\ominus} \quad (18)$$

$$\text{Ag}^+\cdot\text{solvent} \rightleftharpoons \text{Ag}^+ + \text{solvent};\ \Delta H_2^{\ominus}, \Delta S_2^{\ominus} \quad (19)$$

$$\text{HL} + \text{Ag}^+ \rightleftharpoons [\text{Ag(HL)}]^+;\ \Delta H_3^{\ominus}, \Delta S_3^{\ominus} \quad (20)$$

$$\text{solvent} + [\text{Ag(HL)}]^+ \rightleftharpoons [\text{Ag(HL)}]^+\cdot\text{solvent};\ \Delta H_4^{\ominus}, \Delta S_4^{\ominus} \quad (21)$$

observed enthalpy and entropy changes are then given by equations (22) and (23). In comparing the observed

$$\Delta H_{\text{obs.}}^{\ominus} = \Delta H_1^{\ominus} + \Delta H_2^{\ominus} + \Delta H_3^{\ominus} + \Delta H_4^{\ominus} \quad (22)$$

$$\Delta S_{\text{obs.}}^{\ominus} = \Delta S_1^{\ominus} + \Delta S_2^{\ominus} + \Delta S_3^{\ominus} + \Delta S_4^{\ominus} \quad (23)$$

enthalpy changes for two olefins, $\Delta H_2^{\ominus}$ can be neglected since it is a common term. Now in all the four solvents $\Delta H_{\text{obs.}}^{\ominus}$ (prop-2-en-1-ol) $>$ $\Delta H_{\text{obs.}}^{\ominus}$ (pent-4-en-1-ol). Since the solvation of the olefins is largely effected by their hydroxyl groups (this will be true even in propylene carbonate since hex-5-en-1-ol is soluble in this solvent whereas hex-1-ene is not), $\Delta H_1^{\ominus}$ for prop-2-en-1-ol must be more positive than $\Delta H_1^{\ominus}$ for pent-4-en-1-ol, so that olefin-solvation effects alone predict $\Delta H_{\text{obs.}}^{\ominus}$ (prop-2-en-1-ol) $>$ $\Delta H_{\text{obs.}}^{\ominus}$ (pent-4-en-1-ol). The solvation of the $[\text{Ag(HL)}]^+$ complex ($\Delta H_4^{\ominus}$) will be greater for prop-2-en-1-ol than for pent-4-en-1-ol, so that this term would predict $\Delta H_{\text{obs.}}^{\ominus}$ (prop-2-en-1-ol) $<$ $\Delta H_{\text{obs.}}^{\ominus}$ (pent-4-en-1-ol). Clearly these mutually opposite solvation effects ensure that we can make no predictions from the present data as to the influence of the olefin on the enthalpy of formation of the silver(I)–olefin bond ($\Delta H_3^{\ominus}$). Exactly analogous arguments and conclusions apply to the entropy terms.

(*ii*) Whilst the free energy and entropy plots for water as solvent are smooth curves, for reactions in the other solvents each of these plots shows a sharp discontinuity at but-3-en-1-ol ($C_4$). This discontinuity, which especially favours complex formation by but-3-en-1-ol, is ascribed to chelate formation [19,20] which results in an increased number of solvent molecules being displaced from $\text{Ag}^{\text{I}}$ on olefin complex formation. Since chelate formation (Figure 3) involves hydroxyl group co-ordination to $\text{Ag}^{\text{I}}$, which is similar to the co-ordinate bond formed when methanol and ethanol are the solvents, it is not surprising that the enthalpy plots in Figure 2 for reactions in these two solvents show no discontinuity at but-3-en-1-ol. In propylene carbonate, which, as noted above, forms a weaker complex than the hydroxyl-group-containing solvents, there is a sharp favourable enthalpy change at but-3-en-1-ol as a consequence of chelate formation.

The extra stability of the but-3-en-1-ol complex consequent on chelate formation can be seen from Figure 2(*b*)—(*d*) to be *ca.* 2 kJ mol$^{-1}$. This is far less than is usually associated with chelation reactions involving ligands which are inherently stronger complexing groups than the solvent, for example nitrogen donors.[20] However, it is comparable to the 4.8—3.5 kJ mol$^{-1}$ observed previously [21,22] for but-1-enyl-thioether and -selenoether ligands respectively complexing to $\text{Ag}^{\text{I}}$. The thioether and selenoether groups in these latter ligands are both 'softer' than the present hydroxyl group and thus the incidence of chelation with the 'soft' silver(I) ion would be expected to be less in the case of the hydroxylic ligand. In addition the hydroxyl group of the unsaturated alcohol has to compete with similar groups on the solvent (propylene carbonate also co-ordinates through oxygen) so that the increase in stability due to chelate formation would be expected to be small in the present conditions. The lack of any evidence for chelation by but-3-en-1-ol in water is ascribed to competition between water and the ligand hydroxyl group, the small solvent molecule competing effectively for the co-ordination site. The 'five-and-a-half-membered' chelate ring cannot meet the usual linear geometry of two-co-ordinate $\text{Ag}^{\text{I}}$. However, the fact that silver(I) fluoride can be crystallised from solution as a tetrahydrate suggests that in water silver(I) ions probably exist as tetrahedral $[\text{Ag(OH}_2)_4]^+$; [23] this tetrahedral geometry could be maintained in the 'five-and-a-half-membered' chelate-ring complexes.

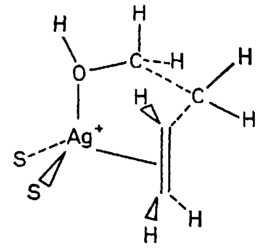

FIGURE 3 Probable structure of the silver(I)–but-3-en-1-ol chelate complex (S = solvent)

It should be noted that the present work has provided thermodynamic evidence in support of chelate-complex formation by but-3-en-1-ol which was suggested independently on the basis of free-energy data alone obtained in n-propanol in a paper published during the course of the present work.[24] The present data provide no evidence for any chelate formation by pent-4-en-1-ol and hex-5-en-1-ol, which also supports Novak *et al.*[24] in

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[19] A. E. Martell, *Adv. Chem. Ser.*, 1976, **62**, 272.

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refuting earlier suggestions based on partition-coefficient data that these latter unsaturated alcohols give rise to chelate-ring formation.[25] It is apparent that the cautions that we raised previously concerning the interpretation of partition-coefficient data [1] must be taken seriously even when comparing a series of homologous ligands.

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