DETERMINATION OF COMPLEX ASSOCIATION CONSTANTS FROM GAS CHROMATOGRAPHIC DATA

II. COMPLEXES OF SILVER IONS WITH SUBSTITUTED ALKENES IN ETHYLENE GLYCOL AT 40°C

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SUMMARY

Association constants of substituted alkenes with silver ions in ethylene glycol have been determined by means of a previously proposed gas chromatographic method.

The results have been interpreted in terms of the electronic and steric effects of the substituents and have given some indication of the type of bonding in these complexes.

Some data are given on the salting out of organic compounds by electrolyte solutions in ethylene glycol.

INTRODUCTION

In a previous paper[1], a method was described for the determination of complex association constants from gas chromatographic data. The novel features of this method are that the equilibria involved are represented in terms of activities (rather than concentrations, as is usually done) and that a reference solute is used. This has the advantage that activity coefficients partially cancel and that only *relative* retention volumes are required.

This method has now been applied to the determination of association constants of complexes of silver ions with substituted alkenes in ethylene glycol at 40°.

Alkene–silver ion complexes are both theoretically interesting and practically important, *e.g.*, for the gas chromatographic separation of alkene isomers[2–7] and the thin-layer chromatographic separation of unsaturated lipids and terpenes[8].

Our aims were (1) to demonstrate the application of the proposed method, (2) to assess the importance of electronic and steric effects of substituents on alkene–silver ion association and (3) to elucidate some details of the bonding in these complexes.

THEORETICAL

Determination of complex association constants from gas chromatographic data
The determination is based on eqn. 8a of ref. 1:

$$\frac{\left[\left(\frac{V_A}{V_{A^*}}\right)_{(S+B)} \cdot \left(\frac{V_{A^*}}{V_A}\right)_{(S+C)} - 1\right]}{x_B} = K_x \left(\frac{f_A f_B}{f_{AB}}\right)_{(S+B)} \tag{1}$$

where:

V = retention volume, corrected for the gas hold-up in the apparatus, at the mean column pressure and the column temperature.

A = complex-forming solute (in this instance an alkene).

A^* = solute that is closely related to A but does not form a complex (in this instance the corresponding saturated compound).

S = solvent (in this instance ethylene glycol).

B = complex-forming compound, dissolved in S (in this instance $AgNO_3$).

C = compound that is closely related to B but does not form a complex (in this instance $LiNO_3$).

x = mole fraction.

K_x = association constant (mole fraction scale).

f = activity coefficient (mole fraction scale).

In the present work we prefer to use the molality scale. Then eqn. 1 becomes:

$$\frac{\left[\left(\frac{V_A}{V_{A^*}}\right)_{(S+B)} \cdot \left(\frac{V_{A^*}}{V_A}\right)_{(S+C)} - 1\right]}{m_B} = K_m \left(\frac{\gamma_A \gamma_B}{\gamma_{AB}}\right)_{(S+B)} \tag{2}$$

It follows from eqn. 2 that, apart from m_B, only the ratios of the retention volumes of A and A^*, on columns containing the complex-forming stationary phase $S + B$ and the reference stationary phase $S + C$, must be measured. These ratios are simply equal to the ratios of the corresponding distances on the recorder chart. No knowledge of the amount of stationary phase, inlet and outlet pressure, room temperature, gas velocity and recorder chart speed is required. Further, any effects of adsorption of the solutes on the support or on the surface of the stationary phase, of non-zero sample size and non-ideality of the column on the retention volume will cancel out for a large part.

However, we determined also the individual retention volumes, so as to be able to judge if appropriate reference stationary phases and reference solutes had been chosen.

The standard solvent, in which the activity coefficients γ are by definition equal to unity, can be chosen arbitrarily. In the present instance, the most appropriate standard solvent is ethylene glycol. Accordingly, we determined the right-hand side of eqn. 2 for $m_B \approx 0.25$, 1, 2 and 3 M $AgNO_3$ and then calculated K_m in ethylene glycol by a linear extrapolation to $m_B = 0$ by the method of least squares.

Complexes of silver ions and unsaturated compounds
The bonding in these complexes can be described in the following way[9]: a

σ-type bond, which is the result of the donation of π-electrons from the occupied $2p$ bonding orbital of the unsaturated compound into the vacant $5s$ orbital of the silver ion, and a π-type bond, which is the result of back-donation of d-electrons from occupied $4d$ orbitals of the silver ion into the unoccupied π^*–$2p$ antibonding orbitals of the unsaturated compound.

Both the σ- and π-type bonds are important for complex stability. Their relative importance can be judged from the electronic effects of substituents on stability. An increased electron density at the carbon–carbon double bond should enhance σ-type formation and weaken the π-type bond.

The association constants of benzene[10] and styrene[11] derivatives are larger as the substituents are more electron-donating. Furthermore, a calculation of the stabilization energy due to delocalization of π-electrons from the occupied carbon $2p$ orbitals of the aromatic hydrocarbon to the $5s$ orbital of the silver ion, thus taking into account only σ-type bonding, has presented values which indeed are a measure of the relative stabilities of complexes of monosubstituted benzenes and styrenes[12, 13]. Consequently, σ-type bonding seems to enhance the stability of arene–silver ion complexes.

For alkene–silver ion complexes, the situation is less clear[14]. On the one hand, the association constants of vinyl derivatives seem to be larger as the substituents are more electron-donating[15]. However, it is possible that steric effects play a large role in this instance. On the other hand, from a theoretical analysis of the electronic structure of the cyclohexene–silver ion complex, it was concluded that the d-electrons of the silver ion contribute appreciably to the stabilization of alkene-silver ion complexes; from this it was concluded that the σ-type and π-type contributions might be equally important[16].

EXPERIMENTAL

Chemicals

The alkenes and the corresponding saturated compounds, of the purest quality available, were obtained from Fluka, Baker or Merck. Ethyl propyl ether was synthesized by the authors. Ethylene glycol, $AgNO_3$ and $LiNO_3$, all p.a. grade, were obtained from Merck, Drijfhout and U.C.B., respectively. Kieselguhr K, 150–200 mesh, washed with acid and alkali (Camag), was used as the support for the stationary phase.

Apparatus

A Becker gas chromatograph equipped with a flame ionization detector was used.

Procedure

Stainless-steel columns, length 2 m, I.D. 4 mm, were used.

To depress adsorption effects, a large amount of stationary phase (40 %) was used.

Columns containing the following stationary phases — ethylene glycol or 0.25, 1, 2 or 3 M $AgNO_3$ or 1, 2 or 3 M $LiNO_3$ — were prepared by dissolving the com-

ponents of the stationary phase in methanol, adding the support and evaporating the methanol in a rotating evaporator still at 40°. With the $AgNO_3$ columns, all manipulations were carried out in darkness and in a nitrogen atmosphere.

Notwithstanding these precautions, some decomposition of the $AgNO_3$ columns occurred during the preparation, during the measurements and even during storage at $-10°$ in a nitrogen atmosphere.

Therefore, measurements on a standard, n-heptene, were made each day when the columns were in use and also after completion of the determinations. Immediately afterwards, the molality of the silver nitrate was calculated from the amounts of silver nitrate and of stationary phase in the column. The former was determined by potentiometric titration of part of the column filling with 0.1 M NaCl, the latter by extraction of another part of the column filling with methanol. Then, the right-hand side of eqn. 2 was calculated for the standard n-heptene, and, assuming that its value is not influenced by the proceeding decomposition, the molality of the silver nitrate on each day when the columns had been in use was calculated.

To be able to calculate the individual retention volumes per gram of ethylene glycol, the amount of ethylene glycol in the reference columns was determined by drying the filling at 110°.

Samples of 2–250 μl of the vapour above a mixture of an alkene and the corresponding saturated compound were injected by means of Hamilton gas-tight syringes, together with some methane as a dead-volume marker. The amount of vapour was chosen so that a convenient peak height was observed. It was verified that variation of sample size from 5 to 50 μl, for heptane and heptene on ethylene glycol and 1 M $AgNO_3$, did not influence the retention volumes.

All measurements were made in duplicate.

RESULTS

The results are given in Tables I and II.

DISCUSSION

Choice of the reference stationary phase

One may raise the question whether it is necessary to use as the reference stationary phase a $LiNO_3$ solution of the same molality as that of the $AgNO_3$ in the complex-forming stationary phase, and whether pure ethylene glycol is not just as good a reference stationary phase.

This is equivalent to the question whether $(V_A*/V_A)_{S+C}$ depends on the $LiNO_3$ molality, which can be judged from the data in Table III.

It follows that $(V_A*/V_A)_{S+C}$ for normal and branched alkane–alkene pairs increases slightly with increasing $LiNO_3$ molality, whereas this ratio decreases slightly for substituted alkane–alkene pairs. It is therefore advisable to use $LiNO_3$ solutions of the appropriate molalities as reference stationary phases.

Choice of the reference solute

Whether or not the choice of the reference solute is very critical can be judged from the values of $V_A*_{(S+C)}/V_A*_{(S+B)}$ in Table IV.

TABLE I

NET RETENTION VOLUME, V (cm^3), PER GRAM OF ETHYLENE GLYCOL, AT THE MEAN COLUMN PRESSURE AND A COLUMN TEMPERATURE OF 40°

Solute	Stationary phase							
	Ethylene glycol	0.25 M AgNO$_3$	1 M LiNO$_3$	1 M AgNO$_3$	2 M LiNO$_3$	2 M AgNO$_3$	3 M LiNO$_3$	3 M AgNO$_3$
Propene	0.39	0.90	0.42	3.42	0.37	6.28	0.23	9.85
Butene-1	0.77	1.88	0.77	7.52	0.64	13.1	0.50	20.0
Pentene-1	1.28	2.94	1.30	10.9	1.07	18.5	0.82	26.3
Hexene-1	2.35	5.19	2.22	18.7	1.75	30.7	1.35	43.5
Heptene-1	4.05	8.68	3.69	30.5	2.88	47.7	2.14	66.0
Octene-1	6.79	14.2	6.05	48.5	4.70	73.5	3.58	99.7
3-Methylbutene-1	0.94	2.25	0.94	9.18	0.81	15.9	0.62	22.8
3,3-Dimethylbutene-1	1.15	2.55	1.09	9.87	0.89	16.3	0.67	23.9
2-Methylhexene-1	4.28	6.74	4.01	19.1	3.10	29.5	2.31	40.3
3-Methylhexene-1	2.79	5.59	2.62	19.1	2.03	30.1	1.52	41.5
4-Methylhexene-1	3.43	6.31	3.21	20.1	2.38	31.3	1.84	42.9
5-Methylhexene-1	3.10	6.72	2.93	24.2	2.24	38.6	1.63	53.4
Allyl chloride	16.4	18.6	16.3	30.3	13.8	39.7	11.5	53.9
Allyl bromide	34.8	149.6	34.6	199.6	29.1	216.1	24.1	250.6
Allyl iodide	71.9	152.4	69.2	198.0	57.8	215.4	46.9	251.8
Ethyl allyl ether	26.0	33.4	24.3	77.2	22.2	117.0	18.7	170.3
Allyl acetate	185.0	197.6	178.0	365.1	169.7	536.0	159.3	768.6
Propane	0.19	0.19	0.19	0.17	0.15	0.15	0.11	0.14
Butane	0.38	0.36	0.39	0.38	0.31	0.31	0.20	0.24
Pentane	0.74	0.77	0.73	0.70	0.61	0.63	0.42	0.44
Hexane	1.34	1.30	1.27	1.21	0.99	0.98	.76	0.78
Heptane	2.33	2.30	2.16	2.18	1.66	1.59	1.33	1.38
Octane	4.00	3.89	3.66	3.85	2.92	2.77	2.29	2.42
2-Methylbutane	0.62	0.59	0.60	0.60	0.53	0.53	0.41	0.41
2,2-Dimethylbutane	0.78	0.77	0.79	0.80	0.63	0.63	0.52	0.53
2-Methylhexane	1.75	1.76	1.69	1.64	1.29	1.33	1.03	1.07
3-Methylhexane	2.06	2.02	1.92	1.93	1.53	1.49	1.20	1.27
Propyl chloride	10.1	10.3	10.0	10.9	8.30	9.45	6.85	8.63
Propyl bromide	20.9	21.9	20.8	26.8	17.1	82.5	13.9	70.6
Propyl iodide	40.9	101.8	39.7	103.6	32.6	83.6	25.9	71.8
Ethyl propyl ether	14.3	13.6	13.3	13.9	11.7	11.3	9.5	10.0
Propyl acetate	132.8	123.5	127.0	128.4	121.2	107.6	114.4	96.3

TABLE II

DECREASE OF THE AgNO$_3$ MOLALITY, m_B

0.25 M AgNO$_3$		1 M AgNO$_3$		2 M AgNO$_3$		3 M AgNO$_3$	
Date	m_B	Date	m_B	Date	m_B	Date	m_B
10.11.1971	0.19	15.10.1971	0.97	22.10.1971	1.92	29.10.1971	3.00
11.11.1971	0.17	18.10.1971	0.95	25.10.1971	1.90	1.11.1971	2.99
12.11.1971	0.15	19.10.1971	0.94	26.10.1971	1.84	2.11.1971	2.97
22. 3.1972	0.14	20.10.1971	0.91	27.10.1971	1.79	3.11.1971	2.93
		28. 3.1972	0.88	29. 3.1971	1.75	4. 4.1972	2.86

TABLE III

INFLUENCE OF THE LiNO$_3$ MOLALITY ON V_A*/V_A

Alkane–alkene	Stationary phase			
	Ethylene glycol	$1 \ M \ LiNO_3$	$2 \ M \ LiNO_3$	$3 \ M \ LiNO_3$
Hexane–hexene-1	0.57	0.57	0.57	0.57
Heptane–heptene-1	0.57	0.58	0.58	0.62
Octane–octene-1	0.59	0.61	0.62	0.64
2-Methylhexane–2-methylhexene-1	0.41	0.42	0.42	0.45
3-Methylhexane–3-methylhexene-1	0.74	0.73	0.76	0.78
3-Methylhexane–4-methylhexene-1	0.60	0.60	0.64	0.66
2-Methylhexane–5-methylhexene-1	0.56	0.58	0.58	0.64
Propyl chloride–allyl chloride	0.62	0.62	0.60	0.59
Propyl bromide–allyl bromide	0.60	0.60	0.60	0.59
Propyl iodide–allyl iodide	0.57	0.57	0.56	0.55
Ethyl propyl ether–ethyl allyl ether	0.55	0.55	0.53	0.51
Propyl acetate–allyl acetate	0.72	0.71	0.71	0.72

TABLE IV

VALUES OF $V_A*(s+c)/V_A*(s+n)$

Solute	Molality				
	0.25	1	2	3	Mean
Hexane	1.03	1.04	1.01	0.98	1.02
Heptane	1.02	0.99	1.04	0.96	1.00
Octane	1.03	0.95	1.05	0.94	0.99
2-Methylhexane	0.99	1.03	0.97	0.96	0.99
3-Methylhexane	1.02	1.00	1.02	0.94	1.00
Ethyl propyl ether	1.05	0.96	1.03	0.94	0.99
Propyl acetate	1.07	0.99	1.13	1.19	
Propyl chloride	0.98	0.91	0.88	0.79	
Propyl bromide	0.95	0.78	0.21	0.20	
Propyl iodide	0.40	0.38	0.39	0.36	

It follows that three cases can be distinguished:

(1) for normal or branched alkanes and ethyl propyl ether, neither the individual values of $V_A*(s+c)/V_A*(s+B)$ at the various molalities nor their means show any effect of size or shape of the alkane, the ratios being close to unity;

(2) for the strongly polar propyl acetate, the ratio is much greater than unity;

(3) for the propyl halides, the ratio is much less than unity. This is probably caused by complex formation of the alkyl halides with silver ion[17]. For propyl chloride, an association constant $K_m = 0.09$ is found (omitting the reference solute). This association constant is so small that we think it is possible to determine the association constant of silver ion with the double bond in allyl chloride, using propyl chloride as the reference solute. For propyl bromide and iodide, the values of $K_m \gamma_{AB}/\gamma_{AB}$ are larger and vary irregularly with the silver nitrate molality. Consequently, we think it is impossible to determine the association constant of silver ion with the double bond in allyl bromide or iodide.

Association constants

The values of $K_m\gamma_A\gamma_B/\gamma_{AB}$ and K_m are given in Table V. A representative example of the extrapolation of the values of $K_m\gamma_A\gamma_B/\gamma_{AB}$ to K_m is shown in Fig. 1.

Also given in Table V, for comparison with literature data, are the values of $K_c = K_m/d$ (d = density of ethylene glycol[18]). Our data are in good agreement with those of CVETANOVIC et al.[19], but differ considerably from those of MUHS AND WEISS[20]. The latter are lower than our data, except for propene and butene.

The cause of the difference is two-fold, as is illustrated in Fig. 2, where data from our work and from MUHS AND WEISS on the retention volumes of pentene on ethylene glycol and $AgNO_3$ columns are compared.

Firstly the values of MUHS AND WEISS of the retention volumes of the alkenes on ethylene glycol are higher than ours. The difference increases with increasing chain-length of the alkene, up to a factor of 2 for octene. This is probably caused by

TABLE V

VALUES OF $K_m\gamma_A\gamma_B/\gamma_{AB}$, K_m, K_c AND SOME LITERATURE DATA ON K_c

Solute	$K_m\gamma_A\gamma_B/\gamma_{AB}$				K_m	K_c	K_c (ref. 19)	K_c (ref. 20)
	$m_B =$ 0.19	$m_B =$ 0.97	$m_B =$ 1.92	$m_B = 3$				
Propene	6.7	8.5	9.7	10.7	6.8 ± 0.4	6.2	5.9	9.1
Butene-1	7.1	8.0	10.0	10.5	7.0 ± 0.4	6.4	6.8	7.7
Pentene-1	6.2	7.9	8.3	9.9	6.2 ± 0.4	5.6	5.2	4.9
Hexene-1	6.6	8.0	8.8	10.0	6.6 ± 0.3	6.0		4.3
Heptene-1	6.0	7.4	8.5	9.6	6.0 ± 0.2	5.5		3.2
Octene-1	6.0	6.8	8.0	8.4	5.9 ± 0.3	5.4		2.6
3-Methylbutene-1	6.2	9.1	9.7	11.4	6.5 ± 0.7	5.9	6.1	5.1
3,3-Dimethylbutene-1	6.6	8.2	9.3	10.6	6.6 ± 0.3	6.0		3.6
2-Methylhexene-1	3.0	4.0	4.5	5.3	3.0 ± 0.2			
3-Methylhexene-1	5.5	6.5	7.5	8.3	5.5 ± 0.1	5.0		2.7
4-Methylhexene-1	4.5	5.3	6.6	8.5	4.0 ± 0.2	3.6		2.3
5-Methylhexene-1	5.9	7.7	8.3	10.3	5.8 ± 0.4	5.3		3.1
Allyl chloride	0.62	0.75[b]	0.83[b]	0.92[c]	0.62 ± 0.03			
Ethyl allyl ether	1.8	2.1[a]	2.4[b]	2.6[c]	1.8 ± 0.1			
Allyl acetate	0.90[d]	1.10[e]	1.43[f]	1.62[g]	0.87 ± 0.06			

[a] $m_B = 0.95$.
[b] $m_B = 1.84$.
[c] $m_B = 2.98$.
[d] $m_B = 0.17$.
[e] $m_B = 0.94$.
[f] $m_B = 1.79$.
[g] $m_B = 2.93$.
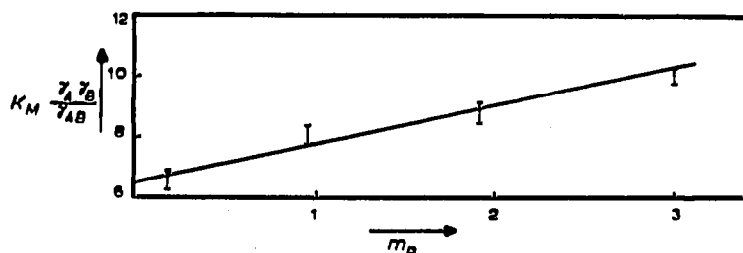
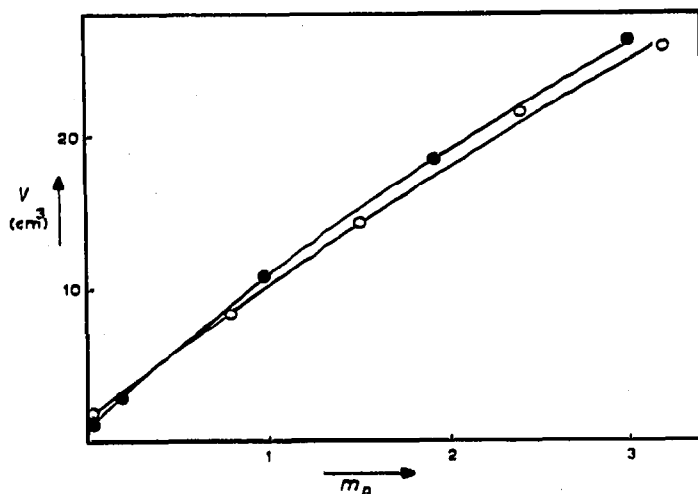Fig. 1. Extrapolation of $K_m\gamma_A\gamma_B/\gamma_{AB}$ to K_m at $m_B = 0$ for hexene-1.

Fig. 2. Net retention volume, V, per gram of ethylene glycol, as a function of m_B for pentene-1. ●, Present work; ○, MUHS AND WEISS[20].

adsorption on the surface of the stationary phase (MUHS AND WEISS used only 22 wt.-% ethylene glycol, whereas we used 40 wt.-%), or by an increase of the distribution coefficient due to their much larger sample size (more than an order of magnitude larger than ours).

Secondly, the values of MUHS AND WEISS of the retention volumes on $AgNO_3$ columns are lower than ours, probably because they did not take into account the decomposition of $AgNO_3$ columns during preparation, storage and use.
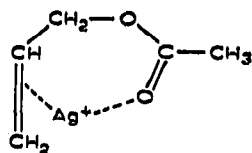
Electronic effects of substituents

In the compounds investigated, resonance between the substituents and the reaction centre is impossible. Therefore, the following functional relationship can be expected:

$$\log K_m/K_m^0 = \rho_I \sigma_I \qquad (3)$$

where K_m^0 is the association constant of the unsubstituted alkene (propene), ρ_I is the reaction constant and σ_I (ref. 21) is the inductive substituent constant.

Fig. 3 shows that this relationship is very well obeyed by the substituents $-CH_3$, $-OC_2H_5$, $-OCOCH_3$ and $-Cl$, and ρ is -2.3. This means that the association constants are much larger as the substituents are more electron donating, which is another argument in favour of the view that σ-type bonding predominates in the stability of alkene–silver ion complexes, as it appears to do in the case of arene–silver ion complexes.

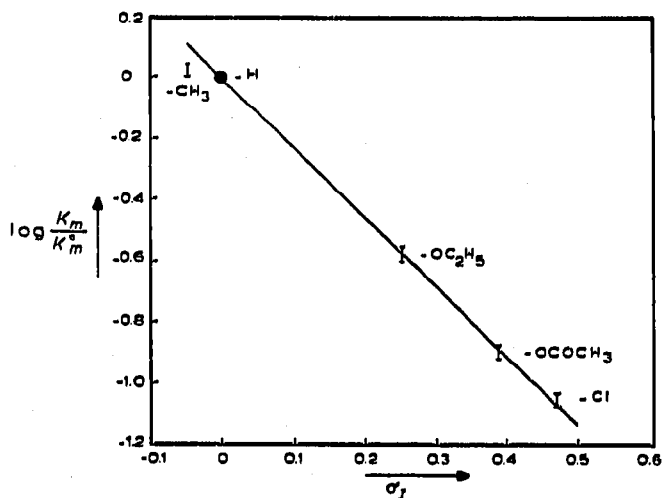It is interesting that the substituent $-OCOCH_3$ conforms to eqn. 3. This shows that the chelate

Fig. 3. Log K_m/K_m^0 as a function of σ_I.

is not formed. Chelates of this type have been suggested[14] but we adhere to the view[22] that it is doubtful that oxygen compounds form chelates with silver ion.

Steric effects of substituents

Whereas even three methyl substituents at position 3 do not exert a significant steric effect, the data on heptene, octene and 3-methylhexene show that n-butyl and larger n-alkyl groups, or the combination of a methyl and an n-propyl group, attached to position 3, have a slight steric effect.

The data on hexene, the methylhexenes and heptene show that the steric effect of a methyl group depends as follows on its position: $2 > 4 > 3 \geqslant 5 \geqslant 6$. The same sequence was found by MUHS AND WEISS[20].

Salting out by LiNO₃ solutions in ethylene glycol

Our data on the retention volumes on ethylene glycol and LiNO₃ columns can be used to investigate the salting out of organic compounds by LiNO₃ solutions in ethylene glycol. The activity coefficient of the compound concerned in a LiNO₃ solution, referred to pure ethylene glycol, is given by:

$$\log \gamma = \log V_{(s)}/V_{(s+c)} \tag{4}$$

It follows from our data that log γ is not influenced by the size or shape of the

TABLE VI

VALUES OF LOG $\gamma = $ LOG $V_{(s)}/V_{(s+c)}$

Compounds	I M LiNO₃	2 M LiNO₃	3 M LiNO₃
Alkanes, alkenes	0.02	0.12	0.25
Ethyl propyl ether, ethyl allyl ether	0.03	0.08	0.16
Propyl halides, allyl halides	0.01	0.09	0.17
Propyl acetate, allyl acetate	0.01	0.04	0.07

compound concerned or by the presence of a double bond. Log γ decreases as the polarity increases, in accordance with expectation[23]. Our data can be summarized as shown in Table VI.

CONCLUSIONS

Association constants of substituted alkenes with silver ions in ethylene glycol can be determined with a precision of about 5 %, by means of a gas chromatographic method in which $LiNO_3$ solutions in ethylene glycol are used as reference stationary phases and the corresponding substituted alkanes as reference solutes.

The association constants correlate very well with the inductive σ_I constants of the substituents. The reaction constant is -2.3, which means that the association constant is much greater as the substituent is more electron donating.

Consequently, σ-type bonding predominates in the stability of alkene–silver ion complexes.

When large alkyl groups are substituted at position 3, steric effects become apparent and the association constant decreases.

The steric effect of a methyl group depends as follows on its position: $2>4>3\geqslant5\geqslant6$.
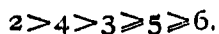
Salting out of organic compounds by $LiNO_3$ solutions in ethylene glycol depends only on their polarity, not on their size or shape or on the presence of a double bond.

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