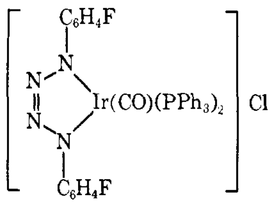
Table III. Electronic Spectra of Some Representative Complexes

Compound	λ_{max}, nm (ϵ)[a]
$Ir(1,2\text{-}O_2C_6Cl_4)(CO)Cl(PPh_3)_2$	460 (770), 318 (6500 sh), 310 (32,000) (sh)
$Ir(1,2\text{-}O_2C_6Cl_4)(CO)Br(PPh_3)_2$	480 (890), 320 (5800) (sh), 265 (29,000) (sh)
$Ir(1,2\text{-}O_2C_6Br_4)(CO)Cl(PPh_3)_2$	370 (1300) (sh), 310 (13,000)
$Rh(1,2\text{-}O_2C_6Cl_4)(CO)Cl(PPh_3)_2$	533 (1600), 323 (32,000)
$Rh(1,2\text{-}O_2C_6Cl_4)(C_6H_6N)Cl(PPh_3)_2$	721 (640), 504 (840), 330 (9800) (sh), 265 (37,000)
$Rh(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2Cl$	725 (3600), 490 (1600), 390 (1200) (sh), 330 (13,000) (sh), 260 (28,000) (sh)

[a] Measured in dichloromethane solution.

chloro-1,2-benzoquinone and $Pt(PPh_3)_2Cl_2$ or $Pd(py)_2Cl_2$. Prolonged refluxing of a chloroform solution containing this quinone and $Pd(PPh_3)_2Cl_2$ leads to the eventual precipitation of red, crystalline $[Pd(PPh_3)Cl_2]_2$[33] but no addition of the *o*-quinone occurs.

Attempts to extend this class of reaction to the addition of analogous nitrogen donors has been unsuccessful. The isolation of **13**[34] suggests that α-diimines may add to $Ir(CO)Cl(PPh_3)_2$, although **13** was



13

formed *via* a quite different route. However, attempts to add the α-diimine biacetylbisanil[35] to $Ir(CO)Cl(PPh_3)_2$ with either thermal or photochemical activation have led only to the recovery of starting material.

Acknowledgment. This research was supported by Grant No. GM-18357 from the National Institutes of Health.

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Solvation of Ions. XVI.[1] Solvent Activity Coefficients of Single Ions. A Recommended Extrathermodynamic Assumption

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Received February 22, 1971

Abstract: Four groups of popular extrathermodynamic assumptions give much the same solvent activity coefficients for transfer of silver cation from acetonitrile to 14 other solvents at 25°. It is therefore strongly recommended that chemists adopt the simplest of these, the assumption of negligible liquid junction potential between $Ag|AgClO_4$ (0.01 *M*) half-cells in different solvents, when linked by a salt bridge of 0.1 *M* tetraethylammonium picrate in either solvent. We note that the Ph_4AsBPh_4 assumption gives very similar values.

The evaluation of single-ion solvent activity coefficients, $^{0}\gamma^{S}_{A^+}$ and $^{0}\gamma^{S}_{B^-}$, for transfer of cations, A^+, or of anions, B^-, from a reference solvent (superscript 0) to another solvent (superscript S) is one of the unresolved classical problems of solution chemistry.[3] It is a problem outside the realm of rigorous thermodynamics and so is of no interest to a few chemists. Those of us who are interested are seeking a universally acceptable means of communicating, interpreting, and predicting the chemistry of ions in different solutions.

In part XIII[5] we were preparing to interpret and predict rates and mechanism of reactions in a variety of solvents. The reactants were usually 0.01–0.04 *M* so we decided to use the molar concentration scale, to compare behavior in 0.01–0.04 *M* solutions, rather than calculate salt (Debye–Hückel) activity coefficients and to not use log $^{0}\gamma^{S}_{Ag^+}$ as derived from any *one* assumption, but rather to take biased mean values. The numbers obtained, by an intuitive estimate of log $^{0}\gamma^{S}_{Ag^+}$ from many assumptions, were most useful.[9,10] In this paper we are anxious to establish an acceptable scale

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(1) Part XV: A. J. Parker and E. C. F. Ko, *J. Amer. Chem. Soc.*, **90**, 6447 (1968).

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(3) The current status of the problem has been reviewed splendidly by Popovych[4] and less comprehensively in part XIII.[5] Some other useful reviews and papers have appeared.[6-8] The reader is referred to ref 4–8 for a more detailed introduction and acknowledgment of the important work of others in this area. We would like, however, to acknowledge the influence of E. Grunwald, G. Baughman, and G. Kohnstam, *J. Amer. Chem. Soc.*, **82**, 5801 (1960), on our work. Some authors[7] prefer the term "medium effect" or "medium activity coefficient" to "solvent activity coefficient," and we have no strong feelings about such terminology.

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Table I. Solubility Products (K, mol^2 l.$^{-2}$) of Solutes at 25° (Reference Solvent Acetonitrile[c] (Superscript 0))

		$pK^{S} - pK^{0} = \text{Log } {}^{0}\gamma^{S}_{A^+} + {}^{0}\gamma^{S}_{B^-}$ in the solvent[a,b]														
Solute AB	pK^{MeCN}	MeCN 1.543	TFE[2] 2.657	$MeNO_2$ 1.479	PC 0.661	Me_2CO 3.760	TMS (30°) 1.244	MeOH 1.900	EtOH 2.956	H_2O 0.509	$HCONH_2$ 0.309	DMF 1.551	DMA 1.551	NMePy 2.004	DMSO 1.115	HMPT 2.201
Ph_4C^{d}	3.2^{d}	0.0		+0.2	0.0	−0.4	−0.5	0.5	0.5		1.7	−0.7	−0.8	−1.2	−0.8	−0.9
AgCl	13.2^{e}	0.0	4.0^{i}	$6.8^{e,i}$	6.8^{i}	8.0^{i}	5.2^{e}	0.2^{e}	0.9^{i}	-3.4^{e}	-3.7^{e}	1.6^{e}	1.4^{e}	1.0^{e}	-2.6^{e}	-0.9^{h}
AgBr	13.2^{e}	0.0	6.5^{i}	8.7^{i}	7.4^{i}	7.9^{i}	5.5^{i}	2.3^{e}	2.9^{i}	-0.9^{e}	-1.7^{e}	2.1^{e}	1.6^{e}	1.0^{h}	-2.4^{e}	-0.5^{h}
AgN_3	9.9^{e}	0.0		$7.7^{e,i}$	6.6^{i}	7.8^{i}	5.0^{i}	1.6^{e}	2.2^{i}	-1.3^{e}	-1.9^{e}	1.4^{e}	1.2^{e}	1.7^{h}	-3.0^{e}	-0.5^{h}
AgSCN	10.3^{e}	0.0		$7.8^{e,i}$	6.1^{i}			3.9^{e}		1.6^{e}	-0.3^{e}	1.5^{e}	0.5^{e}	0.9^{e}	-2.8^{e}	-2.0^{h}
AgI	14.5^{e}	0.0	8.9^{i}	8.2^{i}	6.4^{i}	7.5^{i}	4.5^{i}	4.1^{e}	4.6^{i}	1.5^{e}	0.1^{e}	1.6^{e}	0.5^{e}	0.5^{e}	-2.9^{e}	-0.8^{h}
Ph_4AsI	2.7	0.0		−0.6	−1.0	1.8	−0.2	−0.4	+1.0	+2.4	−0.7	−0.8	−0.3	−0.6	−0.4	+1.1
$AgBPh_4{}^{j}$	7.5	0.0		8.1	5.3	5.6	2.7	6.0^{e}	6.9	4.2^{e}	2.8^{e}	−0.4	-1.3^{e}	−2.6	−2.4	
CsCl	6.8	0.0		−0.5				−4.2				−1.7	−1.4			0.0
KCl	7.2^{e}	0.0	−3.2					-4.2^{e}	-1.9^{e}	-7.5^{e}	-6.5^{e}	-1.7^{e}				
KBr	5.7^{e}	0.0	−2.0	+0.7				-3.1^{e}	−1.2			-2.7^{e}	−2.2		-4.4^{e}	−1.3
$KBPh_4$	2.9^{e}	0.0						2.2^{e}		4.6^{e}	0.0^{e}					
KPic	4.7^{e}	0.0						-0.3^{e}	−0.6	-1.4^{e}		-3.7^{e}				
Ph_4AsPic	2.6^{e}	0.0						1.3^{e}		6.2^{e}						
Ph_4AsBPh_4	5.8	0.0		−0.1	−1.2	2.2	−0.6	3.2	3.6		3.0	−1.9	−1.8	−2.5	−2.2	−2.1
$Ph_4AsBPh_4{}^{f}$	5.8	0.0		−0.7	−2.1	−0.1	−2.0	1.5	3.3	5.1	2.0	−2.8	−2.1	−3.7	0.1	
$Ph_4AsBPh_4{}^{g}$	5.8	0.0						3.8		12.2						

[a] Abbreviations are Pic = picrate; TFE, trifluoroethanol; PC, propylene carbonate; TMS (30°), tetramethylene sulfone at 30°; DMF, dimethylformamide; DMA, dimethylacetamide; NMePy, *N*-methyl-2-pyrrolidone; DMSO, dimethyl sulfoxide; HMPT, hexamethylphosphoramide. [b] Values below solvents are the Debye–Hückel *A* parameter, *i.e.*, $1.823 \times 10^{6}/(\epsilon T)^{3/2}$, with dielectric constants from ref 10. [c] Data from this work unless stated otherwise; solubility products (±0.1 in log *K*) have been corrected for salt activity coefficients, using the Davies equation (1). [d] These are from solubilities not solubility products, measured by vpc (on an SE 30 column) of saturated solutions. [e] Reference 5 but corrected to infinite dilution through salt activity coefficients. [f] Calculated from eq 5. [g] Calculated from eq 6. [h] From potentiometric titration of 0.01 *M* NEt_4X wih 0.01 *M* $AgClO_4$; *i.e.*, ionic strength is 0.01–0.005 *M* over the period of titration. [i] From potentiometric titration of 0.005 *M* NBu_4X with 0.005 *M* $AgClO_4$; *i.e.*, ionic strength is 0.005–0.0025 *M* over the period of titration. [j] Titration were with $NaBPh_4$ and $AgClO_4$.

Table II. Solvent Activity Coefficients for Anions and Cations at 25°[a,b]

Ion	MeCN	TFE	$MeNO_2$	PC	Me_2CO	TMS 30	MeOH	EtOH	H_2O	$HCONH_2$	DMF	DMA	NMePy	DMSO	HMPT
$Ag^{+\,c}$	0.0	12.4	9.1	6.9	5.4	5.1	4.6	4.4	3.0	1.0	0.7	−0.4	−0.5	−2.6	−3.9
$K^{+\,f}$	0.0	4.6	2.0				0.2	1.0	−3.2	−1.8	−3.3	−4.2		−4.2	−4.7
$Ph_4As^{+\,e}$	0.0		0.3	−0.5	−0.3	−0.1	0.1	0.8	6.5^{h} $(3.9)^{e}$	0.2	−1.7	−1.2	−1.6	−0.1	−2.0
Ph_4C^{j}	0.0		0.2	−0.0	−0.4	−0.5	$0.5^{e,h}$	0.5		1.7	−0.7	−0.8	−1.2	−0.8	−0.9
$Ph_4B^{-\,d}$	0.0		−1.0	−1.6	0.2	2.4	1.4 $(-0.5)^{g}$	2.5	5.7^{g} $(1.2)^{d}$	$1.8^{g,d}$	−1.1	−0.9	−2.1	0.2	−0.1
$Cl^{-\,d}$	0.0	−8.4	−2.3	−0.1	2.6	0.1	−4.4	−3.5	−6.4	−4.7	0.9	1.8	1.5	0.0	3.0
$Br^{-\,d}$	0.0	−5.9	−0.4	0.5	2.5	0.4	−2.3	−1.5	−3.9	−2.7	1.4	2.0	1.5	0.2	3.4
$I^{-\,d}$	0.0	−3.5	−0.9	−0.5	2.1	−0.6	−0.5	0.2	−1.5	−0.9	0.9	0.9	1.0	−0.3	3.1
$N_3^{-\,d}$	0.0		−1.4	−0.3	2.4	−0.1	−3.0	−2.3	−4.3	−2.9	0.7	1.6	2.2	−0.4	3.4
$SCN^{-\,d}$	0.0		−1.3	−0.8			−0.7		−1.4	−1.3	0.8	0.9	1.4	−0.2	1.9
$Pic^{-\,i}$	0.0						−0.5	−1.6	+1.8		−0.4				

[a] Molar scale, reference solvent acetonitrile, assumption of negligible liquid junction potential. The assumption is that there is no liquid junction potential in the cell of Table IV. [b] Abbreviations are as in Table I. [c] From Table IV. [d] Log ${}^{0}\gamma^{S}_{Ag^+} + {}^{0}\gamma^{S}_{X^-}$ (Table I) − log ${}^{0}\gamma^{S}_{Ag^+}$ (this table). [e] Log ${}^{0}\gamma^{S}_{Ph_4As^+} + {}^{0}\gamma^{S}_{I^-}$ (Table I) − log ${}^{0}\gamma^{S}_{I^-}$ (this table). [f] Log ${}^{0}\gamma^{S}_{K^+} + {}^{0}\gamma^{S}_{X^-}$ (Table I) − log ${}^{0}\gamma^{S}_{X^-}$ (this table), mean value where more than one KX is available. [g] Log ${}^{0}\gamma^{S}_{K^+} + {}^{0}\gamma^{S}_{BPh_4^-}$ (Table I) − log ${}^{0}\gamma^{S}_{K^+}$ (this table). [h] Log ${}^{0}\gamma^{S}_{Ph_4As^+} + {}^{0}\gamma^{S}_{Pic^-}$ (Table I) − log ${}^{0}\gamma^{S}_{Pic^-}$ (this table). [i] Log ${}^{0}\gamma^{S}_{K^+} + {}^{0}\gamma^{S}_{Pic^-}$ (Table I) − log ${}^{0}\gamma^{S}_{K^+}$ (this table). [j] From Table I.

Table III. Association Constants (K_A, M^{-1}) in Nonaqueous Solvents at 25°

Salt	Log K_A MeOH	EtOH	Me_2CO	MeCN	$MeNO_2$	DMF	DMA	TMS (30°)	TFE
LiPic		2.00[a]	2.91[b]	2.82[c]	4.2[c]				
NaBr	1.00[d]	1.61[c]				0.90[e]	0.75[f]		
KPic	1.11[g]		2.46[b]	2.18[h]		s[i]	s[f]		
KI	1.11[d]	1.70[j]	2.26[k]	0.30[l]	1.60[m]	s[n]	s[f]	0.81[m]	
NEt_4Pic	1.26[o]	1.84[p]	1.65[b]	1.00[q]	s[c]				
NBu_4Cl	s[r]	1.59[s]	2.78[k]		s[t]	1.34[u]			s[a]
NBu_4I	1.20[r]	2.09[s]	2.37[a]	0.48[v]		0.92[z]	s[f]		1.95[a]
NBu_4BPh_4	1.57[w]			s[x]		1.34[a]			
NEt_4I	1.36[c]	2.11[s]	2.11[a]	0.70[y]	s[c]	1.08[z]	s[f]	0.56[m]	
$AgNO_3$	1.89[j]	2.41[j]	5.43[aa]	1.85[bb]		1.60[n]			
$AgClO_4$	s[c]	1.56[c]	2.26[a]	s[bb]	s[c]				
NBu_4ClO_4			2.06[a]						

[a] A. J. Parker and D. A. Palmer, unpublished work. [b] M. R. Reynolds and C. A. Kraus, *J. Amer. Chem. Soc.*, **70,** 1709 (1948). [c] Reference 12. [d] R. E. Jervis, D. R. Muir, J. P. Butler, and A. R. Gordon, *J. Amer. Chem. Soc.*, **75,** 2855 (1953). [e] D. P. Ames and P. G. Sears, *J. Phys. Chem.*, **59,** 16 (1955). [f] G. R. Lester, T. A. Gover, and P. G. Sears, *ibid.*, **60,** 1076 (1956). [g] D. F. Evans and T. L. Broadwater, *ibid.*, **72,** 1037 (1968). [h] I. M. Kolthoff, M. K. Chantooni, and S. Bhownik, *J. Amer. Chem. Soc.*, **88,** 5430 (1966). [i] P. G. Sears, R. R. Wolford, and L. R. Dawson, *J. Electrochem. Soc.*, **108,** 633 (1956). [j] G. Charlot and B. Tremillon, "Chemical Reactions in Solvents and Melts," Pergamon Press, London, 1969. [k] L. G. Savedoff, *J. Amer. Chem. Soc.*, **88,** 664 (1966). [l] G. J. Janz and M. J. Tait, *Can. J. Chem.*, **45,** 1101 (1967). [m] R. Fernandez-Prinz and J. E. Prue, *Trans. Faraday Soc.*, **62,** 1257 (1966). [n] J. E. Prue and P. J. Sherrington, *ibid.*, **57,** 1795 (1961). [o] F. Accascina, A. D'Aprano, and R. M. Fuoss, *J. Amer. Chem. Soc.*, **81,** 1058 (1959). [p] R. Whorton and E. S. Amis, *Z. Phys. Chem. (Frankfurt am Main)*, **17,** 300 (1958). [q] C. M. French and D. F. Muggleton, *J. Chem. Soc.*, 2131 (1957). [r] R. L. Kay, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.*, 69, 4208 (1965). [s] D. F. Evans and P. Gardam, *ibid.*, **72,** 3281 (1968). [t] R. L. Kay, S. C. Blum, and H. I. Schiff, *ibid.*, **67,** 1223 (1963). [u] H. Elias and H. Strecker, *Chem. Ber.*, **99,** 1019 (1966). [v] D. F. Evans, C. Zawoyski, and R. L. Kay, *J. Phys. Chem.*, **69,** 3878 (1965). [w] M. A. Coplan and R. M. Fuoss, *ibid.*, **68,** 1177 (1964). [x] D. S. Berns and R. M. Fuoss, *J. Amer. Chem. Soc.*, **82,** 5585 (1960) [y] A. I. Popov and N. E. Skelly, *ibid.*, **76,** 5309, (1954). [z] P. G. Sears, E. D. Wilhoit, and L. R. Dawson, *J. Phys. Chem.*, **59,** 373 (1955). [aa] V. S. Griffiths and K. S. Lawrence, *J. Chem. Soc.*, 1208 (1955). [bb] H. L. Yeager and B. Kratochvil, *J. Phys. Chem.*, **73,** 1963 (1969).

of single-ion solvent activity coefficients, so the approach is different. Butler's success[11] has encouraged us to calculate salt activity coefficients in dipolar aprotic solvents from equations closely related to the Davies[12] equation (1). Thus our new values are for infinitely dilute solutions, as estimated from measurements on nonaqueous solutions which in rare cases are up to 0.1 *M*, but are usually *ca.* 0.01 *M*. We still use the molar concentration scale, but conversion to molal or mole fraction scales is a simple matter.[4,6] Finally, the single-ion solvent activity coefficients suggested in the final table in this paper are now based on a single assumption, that of negligible liquid junction potential in cell A.[13]

It is important to realize that, just as no experiment can be devised which will yield a single-ion solvent activity coefficient which is thermodynamically meaningful, so we are never faced with an experiment whose interpretation depends only on one "real value" of log ${}^{0}\gamma^{S}_{i}$. Experiments give us "real log ${}^{0}\gamma^{S}_{i}$" in conjunction with another unknown number, be it "real log ${}^{0}\gamma^{S}_{i}$" for another ion, a liquid junction potential, or a standard potential, and so on. One might conclude from this that single ion solvent activity coefficients are unnecessary, but we are convinced that they give the simplest and by far the most effective method for communicating ideas and for interpreting, predicting and recording data on the chemistry of ions in solution.

Results

Solubility Products. The solubility products (K^{MeCN} in mol^2 l.$^{-2}$) at 25° in acetonitrile of the solutes considered in this paper are recorded as pK^{MeCN} (*i.e.*, $-\log K^{MeCN}$) in Table I. Acetonitrile is the reference solvent (superscript 0) and solubility products of salts AB in other solvents (superscript S) are recorded as solvent activity coefficients $pK^S - pK^0 = \log {}^{0}\gamma^{S}_{A^+} \cdot {}^{0}\gamma^{S}_{B^-}$. Some of the solubility products ($pK^S(I)$) at various ionic strengths, *I*, have been reported previously,[5,14] but the values (pK^S) which are recorded in Table I are corrected to infinitely dilute solution (*i.e.*, $pK^S = pK^S(I) + 2 \log \gamma_{\pm}$) by using mean salt activity coefficients ($\gamma_{\pm}$), as calculated from the Davies equation (1).[12]

$$\log \gamma_{\pm} = -A[\sqrt{I}/(1 + \sqrt{I}) - {}^{1}/_{3}I] \qquad (1)$$

Values of *A* for this equation were calculated from $1.823 \times 10^6/(\epsilon T)^{3/2}$ and are shown in Table I. The solubility products and ionic strengths for solutions in acetone, ethanol, and trifluoroethanol were adjusted to infinite dilution by iteration, to allow for incomplete dissociation of electrolytes in these relatively low dielectric solvents. Association constants for tetraalkylammonium salts and iodides are similar in solvents of the same dielectric constant[12] (Table III) so that strengths of electrolytes, if not known, were estimated from the strengths of related electrolytes.[12] Some representative association constants are in Table III. We estimate from this table an association constant of 150 M^{-1} for Ph_4AsI in acetone and <100 M^{-1} for $AgClO_4$ in all of the solvents, except acetone.

Solubility products of silver salts were determined from a potentiometric titration curve of 0.01 *M* solu-

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(11) J. N. Butler and J. C. Synnott, *J. Amer. Chem. Soc.*, **92,** 2602 (1970).

(12) C. W. Davies, "Ion Association," Butterworths, London, 1962.

(13) Although the new values in Table II differ from those used previously,[5,9,10] by a constant amount, which is positive for anions, negative for cations, in each solvent, none of the conclusions about solvent effects on rates and equilibria need be changed. This is because all the previous interpretations were of differences in log ${}^{0}\gamma^{S}_{i}$ between two anions, or of sums of log ${}^{0}\gamma^{S}_{i}$ for an anion and a cation. Thus a constant deviation from the "real value" was cancelled.

(14) R. Alexander and A. J. Parker, *J. Amer. Chem. Soc.*, **89,** 5549 (1967).

Table IV. Rate Constants (k^1, M^{-1} sec^{-1}) of Nucleophilic Substitution Reactions at 25°.
The Reactant–SN2[a] Transition State and Reactant–SNAr[a] Transition State Assumptions (Reference Solvent Acetonitrile (Superscript 0))

Reactants RX + Y$^-$	Log k^0	— Log (k^S/k^0) = Log $^0\gamma^S{}_{Y^-}$ + Log $^0\gamma^S{}_{RX}$ − Log $^0\gamma^S{}_{\ddagger}$[e] in the solvent[c] — MeCN	PC	TFE	EtOH	Me$_2$CO	DMSO	NMePy
		SN2						
CH_3I + NEt_4SCN	−1.82	0.0	0.13			+1.0	+0.50[d]	+2.1
CH_3I + NEt_4Br	−1.20	0.0		−4.2[d]	−2.3[d]	+2.2		
		SNAr						
4-$NO_2C_6H_4F$ + NEt_4N_3	−3.3	0.0	+0.3[d]			1.0	0.0	1.4
log $^0\gamma^S{}_{Ag^+}$$^0\gamma^S{}_{Y^-}$[b] − log ($k^S/k^0$(SN2)		0.0	6.0	10.7	5.2	5.7	−3.3	−1.2
log $^0\gamma^S{}_{Ag^+}$ + $^0\gamma^S{}_{Y^-}$[b] − log (k^S/k^0)(SNAr)		0.0	6.3				−3.0	0.3[d]

[a] SN2 is a bimolecular nucleophilic substitution reaction of methyl iodide, SNAr is a bimolecular nucleophilic sucstitution reacion of 4-nitrofluorobenzene. Rate constants from ref 10 unless stated otherwise, reactants at 0.02–0.04 M. [b] Solvent activity coefficients for transfer of AgY from acetonitrile to solvent S at 25° are from Table I. [c] Abbreviations are as for Table I. [d] This work. [e] ‡ denotes transition state.

tions of NEt_4^+ salts or of 0.01 M $NaBPh_4$ with 0.01 M $AgClO_4$.[14] In ethanol, acetone, nitromethane, and trifluoroethanol, 0.005 M NBu_4^+ salts were titrated with 0.005 M $AgClO_4$. The ionic strength at the midpoint along the titration curve was used in eq 1. The solubility of $AgBPh_4$ in hexamethylphosphoramide (HMPT) was judged too great (>0.5 M or >0.2 mole fraction) for a meaningful measurement. The solubility (mol l.$^{-1}$) of tetraphenylmethane was obtained by vpc analysis of saturated solutions, but was too low for measurement in water and trifluoroethanol.

The solubility products of Ph_4AsBPh_4, Ph_4AsI, CsCl, KCl, KBr, and $KBPh_4$ were estimated by volumetric analysis of saturated solutions, using silver nitrate. Very dilute solutions of tetraphenylborates were measured by spectrophotometry. These salts were estimated to have much the same small degree of association[12] at saturation, being least soluble in those solvents in which the association constant was greatest. The association constants are likely to be <100 in most of the solvents considered (*cf.* Table III),[12] but the numbers in Table I for these salts are less precise than those for the silver salts.

The solubility of Ph_4AsBPh_4 was too low for measurement in water and in trifluoroethanol. The tetraphenylboride anion decomposed rapidly in trifluoroethanol and very slowly in other hydroxylic solvents.

Rate Constants.[9,10] Second-order rate constants (k^{MeCN}, M^{-1} sec^{-1}) for bimolecular nucleophilic substitution reactions of methyl iodide and of 4-fluoronitrobenzene with 0.02–0.03 M NEt_4SCN, NEt_4Br, and NEt_4N_3 in acetonitrile at 25° are in Table III. The rate constants for these reactions in other solvents (k^S) are recorded as log k^S − log k^{MeCN} in Table IV. The reactions of azide ion with 4-nitrofluorobenzene in dipolar aprotic solvents at 25° can be easily and rapidly followed spectrophotometrically for production of 4-nitroazidobenzene under pseudo-first-order conditions. In earlier work[9] we estimated consumption of azide ion by titration with silver nitrate. The reactions of methyl iodide were followed by titration of iodide ion with silver nitrate.

Emf of Silver Cells. The emf of cell A, thermostated at 25°, is recorded as ΔE mV in Table V. Solutions of $AgClO_4$ were 0.005 M in nitromethane and trifluoroethanol but 0.01 M in other solvents. The bridge was an inverted U tube and gave the same emf with either sintered glass frits or liquid sleeve junctions. It contained 0.1 M tetraethylammonium picrate in either acetonitrile or solvent S, whichever was the weaker solvator of silver cations. The same ΔE (to within ±2 mV) was obtained with 0.005 and 0.001 M solutions of $AgClO_4$ in all solvents. The Nernst equation was obeyed between 0.01 and 0.001 M, after due allowance through eq 1 for changes of activity with ionic strength. Silver perchlorate at 0.005 M is a strong electrolyte in acetone (Table III), and since acetone is expected to be the least dissociating solvent for silver salts, the silver perchlorate solutions in other solvents are assumed to be dissociated. A three-compartment cell with the salt bridge solution between two glass frits gave the same ΔE as cell A. As shown in Table III, the value of ΔE in cell A was less by 280 ± 20 mV for all solvents, if 0.01 M $AgClO_4$ in methanol replaced the 0.01 M $AgClO_4$ in acetonitrile as reference. As expected, this is close to the value of 270 mV observed between acetonitrile and methanol solutions in cell A.

Cell A

Ag	$AgClO_4$ 0.01 M MeCN	NEt_4Pic 0.1 M MeCN or S	$AgClO_4$ 0.01 M Solvent S	Ag

The final four columns in Table V record $\Delta E/0.059$ as log $^0\gamma^S{}_{Ag^+}$, with acetonitrile as reference, on the assumption[5] (*vide infra*) that there is negligible liquid junction potential in cell A. The observed values have been corrected to zero ionic strength, using salt activity coefficients calculated from eq 1 and assuming that 0.01 or 0.005 M $AgClO_4$ solutions are dissociated. They are compared in Table V with values measured against methanol solutions which have had 4.6 (*i.e.*, log $^{MeCN}\gamma^{MeOH}{}_{Ag^+}$) added to them. They are also compared with the *mean* values (±15 mV) reported in part XIII.[5] These were from related cells, with a variety of bridges, both $AgNO_3$ and $AgClO_4$ and with a variety of reference solvents. In part XIII we did not allow for Debye–Hückel activity coefficients, although some attempt was made to allow for incomplete dissociation of 0.01 M $AgNO_3$. Despite these differences, the mean values agree remarkably well with the new values in Table V.

Solvents which poorly solvate silver cation relative to water, *e.g.*, trifluoroethanol, nitromethane, sulfolane, and propylene carbonate, needed very careful purification and drying, followed by immediate use, if reproducible results were to be obtained. In earlier work,[5] lower values of log $^0\gamma^S{}_{Ag^+}$ for transfer of Ag^+ from acetonitrile to nitromethane were measured and we suspect that Ag^+ was "solvated" by impurities in the nitromethane, rather than by nitromethane, for example.

In Table VI we record the emf of cell A, with salt

Table V. Emf (25°) of the Cells

Ag	$AgClO_4$	NEt_4Pic	$AgClO_4$	Ag
	0.01 *M*	0.1 *M*	0.01 *M*	
Ref	Solvent 0	Solvent[e]	Solvent S	

Solvent S	Bridge solvent[e]	ΔE_{obsd}, mV	Log ${}^0\gamma^S_{Ag^+}$ Obsd	Cor[b]	MeOH[c]	Parker–Alexander[d]
		(a) Reference Solvent Acetonitrile (Superscript 0)				
$MeNO_2$[f]	$MeNO_2$	520		9.1	8.9	7.9
PC	PC	414	7.02	6.9	6.8	
Me_2CO	Me_2CO	308	5.22	5.4	5.4	
TMS (30°)	TMS (30°)	300	5.08	5.1	5.1	5.2
DMF	DMF	40	0.68	0.7	1.0	0.8
NMePy	NMePy	−28	−0.47	−0.5	0.0	
DMA	DMA	−25	−0.42	−0.4	−0.3	−0.5
DMSO	MeCN	−152	−2.58	−2.6	−2.2	−2.5
HMPT	MeCN	−230	−3.90	−3.9	−3.7	−3.4
MeOH	MeOH	270	4.58	4.6	4.6	4.3
EtOH	EtOH	250	4.24	4.4	4.2	
$HCONH_2$	$HCONH_2$	65	1.10	1.0	1.1	0.5
H_2O	MeCN	185	3.14	3.0	3.1	2.3
TFE[f]	TFE	710		12.4	11.9	
		(b) Reference Solvent Methanol (Superscript 0)				
$MeNO_2$[a,f]	$MeNO_2$	241		4.3		3.4
PC	PC	133	2.25	2.2		
Me_2CO	Me_2CO	38	0.64	0.8		
TMS (30°)	TMS (30°)	30	0.51	0.5		1.0
DMF	MeOH	−210	−3.56	−3.6		−3.2
MeCN	MeOH	−270	−4.58	−4.6		−4.3
NMePy	MeOH	−270	−4.58	−4.6		
DMA	MeOH	−288	−4.88	−4.9		−4.2
DMSO	MeOH	−400	−6.78	−6.8		−6.6
HMPT	MeOH	−491	−8.32	−8.3		−7.2
EtOH	MeOH	−29	−0.49	−0.4		
$HCONH_2$	MeOH	−198	−3.36	−3.5		−3.6
H_2O	MeOH	−81	−1.37	−1.5		−1.5
TFE[f]	TFE	410		7.3		

[a] Measured on a Radiometer pH meter 26, using the expanded scale facility. [b] Corrected for concentration differences and Debye–Hückel activity coefficients (eq 1) where appropriate. [c] Indirect value, calculated by adding +4.6 to the values recorded below for methanol as reference solvent. [d] Reference 5. [e] Bridge solvent is the least solvating of 0 and S for Ag^+. [f] 0.005 *M* $AgClO_4$ in solvent S and 0.01 *M* $AgClO_4$ in reference solvent.

Table VI. Emf (25°[b]) of the Cells[d]

Ag	$AgClO_4$	0.1 *M* NEt_4Pic	$AgClO_4$	Ag
	0.01 *M*		0.01 *M*	
	MeCN	Solvents	Solvent S	

Bridge solvent[a]	ΔE, mV,[c] 0.01 *M* $AgClO_4$ DMSO	$HCONH_2$	H_2O	MeOH
MeCN	−152	68	185	265
DMSO	−149	30	119	243
$MeNO_2$	−153	77	219	275
PC	−156	62	202	263
MeOH	−149	76	179	265
TMS (30°)	−152	59	178	267
Me_2CO	−161	56	162	267
NMePy	−162	33	119	232
DMF	−157	32	134	251
$HCONH_2$	−107	65	150	261

[a] Abbreviations as in Table I. [b] Measured on a Radiometer pH meter 26, using the expanded scale facility. [c] The cell consists of this half-cell in the solvent shown, linked to a 0.01 *M* Ag half-cell in acetonitrile through a salt bridge of 0.1 *M* NEt_4Pic in the "bridge solvent" shown. [d] Reference half-cell in acetonitrile, effect of salt bridges.

Table VII. The Ferrocene Assumption at 25°. Cyclic Voltammetry in the Cell[c]

Ag	$AgClO_4$ 0.01 *M*	NEt_4Pic	Ferrocene 0.002 *M*
	NEt_4ClO_4 0.01 *M*	0.1 *M*	NEt_4ClO_4 0.02 *M*
	Solvent S	Solvent S	Solvent S

Solvent S[b]	E (0.01 *M* Ag^+),[a] mV	$\dfrac{E(0.01\,M\,Ag^+)^S - E(0.01\,M\,Ag^+)^0}{59} = \log {}^0\gamma^S_{Ag^+}$
MeCN	−90	0
TFE	628	12.2
$MeNO_2$	452	9.2
PC	357	7.6
Me_2CO	185	4.7
TMS (30°)	237	5.5
MeOH	145	4.0
EtOH	78	2.8
H_2O	272	6.1
$HCONH_2$	61	2.6
DMF	−23	1.1
DMA	−103	−0.2
NMePy	−88	0.0
DMSO	−190	−1.7
HMPT	−286	−3.3

[a] E (0.01 *M* Ag^+) − $E_{1/2}$ (ferrocene) *vs.* Ag(0.01 *M*) (reference electrode) by cyclic voltammetry on a Beckman Electroscan with a platinum disk electrode. [b] Abbreviations as in Table I. [c] Reference solvent acetonitrile (superscript 0).

bridges containing 0.1 *M* NEt_4Pic in a variety of solvents. These experiments were designed to see if we should expect a liquid junction potential in cell A. If a bridge of 0.1 *M* NEt_4ClO_4 was used in place of 0.1 *M* NEt_4Pic, emf's differing by up to 30 mV from these values were obtained.

$E_{1/2}$ of Ferrocene. A Beckman Electroscan was used for cyclic voltammetry, at a Beckman platinum button electrode, of solutions of 2×10^{-4} *M* ferrocene in 0.02 *M* NEt_4ClO_4. The reference electrode was 0.01 *M* $AgClO_4$ plus 0.01 *M* NEt_4ClO_4 in the same solvent at

Table VIII. Comparison of Extrathermodynamic Assumptions for Estimating Log $^0\gamma^S_{Ag^+}$ at 25° (Reference Solvent Acetonitrile (Superscript 0))

		Log $^0\gamma^S_{Ag^+}$							
		Group 1	Group 2			Group 3		Group 4	
Solvent[a]	ϵ[l]	$^0\gamma^S_{Ph_4As^+} = {}^0\gamma^S_{Ph_4B^-}$[g]	$^0\gamma^S_{Ph_4B^-} = {}^0\gamma^S_{Ph_4C}$[b]	$^0\gamma^S_{\ddagger^-} = {}^0\gamma^S_{ArX}$[c]	$^0\gamma^S_{\ddagger^-} = {}^0\gamma^S_{MeI}$[d]	$^0\gamma^S_{F^+} = {}^0\gamma^S_{F}$[e]	$^0\gamma^S_{Ph_4As^+} = {}^0\gamma^S_{Ph_4C}$[f]	Mean[i]	Negl E_{lj}[j]
TFE	26.1[m]				10.7[k]	12.2		11.5	12.4
$MeNO_2$	38.6	8.1	7.6	8.3	8.1	9.2	9.0	8.4	9.1
PC	64.4[n]	5.9	5.3	6.3	6.0	7.6	7.4	6.4	6.9
Me_2CO	20.7[n]	4.5	6.0		5.7	4.7	5.3	5.1	5.4
TMS (30°)	44[n]	3.0	3.2	4.2		5.5	4.2	3.9	5.1
MeOH	32.6	4.4	5.5	5.4	5.3	4.0	5.0	4.8	4.6
EtOH	24.3[m]	5.1	6.4	5.6	5.2[k]	2.8	4.1	4.8	4.4
H_2O	78.5	1.6[h]		2.7[o]	3.2	6.1		3.6	3.0
$HCONH_2$	109.5	1.3	1.1	1.6	0.6	2.6	2.5	1.6	1.0
DMF	36.7	0.6	0.3	0.8	0.8	1.1	1.7	0.9	0.7
MeCN	37.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
DMA	37.8	−0.4	−0.5	0.1	−0.6	−0.2	0.0	−0.3	−0.4
NMePy	31.5	−1.4	−1.4	0.3	−1.2	0.1	−0.1	−0.7	−0.5
DMSO	48.9	−1.3	−1.6	−3.0	−3.3	−1.7	−3.3	−2.1	−2.6
HMPT	29.6	−3.0		−3.2	−4.1	−3.3	−2.8	−3.2	−3.9

[a] Abbreviation as in Table I plus F = ferrocene, F^+ = ferricinium, Ar = 4-nitrophenyl, X is F or I; $\ddagger^-$ is a transition-state anion. [b] Equation 8, data from Table I. [c] Equation 12, data from Table III, ref 5. [d] Equation 11, data from Tables I and III, ref 5. [e] Data from Table VII. [f] Equation 14, data from Table I. [g] Equation 2, data from Tabe I. [h] Equation 3; eq 4 gives 5.2, using 12.2 for log $^0\gamma^S_{Ph_4As^+}{}^0\gamma^S_{BPh_4^-}$ (Table I). [i] A mean value for groups 1–3 giving equal weight to the mean value within each group of assumptions. [j] Data from Table V corrected for ionic strength effects, assuming negligible liquid junction potential in cell A. [k] The substrate is methyl bromide rather than methyl iodide. [l] Dielectric constants ϵ from ref 10 unless recorded otherwise. [m] L. M. Mukherjee and E. Grunwald, *J. Phys. Chem.*, **62**, 1311 (1958). [n] C. K. Mann, *Electroanal. Chem.*, **3**, 57 (1969). [o] B. G. Cox, unpublished work.

25°. The half-cells were connected by a 0.1 *M* salt bridge of NEt_4ClO_4 in the same solvent. We used low concentrations of supporting electrolyte to minimize salt effects and expect a negligible liquid junction potential, following the Henderson equation.[15] Salt activity coefficient corrections are unnecessary, because the ionic strength in the test solution and reference is the same. At *slow* scan rates (1 V/min) and with the dilute ferrocene solutions, the cyclic voltammograms were normal and typical for a reversible one-electron process.[16] Thus ΔE_p was 60–70 mV, with the exception of ethanol (90 mV) and HMPT (80 mV). The $E_{1/2}$ values, *i.e.*, E_p − 29 mV, are close to $E°$ values, because the diffusion coefficients of ferrocene and ferricinium cation are similar. They are recorded in Table V as E(0.01 *M* Ag^+) against the $E_{1/2}$ of the ferrocene|ferricinium couple.

Where there is duplication, our values usually agree well with results which are scattered through the literature.[4,6,17] The literature values were measured in a variety of ways, using various supporting electrolytes. Agreement is poor for the ferrocene|ferricinium|| $AgClO_4$|Ag cell in methanol, where the literature values[18] for *potentiometric* measurements on this cell are +228 mV, whereas we consistently find E(0.01 *M* Ag^+) as +145 mV by cyclic voltammetry. Ferricinium solutions were found to be unstable in methanol, so that potentiometric measurements give more positive values than cyclic voltammetry. We found that reverse current chronopotentiometry[16] of ferrocene solutions in methanol on the Electroscan gave curves typical of electron transfer followed by a chemical reaction of the oxidized product, *i.e.*, of an EC process. Solutions of ferricinium perchlorate, in methanol when generated electrochemically at platinum from ferrocene, very rapidly lost their blue color on standing, whereas solutions of ferricinium perchlorate in acetonitrile, for example, were stable for more than an hour.

Discussion

Popovych[4] favors the "reference electrolyte" method, and accepts Strehlow's[6] ferrocene assumption as his second preference for the evaluation of single ion solvent activity coefficients. He also advocates the use of structural ion–molecule analogs to evaluate the neutral component of solvation energy.[19] We support these opinions, but we cannot agree with his conclusion that the assumption of negligible liquid junction potential[20] is unsound. In Table VIII we compare values from this assumption with values of log $^0\gamma^S_{Ag^+}$, for transfer from acetonitrile to other solvents at 25°, as calculated from those assumptions which Popovych and ourselves find tolerable. A description and justification of each assumption follow, but it is very brief because our thoughts are no different from those expressed in detail by Popovych.[4]

We would like, however, to present first some results and speculation which might influence opinion on the assumption of negligible liquid junction potential in cell A.

Tetraethylammonium picrate was chosen[21] as bridge electrolyte because it provided "inert" ions of very similar mobility in a variety of solvents. Some limiting ionic conductances are in Table IX. It can be seen

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Table IX. Limiting Equivalent Conductances for Ions at 25° [a]

	λ							
	MeCN[b]	MeOH[c,d]	EtOH[d,e,f]	H_2O[g]	DMF[c,h,i]	DMAC[j]	DMSO[k,l]	Me_2CO[m]
NEt_4^+	85.1	60.5	29.3	32.6	35.4	32.7	17.1	91.2
Pic^-	77.3	47.1	24.6	30.4	37.5	41.5	17.3	85.3
ClO_4^-	103.4	71.0	33.5	67.3	52.4	42.8	24.6	115.3

[a] Solvent abbreviations as in Table I. [b] J. F. Coetzee and G. P. Cunningham, *J. Amer. Chem. Soc.*, **87,** 2529 (1965). [c] J. E. Prue and P. J. Sherrington, *Trans. Faraday Soc.*, 1795 (1961). [d] R. L. Kay, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.*, **69,** 4208 (1965). [e] D. F. Evans and P. Gardam, *ibid.*, **72,** 3281 (1968). [f] "Handbook of Analytical Chemistry," L. Meites, Ed., McGraw-Hill, New York, N. Y., 1963, pp 5–34. [g] "Electrolytic Solutions," R. A. Robinson and R. H. Stokes, Ed., Butterworths, London, 1959, p 463. [h] P. G. Sears, R. K. Wolford, and L. R. Dawson, *J. Electrochem. Soc.*, **103,** 633 (1956). [i] P. G. Sears, E. D. Wilchoit, and L. R. Dawson, *J. Phys. Chem.*, **59,** 373 (1955). [j] G. R. Lester, T. A. Gover, and P. G. Sears, *ibid.*, **60,** 1076 (1956). [k] D. E. Arrington and E. Griswold, *ibid.*, **74,** 123 (1970). [l] P. G. Sears, G. R. Lester, and L. R. Dawson, *ibid.*, **60,** 1433 (1956). [m] M. B. Reynolds and C. A. Kraus, *J. Amer. Chem. Soc.*, **70,** 1709 (1948).

that $NEtClO_4$ solutions are less suitable than NEt_4Pic as salt bridges, because perchlorate is considerably more mobile than tetraethylammonium cation. Thus that part of the liquid junction potential (if any) which arises from differences in mobility of anions and cation[4] should be minimized by a high concentration of NEt_4Pic in the salt bridge. We also note that the dielectric constants of most of the solvents in Table V (except water, formamide, and propylene carbonate) are similar and that NEt_4Pic is of comparable solubility[4] in most of the solvents, except for its low solubility in water.

Some emf's of cells like A, with different types of salt bridge, are shown in Table VI. The emf is different by up to 30 mV if 0.1 *M* NEt_4ClO_4 is used in place of 0.1 *M* NEt_4Pic. This is expected from the different mobilities (Table VII) of picrate and perchlorate anion. The really significant point is that with the exception of junctions at which water is a component and one junction of formamide with DMSO, it makes very little difference to the emf of a particular cell A, whether the salt bridge of 0.1 *M* NEt_4Pic is in any of the solvents of Table VI, other than water. The emf of the cell

$$\begin{array}{l|l||l|l} \mathrm{Ag} & \mathrm{AgClO_4} & \mathrm{AgClO_4} & \mathrm{Ag} \\ & 0.01\ M & 0.01\ M & \\ & \mathrm{MeCN} & \mathrm{DMSO} & \end{array}$$

is virtually constant (155 ± 6 mV) no matter which solvent is used for the 0.1 *M* NEt_4Pic in the salt bridge. There are 20 junctions between different pairs of solvents, but the emf is virtually unchanged. It is highly unlikely that the junctions are all large but equal and opposed in each cell. By far the most reasonable explanation is that the liquid junction potential in cell A is negligible. The differences of up to 100 mV when water is involved need further consideration, but we note that formamide (another high dielectric protic solvent of pronounced structure) behaves more reasonably. A half-cell in methanol (a hydroxylic solvent like water) shows outstandingly constant values for different bridges when linked to an acetonitrile half-cell. Tetraethylammonium picrate is very sparingly soluble in water, but is much more soluble in all the other solvents of Table VI. The variation at the water junction seems to be qualitatively related to the ability of the bridge solvent to solvate NEt_4Pic.

We will now examine some of the other assumptions, which have been gathered into three groups. The basic reasoning is the same within each group.

Group 1. The Reference Electrolyte Assumption (*i.e.*, **$\log {}^0\gamma^S{}_{A^+} = \log {}^0\gamma^S{}_{B^-}$**). This is applied to situations where A^+ and B^- are large symmetrical ions of similar size and structure.[4] Nonelectrostatic (neutral) contributions to solvation are assumed to be the same for anion and cation, because the charge is on an atom which is buried under the same ligands. The ions should be of a type which are incapable of specific interactions with the solvent (*e.g.*, H-bond donation, H-bond acceptance, Lewis acid–base interactions). Within the framework of the Born equation,[22] the assumption should be useful, even for solvents of different dielectric constants, because we are equating solvation of solutes of the same size and charge density. Tetraphenylarsonium tetraphenylboride is a suitable solute for this assumption. A disadvantage is the very low solubility of this salt in water, the instability of tetraphenylboride anion in acidic solvents, and the uncertainty surrounding the solvent activity coefficients of silver tetraphenylboride in water and in methanol (*vide intra*). It is highly desirable of course that we be able to link solvation by water with solvation by other solvents, but routes involving BPh_4^- in water are uncertain.

Solvent activity coefficients of silver cation, on transfer from acetonitrile to other solvents at 25°, are calculated on the basis of this assumption as in eq 2, using data from Table I. They are recorded in Table I.

$$\log {}^0\gamma^S{}_{Ag^+} = \log {}^0\gamma^S{}_{Ag^+}{}^0\gamma^S{}_{BPh_4^-} - \tfrac{1}{2}\log {}^0\gamma^S{}_{Ph_4As^+}{}^0\gamma^S{}_{BPh_4^-} \quad (2)$$

The value for water was calculated indirectly, as in eq 3, because $\log {}^0\gamma^S{}_{Ph_4As^+}{}^0\gamma^S{}_{Ph_4B^-}$ cannot be measured directly. However the value for $\tfrac{1}{2}\log {}^0\gamma^S{}_{Ag^+}{}^0\gamma^S{}_{BPh_4^-}$

$$\log {}^0\gamma^S{}_{Ag^+} = \tfrac{1}{2}\log {}^0\gamma^S{}_{Ag^+}{}^0\gamma^S{}_{BPh_4^-} - \tfrac{1}{2}\log {}^0\gamma^S{}_{Ph_4As^+}{}^0\gamma^S{}_{I^-} + \tfrac{1}{2}\log {}^0\gamma^S{}_{Ag^+}{}^0\gamma^S{}_{I^-} \quad (3)$$

is uncertain, for the reasons discussed below, so this result must be treated with caution. The value of $\log {}^0\gamma^S{}_{Ag^+}$ for transfer of silver cation from acetonitrile to hexamethylphosphoramide was calculated as in eq 4, because $\log {}^0\gamma^S{}_{Ag^+}{}^0\gamma^S{}_{BPh_4^-}$ could not be measured accurately, the salt being extremely soluble in HMPT. Equation 4 is an alternative to (2) but contains an additional term (*i.e.*, two extra solubility products) for a

$$\log {}^0\gamma^S{}_{Ag^+} = \log {}^0\gamma^S{}_{Ag^+}{}^0\gamma^S{}_{I^-} - \log {}^0\gamma^S{}_{Ph_4As^+}{}^0\gamma^S{}_{I^-} + \tfrac{1}{2}\log {}^0\gamma^S{}_{Ph_4As^+}{}^0\gamma^S{}_{BPh_4^-} \quad (4)$$

relatively soluble salt, Ph_4AsI. There is also a little more uncertainty about $\log {}^0\gamma^S{}_{Ag^+}{}^0\gamma^S{}_{I^-}$ than about $\log {}^0\gamma^S{}_{Ag^+}{}^0\gamma^S{}_{BPh_4^-}$ in these solvents because of $Ag_3I_4^-$

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(22) M. Born, *Z. Phys.*, [1] 45 (1920).

formation in HMPT, and DMSO, so that eq 2 is preferred for this assumption, when a choice is possible.

It is unfortunate that the assumption of Ph_4AsBPh_4 as a reference electrolyte cannot be applied with any confidence to the important aqueous solutions. The three sets of data for $\log {}^{0}\gamma^{S}{}_{\mathrm{Ph_4As^+}}{}^{0}\gamma^{S}{}_{\mathrm{BPh_4^-}}$ at the bottom of Table I highlight the difficulty. The first set records values as calculated directly from solubility products for this salt, but the solubility in water is too low for measurement. The second set shows values calculated from eq 5 and the third shows calculations from eq 6. The two indirect calculations of $\log {}^{0}\gamma^{S}{}_{\mathrm{Ph_4As^+}}{}^{0}\gamma^{S}{}_{\mathrm{BPh_4^-}}$

$$\log {}^{0}\gamma^{S}{}_{\mathrm{Ph_4As^+}}{}^{0}\gamma^{S}{}_{\mathrm{BPh_4^-}} = \log {}^{0}\gamma^{S}{}_{\mathrm{Ph_4As^+}}{}^{0}\gamma^{S}{}_{\mathrm{I^-}} + \log {}^{0}\gamma^{S}{}_{\mathrm{Ag^+}}{}^{0}\gamma^{S}{}_{\mathrm{BPh_4^-}} - \log {}^{0}\gamma^{S}{}_{\mathrm{Ag^+}}{}^{0}\gamma^{S}{}_{\mathrm{I^-}} \quad (5)$$

$$\log {}^{0}\gamma^{S}{}_{\mathrm{Ph_4As^+}}{}^{0}\gamma^{S}{}_{\mathrm{BPh_4^-}} = \log {}^{0}\gamma^{S}{}_{\mathrm{Ph_4As^+}}{}^{0}\gamma^{S}{}_{\mathrm{Pic^-}} - \log {}^{0}\gamma^{S}{}_{\mathrm{K^+}}{}^{0}\gamma^{S}{}_{\mathrm{Pic^-}} + \log {}^{0}\gamma^{S}{}_{\mathrm{K^+}}{}^{0}\gamma^{S}{}_{\mathrm{BPh_4}} \quad (6)$$

for transfer from acetonitrile to water lead to grossly different results of 5.1 and 12.2.

The differences show that one or more of the terms in eq 5 and 6 is not obeying the assumptions which are inherent in the determination of solvent activity coefficients through solubility products.[5] These assumptions are that the solid phase be in equilibrium with saturated solutions and that these contain only the dissociated ions. The solid phase (even if a solvate) is assumed to have the same free energy in each solvent. We suspect that the solubility products of $AgBPh_4$ in water and methanol are the source of the discrepancies in Table I. The solubility products are not reproducible and vary with the time allowed for equilibration during the potentiometric titration. Spectrophotometric measurements detected some decomposition of tetraphenylboride anion in hydroxylic solvents, particularly in trifluoroethanol. Despite our suspicions, we cannot be certain that only $AgBPh_4$ is at fault, so that assumptions based on transfer of Ph_4As^+ and Ph_4B^- from acetonitrile to water, and to a lesser extent to methanol, cannot be accepted with confidence. We are confident about values for the other solvents however. Values of $\log {}^{0}\gamma^{S}{}_{\mathrm{Ph_4As^+}}{}^{0}\gamma^{S}{}_{\mathrm{Ph_4B^-}}$ as calculated from eq 5 are admittedly up to 1 unit more negative than those calculated directly from the solubility of Ph_4AsBPh_4, but as noted, eq 5 involves differences in six solubility products each with an uncertainty of ±0.3 log unit, whereas the direct calculations only involve differences in two solubility products. We therefore expect the direct calculation to be much more reliable.

Group 2. The Anion–Molecule Assumptions (*i.e.*, $\log {}^{0}\gamma^{S}{}_{\mathrm{B^-}} = \log {}^{0}\gamma^{S}{}_{\mathrm{C}}$).[4,5,21] The solutes are chosen so that the large uncharged species, C, is thought to have the sum of all its "neutral" interactions with the solvent the same as those of the large anion, B^-. Thus the structure, size, and composition of B^-, should be as similar as possible to that of C. The electrostatic interaction of very large anions, B^- with the solvent is assumed to be unchanged, for transfer through a series of solvents of comparable high dielectric constant (*e.g.*, 20–40), but like Popovych,[4] we would expect that even very large anions would have stronger electrostatic interactions with water ($\epsilon = 80$) or formamide ($\epsilon = 110$) and much weaker electrostatic interactions with nonpolar solvents like hexane or benzene than with solvents of dielectric constant 20–40. Thus this group of assumptions might possibly be best applied to a series of solvents of similar polarity, as is the general case here.

The tetraphenylmethane–tetraphenylboride assumption (eq 7) is admirably suited to this group, for reasons

$$\log {}^{0}\gamma^{S}{}_{\mathrm{Ph_4B^-}} = \log {}^{0}\gamma^{S}{}_{\mathrm{Ph_4C}} \quad (7)$$

given by Popovych.[4] Values of $\log {}^{0}\gamma^{S}{}_{\mathrm{Ag^+}}$ are in Table VIII. The calculation is *via* eq 8, using data from

$$\log {}^{c}\gamma^{S}{}_{\mathrm{Ag^+}} = \log {}^{0}\gamma^{S}{}_{\mathrm{Ag^+}}{}^{0}\gamma^{S}{}_{\mathrm{BPh_4^-}} - \log {}^{0}\gamma^{S}{}_{\mathrm{Ph_4C}} \quad (8)$$

Table I. The insolubility of tetraphenylmethane in water and trifluoroethanol prevented calculations for these solvents. The value for formamide is not unreasonable, in terms of the other assumptions, despite the reservations noted for this high dielectric solvent relative to a lower dielectric reference solvent.

Bimolecular nucleophilic substitution reactions of methyl iodide (SN2) and of 4-nitrohalobenzenes (SNAr) with thiocyanate, bromide or azide ions proceed through "tight" transition state anions containing the organic substrate and the anionic base.[1,10] The mechanism of SN2 reactions is quite different from that of SNAr reactions, but in both transition states, the negative charge is dispersed and both substrate and transition state anion are large; the substrate and its transition state are also of comparable size, composition, and structure.[10] If we accept that transition state anions are in equilibrium with both the reactants and with their environment, then the rate constants for these reactions in different solvents (k^S and k^0) allow us to apply two further group 2 anion–molecule assumptions,[5] as expressed in eq 9 and 10 and calculated as in eq 11 and 12.

$$\log {}^{0}\gamma^{S}{}_{\mathrm{CH_3I}} = \log {}^{0}\gamma^{S}{}_{\mathrm{NCSCH_3I^{-\ddagger}}} \quad (9)$$

$$\log {}^{0}\gamma^{S}{}_{\mathrm{ArHal}} = \log {}^{0}\gamma^{S}{}_{\mathrm{Ar_{N_3}{-}Hal^{\ddagger}}} \quad (10)$$

$$(\mathrm{Ar} = 4\text{-}\mathrm{NO_2C_6H_4})$$

Results from these assumptions are in Table VIII, using data from Tables I and IV and from the literature.[10] Values of $\log {}^{c}\gamma^{S}{}_{\mathrm{Ag^+}}$ from eq 11 and 12 agree remarkably

$$\log {}^{0}\gamma^{S}{}_{\mathrm{Ag^+}} = \log {}^{0}\gamma^{S}{}_{\mathrm{Ag^+}}{}^{0}\gamma^{S}{}_{\mathrm{SCN^-}} - \log (k^S/k^0) \quad (\mathrm{SCN^-} + \mathrm{CH_3I}) \quad (11)$$

$$\log {}^{0}\gamma^{S}{}_{\mathrm{Ag^+}} = \log {}^{0}\gamma^{S}{}_{\mathrm{Ag^+}}{}^{0}\gamma^{S}{}_{\mathrm{N_3^-}} - \log (k^S/k^0) \quad (\mathrm{N_3^-} + \mathrm{ArHal}) \quad (12)$$

(Ar = 4-nitrophenyl, reactants in parentheses)

well with those from the assumption of eq 7 and this provides further evidence that transition-state anions are solvated like "real" anions.[10]

In part XIII[5] we included in this group an assumption that $\log {}^{0}\gamma^{S}{}_{\mathrm{I_2}} = \log {}^{0}\gamma^{S}{}_{\mathrm{I_3^-}}$. We were surprised[5] at the apparent success of this assumption because iodine is a Lewis acid with strong specific interactions with many basic solvents. The results now reported lead us to discard this assumption. It gives anomalous values of $\log {}^{0}\gamma^{S}{}_{\mathrm{Ag^+}}$, in solvents, *e.g.*, DMSO which have very different iodine basicity than acetonitrile.

Group 3. The Cation–Molecule Assumption ($\log {}^{0}\gamma^{S}{}_{\mathrm{A^+}} = \log {}^{0}\gamma^{S}{}_{\mathrm{C}}$). The reasoning is as outlined for group 2 and as reviewed by Popovych.[4] The assumption is in principle also limited to solvents of comparable dielectric constant, as noted for group 2. Two examples of this group are in Table VIII. The first is the

Strehlow assumption,[6,23] which for reasons which have often been stated[4,17] equates the solvent activity coefficients of ferrocene and the ferricinium cation. The assumption is applied here by assuming that $E_{1/2}$ for oxidation of dilute ferrocene at a platinum electrode under the conditions of slow cyclic voltammetry,[16] is not changed by solvent transfer and that the change in emf observed in different solvents is due to a change in the potential of the Ag|0.01 *M* $AgClO_4$ reference electrode, with the same solvent transfer. Thus $\log {}^{0}\gamma^{S}_{Ag^+}$ on this assumption follows from eq 13, using the data

$$\log {}^{0}\gamma^{S}_{Ag^+} = (1/0.059)(E^{S}_{0.01\,M\,Ag^+} - E^{0}_{0.01\,M\,Ag^+} \quad (13)$$

in Table VII.

The second example in group 3 equates the solvent activity coefficients of tetraphenylarsonium cation with those of tetraphenylmethane.[4] The assumption is applied to the data in Table I through eq 14. The

$$\log {}^{0}\gamma^{S}_{Ag^+} = \log {}^{0}\gamma^{S}_{Ag^+}{}^{0}\gamma^{S}_{I^-} - \log {}^{0}\gamma^{S}_{Ph_4As^+}{}^{0}\gamma^{S}_{I^-} + \log {}^{0}\gamma^{S}_{Ph_4C} \quad (14)$$

solubility of tetraphenylmethane in water and trifluoroethanol was too low for measurement, so the assumption is not applied to these solvents. Equation 14 is preferred to eq 15 because it avoids the alternative

$$\log {}^{0}\gamma^{S}_{Ag^+} = \log {}^{0}\gamma^{S}_{Ag^+}{}^{0}\gamma^{S}_{BPh_4^-} - \log {}^{0}\gamma^{S}_{Ph_4As^+}{}^{0}\gamma^{S}_{BPh_4^-} + \log {}^{0}\gamma^{S}_{Ph_4C} \quad (15)$$

route to $\log {}^{0}\gamma^{S}_{Ag^+}$ *via* the slightly suspect solubilities of $AgBPh_4$ and so gives greater variety. Equations 2 and 8, for example, depend on the solubility of $AgBPh_4$. Values of $\log {}^{0}\gamma^{S}_{Ag^+}$ from the ferrocene assumption (eq 13) give good agreement with values from eq 14, except for serious discrepancies with transfer from acetonitrile to methanol, ethanol, or dimethyl sulfoxide.

Mean Values. We have now considered the three possible comparisons of anions, cations, and neutral species of comparable structure. The values of $\log {}^{0}\gamma^{S}_{Ag^+}$ are remarkably similar, with some exceptions. There are undoubtedly differences in solvent orientation about the different charge types. There may also be different specific interactions, such as Lewis acid–base, hydrogen bonding, and dispersion forces,[10] but if these differences exerted a substantial effect, or if there were solvate formation, or if solutes were solvolyzed, then differences in $\log {}^{0}\gamma^{S}_{Ag^+}$ from the three groups of assumptions, involving nine different solutes (including two transition states), would surely appear. The agreement shown in Table VIII is most encouraging, in that no unexpected type of interaction, peculiar to any one solute, is apparent.

The six assumptions of groups 1–3 have been averaged in Table VIII to give a mean value of $\log {}^{0}\gamma^{S}_{Ag^+}$. Equal weight was given to each group, irrespective of how many assumptions that group contained. This of course dampens many of the irregularities inherent in any one assumption. We now compare these mean values with $\log {}^{0}\gamma^{S}_{Ag^+}$, as derived from the assumption that we are strongly advocating, the assumption of negligible E_{lj}.

Group 4. Negligible E_{lj}.[5,20] The data for this assumption are in Table V and values of $\log {}^{0}\gamma^{S}_{Ag^+}$ are in Table VIII. We do not claim that E_{lj} is negligible in *all* electrochemical cells, but suggest that, except when water is involved, it is negligible in cell A when the bridge is 0.1 *M* tetraethylammonium picrate in either solvent. We base this claim on the extraordinarily good correlation of $\log {}^{0}\gamma^{S}_{Ag^+}$ from this assumption with both the mean values and individual values from other quite unrelated assumptions. We cover a range of 10^{16} in ${}^{0}\gamma^{S}_{Ag^+}$, yet even the greatest discrepancy between group 4 values and the mean is <10. The largest discrepancy is for transfer from acetonitrile to trifluoroethanol, a solvent for which only two assumptions, of a possible six, were available for calculating the mean value. The correlation shown, coupled with the observations in Table VI on constant emf in a cell A, even with bridges containing different solvents, is a strong argument in favor of the assumption of negligible E_{lj}.

The assumptions in our first three groups perhaps place too much emphasis on the behavior of large "organic" solutes in solvents of similar dielectric constant. All but the ferrocene assumption depend in whole or in part upon a comparison of solubility products. No such criticisms can be leveled at the assumption of negligible liquid junction potential: it is entirely unrelated to any of the assumptions in groups 1–3, including the ferrocene assumption, and yet it gives virtually much the same results for $\log {}^{0}\gamma^{S}_{Ag^+}$.

The position now is as shown in Figure 1. We have plotted the free energies of transfer of the hypothetical 1 *M* solutions of silver cation, ideal with respect to Henry's law, from acetonitrile to 14 other solvents at 25°. Points for 95 of the possible 105 determinations, using the seven assumptions discussed in this paper, are shown. The values from the assumption of negligible liquid junction potential are starred, so as to illustrate how, in many cases, they are close to the mean values of other assumptions. The behavior shown in Figure 1 is our justification for advocating the assumption of negligible liquid junction potential. Those who would argue that it cannot be valid and must be grossly in error must be prepared also to treat the other currently popular assumptions as invalid. Deviations abound, they are expected, but they are less disturbing if it is remembered that we are presenting a correlation covering differences of *ca.* 20 kcal mol^{-1} in the solvation energy of silver cation. This will lead to differences of *ca.* 20 kcal mol^{-1} in the solvation energy of some anions.

Water. The behavior shown by water as solvent in Tables I, VI, and VIII and Figure 1 is sobering. Our mean of three values in Table VIII, ranging from 1.6 to 6.1, is in fair agreement with 3.0 from the assumption of negligible liquid junction potential, but to take a mean over this range is ridiculous and, in any case, the assumption of negligible liquid junction potential is in doubt, following the variable potentials recorded in Table VI when there is a junction at water. We have noted the difficulties with the tetraphenylarsonium tetraphenylboride assumption in water; indeed we could calculate $\log {}^{0}\gamma^{S}_{Ag^+}$ as 5.5, rather than 1.6, were we to calculate *via* silver and tetraphenylarsonium iodides, potassium and tetraphenylarsonium picrates, and potassium tetraphenylboride. Thus we could legitimately ignore the value of 1.6 given in Table VIII from this assumption, but we cannot see why the 6.1

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[23] H. Strehlow and H. M. Koepp, *Z. Elektrochem.*, 62, 373 (1958).

from Strehlow's ferrocene assumption[6] is so different from the 3.2 of the anion-molecule assumption (eq 9), the 3.0 of the assumption of negligible liquid junction potential, the 3.1 of the modified Born equation,[4,8] and the 3.2 estimated by Izmaylov.[4] Until these anomalies are explained, together with the behavior in Table VI, where emf's of cell A differ by up to 100 mV with different bridges, the all important link between water and the other 14 solvents in Table VIII must remain uncertain. On the credit side, however, we do have a majority of assumptions favoring 3.0, so, for consistency with the following recommendation, we propose that log $^0\gamma^S{}_{Ag^+}$ for transfer from acetonitrile to water at 25° be accepted as +3.0 until the behavior of solutes in water is clarified.

Single-Ion Solvent Activity Coefficients. In Table II we present some representative solvent activity coefficients for single anions and cations.[13] *These replace all values previously reported from our laboratories*[5,10,21] and are based on the assumption of negligible liquid junction potential in cell A. The numbers in Table II are immediately satisfying to a well-developed chemical intuition, particularly the structural intuition of a physical organic chemist, and this is the final argument in favor of the assumption of negligible E_{lj}. It is reasonable that methanol and ethanol should be less effective solvators of cations than is water, because bulky alkyl groups are about the basic oxygen in the alcohols. Trifluoroethanol (CF_3CH_2OH) is particularly satisfying, when compared with ethanol (CH_3CH_2OH) of similar dielectric constant. The electron-withdrawing CF_3 group relative to CH_3 strongly decreases the basicity of the alcoholic oxygen, but strongly increases the hydrogen-bond donor strength of trifluoroethanol, relative to ethanol. Thus trifluoroethanol should be a much weaker solvator of cations but a much stronger solvator of anions than is ethanol, and this expectation is realized by the numbers in Table II. The difference in anion solvation between ethanol and trifluoroethanol is greater for chloride than for bromide than for iodide, in agreement with chloride ion as the most powerful hydrogen-bond acceptor of the three.

The numbers in Table II show that small anions are much more solvated by protic than by dipolar aprotic solvents of much the same dielectric constant. This is reasonable,[10] because the protic solvents but not the dipolar aprotics can donate hydrogen bonds to the small anions, which are strong hydrogen bond acceptors. Very large cations and anions are recorded as poorly solvated by water relative to the other solvents. This is typical of most large solutes and is expected in this most structured of solvents.[10]

The numbers suggest that acetonitrile is a stronger solvator of silver cation than is water, but that water is a stronger solvator of many anions. This is reasonable in terms of the solvent sorting (Ag^+MeCN), ($NO_3^-H_2O$) observed in solutions of silver nitrate in water–acetonitrile mixtures.[28] Chloride ion is shown as rather similarly solvated in DMF, DMAC, sulfolane, *N*-methyl-2-pyrrolidone, propylene carbonate, and acetonitrile. This is reasonable, because these are solvents of comparable dielectric constant and do not have specific interactions with the small chloride ion.[10] HMPT, DMAC, and DMSO are recorded as excellent solvators of closed-shell cations, which is expected from the structure of the solvent molecules; *i.e.*, they have unsaturated oxygen carrying a substantially negative portion of a strong dipole.[10]

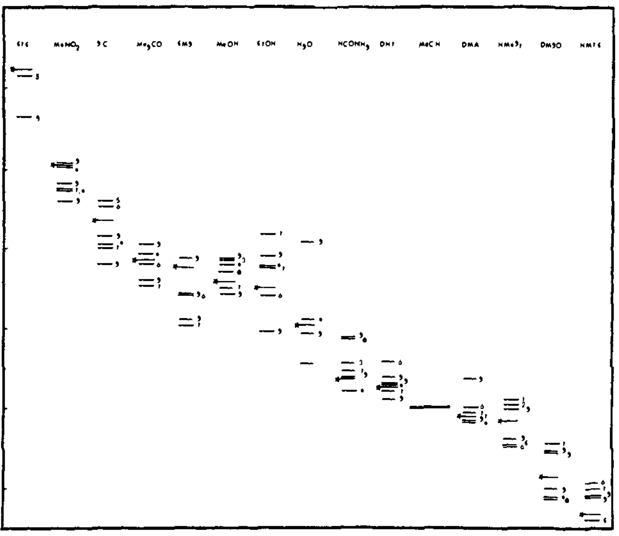

Figure 1. A comparison of extrathermodynamic assumptions, leading to the free energy of transfer [U_{Ag^+}(solvent) − U_{Ag^+}(CH_3CN)] for transfer of 1 *M* silver cation from acetonitrile to other solvents at 25°. The values from the assumption of negligible liquid junction potential in cell A are starred. The assumptions, as numbered in the figure, are (1) log $^0\gamma^S{}_{Ph_4As^+}$ = log $^0\gamma^S{}_{Ph_4B^-}$; (2) log $^0\gamma^S{}_{Ph_4B^-}$ = log $^0\gamma^S{}_{Ph_4C^+}$; (3) log $^0\gamma^S{}_{AsF}$ = log $^0\gamma^S{}_{ArN_3F^{-\mp}}$ (Ar = 4-nitrophenyl); (4) log $^0\gamma^S{}_{CH_3I}$ = log $^0\gamma^S{}_{NCSCH_3I^{-\mp}}$; (5) log $^0\gamma^S{}_{Fe(C_5H_5)_2}$ = log $^0\gamma^S{}_{Fe(C_5H_5)_2{}^+}$; (6) log $^0\gamma^S{}_{Ph_4As^+}$ = log $^0\gamma^S{}_{Ph_4C}$.

The point need not be labored; suffice to say that the numbers in Table II, which suggest differences in various solvents of over 20 kcal mol^{-1} for solvation of cations and of over 12 kcal mol^{-1} for anions, are very much as expected, from the molecular structure of solvents and solutes, combined with a qualitative understanding of solute–solvent interactions.[10] As noted, we regard the intuitively satisfying numbers in Table II as additional evidence in favor of the assumption of negligible liquid junction potential.

Recommendation. Chemists must resolve the question of single-ion solvent activity coefficients without delay. A variety of assumptions are appearing in the literature and a universal assumption must be agreed upon, before too many different numbers with an obscure history are recorded. We will never know if any one assumption is "correct," so that provided a single method of recording, interpreting, and predicting solvent effects on the chemistry of ions is devised, then we have nothing to lose and everything to gain by agreeing upon a universal assumption.

Popovych[4] has stated correctly that the assumption of negligible liquid junction potential in cell A has received no strong endorsement. Our presentation in part XIII was weak,[5] but it is now a much more convincing assumption. It is in our opinion the easiest to measure, the easiest to communicate, and the easiest to comprehend of any we have noted. There is no immediately obvious reason why it might not be a valid assumption. Our test in Table V suggests that it is valid. It leads directly to log $^0\gamma^S{}_{Ag^+}$, which is perhaps the most useful cation for linking up anions through their sparingly soluble silver salts. The Ag|

0.01 *M* $AgClO_4$ couple is an excellent reference electrode for nonaqueous electrochemistry. When it is linked through a 0.1 *M* tetraethylammonium picrate salt bridge to other electrodes in various solvents, a host of electrochemical measurements, meaningful within the framework of the assumption, are possible.

We therefore recommend that the following extrathermodynamic assumption be considered. *There is a negligible liquid junction potential in a cell composed of silver wires in 0.01 M silver perchlorate solutions in two solvents connected by a bridge of 0.1 M tetraethylammonium picrate in that solvent of the pair which is the weaker solvator of silver cations.* We note that further work is required before this assumption can be accepted with confidence for aqueous solutions. Our interpretation of "negligible" is ±20 mV.[24]

(24) NOTE ADDED IN PROOF Recent work by I. M. Kolthoff and M. K. Chantooni [*Anal. Chem*.. **44**, 194 (1972); *J. Amer. Chem. Soc*., **93**, 7104 (1971)] has convinced us that the solubility product of $AgBPh_4$ is 14.4 in methanol and 17.2 in water, and of Ph_4AsBPh_4 is 17.3 in water. Thus values in Tables I, II, and VIII must be adjusted accordingly. Most important is the new value of 3.7 in Table VIII for transfer of Ag^+ from acetonitrile to water by the $Ph_4As^+ = Ph_4B^-$ assumption. This new value substantially changes our reservations about the assumptions of group I, insofar as they are applied to aqueous solutions. Our discussion should be read with the new values in mind. We are now confident that the all-important log γ_{Ag^+} for transfer from acetonitrile to water at 25° lies between 3 and 4 and that the value of 6.1 given by the ferrocene assumption is misleading. We thank Professor Kolthoff for communicating with us prior to publication of his papers.

A Quantitative Analysis of Cyclopropyl β Hyperfine Splittings[1]

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Abstract: The 4-(2-cyclopropyl-1-ethynyl)nitrobenzene anion radical and the (2-cyclopropyl-1-ethynyl)tropenyl radical, two π radicals having the cyclopropyl group attached to digonal carbon, have been synthesized and studied by esr spectroscopy. The corresponding methyl analogs were also synthesized and shown to have essentially equivalent spin distributions. The isopropyl analog was also prepared in the first, anion radical, series. Small, but appreciable, differences in spin densities (hfs) are observed for this anion radical in comparison to its methyl and cyclopropyl relatives. The esr data show that the cyclopropyl methine β hfs are smaller by factors of 0.83 and 0.77, in the anion radical and radical cases, respectively, than the methyl hfs even though the spin distributions are closely similar. These ratios are used, in conjunction with data previously collected, to calculate the explicit equation relating cyclopropyl β hfs to dihedral angle. This equation can be used to obtain cyclopropyl rotational barriers from a single esr measurement. A three-term equation for cyclopropyl β hfs involving (1) hyperconjugative, (2) cyclopropyl–cyclobutyl conjugative, and (3) σ electron spin transmission mechanisms has been further substantiated and the respective contributions of these various mechanisms calculated as a function of dihedral angle.

Esr hyperfine splittings (hfs) of the β type have found increasingly frequent use in the conformational analysis of radicals because of their pronounced orientation dependence.[3–7] Most analyses have used the simple form of eq 1 for the conformation dependence. According to this, the hfs (a_H) of a β proton is directly proportional to the spin density, ρ_α, at the α carbon and to $\langle\cos^2\theta\rangle_{av}$, where θ is the dihedral angle between the C_β–H bond and the relevant p orbital on C_α. However, eq 2 is more accurate.[8] It contains, in addition, a conformation-independent term $B_0\rho_\alpha$ representing, in part, spin transmission through the σ bonds. Evidence is available that the $B_0\rho_\alpha$ term is by no means negligible in general.[9]

$$a_H = B_2\langle\cos^2\theta\rangle_{av}\rho_\alpha \qquad (1)$$

$$a_H = [B_0 + B_2\langle\cos^2\theta\rangle_{av}]\rho_\alpha \qquad (2)$$

Availability of a methyl analog ($CH_3\dot{C}<$) to the pertinent system ($R\dot{C}<$) greatly facilitates the analysis, since $\langle\cos^2\theta\rangle_{av}$ is 0.500 for a rapidly rotating cylindrically symmetrical group and since ρ_α is often essentially identical for the two radicals. A conformational index *C*(R) has been defined as in the first segment of eq 3.[7] Application of eq 2 and cancellation of ρ_α lead to the right-hand side. If, instead, eq 1 is used the simplified relation of eq 4 results. The final form of eq 4 also requires the assumption of equal B_2's for R and CH_3. If one is willing to make all of these assumptions, the experimental *C*(R) values can be translated quite simply

$$C(R) = a_H(R)/a_H(CH_3) = [B_0(R) + B_2(R)\langle\cos^2\theta\rangle_{av}{}^R]/[B_0(CH_3) + B_2(CH_3)0.500] \qquad (3)$$

$$C(R) = a_H(R)/a_H(CH_3) = B_2(R)\langle\cos^2\theta\rangle_{av}{}^R/0.500B_2(CH_3) = 2\langle\cos^2\theta\rangle_{av}{}^R \qquad (4)$$

(1) This research was supported by the Welch Foundation, Grant F-149.

(2) To whom correspondence should be addressed.

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