Table I. Infrared Spectra and $\sigma_R{}^0$ Values of Monosubstituted Ethylenes[a]

Substituent	$\nu_{C=C}$	A^b	$\pm\sigma_R{}^{0\,c}$	$\sigma_R{}^{0\,d}$
Br	1597	1640	0.23	−0.16
I	1587	1209	0.22	−0.14
OEt	1638, 1652 1612	5149	0.44	...
OBu	1636, 1652 1612	5263	0.42[e]	...
OCOMe	1648	2115	0.23	−0.21
n-Pr	1641	470	0.11	...
sec-Bu	1641	460	0.11	...
t-Bu	1641	512	0.12	−0.17[f]
$CH(CH_2)_5$	1638	528	0.13	...
CH_2Ph	1638	359	0.12	−0.08
Ph	1630	339	0.10	−0.09
CH_2OH	1646	177	0.00	−0.07
CH_2Cl	1646 (sh), 1642	123	0.00	−0.03
CH_2Br	1646 (sh), 1638	87	0.00	...
$SiCl_3$	1598	301	0.09[e]	...
COOH	1637 1618	2304	0.29	+0.21
COOMe	1635 1622	733	0.15	...
COOEt	1638 1622	887	0.18	+0.19
CN	1650 1608	117	0.09	+0.21

[a] Frequencies and intensities refer to measurements in CCl_4 solution on a Perkin-Elmer 125 spectrometer. [b] Integrated intensity area in l. mole^{-1} cm^{-2}. [c] $\sigma_R{}^0$ derived from the ir intensity of monosubstituted benzene; taken from ref 3 unless otherwise stated. [d] $\sigma_R{}^0$ derived from the ^{19}F nmr spectra of substituted fluorobenzenes: taken from ref 9 unless otherwise stated. [e] Unpublished work by R. F. Pinzelli. [f] R. W. Taft and W. A. Sheppard, private communication.

that $|\sigma_R{}^0(Me) - \sigma_R{}^0(Cl)|$ is 0.10. We have $\sigma_R{}^0(Cl) = -0.23$ from ir measurements[3] which gives $\sigma_R{}^0(Me) = -0.13$, in fair agreement with the ir value of −0.10 and the ^{19}F value of −0.15 (see Taft, *et al.*, in ref 2).

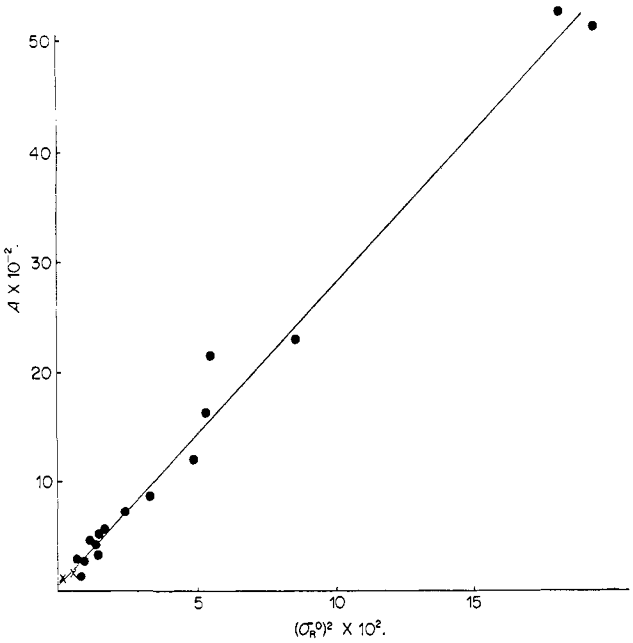

Figure 1. Integrated intensity of the infrared C=C stretching vibration for monosubstituted ethylenes plotted against the square of $\sigma_R{}^0$: ●, ir-derived $\sigma_R{}^0$ values; ×, ^{19}F-derived $\sigma_R{}^0$ values.

A normal coordinate analysis applicable to monosubstituted ethylenes has been carried out by Popov and Kagan[7] who quoted atomic displacements for the carbon and hydrogen atoms. We have, as before,[6] calculated by the CNDO2 method[8] the dipole moment at the equilibrium and stretched states of fluoroethylene and hence[6] found $\partial\mu/\partial Q$ as 39.6. The expected A value of fluoroethylene can be deduced from $\sigma_R{}^0(F) = 0.34$ as $A = 3235$ by reading off from Figure 1. This value of $A = 3235$ is equivalent to $\partial\mu/\partial Q = 67.8$ (*cf.* ref 6).

Acknowledgment. R. F. P. and J. M. A. are grateful to the Centre National de la Recherche Scientifique and the Royal Society for Post Doctoral Fellowships, and M. V. S. acknowledges the award of a 3M Research Studentship.

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(7) E. M. Popov and G. I. Kagan, *Opt. Spectry* (USSR), 12, 102 (1962).

(8) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129, S136 (1965).

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On the Solvation of Ions in Dipolar Aprotic Solvents. Chlorine-35 Nuclear Magnetic Resonance Studies of Chloride Ion in Mixed Solvents[1]

Sir:

Parker and his colleagues[2,3] have concluded that chloride ion activity increases by 8.0 ± 0.3 units on a *log-*

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(1) We acknowledge the financial support of the Directorate of Chemical Sciences, AFOSR, the National Research Council of Canada, and the Ontario Department of University Affairs.

(2) J. Miller and A. J. Parker, *J. Am. Chem. Soc.*, **83**, 117 (1961).

(3) R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *ibid.*, **90**, 5049 (1968); A. J. Parker, *Advan. Phys. Org. Chem.*, **5**, 173 (1967).

arithmic scale on transfer of the ion from water to dimethyl sulfoxide (DMSO). (The qualitative significance of this conclusion is independent of the choice of extrathermodynamic assumptions used to resolve the ion activities.[4]) Quite naturally, ***hydrogen bonding*** of the protic solvent molecule to the small anion has been suggested as the solvation mechanism responsible for the effect. To date, little experimental information is available on the *local* solvent environment of anions. The hydrogen-bonding hypothesis tends to suggest that the requisite stoichiometric amount of a protic solvent in a mixture would strongly *preferentially* solvate the anion. However, the data of 80 vol % DMSO–CH_3OH[3] raises a question about this interpretation. The activity values for small anions are closer to DMSO values than to CH_3OH values in the mixture.

We have undertaken to extend the analysis of preferential solvation from solute chemical shifts suggested by Frankel, Stengle, and Langford[5] to solvation of chloride ion in mixtures of water with dipolar aprotic solvents. The earlier use of solute chemical shift depended upon the argument that solvent-dependent ^{59}Co chemical shifts of Co(acetylacetonate)$_3$ reflect the local environment. Independent evidence for this idea was obtained from relaxation time measurements on the Cr(III) analog of the Co complex. In the case of the Cl^- ion, the local environment may consist of solvent and/or counterions. In fact, it has been shown that $^{23}Na^+$ chemical shifts are anion dependent.[6]

In contrast to $^{23}Na^+$, the choice of cation and *concentration* of salt is of small importance compared to the choice of solvent. The chemical shifts are dominated by *solvent* shifts. This is, in fact, reasonable. If the paramagnetic term[7] in the chemical shift is most important, perturbation theory implies that shifts will depend strongly on the energy of the lowest lying electronic excited state. An excited state, which is probably the lowest lying for a solvated chloride ion, is the charge transfer to solvent (CTTS). Shifts interpreted in terms of chloride CTTS would be the observed "solvent shifts." Unfortunately, Cl^- CTTS bands in the uv spectra in the organic solvents are hidden by solvent absorption. (It is crudely suggestive that I^- CTTS bands lie at lower energy in the solvents of large negative solvent shift.[8])

Given (experimentally) that $^{35}Cl^-$ chemical shifts reflect the solvent environment of the ion, Figure 1 now deserves consideration. It shows ^{35}Cl chemical shifts as a function of solvent composition in mixtures of DMSO and CH_3CN with water. The results for CH_3CN–water mixtures appear to support the hydrogen-bonding hypothesis; there is a strong preference of Cl^- for small amounts of water. But, results for mixtures of DMSO–water do not. There appears to be nearly even competition between the two solvents for sites in the solvation shell of Cl^-.

A deeper examination suggests that the nearly even competition for Cl^- solvation sites may occur in both solvent mixtures. Cl^- solvent preference should be inferred from the change of local chloride environment as the bulk solvent *activity* of the solvent components varies.[9] Partial vapor pressure studies are available for both water–DMSO[10] and water–CH_3CN[11] mixtures. The DMSO–water system was analyzed at 70°. A quantitative comparison is possible for CH_3CN–water mixtures for which 25° thermodynamic data are available. The *straight line* in Figure 1 shows the correlation of ^{35}Cl chemical shift with *bulk* water activity.

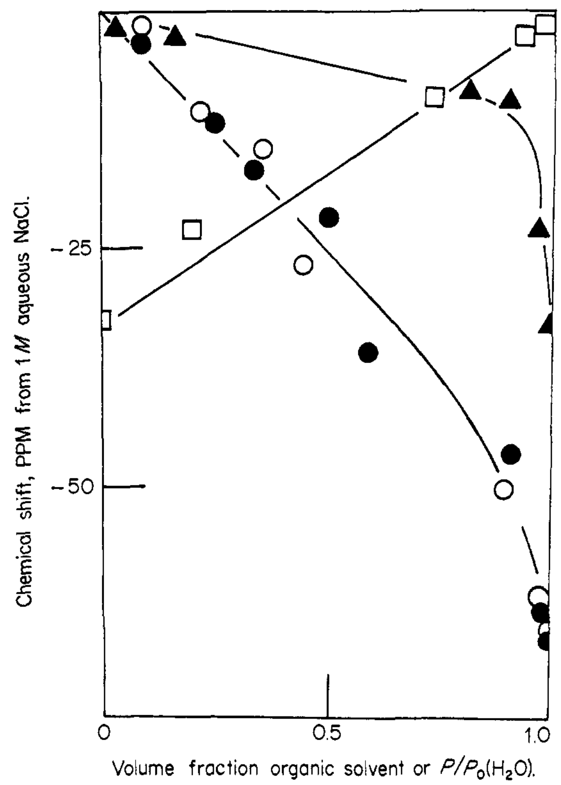

Figure 1. The variation of ^{35}Cl chemical shifts of chloride salts in mixtures of CH_3CN and DMSO with water. Open circles represent 0.25 *M* LiCl in DMSO–water. Closed cirlces represent 0.25 *M* $(C_2H_5)_4NCl$ in DMSO–water. Closed triangles represent 0.25 *M* $(C_2H_5)_4NCl$ in CH_3CN–water. All of these curves are chemical shift as a function of volume fraction of the organic component. The last curve (open squares) represents 0.25 *M* $(C_2H_5)_4NCl$ in CH_3CN–water, this time showing chemical shift as a function of the relative partial pressure of water (approximately relative activity) compared to pure water (P/P_0).

Table I. ^{35}Cl Chemical Shifts of Cl^- in Several Solvents[a]

Solute	Solvent	Concn, *M*	Chem shift, ppm
NaCl	$(CH_3)_2SO$	*Ca.* 0.1 (satd)	−69
LiCl	H_2O	0.25	0
	$(CH_3)_2SO$	0.25, 0.17, 0.12	−66
$(C_2H_5)_4NCl$	H_2O	0.25	0
	$(CH_3)_2SO$	0.25	−65
	CH_3CN	0.25, 0.20, 0.14, 0.11	−33
	$(CH_3)_2NCHO$	0.25	−42
	CH_3NO_2	0.25	−14

[a] Referred to 1 *M* aqueous NaCl.

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[4] A. J. Parker and R. Alexander, *J. Am. Chem. Soc.*, **90**, 3313 (1968).

[5] L. S. Frankel, T. R. Stengle, and C. H. Langford, *Chem. Commun.*, 373 (1965).

[6] E. G. Bloor and R. G. Kidd, *Can. J. Chem.*, **46**, 3425 (1968).

[7] A. Carrington and A. McLachlen, "Introduction to Magnetic Resonance," Harper & Row, New York, N. Y., 1967, p 57.

[8] T. R. Griffiths and M. C. R. Symons, *Trans. Faraday Soc.*, **56**, 1125 (1960).

[9] S. Behrendt, C. H. Langford, and L. S. Frankel, *J. Am. Chem. Soc.*, **91**, 2236 (1969).

[10] J. Kenttamaa and J. J. Lindberg, *Suomen Kemi*, B33, 98 (1960).

[11] V. de Landsberg, *Bull. Soc. Chim. Belges*, **49**, 59 (1940).

The correlation is perhaps surprising. The hydrogen-bonding hypothesis suggests that water should be pulled into the contact solvation shell of Cl^- on a preferential basis and that it should remain the dominating solvating species until bulk water activity has been reduced by a factor comparable to the activity change for transfer of the ion from protic aprotic solvent. The results indicate that, in fact, the immediate environment of Cl^- is related to the long-range structural aspects of solvent mixtures. We can imagine how this occurs if we look closely at the meaning of our numbers. The advantage of the chemical shift parameter as a solvation probe is that it reflects composition of the solvent layers in contact with Cl^-. The activities from vapor pressures characterize the solvent in the solution *at a distance far enough from* Cl^- *to be unperturbed by the ions.* Both of these regions are in equilibrium with an intervening region to which we have no experimental access. A reason why water is not strongly preferred over the aprotic solvent in the layer in contact with Cl^- might well be that a protic solvent molecule hydrogen bonded to Cl^- is strongly polarized so that it presents a "lyate ion like" aspect to the middle solvent region and this "lyate ion like" species is poorly "solvated" by the aprotic solvent. Conversely, an aprotic molecule solvating Cl^- may interact less favorably with the Cl^- but much more favorably with the surrounding solvent layer. In this way, the short-range favorable or unfavorable effects are mitigated and the local environment of the ion comes to reflect long-range interactions.

A final point: lines in the mixed solvents were very wide. They imply a residual assymmetry in the field gradient at the nucleus that is not averaged by tumbling.

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(12) Alfred P. Sloan Research Fellow 1968–1970.

Additions and Corrections

The Mechanism of the Aminolysis of Methyl Formate [*J. Am. Chem. Soc.*, **90,** 2638 (1968)]. By G. M. BLACKBURN and W. P. JENCKS, Graduate Department of Biochemistry, Brandeis University, Waltham, Massachusetts 02154.

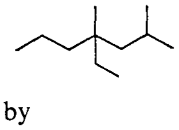
On page 2639, column 2, line 3, the rate constant for alkaline hydrolysis of methyl formate should read $1.95 \pm 0.1 \times 10^3\ M^{-1}\ \text{min}^{-1}$.

Cyclopropyl Conjugation in Olefinic Esters. Conformational Effects on Ultraviolet Absorption [*J. Am. Chem. Soc.*, **90,** 3769 (1968)]. By MARGARET J. JORGENSON and TERESA LEUNG, Department of Chemistry, University of California, Berkeley, California.

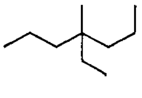
On page 3773, column 1, the second sentence of the third paragraph should read: The values determined for esters **1**, **5**, and **6**, are 9.4, 10.0, and 10.3 cps, respectively.

Biosynthesis of Indole Alkaloids. Vindoline [*J. Am. Chem. Soc.*, **90,** 4144 (1968)] by T. MONEY, I. G. WRIGHT, F. MCCAPRA, E. S. HALL, and A. I. SCOTT, Chemistry Department, University of British Columbia, Vancouver 8, Canada.

On page 4146, Figure 2, the schematic structure



should be replaced by



The Interpretation of Porphyrin and Metalloporphyrin Spectra [*J. Am. Chem. Soc.*, **90,** 6577 (1968)]. By ALSOPH H. CORWIN, ARTHUR B. CHIVVIS, ROBERT W. POOR, DAVID G. WHITTEN, and EARL W. BAKER, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland.

In Table I, column 6, the last value should be 24,530 instead of 24,360. On page 6580, Figures 2 and 3 should be interchanged.

The Acid-Catalyzed Hydrolysis of Acyl Phosphates [*J. Am. Chem. Soc.*, **90,** 6803 (1968)]. By DAVID R. PHILLIPS and THOMAS H. FIFE, Department of Biochemistry, University of Southern California, Los Angeles, California 90053.

In the abstract, the legend to Figure 6, and on page 6808 it should read: plots of ($\log k_{obsd} + H_0$) *vs.* ($\log C_H + H_0$). This expression appeared with the parentheses misplaced.

Spin-Delocalization Mechanisms in Some Paramagnetic Tris-2,2′-bipyridine Complexes of Nickel(II) [*J. Am. Chem. Soc.*, **90,** 6946 (1968)]. By M. WICHOLAS and R. S. DRAGO, William A. Noyes Laboratory, University of Illinois, Urbana, Illinois.

The first compound in Table I should be $Ni(bipy)_3Cl_2 \cdot 2H_2O$. On page 6950, the sentence beginning in column 2, line 37 should read: "The downfield resonance peak is due to either the *ortho* and *para* protons or the *meta* and *para* protons, and the upfield resonance peak is due to either the *ortho* or *meta* protons; however, of these only one assignment is reasonable." The last sentence should read: "If the assignments are correct, the contact shifts are consistent with