

CHEMICAL SHIFTS OF CHARGE-TRANSFER COMPLEXES AND BUCKINGHAM EQUATION

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The ^1H NMR spectra of the charge-transfer complex of 1-ethyl-4-methoxycarbonylpyridinium iodide have been recorded in various dipolar aprotic solvents. An attempt is made to interpret the chemical shifts in terms of Buckingham's reaction field equation for spherical cavities. A linear dependence has been found between the $\delta(2,6)$ values and the square of dielectric function for a spherical cavity, which confirms the validity of the Buckingham equation for this class of compounds.

A polar molecule polarizes the surrounding medium, which generates the reaction field at the solute and causes solvent shifts in NMR spectra. If the contributions other than the polar effect are negligible, the shift should be describable in terms of the reaction field.

Buckingham et al.¹ expressed the shift due to the screening as

$$\delta_E = AE_Z + BE^2 + C, \quad (1)$$

where δ_E is the "polar effect" on the chemical shift, A , B , C are constants, and E_Z is the component of the total field E along X—H bond. The second term is small for a weak interaction. However, for the reaction field perpendicular to the X—H bond the chemical shift would be proportional to E^2 .

Assuming the Onsager model of creation of a spherical cavity by a polar molecule, the polar shift δ_E obtained by Buckingham et al.¹ is given by Eq. (2), where ϵ means the relative permittivity of the solvent, n , μ , and α stand for the refractive index, dipole moment, and polarizability of the solute, respectively, and ϕ is the angle between the solute dipole moment μ and the X—H bond; C is the value of δ_E for $\epsilon = 1$, and D , F are constants different from A , B in Eq. (1).

$$\delta_E = C - 2 \cdot 10^{-12} D \left[\frac{(\epsilon - 1)(n^2 - 1)}{(2\epsilon + 2.5)} \mu \cos \phi / \alpha \right] -$$

$$- 10^{-18} F((\epsilon - 1)/(2\epsilon + 2.5))^2 \mu^2 / \alpha^2 \quad (2)$$

In most cases the angle between the dipole moment and the field (along C—H axis) is zero, and the second term is very small. However, for a compound in which the dipole moment is perpendicular to the C—H axis the chemical shift is determined by the second term.

There is a class of compounds — charge-transfer complexes in which the dipole moment could be perpendicular to the C—H axis. In general, NMR studies of such charge-transfer complexes are connected with the difficulties in preparing the complex in sufficiently high concentrations, because the charge-transfer complexes which are donor-acceptor complexes usually are present together with high concentrations of the donors and acceptors.

Kosower² showed that in the solvatochromic charge-transfer complex 1-ethyl-4-methoxycarbonylpyridinium iodide (*I*) the dipole moment is perpendicular to the plane of the pyridinium ring (Fig. 1). This complex can be synthesized in crystalline form, and solutions of various concentrations can be prepared in various solvents.

Thus this compound offers a test for the Buckingham equation. It may be noted that *I* is a model compound for the biologically important compound NAD, and extensive studies have been carried out on this and derived compounds³. 1-Ethyl-4-methoxycarbonylpyridinium iodide can exist as contact ion pair (tight or loose ion pair), solvent-separated ion pair, and dissociated ions. In aprotic solvents this compound exists mostly (>99%) as the contact (tight or loose) ion pair⁴.

The ¹H NMR spectra of this contact ion pair were recorded and equilibrium between the very tight (CT complex) and caged ion pairs were reported earlier⁵. This present communication deals with application of the Buckingham equation.

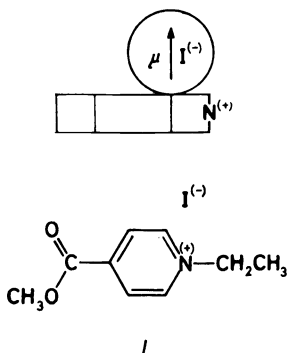


FIG. 1
Dipole model of *I*. Taken from ref.⁹, p. 299.

EXPERIMENTAL

1-Ethyl-4-methoxycarbonylpyridinium iodide was synthesized and purified by standard procedure^{2,6}. The solvents and tetrabutylammonium iodide were purified as given in ref.⁷.

All the ¹H NMR spectra were recorded on a JEOL 60 MHz apparatus, using tetramethylsilane as the internal standard and the solvent peaks as secondary references⁸. The concentration of *I* was 0.2 mol l⁻¹ in all the solvents, however, in chloroform the chemical shifts were recorded at various concentrations of *I* (down to 0.04 mol l⁻¹). The measurements were carried out at room temperature.

RESULTS

Table I presents the chemical shifts of *I* measured in chloroform, methylene chloride, acetonitrile, dimethylformamide, dimethyl sulfoxide, and propylene carbonate. It can be seen that the $\delta_{2,6}$ doublet is significantly affected by the solvents. This is understandable on the basis of model of *I* (Fig. 1 in ref.²). In Table II various properties of the solvents and the square of the dielectric function $\eta^2 = [(\epsilon - 1)/(2\epsilon + 2.5)]^2$ are given. The positions of one of the doublets of $\delta_{2,6}$ are plotted against the square of the dielectric function in Fig. 2.

The values of $\delta_{2,6}$ are also plotted against the dielectric constant ϵ (Fig. 3), concentration of *I* in chloroform (Fig. 4), and concentration of added tetrabutylammonium iodide (TBAI) i.e. the concentration ratio [TBAI] : [*I*] (Fig. 5).

DISCUSSION

The chemical shifts δ observed for a given nucleus in a molecule in a solution differ from that observed in gas phase. The difference δ_{solv} between these chemical shifts thus arises from solute-solvent interactions. Actually δ_{solv} can be written as¹

$$\delta_{\text{solv}} = \delta_{\text{gas}} - \delta_{\text{obs}} = \delta_{\text{b}} + \delta_{\text{w}} + \delta_{\text{a}} + \delta_{\text{E}} + \delta_{\text{S}}, \quad (3)$$

where δ_{b} is due to bulk diamagnetic susceptibility, δ_{w} corresponds to weak (van der Waals) interactions, δ_{a} corresponds to the solvent magnetic anisotropy, δ_{E} is the polar effect, and δ_{S} is the specific interaction with the solvent.

With application of an internal standard and at low concentrations of solute (3–5%), δ_{b} and δ_{w} can be eliminated or minimized or δ_{E} can be separated⁸. The δ_{a} term is minimized by excluding aromatic solvents (like benzene) and alcohols⁸. Thus using TMS as the internal standard (the solvent peaks can also act as secondary standard) and avoiding the above-mentioned solvents we can isolate the δ_{E} term. Hence in the present case δ_{obs} in various solvents is interpreted in terms of the polar effect δ_{E} which is given as in Eqs (1) and (2).

Two points are apparent from Eq. (2): (i) if $\phi = 90^\circ$, then a plot of the square of dielectric function against δ_{obs} should give a straight line whose extrapolation to $\varepsilon = 1$ should provide the constant C ; (ii) the constant C actually is the chemical

TABLE I
The ^1H NMR spectra of pyridinium iodide *I* in various solvents^a

Solvent	Position ^b				
	CH(2, 6)	CH(3, 5)	CH ₂ (7)	CH ₃ COO	CH ₃ (8)
CHCl ₃	9.72, 9.62 (9.05, 8.95)	8.55, 8.45 (8.44, 8.36)	5.35; 5.21; 5.18; 4.98 (4.91, 4.82; 4.67, 4.54)	4.08 (3.98)	1.97, 1.84, 1.60 (1.82, 1.67, 1.57)
CH ₂ Cl ₂ ^c	9.50, 9.29	8.33, 8.23	—	3.80	1.65, 1.53, 1.41
DMF ^d	9.40, 9.29 (8.90, 8.80)	8.38, 8.24 (8.30, 8.20)	4.92, 4.81; 4.68, 4.56	3.78	^h
DMSO ^e	9.30, 9.20	8.45, 8.35	4.83, 4.70; 4.60, 4.47	3.86	ⁱ
MeCN ^f	9.29, 9.19	8.37 ^j	4.96, 4.83; 4.72, 4.60	3.98	^k
PC ^g	9.22, 9.10 (9.05, 9.95)	8.52 ^j (8.43)	^l ^l — —	^l —	^l —

^a The δ values in ppm, TMS as the internal standard, the solvent peaks as secondary reference; ^b the δ values in parentheses are those for the perchlorate salt; ^c methylene chloride; ^d dimethylformamide; ^e dimethyl sulfoxide; ^f acetonitrile; ^g propylene carbonate; ^h under DMF; ⁱ DMSO; ^j broad; ^k under CH₃CN; ^l under propylene carbonate.

TABLE II
The polarity parameters and dielectric functions of the solvents used^a

Solvent	ε^b	Z	η^c	η^2
CHCl ₃	4.8	63.2	0.313	0.098
CH ₂ Cl ₂	9.0	64.2	0.390	0.152
DMF	37.0	68.4	0.471	0.222
DMSO	46.0	71.1	0.476	0.227
MeCN	36.2	71.1	0.470	0.221
PC	64.4	72	0.483	0.233

^a For the abbreviations see Table I; ^b dielectric constant (relative permittivity); ^c the dielectric function $((\varepsilon - 1)/(2\varepsilon + 2.5))$.

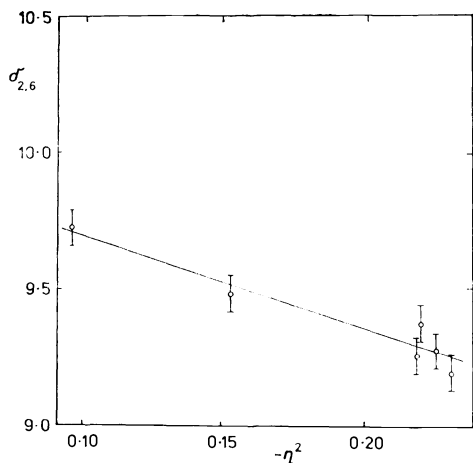


FIG. 2

Dependence of $\delta_{2,6}$ on the square of dielectric function η^2 ; the solid line refers to Eq. (4)

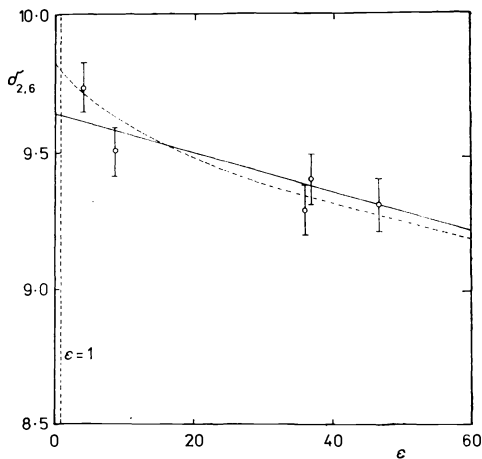


FIG. 3

Dependence of $\delta_{2,6}$ on the dielectric constant ϵ ; the solid line refers to Eq. (6)

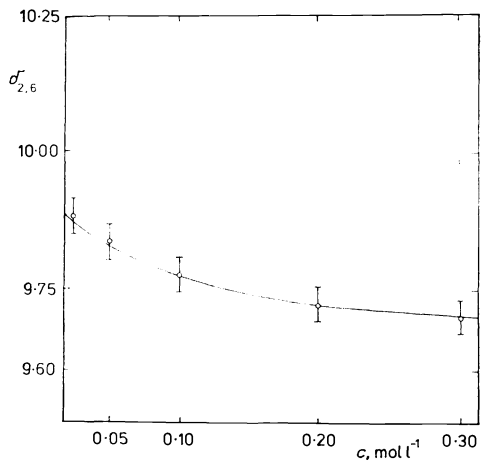


FIG. 4

Dependence of $\delta_{2,6}$ on concentration of I

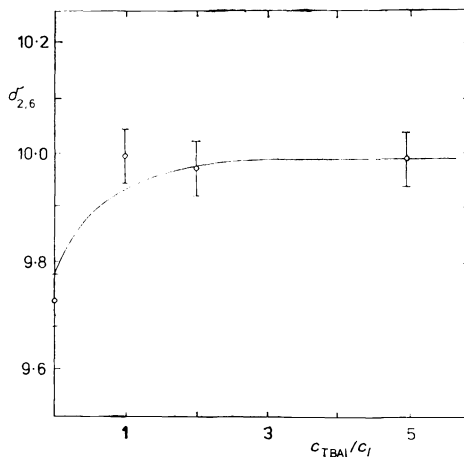


FIG. 5

Dependence of $\delta_{2,6}$ on the concentration ratio [TBAI]: [I]

shift of the polar molecule in a medium with $\epsilon = 1$, i.e. it equals to δ_{vac} or δ_{gas} or δ of the isolated molecule⁸. Thus according to Laszlo a plot of δ_{obs} vs ϵ extrapolated to $\epsilon = 1$ will give δ for an isolated molecule (or $\delta_{\text{vac}} = \delta_{\text{gas}}$)⁸. The same result can also be obtained by plotting δ_{obs} against Z -value and extrapolation to $Z = 54$ (Z -value of vacuum)⁹. In a pyridinium iodide such as *I* the dipole moment is perpendicular to the pyridinium ring² (Fig. 1). Thus if the reaction field is oriented along the pyridinium ring (i.e. along X—H bond), then the angle between the dipole moment and X—H bond is $\phi = 90^\circ$, and the higher term in Eq. (2) should contribute to δ_{E} (or δ_{obs}). In fact, a straight line dependence is obtained between $\delta_{2,6}$ and η^2 . The least square fit gives

$$\delta_{2,6} = 10.02 - 3;20\eta^2 \quad (4)$$

with correlation coefficient 0.97.

The dependence is represented in Fig. 2 as solid line. This expression also gives δ_{vac} or $\delta_{\text{gas}} = 10.02$ for $\eta^2 = 0$ ($\epsilon = 1$). The dependence of $\delta_{2,6}$ on Z -value gives the least square fit equation

$$\delta_{2,6} = 12.49 - 4.5 \cdot 10^{-2}Z \quad (5)$$

(correlation coefficient 0.95) which for $Z = 54$ (i.e. vacuum) gives $(\delta_{2,6})_{\text{vac}} = 10.06$.

The dependence of $\delta_{2,6}$ on ϵ (Fig. 3) is not so perfectly linear. The curve (dotted line) extrapolated to $\epsilon = 1$ gives $\delta_{2,6} = 9.82$; whereas a least square fit straight line (correlation coefficient 0.91)

$$\delta_{2,6} = 9.64 - 7.32 \cdot 10^{-3}\epsilon \quad (6)$$

gives $(\delta_{2,6})_{\text{vac}} = 9.6$.

Figure 4 (the plot of $\delta_{2,6}$ vs concentration of *I* in chloroform) and Fig. 5 ($\delta_{2,6}$ vs concentration of TBAI added) give $(\delta_{2,6})_{\text{vac}} = 9.92$ and 9.98, respectively.

A least square fit straight line is also obtained between $\delta_{2,6}$ and η with correlation coefficient 0.96

$$\delta_{2,6} = 10.52 - 2.57\eta, \quad (7)$$

but this relationship gives $(\delta_{2,6})_{\text{vac}} = 10.52$ which is much too high and not supported by other experimental data. Nevertheless, the linear relationship between $\delta_{2,6}$ and both η and η^2 indicates that the Buckingham equation adequately describes the change in chemical shift for this class of compounds.

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