

A NOTE ON EVALUATION OF SOLVENT SHIFTS IN IR SPECTROSCOPY

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Analysis of ten data sets has proved that for evaluation of solvent effects with the Buckingham equation the cross-term of the Buckingham power series is decisive which has not yet been used for these evaluations. The decisive contribution of this cross-term in the dependence of position of IR absorption bands on relative permittivity and refractive index of the medium explains applicability of the empirical methods used for evaluation of solvents effects on IR spectra as *e.g.* the BHW plot or the G solvent factors of Allerhand and Schleyer.

The Buckingham equation¹ was widely applied for description of solvent shifts of IR absorption bands; its validity is considered to confirm physical nature of collision complexes². Certain limitation in applicability of this equation with respect to selection of solvents and its failure in case of some systems have the result that empirical methods, as *e.g.* the Bellamy–Hallam–Williams method (BHW plot⁴) or the solvent G factors of Alerhand and Schleyer⁵, are still in use for practical purposes³ of evaluation of influence of medium on IR spectra.

The Buckingham equation is used in the form:

$$\nu = A + B(\epsilon - 1)/(2\epsilon + 1) + C(n^2 - 1)/(2n^2 + 1). \quad (1)$$

In this form the equation takes into account the influence of polarity (characterized by relative permittivity ϵ) and polarizability (characterized by refractive index n) of solvent molecules on vibration of the studied group of solute as independent effects, the mutual correlation of the both factors being neglected. Qualitative idea of formation of a collision complex between solute and solvent molecules, however, necessitates the correlation of the both effects. Change in polarity and/or polarizability of solvent will affect stability of the collision complex and, hence, intermolecular distances in the complex. Both the polarity and polarizability effects depend on the distances, thus a change in the intermolecular distance brought about by one effect will affect the magnitude of the other effect on the studied group. Such action of solvent molecules on vibration of bonds in solute could be described by the cross-term $f(\epsilon) \cdot f(n^2)$ of the Buckingham expansion. Significance of this term for evaluation

of solvent effects is now verified by correlation of valence vibrations of a number of bonds in simple compounds using Eqs (1) and (2) without and with the cross-term, respectively.

$$\nu = A + B \frac{\varepsilon - 1}{2\varepsilon + 1} + C \frac{n^2 - 1}{2n^2 + 1} + D \frac{\varepsilon - 1}{2\varepsilon + 1} \cdot \frac{n^2 - 1}{2n^2 + 1} \quad (2)$$

EXPERIMENTAL

The used solvents were dried, rectified and kept over molecular sieve. The IR spectra were measured with a UR-20 spectrophotometer (Zeiss, Jena). The wave-number scale was calibrated according to the published values of C=O and N—H stretching vibrations of benzaldehyde⁶ and aniline⁷, respectively. The solute concentrations were 20 mmol l⁻¹ (0.06 cm NaCl cells). Spectra of gases were measured in a 10 cm cell.

TABLE I
Fundamental Frequencies of the Studied Bonds in Various Solvents

Solvent	f(ε)	f(n ²)	f(ε, n ²)	I	II	III	IV
Gas	0.000	0.000	0.000	3 654	3 408	3 671	3 682
Hexane	0.185	0.185	0.034	3 621	3 355	3 655	3 654
Cyclohexane	0.202	0.204	0.041	3 617	3 346	3 654	3 649
Tetrachloromethane	0.225	0.214	0.048	3 611	3 323	3 649	3 643
Tetrachloroethylene	0.232	0.228	0.053	3 611	3 331	3 648	3 643
Carbon disulphide	0.260	0.261	0.068	3 591	3 317	3 645	3 628
1,1,2-Trichloroethylene	0.309	0.220	0.068	3 602	—	3 646	3 636
1,2-Dichloroethane	0.444	0.210	0.090	3 564	3 272	3 638	3 618
Dichloromethane	0.420	0.202	0.085	3 584	3 276	3 638	3 627
Tribromomethane	0.345	0.254	0.088	3 579	3 257	3 637	3 616
Diiodomethane	0.371	0.287	0.106	3 549	—	3 629	3 593
Dibromomethane	0.403	0.239	0.096	—	—	3 633	—
Acetonitrile	0.480	0.174	0.084	—	—	—	—
Diethyl ether	0.342	0.177	0.060	—	—	—	—
Dibutyl ether	0.289	0.194	0.056	—	—	—	—
Tetrahydrofurane	0.404	0.197	0.080	—	—	—	—
Triethylamine	0.243	0.196	0.048	—	—	—	—
Nitromethane	0.480	0.188	0.090	—	—	—	—

RESULTS AND DISCUSSION

Simple compounds were selected for this study, so that their spectra might be measured in gas phase, too, the compounds having been given more attention in literature. The selection was controlled also by the effort to represent the greatest possible number of types of the systems: I Phenol, $\nu(\text{O—H})$ free, aromatic; II Phenol-tetrahydrofuran complex, $\nu(\text{O—H})$ bonded; III Ionol, $\nu(\text{O—H})$ free, sterically hindered; IV Methanol, $\nu(\text{O—H})$ free, aliphatic; Va Aniline, $\nu(\text{NH}_2)$ antisymmetrical vibration; Vb Aniline, $\nu(\text{NH}_2)$ symmetrical vibration; VI Acetone, $\nu(\text{C=O})$ basic carbonyl group; VII Acetic acid, $\nu(\text{C=O})$ carbonyl group in a complex; VIII Benzaldehyde, $\nu(\text{C=O})$, carbonyl group aromatic; IX Trichloroacetaldehyde, $\nu(\text{C=O})$ little basic carbonyl group; X Acetophenone, $\nu(\text{C=O})$ the basis of the BHW plot and the standard for calculation of the solvent G factors. Out of solvents, for this study the solvents were used which do not form strong complexes on the basis of specific interactions and aromatic solvents.

TABLE I
(Continued)

Va	Vb	VI	VII	VIII	IX	X
3 500	3 418	1 737	1 732	1 718	1 778	1 709
3 485	3 400	1 724	1 717	1 707	—	1 697
3 483	3 397	—	1 716	1 707	1 768	1 696
3 481	3 396	1 719	1 714	1 703	1 766	1 692
3 479	3 395	—	—	—	—	1 693
3 476	3 391	1 718	1 711	1 700	1 763	1 690
3 479	3 396	—	—	1 699	—	—
—	—	—	—	—	1 763	1 686
3 466	3 386	1 713	1 713	1 713	1 761	1 685
3 450	3 373	1 708	1 708	1 694	—	1 680
3 444	3 368	1 707	1 705	1 692	1 757	1 679
—	—	—	1 709	—	—	1 683
—	—	1 715	1 715	1 697	1 759	1 687
—	—	1 721	—	1 703	—	1 694
—	—	—	—	1 704	—	1 694
—	—	—	—	1 700	—	—
—	—	—	—	—	—	1 693
—	—	1 712	—	1 697	—	1 685

The measured data (I, V, VIII) and those taken from literature (II (ref.⁸), III (ref.⁹), VI (ref.¹⁰), VII (ref.¹¹), IX (ref.¹²), X (ref.¹⁰)), are given in Table I. Table II gives the constants *A*, *B*, *C*, *D* of Eqs (1) and (2) calculated by the least squares method along with the respective correlation characteristics – correlation coefficients between the dependent variable and regression *R* and the significance level determined with the use of the Fisher *F*-criterion. In addition to it the Table gives also correlation coefficient of the simple regression between wave numbers of the studied bands and $f/\epsilon, n^2 r$.

The obtained results show that the Buckingham equation, Eq. (2), containing the cross-term correlates better the experimental data than Eq. (1). The correlation coefficients between the dependent variable and regression are markedly increased and the value of the Fisher *F*-criterion is statistically significant for a lower significance level α (5 to 50 times lower). From magnitude of *D* constant and correlation coefficient of the simple regression between the wave numbers of the studied stretching vibrations and the cross-term it follows that the cross-term has a predominant influence on the solvent-induced shifts of absorption bands.

TABLE II
Results of Regression Analysis of Experimental Data Using Eqs (1) and (2)

Values	I	II	III	IV	Va
Equation (1)					
<i>A</i>	3 655	3 415	3 674	3 691	3 507
<i>B</i>	—171.5	—297.3	— 65.7	—103.6	— 93.2
<i>C</i>	— 94.6	— 93.9	— 49.8	—135.5	— 45.4
<i>R</i>	0.929	0.958	0.965	0.924	0.842
Equation (2)					
<i>A</i>	3 654	3 407	3 671	3 682	3 499
<i>B</i>	33.9	20.0	1.4	83.6	87.1
<i>C</i>	17.3	23.6	— 19.5	33.5	25.1
<i>D</i>	—1 103	—1 703	—338.5	—1 005	—883.3
<i>R</i>	0.981	0.984	0.994	0.993	0.957
<i>r</i>	0.980	0.984	0.991	0.978	0.935
$\alpha(1)$	0.05	0.05	0.025	0.05	0.25
$\alpha(2)$	0.001	0.005	0.001	0.001	0.025

This decisive role of a single term of the Buckingham expansion — the cross-term — for expression of dependence of solvent shifts on relative permittivity and refractive index of solvent is obviously the reason of broad applicability of empirical one-parameter equations of the type of BHW plot or applicability of the solvent G factors of Allerhand and Schleyer. Instead of these empirical relations it would, therefore, be possible to use for practical purposes the following one-parameter form of the Buckingham equation:

$$\nu = \nu_0 + Df(\epsilon, n^2). \quad (3)$$

For such practical studies of solvent effects we recommend to use the following solvent series (the value $f(\epsilon, n^2)$ is given in brackets): hexane (0.034), cyclohexane (0.041), tetrachloromethane (0.048), tetrachloroethylene (0.053), carbon disulphide (0.068), trichloroethylene (0.068), dichloromethane (0.085), 1,2-dichloroethane (0.090), dibromomethane (0.096), and diiodomethane (0.106).

TABLE II
(Continued)

Vb	VI	VII	VIII	IX	X
Equation (1)					
3 423	1 739	1 733	1 721	1 779	1 713
— 64.7	— 29.3	— 9.9	— 30.2	— 29.2	— 34.0
— 70.8	— 63.0	— 79.0	— 50.1	— 30.9	— 59.0
0.894	0.951	0.989	0.953	0.985	0.937
Equation (2)					
3 417	1 737	1 732	1 718	1 778	1 709
56.7	— 3.5	— 2.9	2.1	— 13.9	8.9
— 23.3	— 39.0	— 69.2	— 19.8	— 16.8	— 20.8
— 594.5	— 162.9	— 73.9	— 205.5	— 102.4	— 263.7
0.965	0.969	0.994	0.985	0.995	0.980
0.952	0.938	0.867	0.975	0.986	0.967
0.1	0.025	0.01	0.025	0.025	0.025
0.01	0.001	0.001	0.005	0.001	0.005

REFERENCES

1. Buckingham A. D.: *Proc. Roy. Soc. A* 248, 169 (1958).
2. Horák M., Plíva J.: *Spektrochim. Acta* 21, 911 (1965).
3. Sinichi Ueji, Toshio Kinugasa: *Tetrahedron Lett.* 1976, 2037.
4. Bellamy L. J., Hallam H. E., Williams R. L.: *Trans. Faraday Soc.* 54, 1120 (1958).
5. Allerhand A., Schleyer P. R.: *J. Amer. Chem. Soc.* 85, 371 (1963).
6. Thompson H. W., Needham R. W., Jameson D.: *Spektrochim. Acta* 9, 208 (1957).
7. Krueger P. J.: *Can. J. Chem.* 40, 2300 (1962).
8. Osawa E., Yoshida Z.: *Spektrochim. Acta* 23A, 2029 (1967).
9. Horák M., Moravec J., Plíva J.: *Spektrochim. Acta* 21, 919 (1965).
10. Bellamy L. J., Williams R. L.: *Trans. Faraday Soc.* 55, 14 (1959).
11. Lascombe J., Haurie M., Josien M. L.: *J. Chim. Phys. Physicochim. Biol.* 1962, 1233.
12. Horák M., Moravec J.: *This Journal* 36, 2757 (1971).

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