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Viscosimetric Evaluation of Solvent Effects

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The intrinsic viscosities of methylene blue, glucose and dextran were determined in various solvents. They are linear against Y *Winstein-Grunwald* solvent parameters. The relation observed offers an alternative route of the evaluation of the solvent effects by means of viscosimetric measurements.

(Keywords: Correlation analysis; Intrinsic viscosity; Solvent parameters)

Viskosimetrische Auswertung von Lösungsmittel-Effekten

Die Grenzviskositäten von Methylenblau, Glukose und Dextran wurden in verschiedenen Lösungsmitteln bestimmt. Sie sind gegen den *Winstein-Grunwald*-Lösungsmittelparameter Y linear. Die festgestellte Beziehung bietet einen alternativen Weg zur Bestimmung von Lösungsmitteleffekten mittels viskosimetrischer Messungen.

Introduction

Solvent effects are constituted of a number of types of solvent—solute interactions which sometimes are not clearly both specified and identified. The importance of particular types of interactions depends on the nature of both solvent and solute. Therefore, any uniform quantitative treatment of the solvent effect is extremely difficult. The overall solvent effect is usually expressed by means of several sets of so-called solvent parameters which allow to discuss this phenomenon in frame of linear free energy relationships and related equations.

There are several sets of solvent parameters of various origin. These are either derived from the effect of the solvents upon the rates of standard reactions or originate from solvatochromic effects observed in the UV-VIS spectra of some standard dyes. Some sets of such parameters are linear one to another (see for instance books[1–4] and

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reviews[5,6] and reference given therein). Recently *Nummert* and *Palm*[7] have quantitatively analyzed the solvent effect in terms of the influence of varying solvent on the reaction parameter in the *Hammett* equation.

Several properties of matter clearly depend on the solvent and have not been interpreted to date quantitatively in terms of the solvent effect. This report presents results of our preliminary studies on the relation between intrinsic viscosity and Y solvent parameters of *Winstein* and *Grunwald*[8,9]. Our application of viscosimetry for studying solvent effects is different from that of *Rodakov*[10] who proposed viscosimetric evaluation of the solvent effect based on the change of the free energy of viscous flow of a series of liquids.

Experimental

Materials: All the solutes and solvents used were of analytical grade, and dimethylformamide was for spectral use. Water was redistilled. The molecular weight of 70 000 was reported for dextran manufactured by Zakłady Chemiczne Oświecim, Poland.

Apparatus: The dynamic viscosity was measured using a *Zimm* rotatory viscosimeter[11] additionally equipped with an automatic digital recording system[12] for precise measuring speed of rotor. A thermostate maintained the temperature constant with high precision.

Determination of intrinsic viscosity: The solvents and the solution studied are given in Tables 1 and 2. The dynamic viscosities (measured at $298 \pm 0.01\,\mathrm{K}$) of methylene blue and detran solutions were measured at 9 concentrations ranged from 0.05 to $1.00\,\mathrm{kg\,m^{-3}}$ and for glucose solutions from 0.05 to $1.00\,\mathrm{kg\,m^{-3}}$ in every case. The relative deviations for the concentration ($\Delta c/c$) did not exceed 0.6% in every case. The dynamic viscosities, η, (average values of three subsequent runs) were applied for the calculation of reduced viscosities, $<\eta>$, according to Eq. (1)

$$<\eta> = \frac{\eta - \eta_0}{\eta_0 \cdot c} = \frac{t_s}{t_{sv}} \tag{1}$$

where η and η_0 are dynamic viscosities of the solutions and pure solvent, respectively, c is the concentration of the solution, t_s and t_{sv} are the speeds of the rotor in solution and pure solvent, respectively. The intrinsic viscosities, $[\eta]$, were determined graphically from the diagrams of $<\eta>$ versus c.

Correlations: Y-Parameters used for the correlations were taken from[8,9]. The statistical treatment of the results was carried out by the least square method and at the 0.1% confidence level.

Results

The solutes studied were methylene blue, glucose and dextran. The solvents applied were water, methanol, ethanol, dioxane, dimethylformamide (*DMF*) and their aqueous solutions. The concentrations of binary solutions applied are given in Tables 1 and 2.

Table 1. *Intrinsic viscosities* $[\eta] \times 10^{-3}\,[m^3\,kg^{-1}]$ *of methylene blue in various solvents at* $298 \pm 0.01\,K$

C_{vol}	Methanol—H_2O				Ethanol—H_2O				Dioxane—H_2O				*DMF*—H_2O			
[%]	$[\eta_{exp}]$	$[\eta'_c]$	$[\eta_c]$	Y	$[\eta_{exp}]$	$[\eta'_c]$	$[\eta_c]$	Y	$[\eta_{exp}]$	$[\eta'_c]$	$[\eta_c]$	Y	$[\eta_{exp}]$	$[\eta'_c]$	$[\eta_c]$	Y[a]
0	4.3	4.0	4.0	3.493	4.1	4.0	4.0	3.493	3.7	4.0	4.0	3.493	4.0	4.0	4.0	3.493
10	4.0				3.9				4.3				3.7			
20	4.7	4.6	4.6	3.025	4.2	4.4	4.4	3.051	4.0	4.3	4.3	2.877	3.9	4.1	4.1	3.25
30	5.3				4.9				4.2				4.5			
40	5.2	5.4	5.3	2.391	5.3	5.2	5.2	2.196	4.7	4.8	4.8	1.945	4.8	4.4	4.5	2.25
50	5.7				5.4				4.8	5.0	5.2	1.361	4.6			
60	6.9	6.6	6.5	1.492	6.1	6.3	6.2	1.124	5.7	5.5	5.5	0.715	5.0	5.2	5.2	0.65
70	7.8				7.0				5.9	5.9	6.0	0.013	5.4			
75									6.4							
80	8.5	8.2	8.1	0.381	7.3	7.8	7.4	0.000		6.7	6.6	0.833				
90	9.0				8.5	8.7	8.2	—0.747		7.5	7.2	—0.275	6.3	6.5	6.6	—2.35
95						9.3	8.8	—1.287								
100	11.0	10.7	10.3	—1.090		9.9	9.6	—2.033		8.5	8.7	—4.25[a]	7.0	8.0	8.5	—5.74[b]

[a] Data derived by interpolation.

[b] Value taken from[9].

Table 2. *Intrinsic viscosities* ($[\eta] \times 10^{-3}$) [$m^3 kg^{-1}$] *of aqueous ethanolic solutions of glucose and dextran*

	Glucose			Dextran			Y
C_{vol} [%]	$H\eta[_{exp}]$	$[\eta_c']$	$[\eta_c]$	$[\eta_{exp}]$	$[\eta_c']$	$[\eta_c]$	
0	2.6	2.5	2.5	16.0	17.0	17.0	3.493
5				18.0			
10	3.0			18.0			
15				20.0	21.0	18.6	3.051
20	2.5	2.9	2.7	20.0			
25				21.0			
30	3.0			23.0			
40	3.5	3.5	3.2		25.0	20.2	2.196
50	4.0						
60	3.8	4.1	3.9		30.0	26.4	1.124
70	4.6						
75	4.5						
80		5.1	4.6		36.0	31.3	0.000
90		5.9	5.3		39.5	34.7	—0.747
95		6.2	5.5		42.0	37.3	—1.287
100		6.5	6.0		45.0	40.9	—2.033

These Tables show the experimental intrinsic viscosities, $[\eta_{\mathrm{exp}}]$, together with the values calculated from their correlations against the Y-parameters, $[\eta_c']$, as well as the intrinsic viscosities, $[\eta_c]$, calculated from the *Flory* equation (2)[13–15],

$$[\eta] = \varnothing \frac{(\bar{h}^{-2})^{3/2}}{M} \tag{2}$$

[where $(\bar{h}^{-2})^{1/2}$ is the average linear size of the molecule of solute, $\varnothing$ is a universal constant and M is the molecular weight of the solute] modified into the form (3) by introducing Y-parameters.

$$[\eta] = \frac{\varnothing\left[\bar{R}_0^{-2}\left(1 + \frac{Y_w - Y_B}{Y_w - Y_p}\sqrt{\frac{Y_w}{Y_w - Y_p}}\right)\right]^{3/2}}{M} \tag{3}$$

where $(\bar{R}^{-2})^{1/2}$ is the average radius of gyration of the solute in a given solvent, Y_w, Y_p and Y_B are the *Grunwald-Winstein* parameters for water, organic solvent, and their aqueous mixtures, respectively. The derivation of Eq. (3) will be given below. The variation of the intrinsic viscosity with the change of the solvent is also presented in Fig. 1.

The intrinsic viscosities of all solutions of each solute under study nicely correlate with *Winstein-Grunwald* Y-parameters. The correlations are presented in Fig. 2.

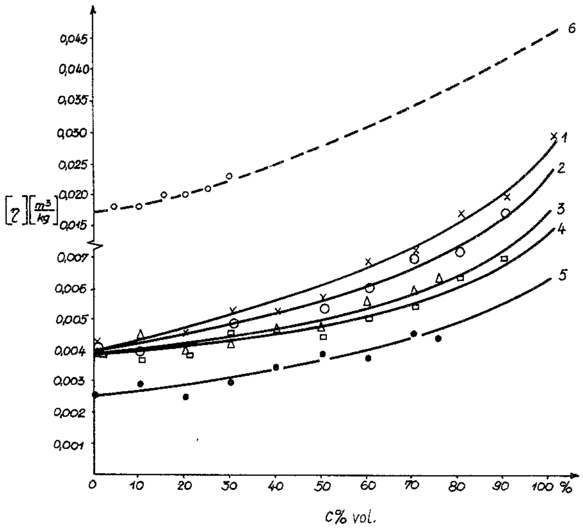

Fig. 1. Variation of the intrinsic viscosity with a change of the composition of binary solvents: *1* (×): methylene blue in aq. methanol; *2* (○): methylene blue in aq. ethanol; *3* (Δ): methylene blue in aq. dioxane; *4* (□): methylene blue in aq. dimethylformamide; *5* (●): glucose in aq. ethanol; *6* (○): dextran in aq. ethanol

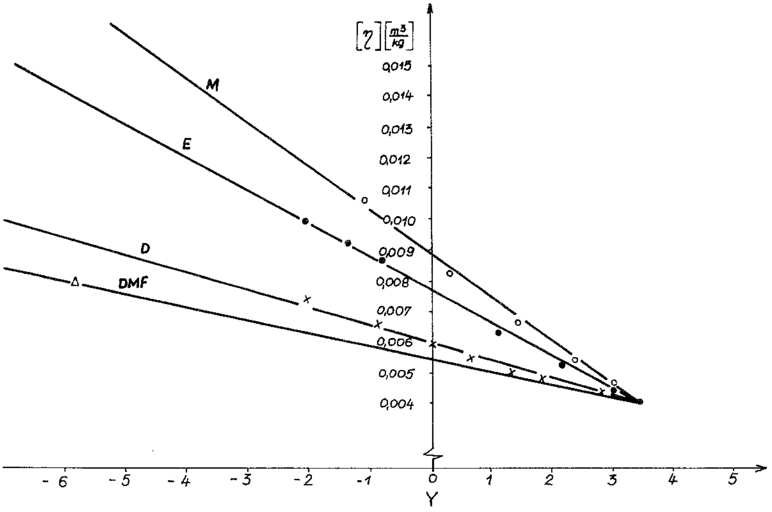

Fig. 2. Correlation of the intrinsic viscosities against the *Y*-parameters for methylene blue solutions in aq. methanol (*M*), aqueous ethanol (*E*), aqueous dioxane (*D*) and aqueous dimethylformamide (*DMF*)

The comparison of the sensitivity of the intrinsic viscosity of the solutions of all solutes studied to the change of the composition of binary solvents is carried out for ethanolic solutions by correlating relative intrinsic viscosities $([\eta_{80}] - [\eta])/[\eta_{80}]$ against Y, where $[\eta_{80}]$ is related to that value in 80% aq. ethanol. The corresponding correlation equations and their statistical evaluation is presented in Table 3.

Discussion

Results presented in this paper show that Eq. (4)

$$[\eta] = m\,Y + \text{constant} \tag{4}$$

is obeyed for the series of solutions of selected solutes in binary aqueous organic solvents (see Table 3).

Several limitations for this relationship may be anticipated. The technique of the measurement and calculation, the applied theory of viscosity as well as not uniform solvent-solute interactions may cause problems.

The technique of measurement and the way of getting intrinsic viscosities should be of sufficient precision. Eq. (1) for calculating the intrinsic viscosity from reduced viscosity points needs satisfactory differences between values of both η and η_0 as well as t_s and t_{sv}. This can be achieved by maintaining a great difference between molecular sizes of solute and solvent. Strong interactions between either molecules of solute or solute and solvent may bring improvement even if the sizes of isolated molecules of solvent and solute do not vary too much from one another. The shape of molecules of solute is also an important property. Depending on whether the molecules of solute have linear, resembling stick, elypsoidal or coiled chain structure either the equations according to *Mark*, *Kuhn* and *Howink*[16,17] [Eq. (5)], *Kuhn*[18] [Eq. (6)] or *Flory*[13–15] [Eq. (2)] may be used. $[\eta]$ is connected with the molecular weight (M) of solute

$$[\eta] = K_\eta M^a \tag{5}$$

where K_η and a are constants characteristic for given solute—solvent system

$$[\eta] = \frac{N_A \cdot v}{M} \nu_p \tag{6}$$

where N_A is the *Avogadro* number, v is the volume of the molecule of solute and ν_p is the number characterizing the elypsoidal shape.

For all three relations a high molecular weight of the solute is of importance for a precise determination of the intrinsic viscosity.

Table 3. *Correlation equations of* $[\eta]$ *and* $\frac{[\eta_{80}]-[\eta]}{[\eta_{80}]}$ *against the Y-parameter for various solutions of methylene blue, glucose and dextran*

Correlated Magnitude	Solute	Binary Solvent[a]	Equation	n^{b}	r^{c}	s^{d}
$[\eta]$	Methylene Blue	Methanol—H_2O	$= -0.015\ Y + 8.9 \times 10^{-3}$	6	0.998	0.002
		Ethanol—H_2O	$= -0.011\ Y + 7.6 \times 10^{-3}$	8	0.998	0.002
		Dioxane—H_2O	$= -0.006\ Y + 6.1 \times 10^{-3}$	9	0.993	0.002
		DMF—H_2O	$= -0.004\ Y + 5.5 \times 10^{-3}$	6[e]		
$\frac{[\eta_{80}]-[\eta]}{[\eta_{80}]}$	Methylene Blue	Ethanol—H_2O	$= 0.142\ Y + 5 \times 10^{-4}$	8	0.998	0.002
	Glucose	Ethanol—H_2O	$= 0.146\ Y + 3 \times 10^{-4}$	8	0.996	0.002
	Dextran	Ethanol—H_2O	$= 0.142\ Y + 1.6 \times 10^{-3}$	8	0.998	0.012

[a] The composition covers the range 0–100%.

[b] Number of experimental points.

[c] Correlation coefficient.

[d] Standard deviations.

[e] The equation is derived from the points for pure water and *DMF*.

Further limitations may result from the variation of the molecular shape of solute under the influence of the solvent. They may lead to swelling of the coiled chain of the solute[19]. Also the ionization of solute and other ions present in the solution influence the intrinsic viscosity of a solution[20]. One of the most essential limitations is the selection of model compounds which are soluble in various pure and binary solvents in a wide range to obtain solutions of sufficiently high concentration. The possibility of a reaction between solute and solvent in the classical chemical sense yields sometimes additional problems.

All this was considered in selecting three solutes which differ very much in their properties. Methylene blue (**1**) has the structure of a salt and ionizes into large, stick-like cation and small anion. α-D-Glucose (**2**) under measurement conditions has a cyclic structure and its hydroxylic groups should moderately interact with solvent molecules but these groups do not ionize. Dextran (**3**) has a molecular weight about 200 resp. 400 times higher than **1** resp. **2**, it does not ionize, exhibits some flexibility of the molecule and may swell in solution.

The intrinsic viscosities of all these solutes in various solvents have been correlated against Y-parameters. The correlations observed (see Table 3) are excellent for all series of solvent studied and for all three solutes. It is striking that the correlation slopes for all three solutes in the same solvent are almost identical i.e. they are not sensitive to the very much varying structure of solutes. Some slight differences are noted in the value of the independent term of Eq. (4) which—probably incidentally—follows the order of increasing molecular weight of the solutes. The effect of change of binary solvents upon the viscosity was studied for methylene blue solutions. These results (Table 3 and Fig. 2) allow to arrange the increasing intrinsic viscosity of the solutions of that solute in the order $H_2O < DMF <$ dioxane $<$ ethanol $<$ methanol. Simultaneously, correlation slopes increase in the order $DMF <$ dioxane $<$ ethanol $<$ methanol. The complex character of the solute—solvent interactions are reflected by the scope of such parameters like dielectric constant (ε), refraction index (n_D), *Lewis* acidity (E) and *Lewis* basicity (B). If data for purely aqueous solutions are rejected the increasing intrinsic viscosity of the remaining solutions follows merely the order of increasing E-parameter (H_2O: $\varepsilon = 78.5$, $n_D = 1.3330$, $E = 21.8$, $B = 123$; DMF: 36.7, 1.4272, 2.60, 159; dioxane: 2.21, 1.4224, 3.98, 129; ethanol: 24.3, 1.3614, 11.57, —; methanol: 32.7, 1.3286, 14.94, —)[5]. This fact suggests that the predominant effect on the intrinsic viscosity results from the *Lewis* acidity of the solvent and the *Lewis* basicity of the solute.

When the intrinsic viscosity of methylene blue in various solvents is calculated using the *Flory* equation [Eq. (2)] assuming $\bar{h}^{-2} = 6\,\bar{R}^{-2}$ the change of the average radius of gyration $(\bar{R}^{-2})^{1/2}$ has to be taken into account which results from the solvent—solute interactions. Assuming the *Flory* coefficient $\varnothing = const$ the influence of the solvent on the solute may be expressed in form of the change of hydrodynamic volume of solute [Eq. (7)]

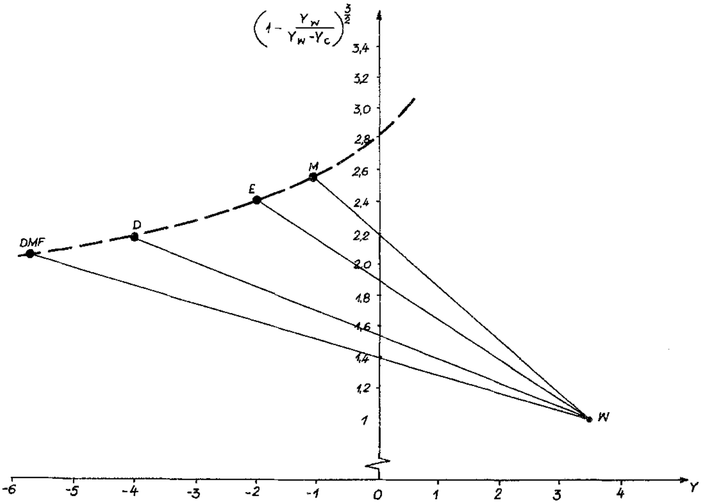

Fig. 3. The relation between the $[1 - Y_w/(Y_w - Y_p)]^{3/2}$ function and Y-parameters for methylene blue solutions: *M* methanol, *E* ethanol, *D* dioxane, *DMF* dimethylformamide, *W* water

$$[\eta] = \varnothing \frac{(\bar{R}_0^{-2} + \Delta\,\bar{R}^{-2})^{3/2}}{M} \tag{7}$$

or

$$[\eta] = \varnothing \frac{(\bar{R}^{-2})^{3/2}}{M} \tag{8}$$

where $(\bar{R}^{-2})^{1/2} = (\bar{R}_0^{-2} + \Delta\,\bar{R}^{-2})^{1/2}$ is the average radius of gyration of the molecule of a solute in a given solvent, $(\bar{R}_0^{-2})^{1/2}$ is the average gyration of that molecule in aqueous solution and M is the molecular weight of the solvated molecule. It can be anticipated that any change of the Y-parameter of the solvent should induce a change of $(\bar{R}^{-2})^{1/2}$. The data given in Table 1 and Fig. 3 allow to present the change of the radius of gyration as the function of the Y-parameter in form of Eq. (9)

$$(\bar{R}^{-2})^{1/2} = \left(\bar{R}_0^{-2} + \bar{R}^{-2} \frac{Y_w - Y_B}{Y_w - Y_p} \sqrt{\frac{Y_w}{Y_w - Y_p}}\right)^{1/2} \tag{9}$$

where Y_w, Y_p and Y_B are the solvent parameters for pure water, pure organic solvent and binary aqueous solvent, respectively. For $Y_B = Y_p$ i.e. for pure solvent Eq. (9) can be reduced to its simpler form (10)

$$(\bar{R}^{-2})^{1/2} = \left(\bar{R}_0^{-2} + \bar{R}^{-2} \sqrt{\frac{Y_w}{Y_w - Y_p}}\right)^{1/2} \tag{10}$$

Introducing Eq. (10) to Eq. (8) yields Eq. (3) which allows to treat the intrinsic viscosity as the function of the solvent effect. A good agreement of intrinsic viscosities calculated by Eq. (3) with experimental ones emphasize the ability of the relation in predicting intrinsic viscosities.

Some deviations observed for aqueous ethanolic solutions of dextran seem to be due to the sparingly soluble substrate in stronger ethanolic solutions.

Fig. 3 suggests a possibility of determination of hydrophobic—lyophilic parameters by viscosity measurements. This assumption will be discussed in a subsequent paper.

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