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The influence of hydration and structure-promoting effects on the viscosity of binary solvent mixtures

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Summary

The viscosity of binary mixtures of water and aprotic or protic polar solvents has been examined and compared with the viscosity of binary mixtures of aprotic polar solvents. In the latter case, ideal behaviour is seen in the sense that the viscosity of the mixture can be expressed as a sum of viscosities. On the contrary, mixtures of water plus a polar solvent (either protic or aprotic) show a maximum in viscosity (expressed as $\Delta\eta_{max}$) corresponding to a well-defined molar ratio of components (expressed as a hydration number, HN_{max}) and resulting from specific water-solvent interactions. Relationships between the two viscosity parameters and various physicochemical properties of the solvents have been investigated, showing that HN_{max} increases or decreases with the capacity of solvents to donate or accept H-bonds, respectively. In contrast, $\Delta\eta_{max}$ results from structure-promoting effects associated with the capacity of the solvent to accept H-bonds from water and to interact hydrophobically.

Introduction

Viscosity is certainly a physical property of major pharmaceutical significance, be it for solvent systems, solutions, emulsions, suspensions, gels, ointments, and the like. The phenomenon arises from a variety of intermolecular interactions of a physicochemical nature which deserves to be better and more explicitely recognized. Binary mixtures of miscible solvents may provide a valuable means for investigating and assessing such interactions, and are used in this study as model systems in a pharmaceutical perspective.

The viscosity (η) of pure non-polar liquids can be described by Eqn. 1 (Vinogradov and Malkin, 1980):

$$\eta = A \cdot e^{(B \cdot V/V_f)} \tag{1}$$

where V is the molecular volume, V_f the free volumes between molecules, and A and B are regression coefficients.

In ideal binary solutions, the molecules of the two solvents do not experience intermolecular interactions different from those occurring in each of the pure solvents. As a consequence, the two solvents do not experience changes in molar

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volume upon mixing, and neither is the free volume between the molecules altered when the two solvents have similar molar volumes. In a number of cases sufficiently close to this ideal situation, the viscosity of binary mixtures has been shown to be the simple addition of the viscosity of the components 1 and 2 (Stairs, 1980):

$$\eta = X_1 \cdot \eta_1 + X_2 \cdot \eta_2 \tag{2}$$

where η is the viscosity of the binary mixture for a given composition, X_1 and X_2 are the molar fractions of solvents 1 and 2, respectively, and η_1 and η_2 are the viscosities of the two pure solvents. A typical example is provided by binary mixtures of acetone and butanone (Stairs, 1980). Based on the theory of Eyring, a slightly different formulation of this equation has been derived for solvents of comparable viscosity (Grunberg and Nissan, 1949; Schott, 1980; Stairs, 1980):

$$\log \eta = X_1 \cdot \log \eta_1 + X_2 \cdot \log \eta_2 \tag{3}$$

In analogy with Eqs. 1 and 2, and after simplification, the ideal viscosity of binary mixtures can also be expressed as the double exponential:

$$\eta = A \cdot e^{B \cdot X} + C \cdot e^{D(1-X)} \tag{4}$$

where X is the molar fraction of one solvent, and $(1 - X)$ that of the other solvent, and where A, B, C and D are regression coefficients.

In the majority of cases, intermolecular interactions result in deviations from ideality. When the resulting viscosity is higher or lower than calculated using e.g. Eqn. 2 or 3, the presence of "structure-making" or "structure-breaking" interactions, respectively, is inferred. Deviations from ideality can thus be expressed as a difference between experimental and ideal (calculated) viscosity ($\Delta\eta_i$) at any point or at all points of a diagram featuring viscosity versus binary mixture composition. In the present study, attention is focused mainly on the peak of viscosity (or maximal viscosity, η_{max}) seen with water/solvent mixtures.

Materials and Methods

Chemicals

The compounds used in this study were chosen according to the following criteria: complete miscibility with water, boiling point higher than 55 ° C, and freezing point lower than 20 ° C (except *t*-butanol). They were obtained from commercial sources (Fluka, Buchs, Switzerland; Siegfried, Zofingen, Switzerland; Merck, Darmstadt, F.R.G.) in the highest available degree of purity and were redistilled before use.

The solutions were prepared by accurate (±0.1 mg) weighing of the solvents and immediately sealed until use in 10 ml vials.

Measurements and calculations

A Low Shear 30 viscosimeter (Contraves, Zürich, Switzerland) with 30 rotation speeds was used. The metallic beaker contained 1.5 ml of solution and was placed in a waterbath thermostated at 20.0 ± 0.1° C. The viscosity of each solution was measured at 5 rotation speeds; all solutions displayed Newtonian behaviour and the S.D. of the 5 measurements was always smaller than 1%. An IBM AT personal computer was used for the calculations.

A polynomial regression equation of 10th degree was used to calculate the curves fitting the experimental viscosities (Wolf and Kudish, 1980). Such a curve has no theoretical foundation but is useful graphically. To express deviations from ideality, it is customary to calculate $\Delta\eta$ values as the difference between experimental and ideal viscosity (for example calculated according to Eqn. 2 or 3) for any composition of the binary mixture. To the $\Delta\eta$ values thus obtained, a differential curve was fitted using a 10th degree polynomial. Such a curve allowed the precise determination of $\Delta\eta_{max}$ values. This maximum corresponds to a well-defined composition of the mixture for which a hydration number can be calculated:

$$HN_{max} = X_{max}/(1 - X_{max}) \tag{5}$$

where HN_{max} is the hydration number, and X_{max} the molar fraction of water, at maximal viscosity. The average error on X_{max} values has been found to be ±0.01, from which an error on HN_{max} can be calculated according to the method of error propagation (Martin et al., 1969). Details on various methods available for the calculation of HN_{max} have been given by Schott (1980).

In the present study, it was consistently found that Eqns. 2 and 3 give practically identical results, and although all calculations have been performed using both equations only values derived from Eqn. 2 are reported. Also, X_{max} and HN_{max} values calculated directly from experimental curves were found to be non-significantly different from the corresponding values calculated as explained above, but are not reported here.

The water-accessible surface areas of the complete molecules and of their apolar part were calculated by the programme MOLSV (QCPE No. 509) from published Van der Waals radii (Testa and Seiler, 1981) and molecular geometries optimized by the quantum-mechanical MNDO method.

Results

Binary mixtures of aprotic polar solvents

In order to better understand the role of H-bonds in the viscosity of binary mixtures, aprotic polar solvents were first investigated. Two pairs of solvents were studied, namely acetone/tetrahydrofuran (THF) and acetone/dimethylsulfoxide (DMSO). The viscosity of the pure solvents at 20 ° C are reported in Table 1. As shown in Fig. 1, the viscosity of the binary mixtures varies monotonously, and no maximum or minimum exists. Mixtures of apolar solvents (e.g. benzene/cyclohexane; Aminabhavi et al., 1982) are known to display ideal viscosity, but the occurrence of electrostatic interactions in the case of polar solvents may results in a non-ideal behaviour, as discussed later.

Binary mixtures of water and a hydroxylated solvent (alkanols, acetic acid)

A number of authors have reported the viscosity of binary water/alkanol mixtures (Ageno and

TABLE 1

Viscosity parameters at 20 ° C

Solvent	η_1 [a]	η_{max} [b]	$\Delta\eta_{max}$ [c]	X_{max} [d]	HN_{max} [e]
Methanol	0.640	1.90	0.98	0.73	2.7 ± 0.1
Ethanol	1.250	2.91	1.83	0.78	3.5 ± 0.2
1-Propanol	2.386	3.24	1.85	0.74	2.8 ± 0.1
2-Propanol	2.401	3.83	2.45	0.75	3.0 ± 0.1
t-Butanol	5.855 [f]	6.43	3.83	0.70	2.3 ± 0.1
Acetic acid	1.260	2.80	1.65	0.49	1.0 ± 0.05
1-Aminobutane	0.531	3.02	2.09	0.80	4.0 ± 0.2
1-Aminopentane	0.694	3.77	2.78	0.80	4.0 ± 0.2
Pyrrolidine	0.835	4.43	3.44	0.75	3.0 ± 0.2
Pyridine	1.004	2.65	1.62	0.70	2.3 ± 0.1
Acetone	0.336	1.63	0.68	0.85	5.7 ± 0.4
Dimethylsulfoxide	2.244	4.34	2.90	0.67	2.0 ± 0.1
Tetrahydrofuran	0.523	2.07	1.11	0.85	5.7 ± 0.4
1,4-Dioxane	1.346	2.32	1.21	0.75	3.0 ± 0.1
Acetonitrile	0.365	1.16	0.19	0.92	11.5 ± 1.4

[a] Viscosity of pure solvent (cP).
[b] Maximal viscosity of binary water/solvent mixtures (η_{max}).
[c] Difference between η_{max} and ideal viscosity at X_{max} defined according to Eqn. 2.
[d] Molar fraction of water at maximal viscosity, derived from eqn. 2 as explained in the text.
[e] Hydration number at maximal viscosity (±S.E.M.), calculated from eqn. 5 as explained in the text.
[f] Extrapolated value.

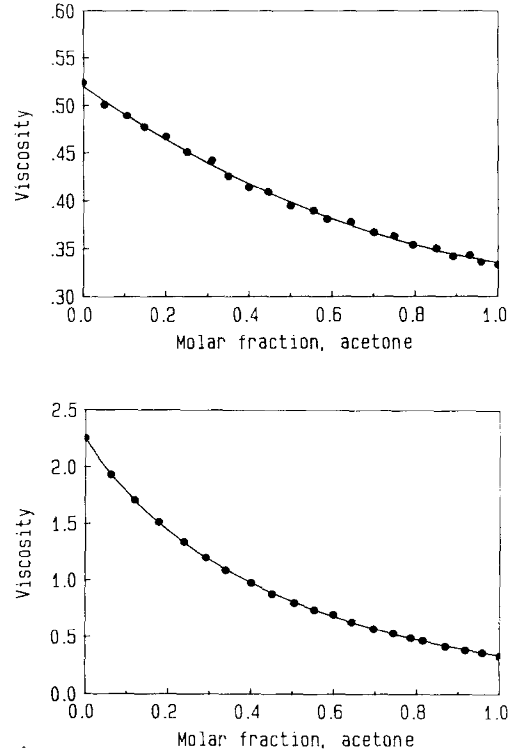

Fig. 1. Viscosity at 20 °C of acetone–tetrahydrofuran (A) and acetone–dimethylsulfoxide (B) mixtures.

Frontali, 1967; D'Aprano et al., 1979; Herskovits and Kelly, 1973; Mikhail and Kimel, 1963; Noda et al., 1982; Wolf and Kudish, 1980; Wolf et al., 1983). We examined the viscosity of binary mixtures of water and every water-miscible alkanol (methanol, ethanol, 1- and 2-propanol, and *t*-butanol). Acetic acid was also included. The viscosity of the pure solvents are reported in Table 1, in good agreement with literature values (Weast, 1976).

The viscosities at 20 °C of the various water/alkanol binary mixtures are presented in Fig. 2. In each curve, a maximum is seen at abscissa values between 0.6–0.8 water molar fraction for the alkanols, and close to 0.5 for acetic acid (see $X_{\max}$ and $HN_{\max}$ values in Table 1). The viscosity values at these maxima ($\eta_{\max}$) are given in Table 1. While clearly detectable, the maximal viscosities are never much higher than the viscosity of the pure organic solvent. This is confirmed by the $\Delta\eta_{\max}$ values reported in Table 1.

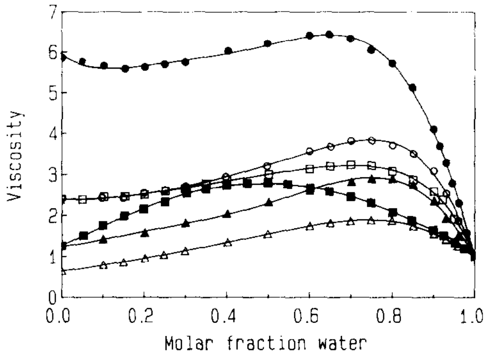

Fig. 2. Viscosity at 20 °C of binary mixtures of water with methanol (△), ethanol (▲), 1-propanol (□), 2-propanol (○), *t*-butanol (●) and acetic acid (■).

Binary mixtures of water and an amine

The behaviour of binary water/amine mixtures is quite different from that noted above. Four water-miscible amines were examined, namely two primary amines (1-aminobutane and 1-aminopentane), one secondary amine (pyrrolidine), and one tertiary amine (pyridine). The viscosity behaviour is depicted in Figure 3. Again a maximum is seen in the viscosities, the corresponding water molar fraction being close to 0.7–0.8 (Table 1). The $\Delta\eta_{\max}$ values (Table 1) are globally comparable to those of water/alkanol mixtures.

Binary mixtures of water and an aprotic polar solvent

Binary mixtures of water and a number of aprotic polar solvents were also examined. The compounds are the two isosteres acetone and

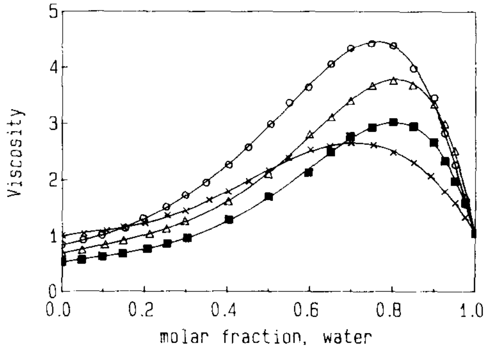

Fig. 3. Viscosity at 20 °C of binary mixtures of water with 1-aminobutane (■), 1-aminopentane (△), pyrrolidine (○) and pyridine (×).

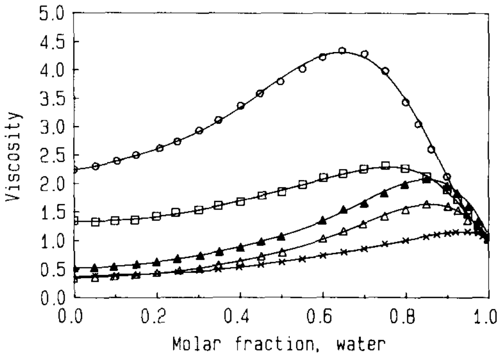

Fig. 4. Viscosity at 20 °C of binary mixtures of water with acetone (△), dimethylsulfoxide (○), tetrahydrofurane (▲), dioxane (□) and acetonitrile (×).

DMSO, two cyclic ethers (THF and 1,4-dioxane), and acetonitrile. The viscosity behaviour (Fig. 4). again shows maxima to exist, with large variations in $\Delta\eta_{\max}$, $X_{\max}$ and $HN_{\max}$ values (Table 1).

Discussion

Binary mixtures not displaying a viscosity maximum

The biexponential Eqn. 4 was used to regress the experimental viscosities of the acetone/THF and acetone/DMSO mixtures, yielding Eqns. 6 and 7:

acetone/THF ($n = 22$)

$$\begin{aligned}\eta &= 0.486(\pm 0.018) \cdot e^{[-0.707(\pm 0.064) \cdot X]} \\ &\quad + 0.034(\pm 0.018) \cdot e^{[1.02(\pm 0.34) \cdot X]}\end{aligned} \tag{6}$$

$r = 0.998$

acetone/DMSO ($n = 20$)

$$\begin{aligned}\eta &= 0.343(\pm 0.110) \cdot e^{[-6.56(\pm 1.89) \cdot X]} \\ &\quad + 1.91(\pm 0.11) \cdot e^{[-1.73(\pm 0.07) \cdot X]}\end{aligned} \tag{7}$$

$r = 0.999$

where X is the molar fraction of acetone. The values in parentheses are the 95% confidence limits of the regression coefficients, showing that every term in these equations is statistically significant. The curves calculated according to Eqns. 6 and 7 (Fig. 1) show an excellent fit with the experimental point.

It thus appears that the acetone/TFH and acetone/DMSO mixtures display viscosities which can be expressed as the summation of the viscosity of the two solvents. In this sense, the two mixtures display ideal viscosities. No specific intermolecular interactions are detectable, in particular specific electrostatic interactions between the two components. It is significant however that the 3 solvents have comparable calculated molar volumes (Testa and Seiler, 1981), namely 51.3, 59.7 and 56.5 cm^3/mol for acetone, DMSO and THF, respectively.

Physicochemical interpretation of the maximal excess of viscosity ($\Delta\eta_{max}$)

When water is one of the two components, strong deviations from ideality are consistently seen in the form of a viscosity maximum. These deviations are expressed here in terms of $\Delta\eta_{\max}$, the difference between calculated and experimental viscosity at the maximum. To better understand the nature of the intermolecular interactions accounting for these structure-promoting effects, we have examined the relationships between $\Delta\eta_{\max}$ and various physicochemical properties of the solvents. Global cohesion parameters are examined first, followed by parameters accounting for specific types of intermolecular forces, i.e. electrostatic interactions (dipolar interactions and H-bonds) and hydrophobic interactions.

Hildebrand cohesion (or solubility) parameter δ (Barton, 1975) is a global descriptor encoding a broad range of physical properties influencing intermolecular interactions. As an additional global descriptor, we have used normalized boiling points (*BP/MW* values), i.e. boiling point divided by molecular weight. The values of these parameters for the solvents investigated are given in Table 2. No correlation between $\Delta\eta_{\max}$ and either δ or BP/MW were found for all solvents examined together. In contrast, good correlations were found when the aprotic and protic solvents were considered separately:

TABLE 2

Physicochemical parameters of the investigated solvents

Solvent	δ [a]	BP/MW [b]	ϵ [c]	α [d]	β [e]	S_{tot} [f]	S_{apol} [g]
Methanol	29.7	2.027	32.7	0.93	0.62	199.0	123.9
Ethanol	26.0	1.704	24.6	0.83	0.77	239.9	173.9
1-Propanol	24.3	1.620	20.3	0.78	NA [h]	275.9	211.0
2-Propanol	23.5	1.371	19.9	0.76	0.95	273.7	217.6
t-Butanol	21.4	1.109	12.5	0.68	1.01	299.0	250.4
Acetic acid	20.7	1.963	–	1.12	NA	239.9	127.6
1-Aminobutane	17.8	1.064	–	NA	0.72	322.1	239.9
1-Aminopentane	17.7	1.198	–	NA	NA	355.3	274.5
Pyrrolidine	19.9	1.247	–	NA	NA	292.8	255.3
Pyridine	21.9	1.460	–	0.00	0.64	281.0	256.2
Acetone	20.3	0.968	–	0.08	0.48	262.1	212.3
Dimethylsulfoxide	24.5	2.419	–	0.00	0.76	276.0	204.1
Tetrahydrofuran	18.6	0.929	–	0.00	0.55	283.1	264.8
1,4-Dioxane	20.5	1.146	–	0.00	0.37	297.0	266.7
Acetonitrile	24.3	1.969	–	0.19	0.31	217.7	122.2

[a] Hildebrand cohesion parameter (Barton, 1975; Vaughan, 1985).

[b] Boiling point (Weast, 1976) divided by molecular weight.

[c] Dielectric constant of pure solvent at 25 ° C (Barton and Ollis, 1977).

[d] Solvatochromic parameter describing the H-bond acidity (Kamlet and Taft, 1976; Kamlet et al., 1983).

[e] Solvatochromic parameter describing the H-bond basicity (Kamlet and Taft, 1976; Kamlet et al., 1983).

[f] Total water-accessible surface area (Å^2).

[g] Apolar water-accessible surface area (Å^2).

[h] Not available.

Aprotic polar solvents

$$\Delta\eta_{\max} = 0.343(\pm 0.323) \cdot \delta - 5.75(\pm 6.86) \qquad (8)$$

$$n = 5; \quad r = 0.890; \quad s = 0.447; \quad F = 11.4$$

$$\Delta\eta_{\max} = 1.35(\pm 0.51) BP/MW - 0.367(\pm 0.765)$$

$$n = 5; \quad r = 0.979; \quad s = 0.199; \quad F = 70.1 \qquad (9)$$

Acetonitrile with its small $\Delta\eta_{\max}$ value behaved as an outlier and is not included in Eqns. 8 and 9. Clearly these equations indicate that the greater the association capacity of these solvents, the greater the structure enhancement of the solution. Examination of the protic solvents yielded Eqns. 10 and 11:

Protic solvents

$$\Delta\eta_{\max} = -0.289(\pm 0.155) \cdot \delta + 9.36(\pm 3.77) \qquad (10)$$

$$n = 6; \quad r = 0.933; \quad s = 0.433; \quad F = 26.8$$

$$\Delta\eta_{\max} = -2.77(\pm 1.02) BP/MW + 6.65(\pm 1.65)$$

$$n = 7; \quad r = 0.952; \quad s = 0.343; \quad F = 48.3 \qquad (11)$$

In Eqn. 10, only the homogenous group of alkanols and pyrrolidine could be taken together, the primary amines and acetic acid being outliers. Eqn. 11 includes acetic acid. The reasons for the peculiar behaviour of the primary amines and acetic acid are not apparent to us.

Eqns. 10 and 11 can be interpreted as indicating that the capacity of protic solvents to form intermolecular associations is detrimental to a maximal increase in viscosity. This result contrasts with that of the aprotic solvents, suggesting the importance of both the existence and directionality (i.e. water-to-solvent vs solvent-to-water) of H-bonds in controlling the magnitude of the structure enhancement in the solution. To test this aspect further, parameters accounting for electrostatic interactions were examined, as reported below.

The results obtained with a chemically homogeneous series of solvents, i.e. the alkanols, were used to assess the role of dipole–dipole interactions. The property examined is the dielectric constant ϵ of the alkanols. Only the ϵ values of the pure solvents were considered (Table 2) since it is known (Franks and Ives, 1966) that all alkanols show the same variation of their dielectric constant upon mixing with water. As shown by Eqn. 12, there is a highly significant correlation between $\Delta\eta_{\max}$ and the dielectric constant:

$$\Delta\eta_{\max} = 0.560(\pm 0.218) \cdot (100/\epsilon) - 0.618(\pm 1.152) \quad (12)$$

$n = 5$; $r = 0.978$; $s = 0.253$; $F = 66.6$

The nature of the H-bond forming atoms being constant ($OH \cdots H$), Eqn. 12 brings clear evidence that the strength of the H-bond is quantitatively related to deviations from ideal viscosity.

To further assess the role of hydrogen bonding, use has been made of the solvatochromic parameters α and β which express the capacity of a compound to give and accept a proton in an H-bond, respectively (Kamlet and Taft, 1976; Kamlet et al., 1983). These parameters can be used to compare compounds belonging to different chemical groups. As seen in Table 2, aprotic solvents have α values of zero or close to it, while there is little variation in the α values of H-bond donors. In contrast, a broad range of β values is displayed by 11 solvents. A good correlation has been found between $\Delta\eta_{\max}$ and the β parameter; adding water ($\Delta\eta_{\max} = 0$; $\beta = 0.18$) as an additional observation yields equation 13:

$$\Delta\eta_{\max} = 4.08(\pm 1.30) \cdot \beta + 0.930(\pm 0.860) \quad (13)$$

$n = 12$; $r = 0.911$; $s = 0.484$; $F = 49.0$

This equation indicates that the magnitude of structure-forming interactions increases with the capacity of the solvent to accept H-bonds from water. Another interesting correlation is that existing for protic solvents between $\Delta\eta_{\max}$ and α values. Here, acetic acid is found to be an outlier in agreement with its marked capacity to form strongly H-bonded dimers. For the 5 other protic solvents plus water ($\alpha = 1.17$), Eqn. 14 was obtained:

$$\Delta\eta_{\max} = -6.97(\pm 3.81) \cdot \alpha + 7.81(\pm 3.32) \quad (14)$$

$n = 6$; $r = 0.931$; $s = 0.532$; $F = 25.8$

This equation indicates that the stronger the H-bond donating capacity of a solvent, the weaker the structure-forming effects seen in the viscosity of its aqueous solutions. Taken together, Eqns. 13 and 14 bring evidence that water-to-solvent H-bonds strongly increase the magnitude of structure-forming water-solvent interactions, in contrast with solvent-to-water H-bonds which decrease such interactions, perhaps inasmuch as they compete with the former type of H-bonds.

To assess the role of hydrophobic interactions on the viscosity of water/solvent mixtures, water-accessible surface areas were calculated and examined. It was found that the ratio of apolar to total surface area gives a good correlation with $\Delta\eta_{\max}$ for a selected group of compounds:

$$\Delta\eta_{\max} = 11.4(\pm 3.9) S_{\text{apol}}/S_{\text{tot}} - 6.30(\pm 2.87)$$

$n = 8$; $r = 0.945$; $s = 0.389$; $F = 50.6$ (15)

The solvents which do not obey this relationship are all cyclic compounds (presumably for steric reasons), and acetone, DMSO and acetic acid (perhaps because the borderline between polar and apolar parts is too fuzzy in these molecules). Eqn. 15, despite its satisfactory statistical character, is not valid below and beyond the explored range of $S_{\text{apol}}/S_{\text{tot}}$ values. Indeed, this equation is not valid for water itself ($\Delta\eta_{\max} = 0$; $S_{\text{apol}}/S_{\text{tot}} = 0$), nor does it account for the fact that $S_{\text{apol}}/S_{\text{tot}} \leq 1$. The calculation of a more general expression would have required a larger number of observations.

Eqn. 15 shows that structure-promoting effects in water-solvent mixtures become larger, albeit to a moderate extent, for larger $S_{\text{apol}}/S_{\text{tot}}$ ratios of the solvents. This may be due to the more organized state of water molecules in the vicinity of apolar surfaces, which would influence viscosity either directly or by strengthening electrostatic water–solvent interactions. A role for hydrophobic solvent–solvent interactions at an optimal water/solvent ratio can also be envisioned.

Physicochemical interpretation of the hydration number at maximal viscosity (HN_{max})

A first obvious question to be examined is whether HN_{max} values display any sort of relationship with $\Delta\eta_{max}$ values. A linear relationship does not exist for all 15 solvents taken together ($r = -0.57$) nor for the 9 protic solvents ($r = 0.11$). When the 6 aprotic solvents are considered separately, a possible relationship may be seen (Fig. 5) such that to be decrease in $\Delta\eta_{max}$ corresponds an exponential increase in HN_{max}. A fairly linear relationship exists ($r = -0.80$), and a statistically significant exponential relationship can be calculated (not reported), but its interest is limited due to the small number of observations. These results indicate that for aprotic polar solvents, high $\Delta\eta_{max}$ values are associated with low values of the hydration number HN_{max}. For protic solvents, the two viscosity parameters are completely unrelated.

In agreement with the above, establishing a general relationship between all HN_{max} values in Table 1 and some physicochemical factor did not prove feasible. Nevertheless, some trends emerge when subgroups of solvents are examined. Thus, the influence of steric hindrance around a given functional group may be deduced from the behaviour of alkanols. While all primary and secondary alkanols have HN_{max} values close to 3.0 (S.D. 0.36), *t*-butanol displays a somewhat lower value which can be postulated to reflect steric factors. It may be noted that such factors have not been found to exert any influence on $\Delta\eta_{max}$.

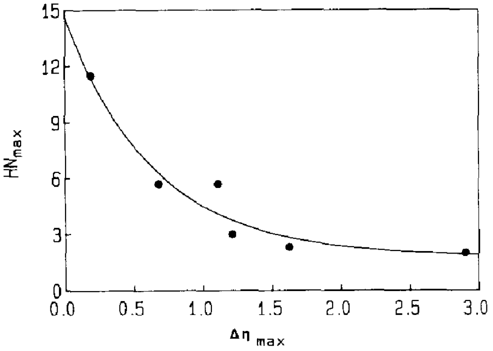

Fig. 5. Plot of HN_{max} versus $\Delta\eta_{max}$ values for the 6 aprotic solvents in Table 1.

For the 4 amines in Table 1, a very good inverse relationship is apparent between HN_{max} and the number of labile protons (NLP):

$$HN_{max} = 0.86(\pm 0.24) NLP + 2.24(\pm 0.35) \qquad (16)$$

$$n = 4; \quad r = 0.996; \quad s = 0.09; \quad F = 250.7$$

Thus, it is their ability to form solvent-to-water H-bonds which is one of the physicochemical factors governing the hydration number of solvents, in contrast with their ability to accept H-bonds which influences their $\Delta\eta_{max}$ value (see above). Such a relationship appears contradictory with the high HN_{max} values displayed by a number of aprotic solvents in Table 1, e.g. THF, acetone and acetonitrile. Interestingly however, the hydration number of these solvents is inversely related to their capacity to accept H-bonds as assessed by the β parameter (equation 17):

$$HN_{max} = -21.6(\pm 12.2) \cdot \beta + 17.3(\pm 6.9) \qquad (17)$$

$$n = 5; \quad r = 0.956; \quad s = 1.29; \quad F = 32.0$$

Dioxane is not included in the equation since it is an outlier presumably due to the presence of two neighbouring hydration sites. Eqn. 17 implies that the weakest aprotic bases are maximally hydrated, in agreement with the inverse relationship between $\Delta\eta_{max}$ and HN_{max} noted above and with Eqn. 13. However, Eqn. 17 does not explain the fact that aprotic polar solvents, despite their incapacity to donate H-bonds, have hydration numbers which are as large or larger that those of the protic solvents. Clearly other factors must also be involved, and it may not be fortuitous that the highly hydrated acetonitrile, besides being the weakest base, also shows the smallest steric hindrance around the polar group.

Conclusion

This study has examined the two viscosity parameters $\Delta\eta_{max}$ and HN_{max} and has related them to a number of physicochemical properties of protic and aprotic polar solvents. Specific structure-promoting effects in binary mixtures of water and a polar solvent (as assessed by $\Delta\eta_{\max}$) increase with the capacity of the latter to accept H-bonds from water (Eqns. 8, 9 and 13) and to interact hydrophobically (Eqn. 15); these effects on the other hand decrease with increasing H-bond donating capacity of the solvent (Eq. 10, 11 and 14).

As opposed to $\Delta\eta_{\max}$, the hydration number at maximal viscosity ($HN_{\max}$) decreases with the capacity of the solvent to accept H-bonds from water, and increases with its acidity. For aprotic polar solvents, the two viscosity parameters are inversely related, indicating that hydration is not a major structure-promoting factor in aqueous solutions of these solvents. A role for hydrophobic interactions is thus indicated but warrants further study.

Acknowledgements

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