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VISCOSITY AND DIELECTRIC PROPERTIES OF LIQUID BINARY MIXTURES

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The stoichiometry of solvates formed in some binary solvent systems is presented and types of interactions in such systems are discussed based on changes in viscosity and dielectric properties.

INTRODUCTION

Viscosity is an important property of liquids and gases in connection with the transport of liquids through pipelines and biological membranes, heat transfer, orientation and reorientation of solutes in liquid media (broadening of chemical shifts in NMR), etc. The viscosity of liquid mixtures is of particular interest for both theoretical and practical reasons. So far it cannot be predicted from the viscosities of individual components. This problem remains unsolved in spite of several models that have been proposed.[1–17] Among others, for this purpose rheology may be a useful tool for studying of intermolecular interactions in liquid media.

It has been reported that viscosity is useful in the determination of the stochiometry of solvates in binary mixtures of solvents.[18,19] The wide range of possible interactions allows the distribution of binary mixtures into four groups and six sub-groups depending on the shape of the viscosity isotherms. The shape of these isotherms usually deviates from theoretical functions constructed under the assumption that the viscosity of both components is additive and that any intermolecular solvent–solvent interactions are effectively absent.[1,13,18] Usually polar intermolecular interactions cause more pronounced deviations from the above-mentioned additivity. They are responsible for either maxima or minima of the isotherms on viscosity–molar fraction diagrams. The maxima correspond to a favourable composition of structural units in solution consisting of solvates of molecules of one solvent surrounded by a certain number of molecules of the second solvent. A lack of maxima on the isotherms is interpreted as the result of intervention of merely weak (exchange) interactions.

It is shown in this paper that this point of view is not generally valid. Moreover, it is shown that the change in viscosity of binary solvents is correlated with a newly introduced $\Delta\varepsilon/\Delta c$ parameter, the absolute concentration coefficient of the dielectric constant. Similarly, a $\Delta\varepsilon/\Delta t$ parameter can be defined, the absolute temperature coefficient of the dielectric constant. The latter is useful in studying the effect of temperature on the dielectric constants of binary systems. Both parameters seem to be convenient tools for investigating interactions between molecules of pure solvents and of binary mixtures. Their application supplements the obvious utility of dielectric constants as parameters for the characterization and classification of solvents[20,21] and also for the interpretation of the behaviour of ionic species in solution.

RESULTS AND DISCUSSION

Table 1 reports viscosities measured as a function of concentration in % (mole/mole) and in % (w/w). The first mode of presentation of the results is useful for the determination of the stoichiometry of solvates, and the second for discussing of the viscosity–dielectric constant interrelations.

These data are additionally illustrated by diagrams for (i) binary mixtures of water with acetone, acetic acid, methanol, ethanol, propan-1-ol, acetonitrile, 1,4-dioxane, dimethyl sulphoxide, pyridine, formamide, and *N,N*-dimethylformamide, with concentrations expressed in % (mole/mole) (Figure 1) and in % (w/w) (Figure 2); (ii) for binary mixtures of cyclohexane with methanol, ethanol, propan-1-ol, 1,4-dioxane, acetone, acetic acid, acetonitrile, formamide and *N,N*-dimethylformamide, with concentrations expressed in % (w/w) (Figure 3); and (iii) for binary mixtures of

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Table 1. Viscosity, η (cP), at 25 °C of some binary mixtures at various concentrations, C

Water–methanol

C (%, w/w)	C (%, mole/mole)	η (cP)
0	0	0·89
7·3	4·3	1·07
13·6	8·2	1·23
19·1	11·8	1·40
24·0	15·1	1·48
32·1	21·1	1·56
38·6	26·3	1·58
44·0	30·8	1·57
49·5	35·8	1·52
56·7	42·6	1·45
66·3	52·7	1·30
72·4	59·7	1·16
79·7	69·0	1·03
88·7	82·0	0·81
100	100	0·54

Water–ethanol

C (%, w/w)	C (%, mole/mole)	η (cP)
0	0	0·89
7·3	2·9	1·16
13·6	5·5	1·43
19·1	8·1	1·71
24·0	10·4	1·93
32·0	14·8	2·16
38·5	18·7	2·30
44·0	22·2	2·37
49·5	26·1	2·41
56·7	31·6	2·47
66·3	40·2	2·25
72·4	46·5	1·90
79·7	55·2	1·66
88·7	67·9	1·34
100	100	1·09

Water–propan-1-ol

C (%, w/w)	C (%, mole/mole)	η (cP)
0	0	0·89
7·4	2·4	1·19
13·8	4·6	1·51
19·4	6·8	1·58
24·3	8·8	1·93
32·4	12·6	2·23
39·0	16·2	2·42
49·4	19·4	2·55
49·9	23·2	2·63
57·1	28·7	2·63
66·6	37·6	2·57
72·2	44·6	2·55
79·9	54·7	2·43
88·9	70·7	2·26
100	100	2·00

Water–*N*,*N*-dimethylformamide

C (%, w/w)	C (%, mole/mole)	η (cP)
0	0	0·89
8·6	2·3	1·07
15·9	4·5	1·27
22·1	6·5	1·44
27·4	8·5	1·66
36·2	12·3	1·94
43·0	15·7	2·15
48·6	18·9	2·25
54·1	22·6	2·47
61·2	28·0	2·49
70·2	36·8	2·34
75·9	43·7	2·24
82·5	53·8	1·86
90·4	70·0	1·36
100	100	0·80

Water–acetone

C (%, w/w)	C (%, mole/mole)	η (cP)
0	0	0·89
7·3	2·4	1·03
13·6	4·7	1·16
19·1	6·9	1·28
24·0	9·0	1·35
32·0	12·9	1·37
38·3	16·5	1·42
44·0	19·8	1·31
49·5	23·6	1·22
56·7	29·1	1·05
66·3	38·2	0·89
72·4	45·1	0·71
79·7	55·2	0·58
88·7	71·2	0·42
100	100	0·30

Water–acetic acid

C (%, w/w)	C (%, mole/mole)	η (cP)
0	0	0·89
9·5	3·2	1·07
17·9	6·2	1·24
23·8	9·0	1·36
29·5	11·6	1·45
38·5	16·5	1·60
45·5	20·8	1·80
51·1	24·7	1·90
56·6	29·1	2·05
63·5	35·3	2·18
72·3	45·1	2·34
77·6	52·1	2·40
83·9	62·1	2·36
91·2	76·6	2·06
100	100	1·13

Water–pyridine

C (%, w/w)	C (%, mole/mole)	η (cP)
0	0	0·89
8·9	2·2	1·07
16·4	4·3	1·23
22·7	6·3	1·40
28·1	8·2	1·54
37·0	11·8	1·74
43·8	15·1	1·90

Water–dimethyl sulphoxide

C (%, w/w)	C (%, mole/mole)	η (cP)
0	0	0·89
9·9	2·0	1·08
18·0	3·9	1·30
24·8	5·7	1·53
30·5	7·5	1·78
40·0	10·8	2·31
46·7	13·9	2·64

(*continued*)

Table 1. *Continued*

Water–methanol

C (%, w/w)	C (%, mole/mole)	η (cP)
49·4	18·2	2·00
54·9	21·8	2·09
62·0	27·1	2·19
70·9	35·8	2·26
76·5	42·6	2·22
83·0	52·7	2·06
90·7	69·0	1·69
100	100	0·88

Water–ethanol

C (%, w/w)	C (%, mole/mole)	η (cP)
52·3	16·8	3·04
57·8	20·2	2·32
64·6	25·2	3·62
73·2	33·6	3·77
78·5	40·2	3·56
84·5	50·2	3·17
91·6	67·0	2·61
100	100	1·96

Water–acetonitrile

C (%, w/w)	C (%, mole/mole)	η (cP)
0	0	0·89
7·2	3·3	0·96
13·5	6·4	0·99
18·9	9·3	0·99
23·7	12·1	0·96
31·8	17·1	0·89
38·3	21·6	0·86
43·7	25·6	0·82
49·2	30·0	0·77
56·4	36·4	0·70
66·0	46·2	0·59
72·1	53·4	0·54
79·5	63·2	0·47
88·6	77·5	0·40
100	100	0·34

Water–1,4-dioxane

C (%, w/w)	C (%, mole/mole)	η (cP)
0	0	0·89
9·3	2·1	1·08
17·1	4·1	1·25
23·6	6·0	1·38
29·1	7·8	1·52
38·1	11·2	1·71
45·1	14·4	1·81
50·7	17·4	1·90
56·2	20·9	1·97
63·1	26·0	1·98
71·9	34·5	1·90
77·4	41·3	1·80
83·7	51·4	1·62
91·1	67·9	1·39
100	100	1·26

Water–formamide

C (%, w/w)	C (%, mole/mole)	η (cP)
0	0	0·89
9·9	2·9	0·96
18·1	5·5	1·03
24·9	8·1	1·11
30·7	10·4	1·18
40·1	14·8	1·21
46·9	18·7	1·36
52·6	22·2	1·44
58·1	26·1	1·53
64·9	31·6	1·60
73·7	40·2	1·71
78·9	46·5	2·06
84·8	53·2	2·21
91·9	67·9	2·52
100	100	3·30

Cyclohexane–methanol

C (%, w/w)	C (%, mole/mole)	η (cP)
62·5		0·61
71·4		0·58
76·9		0·56
83·3		0·55
90·9		0·55
100		0·54

Cyclohexane–ethanol

C (%, w/w)	C (%, mole/mole)	η (cP)
37·5		0·87
44·4		0·86
50·0		0·87
55·5		0·87
62·5		0·88
71·4		0·90
76·9		0·94
83·3		0·96
90·9		1·02
100		1·09

Cyclohexane–propan-1-ol

C (%, w/w)	C (%, mole/mole)	η (cP)
0		0·90
9·1		0·88
16.7		0·91
23·1		0·96
28·6		1·00
37·5		1·10
44·4		1·18
50·0		1·26
55·5		1·32
62·5		1·39
71·4		1·52
76·9		1·59
83·3		1·69
90·9		1·81
100		2·00

cyclohexane–*N*,*N*-dimethylformamide

C (%, w/w)	C (%, mole/mole)	η (cP)
62·5		0·76
71·4		0·76
76·9		0·75
83·3		0·74
90·9		0·78
100		0·80

(*continued*)

Table 1. *Continued*

Water–methanol			Water–ethanol		
C (%, w/w)	C (%, mole/mole)	η (cP)	C (%, w/w)	C (%, mole/mole)	η (cP)
Cyclohexane–acetone			Cyclohexane–acetonitrile		
0		0·90	88·0		0·35
9·1		0·74	92·0		0·34
16·7		0·63	95·0		0·34
23·1		0·57	100		0·34
28·6		0·54			
37·5		0·49	Cyclohexane–acetic acid		
44·4		0·45			
50·0		0·42	0		0·90
55·5		0·40	9·1		0·81
62·5		0·37	16·7		0·72
71·4		0·35	23·1		0·71
76·9		0·34	28·6		0·68
83·3		0·33	37·5		0·69
90·9		0·31	44·4		0·70
100		0·30	50·0		0·72
			55·5		0·74
Cyclohexane–1,4-dioxane			62·5		0·77
			71·4		0·80
0		0·90	76·9		0·82
9·1		0·88	83·3		0·84
16·7		0·87	90·9		0·95
23·1		0·86	100		1·13
28·6		0·86			
37·5		0·89	Methanol–*N*,*N*-dimethylformamide		
44·4		0·91			
50·0		0·94	0		0·54
55·5		1·01	17·0		0·57
62·5		1·02	29·0		0·58
71·4		1·04	38·0		0·59
76·9		1·07	44·0		0·60
83·3		1·12	50·0		0·62
90·9		1·18	56·0		0·64
100		1·26	62·0		0·67
			71·0		0·72
Methanol–ethanol			83·0		0·75
			100		0·80
0		0·54			
17·0		0·55	Methanol–dimethyl sulphoxide		
29·0		0·56			
38·0		0·58	0		0·54
44·0		0·62	17·0		0·57
50·0		0·66	29·0		0·60
56·0		0·70	38·0		0·65
62·0		0·75	44·0		0·70
71·0		0·80	50·0		0·74
83·0		0·85	56·0		0·81
100		1·09	62·0		0·90
			71·0		1·05
			83·0		1·20
			100		1·96

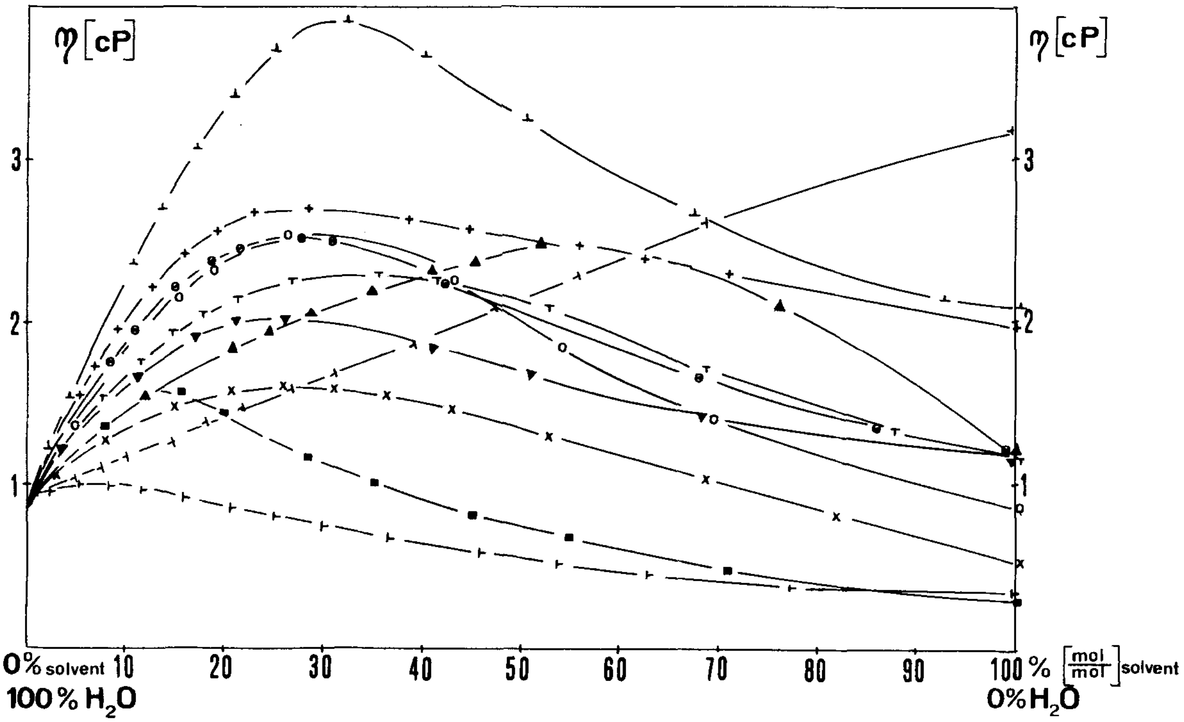

Figure 1. Viscosity–concentration [in % (mole/mole)] isotherms for aqueous binary mixtures with (□) acetone, (△) acetic acid, (×) methanol, (⊢) acetonitrile, (▽) 1,4-dioxane, (+) propan-1-ol, (⊥) dimethyl sulphoxide, (T) pyridine, (○) *N*,*N*-dimethylformamide, ⊙ ethanol and (⊣) formamide

methanol with *N*,*N*-dimethylformamide, ethanol and dimethyl sulphoxide, with concentrations also expressed in % (w/w) (Figure 4).

The stoichiometry of the structural units of the solvent which corresponds to the viscosity maximum of the binary mixtures (if it differs from the viscosity of a pure component) is given in Table 2. These data are calculated based on the position of the maximum on the viscosity–concentration curves, with concentrations given in % (mole/mole).

The variations of the absolute temperature coefficient of the dielectric constant ($\Delta\varepsilon/\Delta t$) for several solvents are given in Table 3, and the variations of the absolute concentration coefficient of the dielectric constant ($\Delta\varepsilon/\Delta c$) for mixtures of water with ethanol, acetone and 1,4-dioxane are given in Table 4.

A graphical presentation of the relationships between the data in Table 4 and the viscosity of these systems is given in Figure 5. The results of a statistical evaluation of these relationships are given in Table 5. These data are related to two sets of points, i.e. to those which describe ascending (from pure water) and descending (to pure non-aqueous solvent) portions of the curves in Figure 2.

It is found that there is no simple relationship between the stoichiometry of the favourable aggregate (solvate) formed in binary solvents and the polarity of the two components expressed as dielectric constants, refractive indices and various sets of empirical solvent polarity parameters such as that of Winstein–Grunwald, Kosower, Dimroth–Reichardt,[24,25] Kamlet[26] and Pytela.[27] Undoubtedly, the lack of such correlations is due to the fact that viscosity is a parameter that describes the overall situation of the solution whereas empirical solvent polarity parameters usually reflect certain well defined components of such overall interactions. Moreover, various parameters considered here differ from one another in their character. Thus, some of them are thermodynamic whereas others (e.g. the dielectric constants) are not.

The rheological properties of a solution depend also on the volume and shape of the molecules which form heterosolvates and homosolvates.[13,28] Therefore, any prediction of the solvate composition responsible for the maximum viscosity of binary systems seems to be impossible. Nevertheless, some qualitative conclusions can be drawn. The curves for aqueous binary mixtures (Figures 1 and 2) usually exhibit maxima, whereas the curves for binary mixtures of cyclohexane (Figure 3) are concave with very broad minima, as already observed a

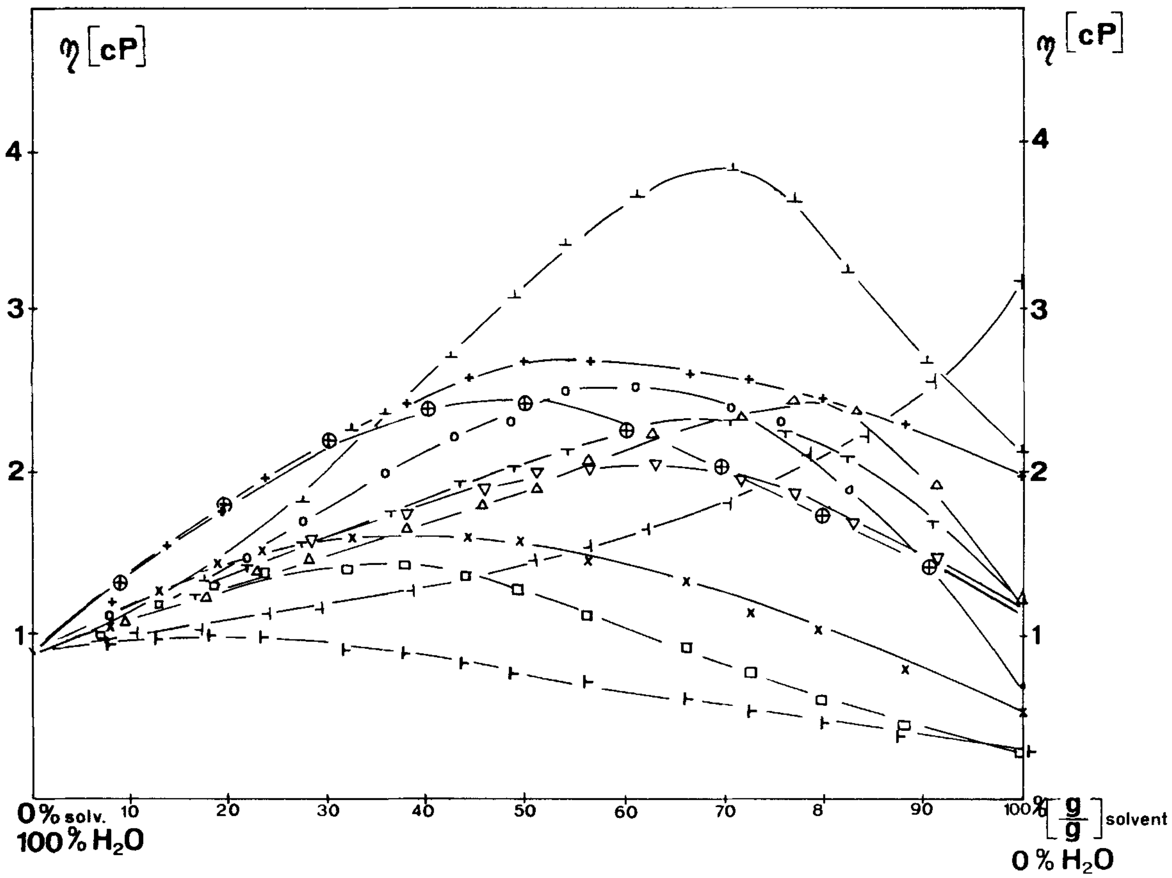

Figure 2. Viscosity–concentration [in % (w/w)] isotherms for aqueous binary mixtures with solvents as specified in Fig. 1. Symbols as in Fig. 1

long time ago.[29] This is also in agreement with earlier statements by Fialkov,[18] who found that such a shape of isotherms is typical of weak exchange interactions between the two components of such binary solvent mixtures.

Surprisingly, even binary mixtures of methanol with *N*,*N*-dimethylformamide, ethanol and dimethyl sulphoxide (Figure 4) do not exhibit any maxima. The assumption that methanol interacts with these solutes via exchange interactions is unlikely. The curve for aqueous formamide is also concave upwards, i.e. the concave downwards pattern of the isotherms for aqueous binary solutions is not a general case. Moreover, it is also difficult to believe that only exchange interactions exist between such highly dipolar molecules. The shape of the isotherms does not depend clearly on the difference in the polarities of the two components of the binary system. It solely reflects the polarity resulting from the mutual orientation of the molecules in solution to form solvates. The polarity of particular kinds of molecules may be high but the solvates formed between them do not necessarily interact with one another very effectively. Comparison of the results presented here for acetic acid with those included for other solvent mixtures clearly supports this statement.

The concave downwards pattern of the isotherms given in Figures 1 and 2 may induce attempts to develop a more quantitative approach to their interpretation. This can be based on the determination of the slope of tangents to ascending (from pure water) and descending (to pure non-aqueous solvent) portions of the isotherms and of the positions of the maxima of these isotherms. However, neither portion of the isotherms is linear and they exhibit more or less concave shapes themselves. This introduces a lack of precision in the treatment. This non-linearity reflects an important factor, namely the hydrodynamic property of the resulting binary mixtures in addition to the polarity of the solvates formed as the composition of the system changes. It is more

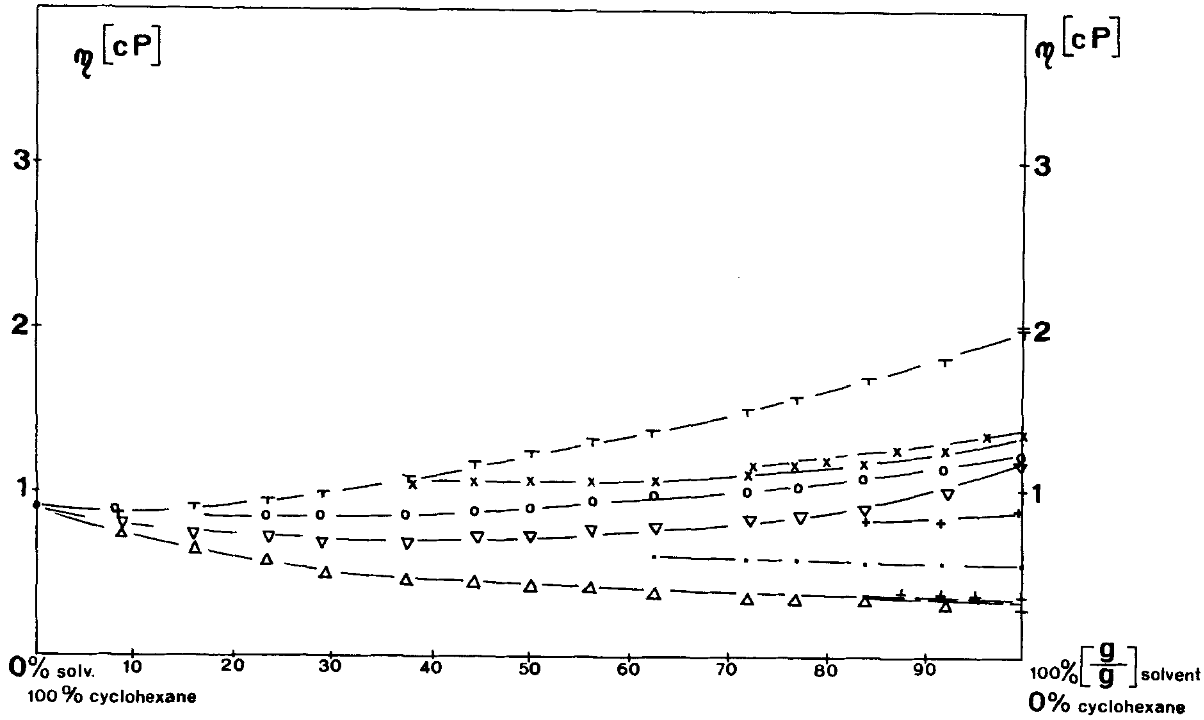

Figure 3. Viscosity–concentration [in % (w/w)] isotherms for binary mixtures of cyclohexane with (•) methanol, (×) ethanol, (○) 1,4-dioxane, (△) acetone, (▽) acetic acid, (⊥) acetonitrile, (+) *N*,*N*-dimethylformamide and (⊤) propan-1-ol

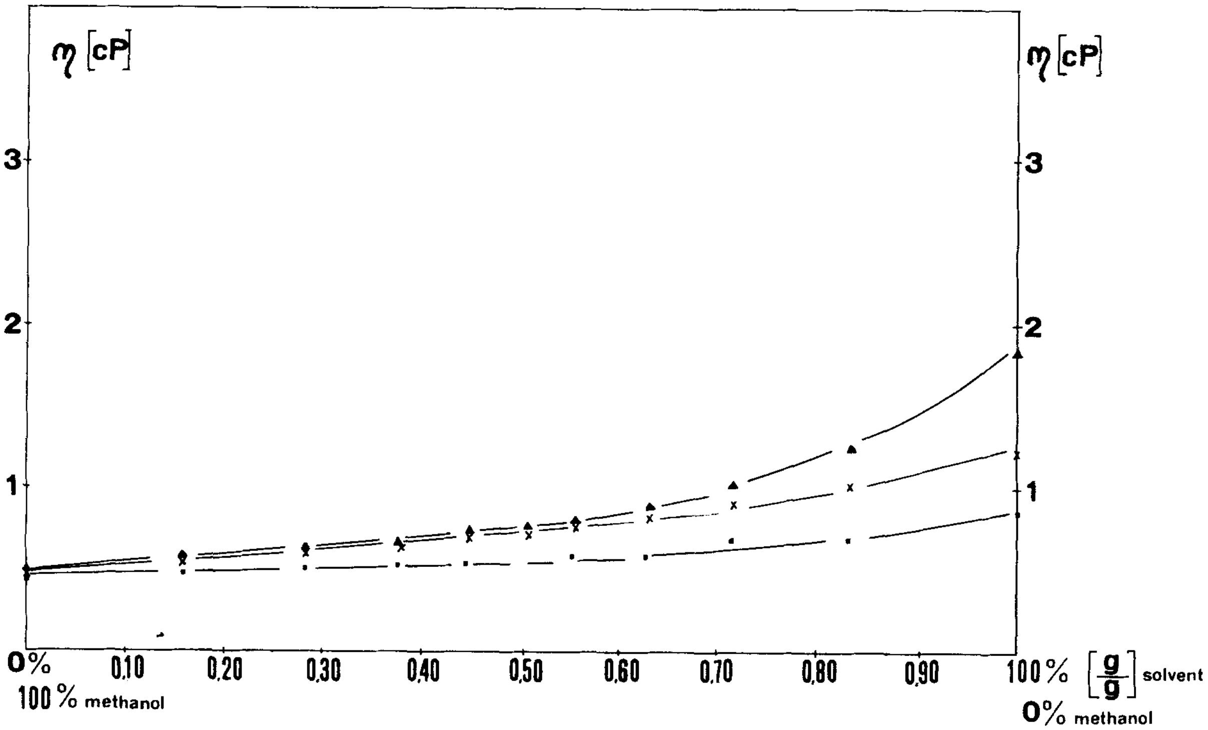

Figure 4. Viscosity–concentration [in % (w/w)] isotherms for binary mixtures of methanol with (•) *N*,*N*-dimethylformamide, (×) ethanol and (△) dimethyl sulphoxide

Table 2. Stoichiometry of some solvates

System	Stoichiometry[a]
Methanol–water	1 : 2
Ethanol–water	1 : 2
Propan-1-ol–water	1 : 3
Dimethyl sulphoxide–water	1 : 2
Acetonitrile–water	1 : 9
N,N-Dimethylformamide–water	1 : 2
1,4-Dioxane–water	1 : 3

[a] Calculated from the maxima of viscosity.

reasonable to shift the discussion in a more quantitative direction, utilizing both of the above-mentioned parameters, i.e. $\Delta\varepsilon/\Delta t$ and $\Delta\varepsilon/\Delta c$. The data in Table 3 show that the change in the former is negligible in the case of binary mixtures of components of low polarity. In contrast it changes noticeably if the components of solutions are polar. Thus, $\Delta\varepsilon/\Delta t$ measures the far-distance ordering of molecules in solution.

The result of the treatment of the experimental data by means of $\Delta\varepsilon/\Delta c$ is illustrated in Figure 5. There are three pairs of linear η–$\Delta\varepsilon/\Delta c$ relationships. The lines labelled 1 relate to ascending portions of the isotherms from Figure 1 and those labelled 2 relate to descending portions of the same isotherms. The deviations of the points from these straight lines measure the hydrodynamic factor, which evidently varies in a different manner in all three binary mixtures under consideration.

Evidently, there are two mechanisms (two distinct compositions of effects) which are responsible for the formation of solvates. They relate to the manner of preparation (either solvent A is diluted with solvent B,

Table 4. Variation of viscosity as a function of the absolute coefficient of the dielectric constant for some binary systems

	Ascending line		Descending line	
Binary system	η (cP)	$\Delta\varepsilon/\Delta c$	η (cP)	$\Delta\varepsilon/\Delta c$
Acetone–water	0·54	0·9696	0·621	1·3635
	0·545	1·1211	0·614	1·2726
	0·549	1·2423	0·606	1·1514
	0·560	1·3332	0·605	1·0605
	0·571	1·3938	0·605	0·9696
	0·595	1·5444	0·595	0·8181
			0·585	0·7272
			0·564	0·6363
			0·544	0·5454
			0·538	0·4545
			0·532	0·3636
Ethanol–water	0·570	1·1211	0·580	2·4543
	0·575	1·3635	0·560	2·3634
	0·580	1·6059	0·550	2·2422
	0·585	1·8180	0·540	2·1210
	0·590	1·9998	0·530	1·9998
	0·600	2·1816	0·520	1·9089
	0·610	2·2725	0·495	1·7574
			0·470	1·6059
			0·425	1·4544
			0·380	1·2726
1,4-Dioxane–water	0·817	0·9999	0·814	2·0301
	0·832	1·1817	0·767	1·9998
	0·847	1·3332	0·721	1·9392
	0·852	1·4241	0·650	1·8180
	0·858	1·5150	0·579	1·6665
	0·866	1·6362	0·482	1·4847
	0·874	1·7271	0·386	1·3332

Table 3. Change of the absolute temperature coefficient of the dielectric constant ($\Delta\varepsilon/\Delta t$) for some solvents[a]

	$\Delta\varepsilon/\Delta t$					
Δt (°C)	Water	Cyclohexane	Benzene	Chloroform	Methanol	Ethanol
0–5	1·95			0·180		
5–10	1·93					
10–15	1·89	0·016	0·020	0·180	2·10	1·63
15–20	1·86					
20–25	1·72	0·016	0·020	0·180	2·00	1·51
25–30	1·89					
30–35	1·75	0·016	0·019	0·166	1·86	1·42
35–40	1·72					
40–45	1·69	0·016	0·020	0·162	1·75	1·34
45–50	1·65					
50–55	1·62	0·016	0·021	0·150		1·25
55–60						
60–70						1·18

[a] Calculated from data tabulated in Refs 22 and 23.

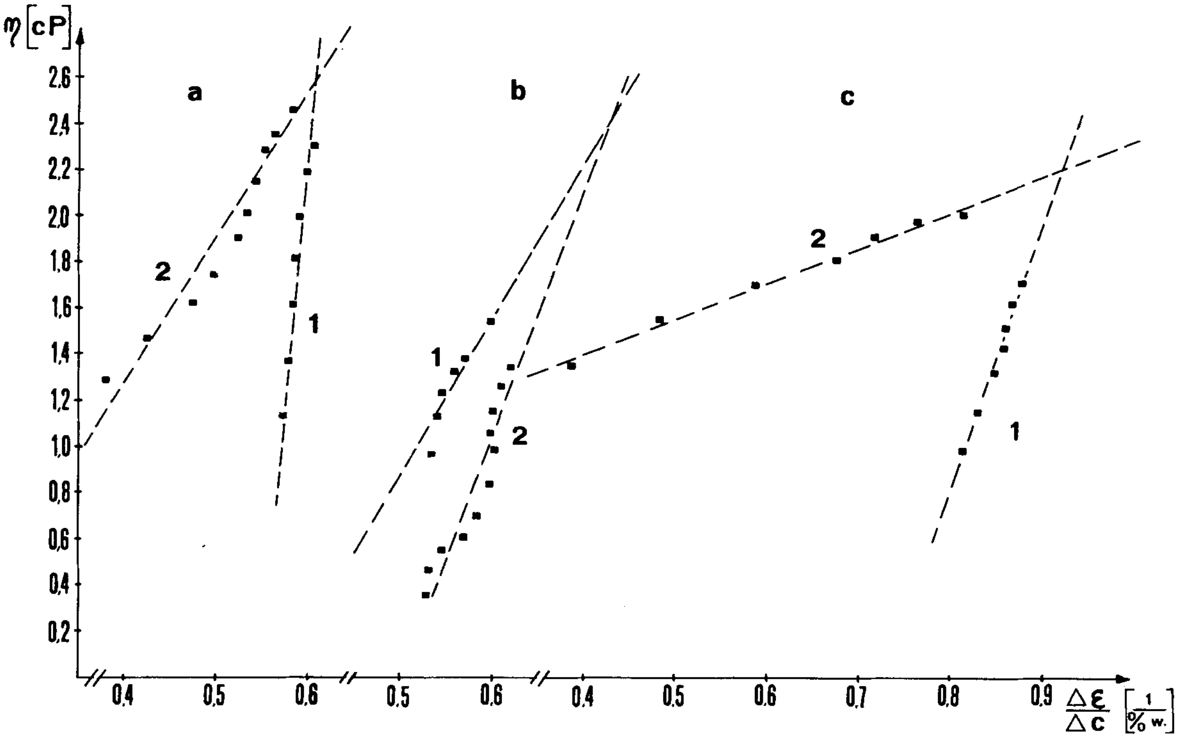

Figure 5. Viscosity–absolute concentration coefficient of dielectric constant relationships for aqueous binary mixtures with (a) ethanol, (b) acetone and (c) 1,4-dioxane

Table 5. Relationships between viscosity and absolute concentration coefficient of dielectric constant [$\eta = a(\Delta\varepsilon/\Delta c) - b$]

Binary system	Line	a	b	r[a]	s[b]	n[c]
Acetone–water	1	7·7 ± 5·8	3·1 ± 3·2	0·882	0·18	6
	2	21·6 ± 4·6	11·7 ± 2·7	0·962	0·34	11
Ethanol–water	1	36·0 ± 8·0	19·0 ± 5·0	0·980	0·43	7
	2	9·6 ± 1·4	2·9 ± 0·7	0·985	0·39	10
1,4-Dioxane–water	1	12·8 ± 1·3	9·4 ± 1·1	0·996	0·25	7
	2	1·7 ± 0·2	0·7 ± 0·2	0·992	0·27	7

[a] Correlation coefficient.
[b] Standard deviation.
[c] Number of experimental points.

or solvent B is diluted with solvent A). One of them causes a change in viscosity of the binary system along lines 1 and the other along lines 2.

Following other attributes, these relationships can be interpreted as follows. The range of variation of $\Delta\varepsilon/\Delta c$ for both solvation mechanisms for a given binary mixture, i.e. $\Delta(\Delta\varepsilon/\Delta c)_1$ and $\Delta(\Delta\varepsilon/\Delta c)_2$, measures the deviation from the additivity of dielectric constants of these systems which takes place when either the first or the second mechanism is involved. These parameters are helpful in deducing whether the structure of the solvate is more or less polar, i.e. whether these solvates are capable of stronger or weaker interactions with one another. Polar solvates interact more strongly and $\Delta(\Delta\varepsilon/\Delta c)$ is small. Hence the hydrodynamic properties of acetone–water and water–acetone binary systems vary significantly and irregularly. These properties vary in the case of ethanol–water whereas in the case of water–ethanol mixtures they are constant. The changes in hydrodynamic properties for 1,4-dioxane–water and water–1,4-dioxane binary mixtures are stable. Addition of ethanol to water leads to the formation of solvates which interact with one another less strongly than solvates resulting from the addition of water to ethanol.

There are very strong interactions between solvates formed from 1,3-dioxane with water added, and much weaker interactions between solvates from water with 1,4-dioxane added.

Both straight lines 1 and 2 are described by the equation $y = ax + b$ with $x = x_1 - x_0$ as the magnitude of the deviations from zero. Thus, the corresponding equations take the following forms, respectively:

$$\eta = [\Delta\eta/\Delta(\Delta\varepsilon/\Delta c)]\,[(\Delta\varepsilon/\Delta c)_1 - (\Delta\varepsilon/\Delta c)_0] + \eta_1 \quad (1)$$

$$\eta = [\Delta\eta/\Delta(\Delta\varepsilon/\Delta c)]\,[(\Delta\varepsilon/\Delta c)_1 - (\Delta\varepsilon/\Delta c)_0] + \eta_2 \quad (2)$$

where $[\Delta\eta/\Delta(\Delta\varepsilon/\Delta c)]$ is the slope ($\tan\alpha$) of the lines, which reflects the hydrodynamic and polar properties of the solvates, and $(\Delta\varepsilon/\Delta c)_0$ corresponds to the original value of this coefficient, i.e. the magnitude of this coefficient for pure solvents which constitute a binary mixture. The statistical treatment of the data points to a high credibility of the proposed approach.

EXPERIMENTAL

The viscosity measurements (with ca 1% accuracy) were carried out by means of a Zimm rotatory viscosimeter,[30] modified by providing for the preparation of binary solutions inside the chamber of the device.[31] The weight of the rotor can be adjusted to the viscosity of the mixture being studied. The apparatus was additionally equipped with an automatic timer measuring the velocity of the rotor under a constant meniscus for pure solvents and their mixtures. The measurement temperatures were 298 and 313 K, maintained with a precision of ±0·01 K.

The solvents used in the measurements were of analytical-reagent grade and water was redistilled.

The dielectric constant data were taken from the literature.[22,23]

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