Viscosities and Activation Energies of Viscous Flow of the 1,2-Ethanediol/*N,N*-Dimethylformamide Binary Solvent System

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Densities (ρ) and absolute viscosities (η) of pure 1,2-ethanediol, *N,N*-dimethylformamide and of their nine mixtures were determined at nineteen temperatures ranging between −10 and +80 °C. The above properties were fitted by empirical equations stating their dependence on temperature and composition of the mixtures. The extrathermodynamic excess functions, such as the excess rheochor $[R^E]$ and the excess Gibbs energy of activation of viscous flow ΔG^E, have been studied. The trend of $[R^E]$ vs. composition of the mixtures shows negative deviations from ideality, indicating extensive molecular interactions between the components of the binary solvent system. Furthermore, activation enthalpies and entropies for viscous flow have been obtained and their variations with composition have also been discussed.

The knowledge of the solution properties for mixed solvents of two, or more, components is frequently required in the understanding of the transport phenomena as well as in the industrial chemical processes. These properties may include density, viscosity, and other common physical parameters such as refractive index, dielectric constant and any related quantity. Relatively few data are available in the literature about amide–alcohol solvent systems, and this fact allows us to plan some extensive studies in this research field in order to investigate the closest interactions between unlike molecules by examining the macroscopic extrathermodynamic parameters. In connection with our previous works on the determination of acid-base properties in nonaqueous solvent systems, where 1,2-ethanediol was used as pure solvent,[1] or in mixture with 2-methoxyethanol[2–5] and water,[6] in this paper density and viscosity are reported at 19 temperatures ranging between −10 to +80 °C, with thermal scanning of 5 °C, and for 9 mixtures covering the whole miscibility field expressed by the mole fraction $X_{1,2\text{-ethanediol}}$ ($0 \leqslant X_{1,2\text{-ethanediol}} \leqslant 1$).

1,2-Ethanediol, amphiprotic in nature, is a very interesting nonaqueous solvent, especially because of its unusual properties, such as a large dipole moment (μ=2.28 D at 20 °C, 1 D=3.3356×10^{-30} C m),[7] associated to a moderately high dielectric constant (ε=37.7 at 25 °C)[7] that makes it a medium dissociating solvent[8] in the general classification of Charlot.[9] Further, it has a high viscosity value, suggesting a highly polymerized structure, in particular at the lowest temperatures; this fact is confirmed by structural and geometrical studies that outlined the possibility to form either intra- and/or intermolecular hydrogen bonds.[10] This cooperative bond network provides strong intermolecular connectivities which may be slackened by increasing the temperature or by mixing with a miscible cosolvent. In fact, the addition of *N,N*-dimethylformamide (DMF) to pure 1,2-ethanediol progressively inhibits the cooperative fluctuations of the –(diol–diol)$_n$– hydrogen-bonding connectivities; these last interactions are progressively replaced by 1,2-ethanediol–cosolvent mixed connectivities, providing a series of micro- and macroscopic evidences in the real behavior of the systems.

On the other hand, DMF, aprotic protophylic, potentially basic medium, is one of the most important organic solvents, largely utilized in analytical and electrochemical applications, owing to its easy purification,[11] and to other properties such as the whole miscibility with almost all common polar and nonpolar solvents and the high solvating power with respect to a wide lot of organic and inorganic substances; this last behavior is probably due to a quite large dipole moment (μ=3.28 D at 25 °C)[7] and to a moderately high dielectric constant (ε=37.5 at 25 °C).[9] The striking tendency to provide hydrogen bonds via acceptor sites –C(=O)–N=, makes DMF a powerful breaker of polymerized structure of hydroxy compounds.

Experimental

Materials. 1,2-Ethanediol and DMF (containing both >0.10% by weight water found by Karl Fischer titration) were Carlo Erba (Milan) high purity grade. The DMF was purified by passage on neutral alumina column before use. The mixtures were gravimetrically prepared on a Mettler analytical balance just before their use, operating in a dry nitrogen atmosphere at 26 °C and then preserved on 3 Å molecular sieves. The probable error in the 1,2-ethanediol mole fraction (X_1) is estimated to be less than 1.5×10^{-4}.

Instrumental. The densities were determined by means of an Anton Paar Mod. DMA 60 digital precision density meter, equipped with a density measuring cell Mod. DMA 602, with a sensitivity up to 0.000001 g cm^{-3}.

This instrument utilizes an oscillating capillary tube, the frequency of which is closely related to the density of fluid sample. The measuring cell DMA 602 was embodied on a plexiglas air thermostated box, which was maintained to the same measure temperature. The instrumental calibration is accomplished with two fluids of accurately known density, such as bidistilled water, liquid Hg, and dried air at each investigated temperature. For the measurements, the period (T) of 10000 oscillation cycles was selected, keeping ca. 30 readouts for every sample at each temperature until the T value becomes constant ±1, and with a maximum variation between each series equal to $\bar{T}\pm3$. The standard deviation (σ) was approximately 1.6×10^{-6}, and the estimated accuracy (95% confidence interval) is $\pm3\times10^{-6}$.

Kinematic viscosity measurements were performed using a Schott-Geräte AVS 400 viscosity-measuring system equipped with a series of Ubbelhode viscometers, covering the $0.6\leq\nu\leq300$ cSt ($1\mathrm{St}=10^{-4}\ \mathrm{m^2\,s^{-1}}$). In all the determinations the kinetic energy correction has been taken into account according to Hagenbach in order to evaluate the absolute viscosity η. In all the cases the experiments were generally performed at least in five replicates for each composition and at each temperature and the results were averaged.

The overall experimental uncertainty (standard deviation) was approximately equal to $\pm1.4\times10^{-3}$ and the estimated accuracy (95% confidence interval) was $\pm4\times10^{-3}$. The temperature control was provided by a Lauda K2R thermostatic bath maintained to ±0.02 °C.

Karl Fischer titrations were performed with an automatic titration system (Crison model KF431) equipped with a digital buret (Crison model 738).

Results and Discussion

The experimental measurements of density (ρ) and viscosity (η) were carried out for the two pure components and for their nine mixtures in the whole composition range $0\leqslant X_1\leqslant1$ working in the −10 to +80 °C temperature range. The letters A,B,···M which appear in the text represent the eleven solvent systems whose compositions are expressed by the mole fraction of 1,2-ethanediol (X_1) and are reported, in different scales, in Table 1.

Table 2 summarizes the experimental density values, and their dependence on temperature was checked by a polynomial equation

$$\rho(t)=\sum_{i=0}^{4}\rho_i t^i \quad t/°\mathrm{C}, \tag{1}$$

for each binary solvent system. The ρ_i coefficients were evaluated by means of the ordinary least-squares method, using a multilinear regression package TSP,[12] and are presented in Table 3. The goodness of this fit equation is ascertained by an average uncertainty of ±0.000027 units of ρ. In order to establish the dependence of ρ on the composition of the binary solvent system, the polynomial equation

$$\frac{1}{\rho(X_1)}=\sum_{j=0}^{4}\frac{1}{\rho_j}X_1^j \tag{2}$$

was used to fit the experimental data at each temperature. The results of this correlation procedure are listed in Table 4, along with the relative standard deviations $\sigma_{(\rho)}$ at each investigated temperature.

Table 1. Binary Composition of 1,2-Ethanediol/*N,N*-Dimethylformamide Solvent System

System	X_1	$V_{\mathrm{ED}}/V_{\mathrm{DMF}}/\%$	Molarity[a] of ED	Molarity[a] of DMF
A	0.0000	0/100	—	12.9364
B	0.1152	10/90	1.7882	11.4468
C	0.2266	20/80	3.5784	10.3694
D	0.3346	30/70	4.8094	9.5644
E	0.4391	40/60	7.1830	7.7916
F	0.5399	50/50	8.2992	7.0726
G	0.6377	60/40	10.7761	5.1984
H	0.7323	70/30	12.0070	4.3893
I	0.8242	80/20	14.3656	2.6026
L	0.9136	90/10	16.1596	1.2976
M	1.0000	100/0	17.8830	—

a) at 25 °C.

Table 2. Experimental Density Values (g cm^{-3}) for 1,2-Ethanediol/*N,N*-Dimethylformamide Solvent System at Various Temperatures

t/°C	System A	System B	System C	System D	System E	System F	System G	System H	System I	System L	System M
−10	0.981485	0.998202	1.013121	1.029651	1.045861	1.063053	1.080514	1.095918	1.110466	1.123325	1.133634
−5	0.976038	0.992910	1.008093	1.024762	1.041254	1.058153	1.075302	1.091094	1.105903	1.119611	1.130452
0	0.970704	0.987714	1.003191	1.020028	1.036778	1.053548	1.070584	1.086648	1.101642	1.115874	1.127069
5	0.965525	0.982676	0.998675	1.015407	1.032242	1.048938	1.065817	1.082218	1.097470	1.112283	1.123664
10	0.960456	0.977735	0.993725	1.010776	1.027955	1.044599	1.061424	1.078071	1.093449	1.108680	1.120296
15	0.955302	0.972872	0.989104	1.006306	1.023669	1.040270	1.057033	1.073914	1.089504	1.105005	1.116906
20	0.950453	0.968111	0.984557	1.001927	1.019486	1.036160	1.052965	1.069980	1.085640	1.101422	1.113440
25	0.945597	0.963372	0.980009	0.997538	1.015337	1.032031	1.048828	1.066087	1.081895	1.097867	1.109913
30	0.940691	0.958710	0.975602	0.993314	1.011241	1.028062	1.044948	1.062255	1.078153	1.094216	1.106512
35	0.935814	0.954035	0.971156	0.989015	1.007107	1.024087	1.041006	1.058483	1.074546	1.090673	1.103089
40	0.931030	0.949375	0.966755	0.984856	1.003174	1.020245	1.037275	1.054829	1.070976	1.087108	1.099747
45	0.926282	0.944615	0.962330	0.980575	0.999083	1.016333	1.033460	1.051121	1.067351	1.083559	1.096312
50	0.921548	0.940030	0.957911	0.976358	0.995009	1.012436	1.029681	1.047389	1.063780	1.079822	1.092946
55	0.916716	0.935305	0.953404	0.972072	0.990945	1.008519	1.025856	1.043670	1.060133	1.076245	1.089471
60	0.911971	0.930520	0.949097	0.967774	0.986722	1.004563	1.022078	1.039974	1.056574	1.072654	1.086011
65	0.907025	0.925659	0.944471	0.963424	0.982651	1.000616	1.018145	1.036175	1.052952	1.068906	1.082634
70	0.902258	0.920705	0.939826	0.958880	0.978339	0.996503	1.014153	1.032376	1.049244	1.065332	1.079003
75	0.897219	0.915645	0.935128	0.954311	0.974013	0.992325	1.010060	1.028494	1.045441	1.061785	1.075369
80	0.892247	0.910463	0.930381	0.949681	0.969686	0.988141	1.005893	1.024572	1.041625	1.058146	1.071699

Table 3. ρ_i Coefficients of Eq. 1 for 1,2-Ethanediol/*N*,*N*-Dimethylformamide Solvent System

System	ρ_0	$\rho_1\times10^4$	$\rho_2\times10^6$	$\rho_3\times10^8$	$\rho_4\times10^{12}$	$\sigma_{(\rho)}\times10^5$
A	0.970730	−10.5148	2.11707	−1.54237	−0.540145	4.7
B	0.987731	−10.2105	2.38126	−2.05331	−7.49344	2.7
C	1.003266	−9.65616	1.71472	−0.742936	−69.2701	7.1
D	1.020014	−9.41794	2.12307	−1.22064	−57.6457	3.2
E	1.036711	−8.95662	2.05180	−1.61720	−6.35283	4.4
F	1.053493	−9.21952	3.17420	−2.30863	−2.96714	3.3
G	1.070510	−9.52328	4.23962	−3.07620	4.06607	4.6
H	1.086607	−8.90502	3.53508	−3.14781	65.7005	3.1
I	1.101643	−8.48416	2.84760	−2.10472	9.89670	3.0
L	1.115904	−7.33575	0.802849	−1.55567	91.7867	4.4
M	1.127083	−6.71053	−1.09692	2.78711	−219.177	4.2

Table 4. $1/\rho_j$ Coefficients of Eq. 2 for 1,2-Ethanediol/*N*,*N*-Dimethylformamide Solvent System

t/°C	ρ_0^{-1}	$\rho_1^{-1}\times10$	$\rho_2^{-1}\times10^2$	$\rho_3^{-1}\times10^2$	$\rho_4^{-1}\times10^2$	$\sigma_{(\rho^{-1})}\times10^4$
−10	1.018659	−1.43672	3.09803	−10.2497	7.88204	4.3
−5	1.024393	−1.48228	3.35059	−9.61683	7.11591	3.2
0	1.030058	−1.52144	3.34506	−8.92413	6.51241	2.8
5	1.035657	−1.59064	4.89227	−10.5831	7.01676	2.2
10	1.041120	−1.60593	4.08951	−9.07544	6.18056	3.1
15	1.046755	−1.66169	4.79998	−9.53258	6.18905	3.5
20	1.052110	−1.68739	4.44953	−8.74172	5.74542	3.8
25	1.057534	−1.72182	4.55991	−8.74565	5.72226	4.4
30	1.063049	−1.76347	4.56806	−8.28118	5.39228	4.2
35	1.068596	−1.80585	4.83390	−8.45681	5.45110	4.3
40	1.074095	−1.83184	4.13101	−7.05691	4.74018	4.3
45	1.079625	−1.85134	3.37372	−5.78351	4.14980	4.2
50	1.085159	−1.87575	2.77701	−4.64643	3.58582	3.7
55	1.090884	−1.90139	2.13546	−3.48398	3.03987	3.9
60	1.096601	−1.93229	1.92428	−3.11629	2.91460	3.3
65	1.102586	−1.95156	0.711255	−0.925256	1.81998	3.5
70	1.108452	−1.95635	−0.402062	0.472997	1.30359	3.9
75	1.114721	−1.98642	−0.852356	1.19856	1.00988	4.6
80	1.120998	−1.99569	−2.18110	3.16596	0.148585	5.7

Table 5. Experimental Viscosity Values (cP) for 1,2-Ethanediol/*N*,*N*-Dimethylformamide Solvent System at Various Temperatures

t/°C	System A	System B	System C	System D	System E	System F	System G	System H	System I	System L	System M
−10	1.371	2.069	3.192	5.026	7.983	12.90	20.55	32.46	50.84	75.71	112.1
−5	1.258	1.863	2.813	4.322	6.693	10.51	16.24	25.03	38.06	55.94	80.35
0	1.157	1.684	2.502	3.750	5.666	8.646	12.99	19.54	29.03	41.88	59.08
5	1.069	1.534	2.234	3.281	4.848	7.242	10.65	15.65	22.70	32.21	44.43
10	0.9934	1.403	2.011	2.889	4.164	6.120	8.844	12.69	18.05	25.12	34.11
15	0.9261	1.290	1.822	2.574	3.643	5.243	7.418	10.46	14.64	19.96	26.68
20	0.8669	1.191	1.660	2.310	3.230	4.532	6.278	8.707	11.93	16.12	21.20
25	0.8136	1.105	1.518	2.081	2.862	3.952	5.380	7.353	9.921	13.24	17.14
30	0.7648	1.027	1.392	1.882	2.552	3.456	4.639	6.225	8.250	10.91	14.02
35	0.7217	0.9570	1.285	1.711	2.289	3.060	4.044	5.360	7.023	9.133	11.58
40	0.6831	0.8951	1.185	1.563	2.064	2.719	3.551	4.644	5.998	7.726	9.684
45	0.6461	0.8414	1.096	1.433	1.873	2.434	3.139	4.054	5.171	6.606	8.202
50	0.6128	0.7911	1.022	1.322	1.711	2.190	2.789	3.563	4.507	5.671	7.032
55	0.5843	0.7455	0.9527	1.219	1.562	1.980	2.495	3.159	3.949	4.942	6.027
60	0.5565	0.7044	0.8922	1.129	1.433	1.799	2.245	2.810	3.472	4.305	5.188
65	0.5322	0.6674	0.8387	1.051	1.320	1.642	2.029	2.516	3.091	3.772	4.538
70	0.5084	0.6319	0.7876	0.9791	1.220	1.505	1.843	2.267	2.761	3.339	3.980
75	0.4846	0.6007	0.7424	0.9174	1.132	1.385	1.683	2.049	2.475	2.977	3.526
80	0.4649	0.5712	0.7027	0.8607	1.055	1.285	1.546	1.877	2.249	2.692	3.119

Table 6. ln η_i Coefficients of Eq. 3 for 1,2-Ethanediol/*N*,*N*-Dimethylformamide Solvent System

System	$\ln \eta_0$	$\ln \eta_1$	$\ln \eta_2 \times 10^4$	$\ln \eta_3 \times 10^6$	$\ln \eta_4 \times 10^{10}$	$\sigma_{(\ln \eta)} \times 10^3$
A	24.095	−0.22387	7.9561	−1.3095	8.1311	1.2
B	36.281	−0.35935	13.943	−2.5194	17.445	0.7
C	59.500	−0.64289	27.397	−5.4014	40.758	1.3
D	81.790	−0.89383	38.326	−7.5486	56.704	1.2
E	101.39	−1.1058	47.191	−9.2177	68.552	2.4
F	113.59	−1.2354	52.803	−10.361	77.639	1.1
G	125.84	−1.3539	57.250	−11.112	82.398	1.7
H	144.79	−1.5650	66.456	−12.943	96.265	1.8
I	154.99	−1.6599	69.903	−13.509	99.779	2.5
L	169.50	−1.8246	77.264	−15.006	111.33	2.6
M	167.61	−1.7514	71.873	−13.509	96.843	2.2

Equation 2 well reproduces the experimental densities, within ±0.000212 units overall the 209 values of Table 2.

The temperature effect on the absolute viscosity of the ED/DMF mixtures (Table 5) was investigated, at first, by using a polynomial equation of the type:

$$\ln \eta = \sum_{i=0}^{4} \ln \eta_i \, T^i. \quad T/\mathrm{K} \tag{3}$$

The ln η_i coefficients are reported in Table 6 for each binary solvent mixture. Equation 3 well reproduces the experimental values with an average difference of $\pm 1.1 \times 10^{-3}$ cP ($1\ \mathrm{P} = 10^{-1}$ Pa s).

In order to establish a function relating viscosity and solvent composition, the rheochor [*R*] was calculated for the various mixtures by means of the equation:[13]

$$[R] = \frac{M}{\rho} \eta^{1/8}, \tag{4}$$

where ρ is the smoothed density data evaluated by Eq. 1 and M is defined as:

$$M = X_1 M_1 + X_2 M_2, \tag{5}$$

M_1 and M_2 being the molecular weight of 1,2-ethanediol and DMF, respectively.

The trend of [*R*] vs. temperature is represented in Fig. 1 and it appears quite interesting, owing to the presence of a characteristic temperature in correspondence of which all the 1,2-ethanediol/DMF mixtures present almost isorheological properties. The plots of [*R*] values vs. X_1 are collected in Fig. 2, and the corresponding data were well fitted by means of the least-squares method, at each temperature, with a polynomial equation of the type

$$[R] = \sum_{i=0}^{4} R_i X_1^i, \tag{6}$$

whose coefficients are reported in Table 7 together with the corresponding standard deviation values.

Now, by combining Eqs. 2, 4, and 6, it is possible to write

$$\eta^{1/8} = \frac{1}{M} \frac{R_0 + R_1 X_1 + \cdots + R_4 X_1^4}{\rho_0 + \rho_1 X_1 + \cdots + \rho_4 X_1^4}, \tag{7}$$

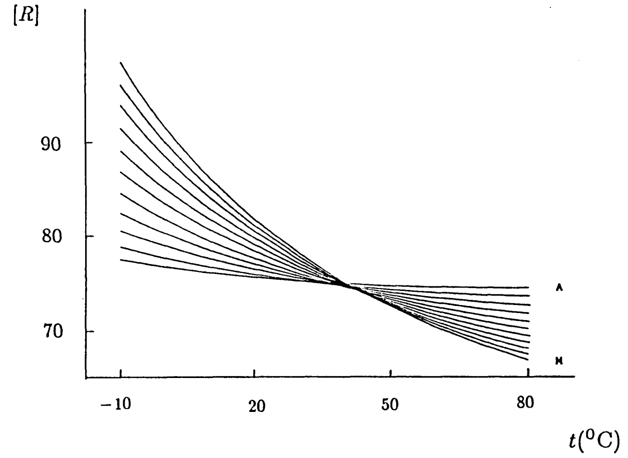

Fig. 1. Plots of [*R*] vs. temperature for the 1,2-ethanediol/*N*,*N*-dimethylformamide solvent system.

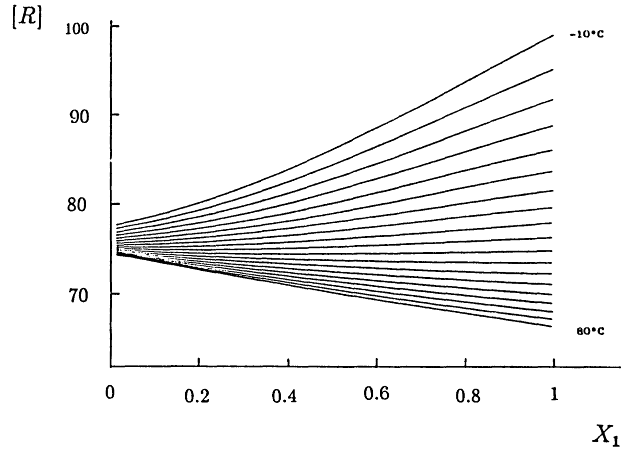

Fig. 2. Plots of [*R*] vs. mole fraction for the 1,2-ethanediol/*N*,*N*-dimethylformamide solvent system at different temperatures from −10 °C (top) to +80 °C (bottom).

where η is expressed as a rational function of two polynomials.

In the literature reports, the advantages deriving by the use for data fittings of rational functions rather than linear polynomials have been pointed out.[14] Also in

Table 7. R_i Coefficients of Eq. 6 for 1,2-Ethanediol/*N*,*N*-Dimethylformamide Solvent System

$t/°C$	R_0	R_1	R_2	R_3	R_4	$\sigma_{([R])}\times10^2$
−10	77.46	10.10	16.02	−3.619	−1.216	7.1
−5	77.05	8.616	13.24	−2.015	−1.892	4.7
0	76.66	7.355	11.05	−2.188	−1.184	4.9
5	76.33	5.843	9.839	−1.954	−1.308	3.9
10	76.04	4.519	7.973	−0.4705	−1.947	5.7
15	75.77	3.396	6.570	−0.02798	−1.943	5.9
20	75.53	2.105	7.158	−3.395	0.2542	3.8
25	75.32	1.167	5.284	−1.537	−0.4724	3.6
30	75.13	−0.08918	6.001	−4.633	1.614	2.9
35	74.97	−0.9829	4.512	−2.814	0.7309	3.6
40	74.84	−2.209	4.842	−3.908	1.399	2.6
45	74.71	−3.066	4.142	−3.670	1.537	1.4
50	74.60	−3.853	3.901	−4.602	2.420	1.1
55	74.55	−4.768	2.789	−2.476	1.229	1.1
60	74.49	−5.449	1.687	−1.082	0.5764	1.5
65	74.47	−6.241	1.218	−0.7482	0.5664	0.8
70	74.45	−6.999	0.7313	0.008343	0.1706	0.8
75	74.42	−7.273	−0.7466	1.222	−0.06020	1.8
80	74.44	−7.579	−3.326	5.949	−2.713	1.9

Table 8. Excess Reochor Values $[R^E]$ for 1,2-Ethanediol/*N*,*N*-Dimethylformamide Solvent System at Various Temperatures

$t/°C$	System B	System C	System D	System E	System F	System G	System H	System I	System L
−10	−1.1259	−1.7334	−2.1159	−2.2150	−2.0209	−1.8373	−1.4033	−0.8334	−0.5729
−5	−0.9469	−1.4421	−1.7483	−1.8133	−1.6179	−1.4671	−1.0888	−0.6438	−0.3696
0	−0.7982	−1.1690	−1.4393	−1.4998	−1.3314	−1.2287	−0.9141	−0.5373	−0.3229
5	−0.6699	−0.9786	−1.1969	−1.2520	−1.0625	−0.9477	−0.7009	−0.4043	−0.2283
10	−0.5712	−0.8065	−1.0180	−1.1148	−0.8770	−0.7374	−0.5664	−0.3125	−0.2022
15	0.4857	−0.6606	−0.8340	−0.9254	−0.7069	−0.5969	−0.4455	−0.2109	−0.1779
20	−0.4230	−0.5396	−0.6750	−0.7145	−0.5738	−0.5056	−0.3766	−0.2133	−0.1389
25	−0.3576	−0.4515	−0.5725	−0.6204	−0.4819	−0.4320	−0.3171	−0.1719	−0.1017
30	−0.3091	−0.3796	−0.4849	−0.5307	−0.4387	−0.3896	−0.3264	−0.2347	−0.1309
35	−0.2764	−0.3033	−0.4171	−0.4556	−0.3610	−0.3309	−0.2641	−0.1657	−0.1100
40	−0.2529	−0.2889	−0.3696	−0.4090	−0.3372	−0.3002	−0.2476	−0.1771	−0.1004
45	−0.1895	−0.2676	−0.3282	−0.3575	−0.3085	−0.2877	−0.2495	−0.1978	−0.0957
50	−0.1618	−0.2288	−0.2842	−0.3115	−0.3118	−0.3102	−0.2805	−0.2183	−0.1590
55	−0.1555	−0.2260	−0.2817	−0.3030	−0.2966	−0.2917	−0.2475	−0.2014	−0.0898
60	−0.1178	−0.1847	−0.2427	−0.2650	−0.2526	−0.2461	−0.2148	−0.1828	−0.0627
65	−0.1041	−0.1718	−0.2380	−0.2725	−0.2686	−0.2662	−0.2405	−0.1826	−0.1199
70	−0.0878	−0.1651	−0.2251	−0.2611	−0.2558	−0.2514	−0.2254	−0.1697	−0.1113
75	−0.0240	−0.1285	−0.1748	−0.2406	−0.2431	−0.2448	−0.2490	−0.2013	−0.1270
80	0.0034	−0.0957	−0.1468	−0.2118	−0.1817	−0.1960	−0.1637	−0.1173	−0.0250

the present case we have found that Eq. 7 reproduces the experimental viscosity values better than a single polynomial, the average uncertainty being $\pm1.8\times10^{-3}$ cP.

Some interesting considerations may be drawn taking into account the rheochor excess function $[R^E]$, which is a nonthermodynamic property very sensible to the molecular interactions. This function is defined by the equation

$$[R^E]=[R]-[R^{id}]=\frac{M}{\rho}\eta^{1/8}-(X_1[R_1]+X_2[R_2]), \tag{8}$$

where $[R^{id}]$ is the ideal rheochor, $[R_1]$ and $[R_2]$ the rheochors of the pure components. The $[R^E]$ calculated values are reported in Table 8 and, according to Redlich and Kister,[15] they are well fitted against mole fraction by the proper Eq. 9,

$$Y^E=X_1X_2\sum_{k=0}^{n}a_k(X_1-X_2)^k, \tag{9}$$

where Y^E represents the excess function under consideration and a_k are the adjustment coefficients. The values of these coefficients are summarized in Table 9 together with the standard deviations.

Figure 3 shows the plots of $[R^E]$ vs. X_1 at each investigated temperature. The trend shows in general a negative deviation in the whole composition range, with a pronounced minimum at $X_1\approx0.4$ and at the lowest temperatures. This minimum becomes quite flattened as the temperature increases up to ca. 40 °C. Upper this value, the $[R^E]$ quantity becomes very small, with a

Table 9. a_k Adjustment Parameters and Standard Deviation ($\sigma_{[R^E]}$) of the $[R^E]$ Fit Eq. 9 for 1,2-Ethanediol/*N*,*N*-Dimethylformamide Solvent System at Various Temperatures

t/°C	a_0	a_1	a_2	a_3	$\sigma_{([R^E])} \times 10^2$
−10	−8.5321	2.9923	0.1627	−0.0536	6.7
−5	−6.9331	2.7069	0.3794	0.6410	4.2
0	−5.7211	2.0512	0.1866	0.7781	4.4
5	−4.6415	2.2279	0.2571	0.1963	3.6
10	−3.9061	2.4306	0.4118	−0.9202	5.1
15	−3.1830	2.1560	0.3827	−0.7866	5.4
20	−2.5392	1.4059	−0.1461	0.1384	3.5
25	−2.1758	1.1797	0.0498	0.2494	3.4
30	−1.8921	0.7070	−0.4469	0.0345	2.7
35	−1.5964	0.6378	−0.2570	0.1743	3.3
40	−1.4454	0.5001	−0.4035	0.2457	2.4
45	−1.3251	0.3204	−0.3767	−0.0412	1.3
50	−1.2462	−0.0963	−0.6322	−0.1078	1.0
55	−1.2185	−0.0805	−0.3027	0.3739	0.8
60	−1.0579	−0.0732	−0.1153	0.2008	1.4
65	−1.0945	−0.1238	−0.1478	−0.2645	0.6
70	−1.0477	−0.0746	−0.0428	−0.3815	0.5
75	−0.9814	−0.3317	0.0520	−0.8169	1.1
80	−0.8321	−0.1993	0.7348	−0.1963	1.8

slight variation around the zero value, indicating an almost ideal behavior of the rheological properties of the systems. This behavior is therefore traced to the complex formation between unlike molecules through intermolecular hydrogen bonding and/or dipole–dipole interactions.[16]

The next step of this work lies in the study of the thermodynamic properties of viscous flow. The energies of activation of the viscous flow, ΔG^*, were calculated by using the Eyring viscosity equation,[17]

$$\eta = \frac{hN}{V_m} e^{\frac{\Delta G^*}{RT}}, \tag{10}$$

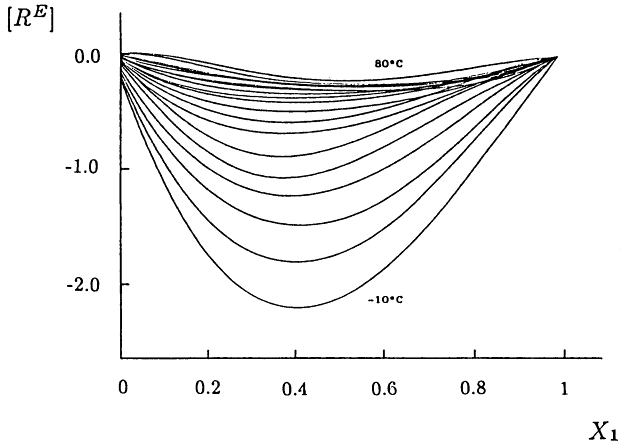

Fig. 3. Excess rheochor $[R^E]$ curves for the 1,2-ethanediol/*N,N*-dimethylformamide solvent system at different temperatures from −10 °C (bottom) to +80 °C (top).

where h is the Planck constant, N the Avogadro's number, R the universal gas constant, and T the absolute temperature. The term V_m is the molar volume of the mixtures, calculated from the corresponding mixture densities and by the following relation:

$$V_m = \frac{X_1 M_1 + X_2 M_2}{\rho}. \tag{11}$$

The obtained ΔG^* values are summarized in Table 10.

Now, it is possible to write

$$\Delta G^* = \Delta H^* - T\Delta S^*, \tag{12}$$

where ΔH^* and ΔS^* are the enthalpy and the entropy of activation of viscous flow, respectively. By combining Eqs. 10 and 12, and plotting the $R \ln(\eta V_m)$ quantity vs. $1/T$ for each binary mixture, Fig. 4, we have found that

Table 10. Free Energy of Activation of Viscous Flow (kJ mol⁻¹) for 1,2-Ethanediol/*N*,*N*-Dimethylformamide Solvent System at Various Temperatures

t/°C	System A	System B	System C	System D	System E	System F	System G	System H	System I	System L	System M
−10	12.150	12.976	13.855	14.779	15.725	16.701	17.647	18.585	19.502	20.323	21.125
−5	12.199	12.999	13.848	14.730	15.631	16.567	17.468	18.363	19.237	20.028	20.790
0	12.251	13.026	13.849	14.692	15.552	16.449	17.309	18.163	18.997	19.760	20.484
5	12.307	13.059	13.855	14.664	15.487	16.346	17.167	17.984	18.780	19.516	20.206
10	12.366	13.096	13.868	14.645	15.434	16.256	17.040	17.823	18.583	19.295	19.953
15	12.428	13.137	13.885	14.633	15.392	16.178	16.928	17.679	18.405	19.093	19.723
20	12.493	13.181	13.907	14.628	15.358	16.111	16.829	17.549	18.244	18.909	19.513
25	12.560	13.229	13.933	14.629	15.333	16.053	16.741	17.433	18.098	18.741	19.322
30	12.630	13.280	13.961	14.634	15.314	16.003	16.663	17.328	17.966	18.587	19.147
35	12.702	13.334	13.993	14.644	15.301	15.960	16.594	17.233	17.845	18.446	18.987
40	12.776	13.390	14.027	14.657	15.293	15.924	16.533	17.148	17.736	18.317	18.839
45	12.852	13.449	14.063	14.674	15.290	15.893	16.479	17.071	17.636	18.197	18.703
50	12.929	13.509	14.102	14.693	15.290	15.868	16.431	17.001	17.546	18.086	18.577
55	13.007	13.570	14.143	14.715	15.293	15.848	16.390	16.940	17.464	17.985	18.459
60	13.086	13.634	14.186	14.740	15.299	15.833	16.355	16.885	17.390	17.892	18.350
65	13.165	13.698	14.233	14.769	15.309	15.825	16.327	16.838	17.325	17.809	18.248
70	13.245	13.764	14.282	14.801	15.323	15.823	16.305	16.800	17.270	17.735	18.153
75	13.325	13.831	14.336	14.838	15.342	15.829	16.292	16.772	17.225	17.673	18.065
80	13.404	13.900	14.396	14.882	15.367	15.845	16.289	16.754	17.193	17.623	17.986

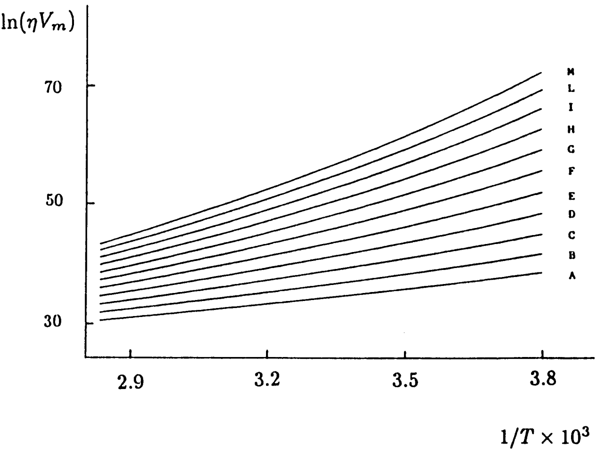

Fig. 4. Plots of R ln (ηV_m) vs. $1/T$ for the 1,2-ethanediol/ *N,N*- dimethylformamide solvent system.

Table 11. Enthalpy (ΔH^*) and Entropy (ΔS^*) of Activation of Viscous Flow for 1,2-Ethanediol/ *N,N*-Dimethylformamide Solvent System from −10 to +80 °C

System	ΔH^* kJ mol^{-1}	ΔS^* J mol^{-1} K^{-1}	r
A	8.411	−52.36	0.999
B	10.196	−48.65	0.998
C	12.212	−44.27	0.998
D	14.353	−39.49	0.998
E	16.567	−34.51	0.997
F	19.029	−28.74	0.996
G	21.393	−23.20	0.996
H	23.681	−17.92	0.995
I	25.963	−12.57	0.995
L	27.901	−8.26	0.995
M	29.861	−3.71	0.995

the plots show a quite linear trend in the DMF rich region and they moderately shift from the linearity as the 1,2-ethanediol mole fraction increases up to the mixture E. For the mixtures from E to M the linear trend is well reproduced up to 3.5×10^{-3} $1/T$ values and then small deviations are observed. Therefore, to a first approximation, these plots may indicate that the ΔH^* values are almost constant in the investigated temperature range.

From this last correlation procedure, the ΔH^* values were obtained from the slopes of the curves, while ΔS^* values were evicted from the intercepts. The results are listed in Table 11 where, in the fourth column, we have reported the linear correlation coefficient r of the logarithmic form of Eq. 10.

On the basis of the fact that the plots of R ln (ηV_m) vs. $1/T$ are reasonably linear from A to E solvent systems, one may suggest that the mechanism of viscous flow for these binary mixtures is a thermally activated single process. The ΔH^* values, as previously determined, are all positive and decrease with an increase of the mole fraction of cosolvent DMF.

The above observations suggest that the formation of the activated species necessary for viscous flow appears quite easy in the DMF rich region, and becomes difficult as the 1,2-ethanediol mole fraction increases.

As regards ΔS^* values, these are all negative and decrease with an increase of DMF. A brief examination of these values makes evident the very large difference (much more than one order of magnitude) encountered on passing from one pure solvent to the other. Therefore, in our opinion it appears unlikely that, in the 1,2-ethanediol rich region, the flow can take place simply by jumping of individual molecular units.

A satisfactory elucidation of these facts probably arises from the more realistic hypothesis of the flow

Table 12. Excess Free Energy of Viscous Flow ΔG^{*E} (J mol^{-1}) for 1,2-Ethanediol/ *N,N*-Dimethylformamide Solvent System at Various Temperatures

t/ °C	System B	System C	System D	System E	System F	System G	System H	System I	System L
−10	−208.0	−328.5	−374.1	−366.2	−294.6	−226.6	−137.3	−45.0	−26.1
−5	−189.8	−297.2	−343.4	−340.0	−270.5	−209.3	−127.0	−42.2	−19.2
0	−173.2	−268.0	−313.8	−313.8	−247.5	−192.9	−116.9	−39.7	−12.9
5	−158.0	−241.3	−285.8	−288.0	−226.0	−177.6	−107.4	−37.6	−7.4
10	−144.1	−217.2	−259.7	−263.2	−206.2	−163.7	−98.8	−36.0	−2.9
15	−131.5	−195.4	−235.4	−239.3	−188.2	−151.2	−91.0	−35.0	0.5
20	−120.1	−176.3	−213.5	−217.0	−172.1	−140.2	−84.5	−34.5	2.7
25	−109.8	−159.7	−193.8	−196.4	−158.0	−130.7	−79.0	−34.7	3.7
30	−100.5	−145.4	−176.3	−177.5	−145.7	−122.5	−74.6	−35.4	3.7
35	−91.9	−133.3	−160.8	−160.3	−135.0	−115.5	−71.1	−36.3	2.8
40	−84.2	−122.8	−147.3	−144.9	−125.9	−109.5	−68.3	−37.3	1.2
45	−77.0	−114.2	−135.6	−131.3	−117.7	−104.2	−65.8	−38.1	−0.6
50	−70.6	−106.4	−125.4	−119.2	−110.3	−99.2	−63.3	−38.3	−2.2
55	−64.4	−99.3	−115.9	−108.0	−102.5	−93.8	−60.1	−37.1	−3.1
60	−58.3	−92.3	−106.8	−97.7	−94.3	−87.4	−55.5	−34.1	−2.5
65	−52.3	−83.9	−96.8	−87.4	−84.3	−79.5	−48.8	−28.6	0.4
70	−45.8	−74.6	−85.9	−76.4	−71.5	−69.3	−38.8	−19.8	6.5
75	−39.5	−62.6	−72.6	−64.0	−55.2	−55.5	−24.8	−6.7	16.9
80	−32.1	−46.8	−55.8	−49.3	−33.5	−37.2	−5.2	12.1	32.8

Table 13. a_k Adjustment Parameters and Standard Deviation ($\sigma_{(\Delta G^{*E})}$) of the ΔG^{*E} Fit Eq. 9 for 1,2-Ethanediol/*N,N*-Dimethylformamide Solvent System at Various Temperatures

t/ °C	a_0	a_1	a_2	a_3	a_4	$\sigma_{(\Delta G^{*E})}\times10^2$
−10	−1.3295	1.2539	0.5525	−0.1635	−0.4589	9.1
−5	−1.2276	1.1306	0.5392	−0.1145	−0.3831	8.1
0	−1.1282	1.0095	0.5156	−0.0533	−0.3143	7.5
5	−1.0328	0.8934	0.4776	0.0119	−0.2415	7.1
10	−0.9431	0.7834	0.4280	0.0759	−0.1655	6.9
15	−0.8591	0.6784	0.3732	0.1392	−0.0982	6.7
20	−0.7823	0.5824	0.3076	0.1930	−0.0249	6.3
25	−0.7131	0.4951	0.2392	0.2359	0.0422	5.8
30	−0.6509	0.4166	0.1659	0.2678	0.1102	5.3
35	−0.5954	0.3477	0.0898	0.2865	0.1807	4.6
40	−0.5470	0.2876	0.0231	0.2955	0.2353	4.1
45	−0.5037	0.2399	−0.0467	0.2896	0.3013	3.8
50	−0.4653	0.2006	−0.1017	0.2807	0.3509	3.7
55	−0.4279	0.1720	−0.1516	0.2662	0.4058	3.8
60	−0.3912	0.1545	−0.1825	0.2506	0.4536	4.0
65	−0.3510	0.1402	−0.1868	0.2531	0.4831	4.0
70	−0.3038	0.1381	−0.1838	0.2638	0.5367	4.2
75	−0.2464	0.1388	−0.1453	0.3136	0.5663	4.3
80	−0.1738	0.1451	−0.0722	0.3981	0.5958	5.4

mechanism of Eyring,[17] which explains the flow by movement of dislocations or discontinuities in the fluid layers. In a dynamic steady state, and in an oversimplified picture, the movement of a dislocation by one layer position requires the cooperation of at least two moving elementary units: one is moving out the standard position and requires energy, and the other is moving into this cavity and gives up energy. Therefore, the enthalpy of activation of viscous flow could be taken as a measure of the cooperation degree between the species taking part in the flow process. Really, in the liquid state the opportunity of the formation of many discontinuities is warrented by statistical fluctuations of local density. In the low temperature range, as well as for highly structured components, one may expect a considerable degree of order, so that transport phenomena take place cooperatively; as a consequence a great heat of activation associated to a relatively high value of flow entropy is observed. When the breaking in the ordered and polymerized fluid structure becomes very quick, by increasing the temperature or by adding a component that breaks a homopolymer hydrogen-bond network, the movement of the individual units becomes more disordered and the cooperation degree is reduced, facilitating the viscous flow via the activated state of molecular species. As a consequence, the overall molecular order in the system should be reduced, and positive ΔS^* values should be expected.

The evidences obtained in this work appear quite intriguing, because at higher temperatures as far as in the DMF rich region, the availability of randomly scattered monomers should be sufficient to provide the activated molecular species which then lead to comparatively increased order as a result of viscous flow, giving the more negative ΔS^* values of Table 11.

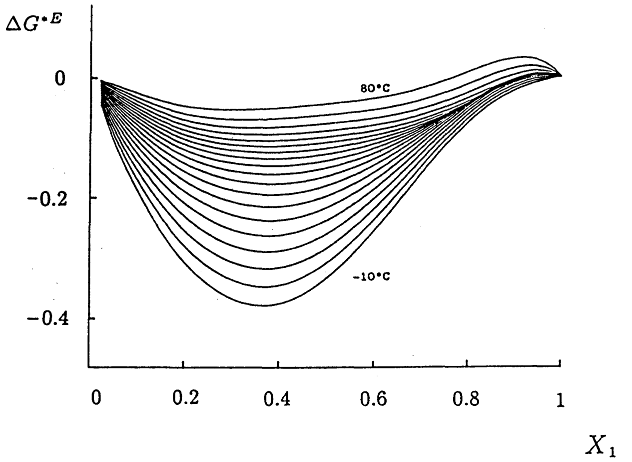

Fig. 5. Excess free energy of activation of viscous flow for the 1,2-ethanediol/*N,N*-dimethylformamide solvent system at different temperatures from −10 °C (bottom) to +80 °C (top).

The excess thermodynamic function ΔG^{*E} values are shown in Table 12 for each of the nine mixtures studied. These values were fitted at each temperature with a polynomial Eq. 9 in the proper form. Table 13 summarizes the a_k coefficients for ΔG^{*E} function and the relative standard deviations. Other authors pointed out that excess free energy of activation may be considered a reliable measure to detect the presence of interactions between unlike molecules.[18–20] Positive deviations of ΔG^{*E} can be seen in binary liquid systems where specific interactions between molecules take place, while negative ΔG^{*E} values indicate a characteristic behavior of mixtures in which dispersion forces are prevailing.

In this work quite negative ΔG^{*E} values were obtained at all the investigated temperatures and only in few cases positive ΔG^{*E} values appeared in the proximity of 1,2-ethanediol pure component. These results are reported in Fig. 5, where the curves show a minimum located at $X_1 \approx 0.35$ (1,2-ethanediol: DMF=1 : 2, stoichiometrical ratio) that is the deeper the lower is the temperature.

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References

1) G. C. Franchini, E. Ori, C. Preti, L. Tassi, and G. Tosi, *Can. J. Chem.*, **65**, 722 (1987).

2) G. C. Franchini, L. Tassi, and G. Tosi G, *J. Chem. Soc., Faraday Trans. 1*, **83**, 3129 (1987).

3) G. C. Franchini, C. Preti, L. Tassi, and G. Tosi, *Anal. Chem.*, **60**, 2358 (1988).

4) G. C. Franchini, A. Marchetti, C. Preti, L. Tassi, and G. Tosi, *J. Chem. Soc., Faraday Trans. 1*, **85**, 1697 (1989).

5) G. C. Franchini, A. Marchetti, C. Preti, L. Tassi, and G. Tosi, *Anal. Chem.*, **61**, 177 (1989).

6) G. C. Franchini, A. Marchetti, L. Tassi, and G. Tosi, *J. Chem. Soc., Faraday Trans. 1*, **84**, 4427 (1988).

7) R. C. Weast, "Handbook of Chemistry and Physics," 66th ed, The Chemical Rubber Co., Cleveland, OH (1985—1986).

8) G. C. Franchini, A. Marchetti, L. Tassi, and G. Tosi, *Anal. Chem.*, **62**, 1004 (1990).

9) G. Charlot and B. Trêmillon, "Les Reactions Chimiques dans les Solvants et les Sels Fondus," Gautiers-Villars, Paris (1963).

10) E. Walder, A Bauder, and Hs. H. Günthard, *Chem. Phys.*, **51**, 223 (1980).

11) J. A. Riddick and E. E. Toops, "Organic Solvents," Interscience Publishers, N. Y. (1955), Vol. VII.

12) "Time Series Processor-TSP-User's Guide," ed by B. H. Hall, TSP International, Stanford, CA (1987).

13) R. Reynaud, *Bull. Soc. Chim. Fr.*, **1971**, 4269.

14) O. W. Kooling, *Anal. Chem.*, **57**, 1721 (1985).

15) O. Redlich and A. T. Kister, *Ind. Eng. Chem.*, **40**, 341 (1948).

16) R. J. Fort and W. R. Moore, *Trans. Faraday Soc.*, **62**, 1112 (1966).

17) H. Eyring and M. S. John, "Significant Liquid Structure," John Wiley & Son, New York (1969).

18) T. M. Reed and T. E. Taylor, *J. Phys. Chem.*, **63**, 58 (1959).

19) R. Meyer, M. Meyer, J. Metzer, and A. Peneloux, *J. Chem. Phys.*, **62**, 405 (1971).

20) S. Oswal and M. U. Rathnam, *Can. J. Chem.*, **62**, 2851 (1984).