Bull. Chem. Soc. Jpn., **68**, 1867—1872(1995)

N,*N*-Dimethylformamide+2-Methoxyethanol Binary Mixtures. Viscosity and Activation Energy of Viscous Flow at Various Temperatures

Fulvio Corradini, GianCarlo Franchini, Andrea Marchetti, Mara Tagliazucchi, and Lorenzo Tassi*

Department of Chemistry, University of Modena, via G. Campi, 183, 41100 Modena, Italy

(Received November 28, 1994)

Dynamic viscosity (η) of binary solvent mixtures of *N*,*N*-dimethylformamide (DMF, component 1)+ 2-methoxyethanol (ME, component 2) has been investigated at 19 temperatures ranging from -10 to $+80$ °C. Some empirical equations have been applied in order to establish the best regression fitting procedures $\eta=\eta(T)$, $\eta=\eta(X_1)$ and $\eta=\eta(T,X_1)$. For this binary solvent system, the viscometric properties are continuous but not linear functions of the mixture composition. Therefore, experimental η values were used to calculate the excess viscosities (η^E) and excess Gibbs activation energies (ΔG^{*E}) of viscous flow. Both these quantities strongly deviate from ideality over the whole composition range of the investigated mixtures. Furthermore, deviations from the ideal behaviour could be very useful in order to evidentiate the formation of solvent–cosolvent complex species and to evaluate their stoichiometrical composition.

Transport properities of irregular liquid mixtures are always governed by intermolecular specific interactions as well as by structure factors (size and shape) of the constitutive molecules. These two aspects are strictly correlated, determining the thermodynamic and thermomechanic properties of mixed systems. Therefore, anomalies shown by the transport properties of liquid mixtures should be related with microheterogeneity of these systems. However, usually both energetic and structural effects cannot be treated separately because of their interconnections to provide macroscopic phenomenologies.

Although the transport properties of ideal binary liquids are nowadays adequately understood within the frame of a simple model, deviations from the ideality cannot be predicted on theoretical basis and they have to be empirically determined. The knowledge of such deviations may provide valuable information about the thermodynamic excess properties, when available.

Along these research lines and in connection with our previous works,[1,2] we report in this paper a detailed investigation on the dynamic viscosity (η) of *N*,*N*-dimethylformamide (DMF, component 1)+2-methoxyethanol (ME, component 2) solvent system, employing the two pure components and 9 binary mixtures of theirs covering the whole miscibility field expressed by the condition $0\leq X_1\leq 1$, and working at 19 temperatures in the range $-10\leq t/°\mathrm{C}\leq 80$, with thermal scanning of 5 °C. Because of the importance of the chosen two pure species for practical and theoretical purposes,[3,4] also their binary mixtures may be usefully employed for electroanalytical studies.[5]

Therefore, the investigation of their dynamic viscosity should help in order to gain deep knowledge about their micro- and macroscopic behavior.

Experimental

Materials. *N*,*N*-Dimethylformamide and 2-methoxyethanol (both containing<0.10 and 0.05% g of water, respectively, determined by Karl–Fischer titrations) were Carlo Erba (Milan) high-purity grade. Both the solvents were purified by passage through a neutral alumina column and stored over molecular sieves 3 Å for many days before use. The final purity was checked by gas chromatography (99.8% DMF, 99.7% ME), confirming the absence of other significant organic components.

Apparatus and Procedures. The solvent mixtures were prepared by weight through a Mettler PM 4800 Δ-range balance, operating in a dry nitrogen atmosphere in order to avoid contact with the atmospheric moisture, and then preserved over molecular sieves 3 Å. The probable error in each mole fraction (X_i) is estimated to be less than 1.5×10^{-4}.

The kinematic viscosity (ν) was measured by use of Ubbelhode-type micro viscosimeters, through a Schott–Geräte AVS 400 viscosity measuring system. The temperature control of the capillary was provided by a Lauda K2R thermostatic bath maintained to ±0.02 °C. The experiments were generally performed at least in five replicates for each composition and at each temperature, and the results were averaged. In all the determinations the kinetic energy correction has been taken into account according to Hagenbach[6] before evaluating the absolute viscosity (η/cP; 1 cp=1 mPa s).

The overall experimental standard deviation $\sigma(\nu)$ was apporoximately equal to 1.4×10^{-3}, while the estimated accuracy with 95 % confidence interval was $\pm3\times10^{-3}$ (statistics were taken at about the middle of the investigated range, for $\nu\simeq1$ cSt). Densites (ρ/g cm^{-3}) were taken from our previous paper.[7]

Results and Discussion

Table 1 summarizes some literature and present η values for pure DMF at various temperatures. Evidently, a poor agreement appears among them, being these values often scattered by several % or more. These discrepancies may be mainly ascribed to the different measurement techniques employed and to the different procedures of samples purification applied by the authors. A very sound analysis of these problems was made in the literature by Fogg et al.[8] Therefore, a careful assessment is recommended and required on these topics, and as many as possible η values from different sources are needed.

Table 1. Some Viscosity Reference Values (η/cP[a]) for DMF at Various Temperatures

t/°C	η/cP	Ref.
5	1.0673	20
	1.069	This work
20	0.9248	21
	0.8668	This work
25	0.7912	20
	0.802	22
	0.7987	23
	0.8135	This work
40	0.7143	21
	0.6829	This work
55	0.6644	23
	0.5840	This work

a) 1 cP=1 mPa s.

The results of our experimental measurements are given in Table 2, along with the binary composition expressed by DMF mole fraction (X_1). The letters A, B,···M which appear along the text refer to the eleven solvent mixtures used.

In order to obtain useful correlation functions between dynamic viscosity and binary mixture composition, the trend of η vs. ME mole fraction (X_2) has been depicted in Fig. 1 at all the experimental temperatures. As one can see, the relationships shown in Fig. 1 are not linear. Therefore, a logarithmic polynomial expansion with high power terms should be taken to represent each isothermal set of experimental points.

The dependence of dynamic viscosity on temperature and binary composition for these liquid mixtures has been investigated by applying a combined polynomial relation

$$\ln\eta(T,X_1)=\sum_{0}^{i}\sum_{0}^{j}c_{ij}T^{i}X_1^{j} \tag{1}$$

in order to quicken the interpolation procedures and to provide the η values as a function of the two independent variables T and X_1.

The empirical c_{ij} coefficients ($0\leq i,\ j\leq4$) of Eq. 1, evaluated by the TSP computer package,[9] are listed in Table 3 along with the overall standard error of deter-

Table 2. Experimental Values of Dynamic Viscosity (η/cP) for the *N*,*N*-Dimethylformamide (1)–2-Methoxyethanol (2) Solvent System at Various Temperatures

X_1=	1.0000	0.9021	0.8038	0.7053	0.6060	0.5063	0.4062	0.3053	0.2044	0.1025	0.0000
T/K	A	B	C	D	E	F	G	H	I	L	M
263.15	1.368	1.558	1.666	1.870	2.113	2.328	2.516	2.742	3.046	3.385	3.557
268.15	1.255	1.421	1.515	1.682	1.886	2.068	2.232	2.425	2.671	2.936	3.093
273.15	1.156	1.300	1.384	1.523	1.692	1.851	1.995	2.159	2.360	2.573	2.711
278.15	1.069	1.196	1.270	1.388	1.532	1.669	1.795	1.935	2.100	2.274	2.392
283.15	0.9927	1.105	1.171	1.271	1.393	1.513	1.624	1.742	1.879	2.023	2.125
288.15	0.9259	1.024	1.082	1.168	1.274	1.379	1.478	1.579	1.693	1.815	1.899
293.15	0.8668	0.9542	1.006	1.079	1.171	1.263	1.350	1.438	1.534	1.637	1.707
298.15	0.8135	0.8911	0.9374	1.001	1.080	1.162	1.239	1.314	1.397	1.485	1.542
303.15	0.7647	0.8341	0.8760	0.9329	1.003	1.074	1.141	1.206	1.277	1.352	1.399
308.15	0.7216	0.7835	0.8204	0.8713	0.9340	0.9961	1.055	1.111	1.173	1.237	1.275
313.15	0.6829	0.7379	0.7710	0.8161	0.8714	0.9281	0.9788	1.028	1.082	1.136	1.166
318.15	0.6458	0.6967	0.7265	0.7659	0.8152	0.8654	0.9109	0.9540	0.9994	1.047	1.071
323.15	0.6133	0.6593	0.6857	0.7207	0.7646	0.8094	0.8493	0.8879	0.9275	0.9671	0.9866
328.15	0.5840	0.6242	0.6485	0.6809	0.7202	0.7586	0.7936	0.8277	0.8637	0.8959	0.9124
333.15	0.5562	0.5943	0.6148	0.6441	0.6787	0.7114	0.7415	0.7721	0.8044	0.8300	0.8460
338.15	0.5319	0.5654	0.5841	0.6099	0.6411	0.6693	0.6953	0.7231	0.7503	0.7716	0.7871
343.15	0.5081	0.5382	0.5548	0.5790	0.6071	0.6311	0.6534	0.6789	0.7026	0.7195	0.7336
348.15	0.4844	0.5128	0.5297	0.5507	0.5755	0.5955	0.6146	0.6368	0.6576	0.6717	0.6851
353.15	0.4647	0.4910	0.5052	0.5250	0.5462	0.5615	0.5775	0.5970	0.6152	0.6271	0.6426

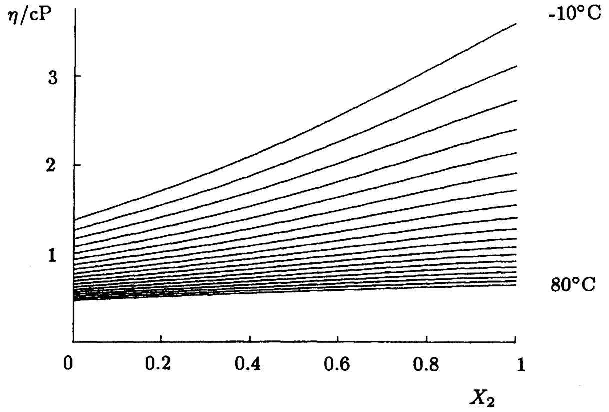

Fig. 1. Plots of η/cP against X_2 for the DMF (1)+ ME (2) solvent system from −10 (top) up to 80 °C (bottom).

Table 3. Coefficients c_{ij} and Standard Deviations $\sigma(\ln\eta)$ of Eq. 1 for the DMF (1)–ME (2) Solvent System

ij	Variable quantity	c_{ij}
00		60.334
01	X_1	−301.04
02	X_1^2	1260.4
03	X_1^3	−1859.4
04	X_1^4	863.86
10	T	−0.63341
11	TX_1	3.9869
12	TX_1^2	−16.791
13	TX_1^3	24.586
14	TX_1^4	−11.377
20	T^2	2.6244×10^{-3}
21	T^2X_1	-1.9893×10^{-2}
22	$T^2X_1^2$	8.3663×10^{-2}
23	$T^2X_1^3$	-1.2158×10^{-1}
24	$T^2X_1^4$	5.6020×10^{-2}
30	T^3	-5.0449×10^{-6}
31	T^3X_1	4.4187×10^{-5}
32	$T^3X_1^2$	-1.8490×10^{-4}
33	$T^3X_1^3$	2.6661×10^{-4}
34	$T^3X_1^4$	-1.2227×10^{-4}
40	T^4	3.7161×10^{-9}
41	T^4X_1	-3.6791×10^{-8}
42	$T^4X_1^2$	1.5292×10^{-7}
43	$T^4X_1^3$	-2.1873×10^{-7}
44	$T^4X_1^4$	9.9803×10^{-8}

$\sigma(\ln\eta)=6.9\times10^{-3}$.

mination $\sigma(\ln\eta)$. This three dimensional model Eq. 1 reproduces the experimental values with a good approximation, within an avarage uncertainty $\overline{\Delta\eta}$, evaluated as follows

$$\overline{\Delta\eta}=\frac{1}{N}\sum_{N}|\eta_{\mathrm{exptl}}-\eta_{\mathrm{calcd}}| \qquad (2)$$

equal to ±0.0067 cP over the 209 (N) experimental values of Table 2.

Excess Function. The experimental curves of Fig. 1 show the general patterns described for the viscometric properties of these mixtures of both polar components. Since departures from linearity are detected to some extent at all the investigated temperatures, algebraic or derivative expressions coming from the empirical η vs. X_2 plots are necessary in order to evaluate the shift from ideal behavior of the real system under study. A simple and more effective measure of nonlinearity in viscometric properties is the excess function (η^{E}) which has been defined as follows:

$$Y^{\mathrm{E}}=Y-(X_1Y_1+X_2Y_2), \qquad (3)$$

where Y is the experimental measured value for the mixtures, Y_1 and Y_2 are the viscosities for the two pure components with mole fractions X_1 and X_2 at each temperature. Clearly, η^{E} is zero for an ideal mixture (linear trend), being $(X_1\eta_1+X_2\eta_2)=\eta_{\mathrm{ideal}}$. The general trend of the obtained excess quantities vs. binary composition can be seen from Fig. 2. The curves of this figure have been represented in analytical form by an equation of the type:[10)]

$$Y^{\mathrm{E}}=X_1X_2\sum_{0}^{n}c_n(X_2-X_1)^n, \qquad (4)$$

where Y^{E} is the investigated quantity, and c_n (for n=5) are the adjustment parameters listed in Table I available as supplementary material and deposited as Document No. 68034 at the Office of the Editor of Bull. Chem. Soc. Jpn. The deviations from ideality for these polar cosolvents are positive and negative to some extent for each mixture, with the exception of the mixture L, where the shift is always positive at each temperature.

The curves of Fig. 2 show some peculiarities due to the presence of some pronounced minima and maxima in the investigated ranges. In particular, starting from the lowest temperature, it is possible to observe two clear minima centered on $X_2\simeq0.3$ (DMF : ME=2 : 1) and $X_2\simeq0.65$ (DMF : ME=1 : 2), going by a gentle sloping inflection at $X_2\simeq0.5$ (DMF : ME=1 : 1), and finally a weak maximum appears at $X_2\simeq0.9$ (DMF : ME=1 : 9).

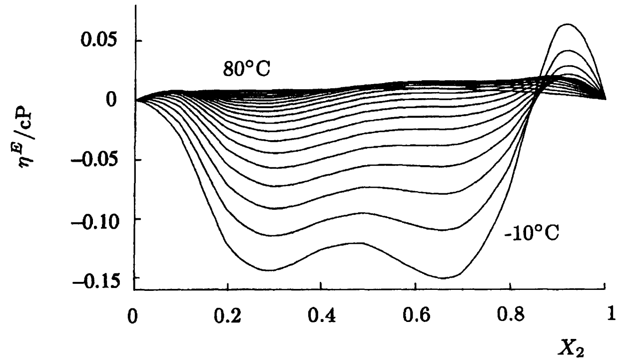

Fig. 2. Plots of η^{E}/cP vs. X_2 for the DMF (1)+ME (2) solvent system from −10 (bottom) up to 80 °C (top).

With the increasing of the temperature up to 40 °C *circa*, the curves tend to become more flattened and slightly oscillating around the zero value. It has been ascertained that deviations from ideality of mixed liquids are probably due to strong dipolar interactions and hydrogen bonds which occur between components.[11] These conjectures appear to be in good agreement with the evidence of this paper, and are strengthened by taking into account the molecular dynamic of the two pure species.

In literature it has been reported by NMR studies that the DMF molecule can exist in different mesomeric forms which can be represented by limiting structures as follows (Chart 1):[12] where the molecular skeleton tends to be planar in the form II with separated charges. The presence of a significant amount of double bond character in the C–N amide bond is stated by the temperature dependent coalescence observed for the chemical shift proton doublet of the $-N(CH_3)_2$ group, which requires about 92 kJ mol^{-1} at ordinary conditions for the activation free energy of reorientation around this bond. Obviously, both structures I and II are able to act as hydrogen bond acceptor via oxygen atom.

Molecular dynamic of ME also has been largely investigated in the literature by different spectroscopic techniques, such as IR and NMR.[4,13,14] In particular, it has been shown that this species can exist in different rotameric forms, and the two limiting structures (*anti* and *gauche*) may be represented as follows (Chart 2):

In the pure species, the *gauche* conformer seems to be more stable than the *anti* rotamer, being the thermodynamic constant $K=10.3$ at 20 °C.[14] In the high density–high entropy *gauche* rotamer, a relatively strong (ca. 7.5 kJ mol^{-1}) intramolecular hydrogen bond is present, this fact resembling the molecule as a pseudocyclic crown ether. This conformation, even if more polar than the low density–low entropy *anti* rotamer, reduces the possibility of interactions with neighboring like and/or unlike molecules, and this rotamer can behave only as an acceptor hydrogen bonding or can interact by weaker dipolar forces. On the other hand, the *anti* conformer may interact more strongly with neighboring units, because of its capability to behave either as a donor or an acceptor of hydrogen bonding.

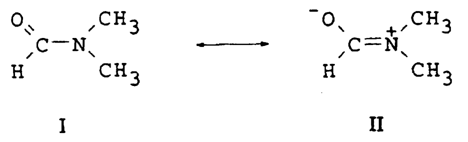

Chart 1.

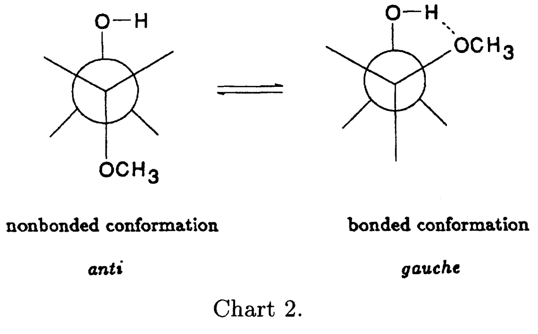

Chart 2.

Turning now to the DMF/ME mixtures and on the basis of the evidence of Fig. 2, it is possible to suppose the existence of different complex moieties, whose probable composition can be determined from the mole fractions at the singular points (minima and maxima) in the patterns of Fig. 2. The results obtained in the present work indicate the formation of some different adducts, namely 2DMF·ME, DMF·ME, and DMF·2ME, while in our opnion the maximum centred on $X_2 \simeq 0.9$ could be preferably attributed to interstitial solvation phenomena rather than to a complex species involving such an high number of molecules. Obviously, when $\eta^E > 0$ we are in presence of a structural promotion in the mixed solvents greater than in the pure species, while the contrary is true for $\eta^E < 0$. All these pictures may be conveniently resumed in terms of SLS theory,[15] where structure-maker and structure-breaker effects are related to different molecular geometries with different dipole moments as a result of different orientation of functional groups. Therefore, on the basis of the actual experimental evidence, we can suggest that the addition of DMF to ME certainly is responsible of hydrogen bonding network breaking, which exists in the pure specie ME and more likely, different molecular arrangements of components should be responsible of the appearance of different complex adducts with different stoichiometric composition and thermostabilities.

Thermodynamics of Viscous Flow. Viscosity data can be analyzed from the thermodynamic viewpoint, in order to obtain further information about these mixed solvents. A more suitable treatment of experimental η values was suggested in the literature by Eyring[16] who, starting from Andrade's approach to the viscosity theory, provided the following equation

$$\eta = \frac{hN_A}{V_m}\exp(\Delta G^*/RT), \tag{5}$$

where h is the Planck constant, N_A the Avogadro's number, R the universal gas constant, and T the absolute temperature. In Eq. 5, V_m represents the molar volume of the mixture, evaluated from the corresponding mixture density data (ρ)[7] by the relationship

$$V_m = \frac{X_1M_1 + X_2M_2}{\rho}. \tag{6}$$

It is interesting to note that in Eq. 5 also the preexponential factor is temperature dependent, while this fact is ignored in Andrade's theory.

Figure 3 represents the trend of $R\ln(\eta V_m/hN_A)$ vs. $1/T$ curves. These plots, even if only slightly, shift from linearity, suggesting that the viscous flow activation energy is not temperature independent. Now, introducing

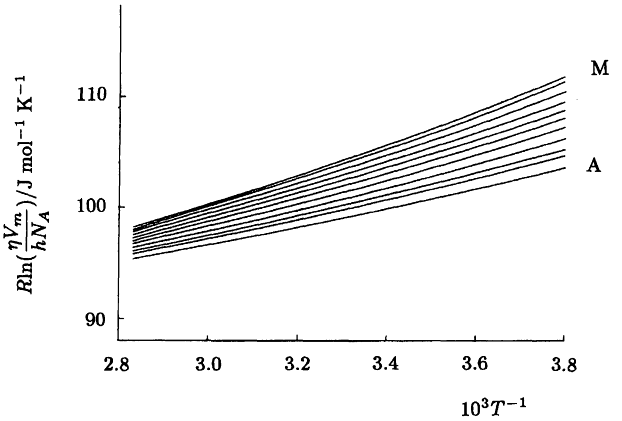

Fig. 3. Plots of $R\ln(\frac{\eta V_m}{hN_A})$ against $1/T$ for DMF (1)+ME (2) solvent system from mixture A (bottom) to M (top).

the standard thermodynamic relation into Eq. 5 it is possible to write

$$\eta = \frac{hN_A}{V_M}\exp\left(\frac{\Delta H^*}{RT} - \frac{\Delta S^*}{R}\right), \tag{7}$$

where ΔH^* and ΔS^* are enthalpy and entropy of activation of viscous flow respectively.

Therefore, these quantities may be evaluated from the tangent slope and the intercept at each investigated temperature, for ΔH^* and ΔS^* respectively.

A more effective and expeditious way to provide these thermodynamic quantities has been recently applied by us[2] in order to investigate viscometric properties of ethane-1,2-diol/water binary mixtures, and can be represented by a polynomial fitting procedure of the type:

$$R\ln\frac{\eta V_m}{hN_A} = d_0 + \frac{d_1}{T} + \frac{d_2}{T^2} + \frac{d_3}{T^3} = \sum_{i=0}^{3}\frac{d_i}{T^i} \tag{8}$$

where d_i are adjustment parameters and, after algebraic manipulation,

$$\Delta H^* = d_1 + \frac{2d_2}{T} + \frac{3d_3}{T^2}, \tag{9}$$

$$\Delta S^* = -d_0 + \frac{d_2}{T^2} + \frac{2d_3}{T^3}. \tag{10}$$

The results are given in Table II and III (deposited document) for ΔH^* and ΔS^* respectively.

ΔH^* is always positive, generally increasing with ME content in the mixtures and decreasing with temperature, taking values ranging from 7.4 (pure DMF at 80 °C) up to 16.0 (pure ME at −10 °C) kJ mol^{-1}. Furthermore, ΔS^* values are all negative, becoming more negative as the temperature increases [−74.3 (DMF at 80 °C)$\leq \Delta S^*$/J mol^{-1} K$^{-1} \leq -50.8$ (ME at −10 °C)]. These evidences suggest that the flow mechanism in DMF/ME binary solvent system should be mainly provided by a transversal motion of cooperative intermolecular adducts when crossing an energy barrier due to a velocity gradient, with no significant contribution of both component monomers through an activated state of the monomeric molecular species.[16] This idea appears corroborated by the very negative ΔS^* values, which confirm that the viscous flow is an ordered and cooperatively activated process.

A more informative quantity related to these measurements is represented by the excess free energy of viscous flow (ΔG^{*E}) evaluated by Eq. 3 in the proper form. These values are represented in a graphical form in Fig. 4. The curves of this figure have been obtained by fitting the ΔG^{*E} quantities through Eq. 4 by setting n=3. The corresponding c_n coefficients at each temperature are listed in Table IV (deposited document) along with a standard error of determination $\sigma(\Delta G^{*E})$. As one can note, ΔG^{*E} is always positive at all the experimental conditions.

In the literature it has been pointed out that the excess free energy of viscous flow in liquid mixtures is a property very sensible to the presence of specific interactions between components and, therefore, to the formation of stable solvent–cosolvent complexes.[17—19] In particular, positive deviations should be detected in binary mixtures where strong specific interactions between unlike molecules, such as hydrogen bonding, take place. In the present case, these specific interactions should be prevailing over all other interactions of any kind, classfiable as dispersion forces which generally are responsible of negative deviations in the ΔG^{*E} property. Bearing in mind the former remarks about the molecular dynamic of pure species, in order to achieve this situation a condition should be required: the ME molecules involved in complex moieties should be present as *anti* rotamers.

The trend of the curves of Fig. 4 shows a maximum centered on $X_2 \simeq 0.65$ at each temperature, indicating that the DMF·2ME solvent–cosolvent adduct probably is the most stable complex moiety formed in these binary mixtures.

The authors gratefully thank Professor Carlo Preti for helpful suggestions and support in the preparation

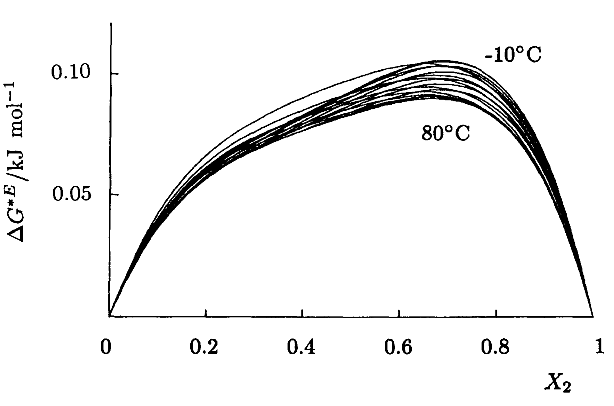

Fig. 4. Plots of the excess free energy of activation of viscous flow (ΔG^{*E}/kJ mol^{-1}) against X_2 for the DMF (1)+ME (2) solvent system at various temperatures from −10 to +80 °C.

of this work. The Ministero dell' Università e della Ricerca Scientifica e Tecnologica (M.U.R.S.T.) of Italy is acknowledged for financial support.

References

1) F. Corradini, L. Marcheselli, L. Tassi, and G. Tosi, *Bull. Chem. Soc. Jpn.*, **66**, 1886 (1993).

2) F. Corradini, A. Marchetti, M. Tagliazucchi, L. Tassi, and G. Tosi, *Aust. J. Chem.*, **48**, 103 (1995).

3) S. J. Bass, W. I. Nathan, R. M. Meighan, and R. H. Cole, *J. Phys. Chem.*, **68**, 509 (1964).

4) L. P. Kuhn and A. R. Wires, *J. Am. Chem. Soc.*, **86**, 2161 (1964).

5) A. Marchetti, C. Preti, M. Tagliazucchi, L. Tassi, and G. Tosi, *Can. J. Chem.*, **69**, 509 (1991).

6) "AVS 400-Viscosity Measuring System-Instruction Manual," Schott-Gerate, Hofheim a. Ts., Germany (1986).

7) L. Marcheselli, A. Marchetti, M. Tagliazucchi, L. Tassi, and G. Tosi, *J. Chem. Soc., Faraday Trans.*, **88**, 3159 (1992).

8) E. T. Fogg, A. N. Hixons, and A. R. Thompson, *Anal. Chem.*, **27**, 1609 (1955).

9) "TSP-Times Series Processor-User's Guide," ed by B. H. Hall, TSP International, Stanford, CA, 94305, July 1987.

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

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

12) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

13) V. Viti and P. Zampetti, *Chem. Phys.*, **2**, 233 (1973).

14) P. Buckley and M. Brochu, *Can. J. Chem.*, **50**, 1149 (1972).

15) H. Eyring and M. S. John, in "Significant Liquid Structures," Wiley, New York (1969).

16) H. Eyring, *J. Chem. Phys.*, **4** 283 (1936).

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

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

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

20) S. Taniewska-Osinska, A. Piekarska, and A. Kacperska, *J. Solution Chem.*, **12**, 717 (1983).

21) C. Della Volpe, G. Guarino, R. Sartorio, and V. Vitagliano, *J. Chem. Eng. Data*, **31**, 37 (1986).

22) J. A. Riddick and W. B. Bunger, in "Organic Solvents," 3rd ed, "Techniques in Chemistry," Wiley, New York (1970), Vol. II.

23) S. S. Joshi, T. M. Aminabhavi, R. H. Balundgi, and S. S. Shukla, *J. Chem. Eng. Data*, **35**, 185 (1990).