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The Eyring Significant Structure Theory Applied to Methanol-Tetrahydrofuran Mixtures

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The dielectric constant of MeOH, T.H.F. and their mixtures have been measured at low temperature. The experimental data are explained by the Eyring significant structure theory. It is shown that the G structure parameter of the solid-like phase is not independent of temperature. For methanol, the behaviour suggests that monomers dominate at the critical point, dimers in the 290 K temperature range and polymers near the melting point. The Eyring model, applied to the dielectric constant calculations of the mixtures, is very satisfactory in the case of the MeOH-T.H.F. solutions.

INTRODUCTION

X-Ray investigations show that a liquid, despite instantaneous and incessant structure changes, has a considerable short-range order.

Such a fact indicates that it is not unreasonable to describe a fluid as a lattice in which the sites are occupied by molecules or by holes of molecular size. Such holes are assumed to confer gas-like properties on a neighbouring molecule which jumps into them. In the more successful hole theory, namely the significant structure theory proposed by Eyring and coworkers,^{1–3} a random distribution of holes and molecules is assumed. Hence, the liquid at a given temperature T , is described as a mixture where the fraction $(V - V_s)/V$ of molecules possesses gas-like degrees of freedom and the remaining fraction V_s/V possesses the solid-like degrees of freedom. V is the molar volume of the liquid at the temperature T and V_s the molar volume

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of the solid at the melting point. According to this theory, M. E. Hobbs, M. S. Jhon and H. Eyring² have proposed a model for the dielectric constant of a H-bonded liquid in which the dielectric constant is related to its refractive index, its molar volume and its dipole moment. In the Eyring relation, a G -term appears, due to correlations between the solid-like dipoles. This structure parameter G corrects the value of the resultant dipole moment of the molecules taken in the gaseous state. In the case of alcohols, G is found to be greater than unity; such a value is interpreted as indicating a slight degree of polymerisation. For a polar non H-bonded liquid, this term generally is lower than unity. The theory is also developed for the calculation of the dielectric constant of two polar solvent mixtures. The model is very satisfactory in the case of water-alcohol mixtures,³ but not in the case of mixtures giving an intermolecular complex^{5,6} for the theory assumes a random distribution of the component molecules.

In previous work,⁴ we have specially studied the transport properties of the lithium perchlorate in methanol-tetrahydrofuran (MeOH-T. H. F.) mixtures. We report here the variations of the dielectric constant of these solvents versus the temperature. We have used the Eyring significant structure model¹⁻³ to interpret our results. Methanol (MeOH) a polar H-bonded solvent and tetrahydrofuran (T. H. F.), a polar non H-bonded solvent, compose a quasi-ideal mixture (in spite of their great difference of chemical nature) and the Eyring model is remarkably verified. We show, besides, that the G term is not absolutely independent of temperature, as was supposed up to now.

EXPERIMENTAL SECTION

Methanol is purified in a closed system in a flask containing magnesium turnings and iodine, then distilled and used immediately. Very pure tetrahydrofuran stabilized to avoid peroxide formation is used, from freshly opened bottles, without further purification (Art. 8107 and 8105 E. Merck-Darmstadt-Germany). The water contents determined by coulometric titration is less than 0.03% for MeOH and less than 0.01% for T. H. F.

The refractive indexes of the liquids are measured at 293 K and 283 K with an Abbe refractometer ($\lambda = 5890 \text{ \AA}$). The low-temperature indexes have been calculated, assuming the validity of the Lorenz-Lorentz formula.

The permittivity cell constant is $12.30 \pm 0.02 \text{ pF}$ (independent of temperature). The dielectric constants are measured at low-frequency (1592 Hz), with a Wayne-Kerr bridge B 642.

At low temperature, all the experiments are made in a dry box. The temperature of the sample is measured in the cell with a calibrated Pt resistance probe ($\pm 0.1 \text{ C}$).

The molar volumes are calculated from density and thermal expansion coefficient data. These measurements are made between 195 K and 293 K with a capillary pycnometer. The molar volumes of the solid phase are obtained by extrapolation to the melting point of the liquid phase results, assuming a percentage expansion on melting of 10%.^{2,3,9}

RESULTS AND DISCUSSION

A Pure solvents

The dielectric constant of a polar liquid A , ϵ_A , is related to the molar volume V_A and the refractive index n_A by^{2,3}:

$$\epsilon_A = \frac{n_A^2}{2} + \frac{n_A^4}{2\epsilon_A} + \frac{6\pi N}{V_A} \left(\frac{V_{SA}}{V_A} \cdot \frac{\mu_A^2 G_A}{kT} + \frac{V_A - V_{SA}}{V_A} \frac{\mu_A^2}{3kT} \right) \times \left(\frac{n_A^2 + 2}{3} \right)^2 \quad (1)$$

V_{SA} is the molar volume in the solid phase, μ_A , the dipole moment in the gaseous state, G_A , the structure term and N , k , T have their usual meanings. First, we give in Table I, the main typical physical properties for both solvents. The dipole moments, the shear viscosities at 293 K, the thermal expansion coefficients are very similar; the boiling points are the same; the difference between the melting points is only 9 K; the molar volume of

TABLE I
Some characteristic properties of methanol (MeOH) and tetrahydrofuran (T.H.F.)

	MeOH	T.H.F.
Viscosity at 293 K (Pa. s)	0.6×10^{-3a}	0.5×10^{-3a}
Dipole moment (Debye)	1.69 ^b	1.76 ^c
Thermal expansion (K ⁻¹)	1.18×10^{-3}	1.19×10^{-3}
Boiling point (K)	338	338
Melting point (K)	175 ^d	166 ^d
Molar volume (cm ³)		
V_m liquid at 293 K	40.485	81.09
Molar volume (cm ³)		
V_s solid at the melting point	31.363 ^e	61.951 ^e

^a From Ref. 4.

^b From Ref. 10, p. 15.

^c From Ref. 8.

^d By D.T.A. measurements.

^e Extrapolation of molar volume of the liquid to the melting point and assuming a volume contraction of 10% (Ref. 9).

T. H. F. is exactly twice that of MeOH. The higher viscosity of MeOH may be attributed to H-bonds.¹⁰ For that reason, also, the dielectric constants are very different.

The polarizability α has been deduced from the refractive index data. We find, for MeOH, $\alpha = 3.26 \times 10^{-24} \text{ cm}^3$ ($\lambda = 5890 \text{ \AA}$) and $dn/dT \simeq -4.16 \times 10^{-4}$. These values are in good agreement with that given by D. Beysens:⁷ $\alpha = 3.23 \times 10^{-24} \text{ cm}^3$ and $-dn/dT = -3.94 \times 10^{-4}$ for $\lambda = 6328 \text{ \AA}$. For T. H. F. we obtain $\alpha = 7.91 \times 10^{-24} \text{ cm}^3$ and $dn/dT = 5.2 \times 10^{-4}$.

The dielectric constants, ϵ , of both solvents have been measured between 293 K and 243 K; some experimental points have been measured at lower temperatures up to the melting point for MeOH. Our ϵ values for that solvent, are intermediate between those given by D. J. Denney,¹² D. N. Davidson¹³ and G. J. Janz,¹⁴ B. P. Jordan.¹⁷ In the case of pure T. H. F., our ϵ values are a little lower than that found by D. J. Metz.¹⁵ In order to calculate the G term, we have assumed the validity of the Eyring relation, for each temperature. The results are reported in Table II. The G parameter is not absolutely constant. For MeOH, it seems to go through a maximum ($G \simeq 1.25$ for $T \simeq 290 \text{ K}$) and then to decrease with temperature up to the melting point ($G \simeq 1.15$). For T. H. F., the G term decreases slightly from $G = 0.365$ at 338 K (boiling point) to $G \simeq 0.275$ at 166 K (melting point), figure 1.

In order to examine the behaviour of the G parameter versus the temperature, we have evaluated its value at high temperature from the M. S. Jhon⁹ and W. Dannhauser¹¹ data; these authors have measured the dielectric constant of liquid methanol up to its critical point ($T_c = 513 \text{ K}$). However, for this calculation, we have taken our values of molar volume and refraction

TABLE II
Variations of the G term for MeOH and T.H.F. at low temperature

T	MeOH				T.H.F.			
	$\epsilon_{\text{obs.}}$	n_M	$V_M \text{ cm}^3 \text{ M}^{-1}$	G	$\epsilon_{\text{obs.}}$	n_M	$V_M \text{ cm}^3 \text{ M}^{-1}$	G
293	33	1.3282	40.485	1.232	7.54	1.407	81.09	0.3467
283	35.40	1.3325	40.007	1.247	7.68	1.4115	80.125	0.3323
273	37.56	1.3369	39.529	1.2445	8.00	1.4150	79.160	0.3297
263	39.98	1.3415	39.052	1.2439	8.39	1.4231	78.195	0.3265
253	42.42	1.3461	38.574	1.2365	8.78	1.4311	77.23	0.3218
243	44.79	1.3509	38.096	1.2199	9.20	1.4374	76.265	0.3182
223	51.30	1.3610	37.140	1.2135	10.0	1.4505	74.335	0.3043
203	59.0	1.3716	36.185	1.1997				
183	67.4	1.3830	35.230	1.1627				
177	70.6	1.3865	34.943	1.1565				

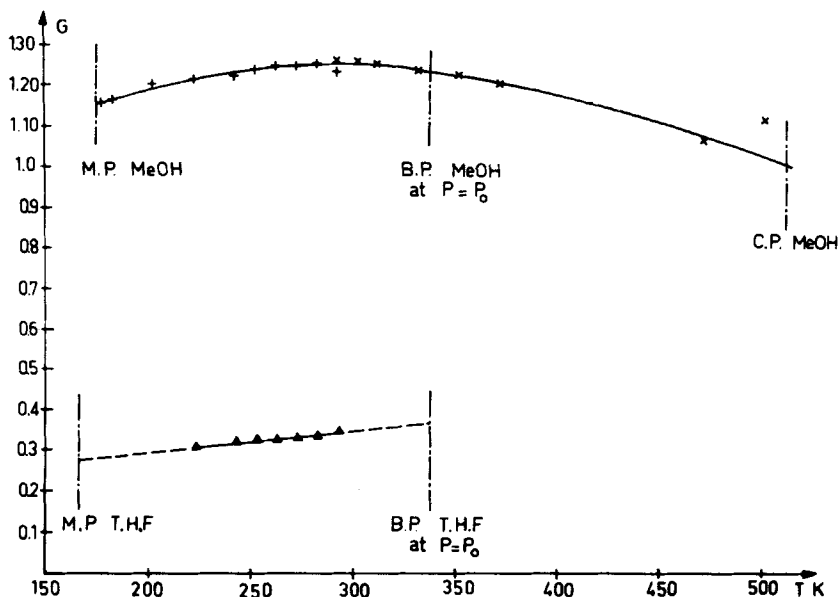


FIGURE 1 Variations as a temperature function of the G parameter for MeOH and T.H.F. +, ▲ our results; × from Ref. 9 and 11.

($V_{SA} = 31.363 \text{ cm}^3$ and $R. M. = 8.218$) (Table III). The G parameter drops gradually when the temperature increases and reaches a value nearly equal to unity at the critical point. In order to interpret these results, we may use the following model: at the critical temperature, the dipole moment of the molecules in the solid-like degree of freedom is the same as that measured in the gas-like state, then methanol should be principally in the monomer form; on decreasing the temperature, some dimers should appear, with a dipole moment higher than that of the monomer (see below paragraph B and Figure 3) and the G term becomes more important. At lower temperature, these dimers tend to networks of polymers; a more ordered structure takes place and then the G factor decreases. Indeed, the average component of the dipole moment, $\mu \cos \theta$, in the direction of maximum polarization domains tends to μ , because $\cos \theta$ approaches unity for perfect tetrahedral bonding.³ With this model, a maximum of dimers should be formed in the liquid phase near 250–300 K.

Other authors^{18–20} have suggested a two state theory to account the variation of excess ultrasonic absorption with temperature and pressure in water and primary alcohols. The two structures assumed are (1) molecules bonded in chains, (2) molecules arranged in pairs with antiparallel dipole

TABLE III

Variations of the G term for MeOH at high temperature

T	$\epsilon^a_{\text{obs.}}$	V_M^b $\text{cm}^3 \text{M}^{-1}$	n^c	G^d
298	32.70	40.480	1.3281	1.260
303	31.80	40.946	1.3241	1.258
313	29.96	41.395	1.3203	1.250
333	26.53	42.409	1.3119	1.236
353	23.46	43.560	1.3029	1.219
373	20.66	44.874	1.2933	1.200
473	9.35	57.940	1.2230	1.063
503	6.32	72.653	1.1758	1.110

^a From Ref. 9.^b From Ref. 9 and Ref. 16.^c Calculated assuming the validity of the Lorenz-Lorentz theorem.^d Calculated with $V_S = 31.363 \text{ cm}^3$.

moments. But these authors do not agree about the variations versus temperature of the mole fraction X_2 of pairs. S. Kor and coworkers¹⁹ give X_2 increasing when the temperature decreases from 323 K to 273 K and K. H. Swamy²⁰ gives X_2 decreasing in the same conditions. Our interpretation of our experimental data is in better agreement with the Kor results: the number of dimers should be maximum near 290 K.

B Solvent mixtures

The thermal expansion coefficients measured between 195 K and 293 K are all the same for the MeOH-T.H.F. mixtures: $\alpha = 1.18 \times 10^{-3} \text{ K}^{-1}$. The molar volumes of the solutions are related by $V_M = X_A V_A + X_B V_B$ ($A = \text{MeOH}$; $B = \text{T.H.F.}$). The excess of volume between the calculated and experimental data is very small; it is maximum for $X_B = 0.33$ ($\Delta V \leq 0.2 \text{ cm}^3 \cdot \text{M}^{-1}$ and $\Delta V/V \leq 3.6 \times 10^{-3}$ at 293 K, see Figure 2).

Similarly, the molar refractions of the M -mixtures are given by: $(R. M)_M = X_A (R. M)_A + X_B (R. M)_B$ (Table IV). In both expressions, X_A and X_B are the mole fractions of MeOH and T. H. F. respectively.

Thus, we may consider the MeOH-T.H.F. mixtures as being "quasi-ideal" solutions: no intermolecular complex is formed and there is a random mixing. In such a case, the Jhon and coworkers theory³ leads to the following relation between the dielectric constant of the mixture ϵ_M , its refractive index n_M and its molar volume V_M :

$$\begin{aligned} \epsilon_M = & \frac{n_M^2}{2} + \frac{n_M^4}{2\epsilon_M} + \frac{6\pi N}{V_M} \left(\frac{n_M^2 + 2}{3} \right)^2 \times \left\{ \left(\frac{X_A V_{SA} + X_B V_{SB}}{V_M} \right) \left(\frac{X_A^2 \mu_A^2 G_A}{kT} \right. \right. \\ & + \frac{X_B^2 \mu_B^2 G_B}{kT} + \frac{2X_A X_B \sqrt{G_A \cdot G_B} \mu_A \cdot \mu_B}{kT} \left. \left. + \frac{V_M - X_A V_A - X_B V_B}{V_M} \right. \right. \\ & \left. \left. \times \left(\frac{X_A \mu_A^2}{3kT} + \frac{X_B \mu_B^2}{3kT} \right) \right\} \end{aligned} \quad (2)$$

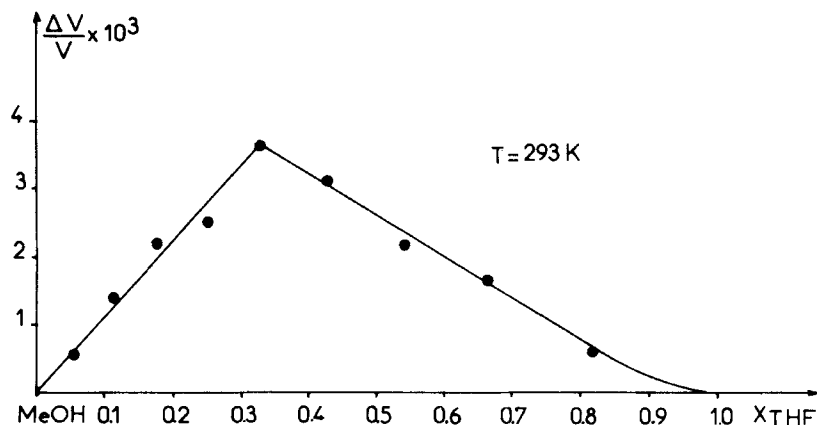


FIGURE 2 Relative differences between the calculated and measured molar volumes of the MeOH-T.H.F. system, at 293 K

TABLE IV
Molar refraction for the MeOH-T.H.F. mixtures measured at 293 K and 283 K

$X_{T.H.F.}$	R.M. ^a	R.M.	R.M.
	293 K	283 K	mean value
0	8.218	8.218	8.218
0.0525	8.849	8.827	8.840
0.11	9.514	9.490	9.502
0.176	10.300	10.251	10.275
0.250	11.150	11.130	11.136
0.333	12.073	12.059	12.068
0.428	13.243	13.236	13.239
0.538	14.547	14.507	14.527
0.666	16.050	16.003	16.026
0.818	17.844	17.784	17.814
0.86		18.198	
0.905		18.741	
1	19.96	20.035	19.998

^a R.M. = $(n^2 - 1)V/(n^2 + 2)$ with n = refractive index and V = molar volume.

TABLE Va
The observed and calculated dielectric constants of the MeOH-T.H.F. mixtures at various temperatures

$\chi_{T,H.F.}$	293 K				283 K				273 K			
	V_M	n_M	ϵ_M obs.	ϵ_M calc.	V_M	n_M	ϵ_M obs.	ϵ_M calc.	V_M	n_M	ϵ_M obs.	ϵ_M calc.
	0.0525	42.59	1.3367	30.78	30.49	42.09	1.3407	33.11	32.63	41.59	1.3452	34.61
0.110	44.89	1.3437	28.44	27.92	44.36	1.3482	29.95	29.83	43.84	1.3528	31.57	31.61
0.176	47.53	1.3518	24.80	25.28	46.97	1.3564	26.59	26.95	46.41	1.3613	28.43	28.56
0.250	50.51	1.3600	22.67	22.64	49.92	1.3640	24.06	24.04	49.32	1.3693	25.69	25.47
0.333	53.67	1.3676	20.29	20.12	53.04	1.3720	21.61	21.30	52.40	1.3775	22.83	22.55
0.428	57.68	1.3762	17.40	17.44	57.00	1.3810	18.11	18.39	56.32	1.3863	19.33	19.43
0.538	62.21	1.3841	14.88	14.84	61.480	1.3880	15.50	15.54	60.74	1.3939	16.31	16.40
0.666	67.42	1.3919	12.44	12.34	66.630	1.3958	13.30	12.83	65.83	1.4019	13.78	13.51
0.818	73.65	1.3997	9.77	9.94	72.79	1.4035	10.39	10.24	71.92	1.4098	10.92	10.75
0.86					74.25	1.4050	9.55	9.65	73.39	1.4104	10.11	10.10
0.905					76.05	1.4075	8.81	9.04	75.15	1.4130	9.26	9.46

TABLE Vb
The observed and calculated dielectric constants of the MeOH-T.H.F. mixtures at various temperatures

$\chi_{T.H.F.}$	263 K						243 K					
	V_M	n_M	ϵ_M obs.	ϵ_M calc.	V_M	n_M	ϵ_M obs.	ϵ_M calc.	V_M	n_M	ϵ_M obs.	ϵ_M calc.
	0.0525	41.08	1.3500	36.60	36.83	40.58	1.3548	38.82	39.06	40.08	1.3597	41.61
0.110	43.32	1.3575	33.59	33.59	42.77	1.3626	35.43	35.66	42.24	1.3677	37.73	37.65
0.176	45.85	1.3661	30.50	30.35	45.28	1.3713	32.15	32.17	44.73	1.3764	36.93	33.94
0.250	48.72	1.3744	27.60	27.05	48.13	1.3795	29.20	28.63	47.53	1.3848	31.28	30.22
0.333	51.77	1.3827	24.26	23.92	51.14	1.3880	25.86	25.29	50.50	1.3936	26.63	26.69
0.428	55.64	1.3916	20.64	20.58	54.96	1.3971	22.02	21.74	54.28	1.4027	23.25	22.92
0.538	60.00	1.3994	17.13	17.34	59.27	1.4050	18.35	18.28	58.54	1.4107	19.41	19.26
0.666	65.03	1.4075	14.5	14.25	64.24	1.4132	14.92	14.98	63.44	1.4191	15.66	15.76
0.818	71.05	1.4155	11.46	11.28	70.18	1.4214	11.99	11.82	69.31	1.4275	12.60	12.41
0.86	72.50	1.4161	10.58	10.59	71.62	1.4219	11.12	11.08	70.75	1.4278	11.71	11.62
0.905	74.26	1.4187	9.72	9.90	73.36	1.4245	10.26	10.35	72.46	1.4306	10.76	10.85

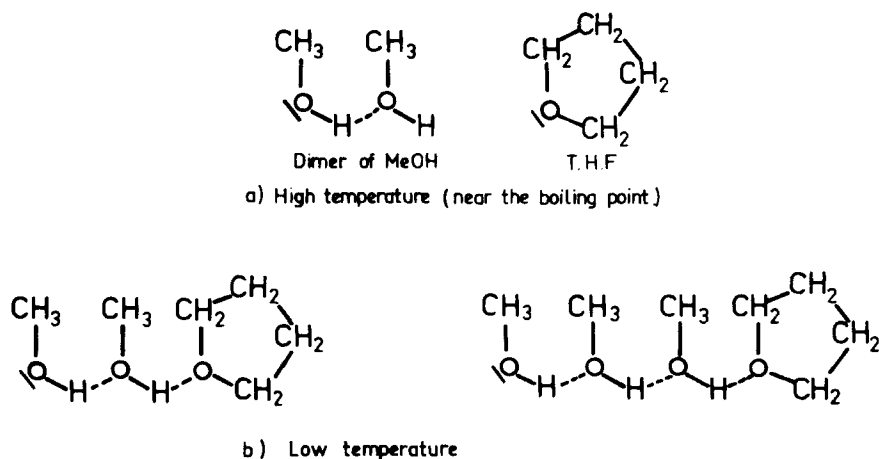


FIGURE 3 Schematic diagram for the dimer (MeOH)-T.H.F. association vs. temperature (note that the molecule of T.H.F. is not a plane).

Hence, from the knowledge of the parameters X , V_S , G , μ , for each solvent and of the n_M and V_M values for the mixture M , the ϵ_M may be deduced. The observed and calculated dielectric constants are presented in Table V, for the temperature range 293 K–243 K. Theory and experiment are in excellent agreement. Such an agreement may be explained, assuming that the MeOH-molecules essentially form dimers in that temperature range. Now, we have seen that a MeOH dimer volume is nearly equal to T.H.F. molar volume. Moreover, such a linear dimer (Figure 3) shows, like T.H.F., an oxygen with a “lone pair” of electrons. This fact allows a H-bonding between another MeOH molecules.

In the MeOH-T.H.F. mixtures, the similarity of electronic structures and steric hindrance of MeOH dimers and T.H.F. molecules must lead to equivalent dimer-dimer, dimer-T.H.F. or T.H.F.-T.H.F. interactions in the ~ 250 – 300 K temperature range. This hypothesis is supported by the very small difference of the shear viscosities shown by these solvents at 293 K and their identical boiling points (Table I). The large increase of viscosity observed at low temperature in the MeOH rich range is probably due to chains or ordering of dimers (Figure 4).

CONCLUSION

Assuming the validity of the Eyring relation for the dielectric constant calculation in the case of polar liquids, we have shown that the structure

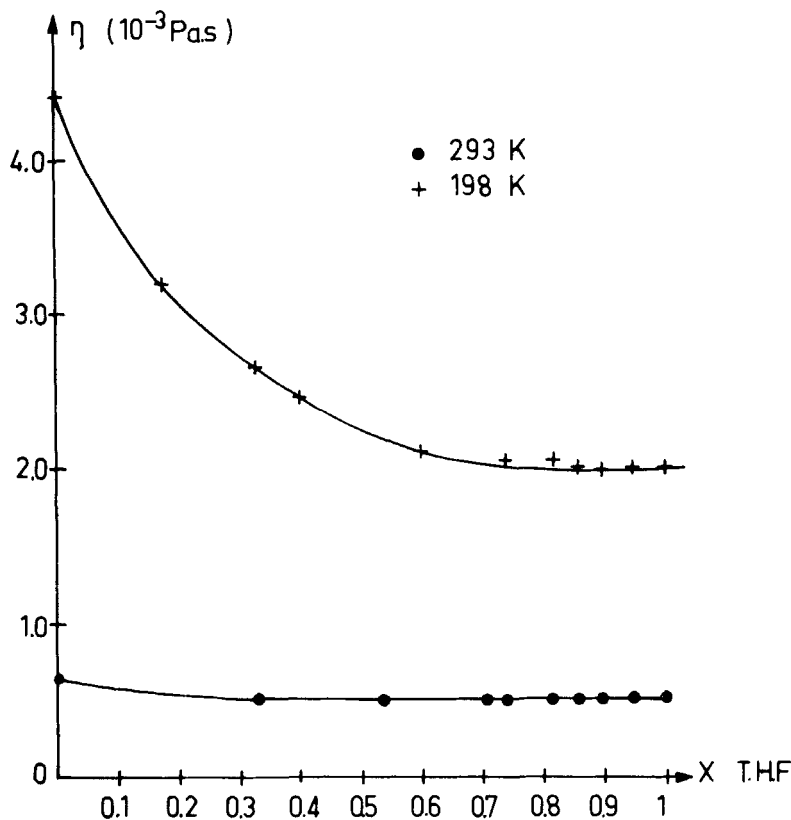


FIGURE 4 Viscosity of the MeOH-T.H.F. mixtures at 293 K and 198 K (from Ref. 4).

parameter G is not absolutely independent of temperature. For MeOH, this term goes through a maximum when the temperature decreases; this behaviour is interpreted as due to the formation of dimers and then of chains. Moreover, the significant structure theory leads to a good explanation of the dielectric constant behaviour found for the MeOH-T. H. F. mixtures.

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