CHAPTER - V

Excess properties of the binary liquid systems 1,2-dimethoxyethane + water and tetrahydrofuran + water at different temperatures

Excess molar volumes (V^E), excess viscosities (η^E) and excess molar free energies of activation of flow (G^{*E}) have been reported for 1,2-dimethoxyethane + water and tetrahydrofuran + water mixtures at 25, 35 and 45°C. The deviations from ideality of thermodynamic and transport functions are explained on the basis of molecular interactions between the components of the mixtures.

During the past decade, significant advances have taken place in the commercial development of batteries using non aqueous electrolyte solutions[1]. Such remarkable progress could not have been achieved without fundamental understanding of the thermodynamic and electrochemical behaviour of the active components in a battery. Since organic mixed solvents offer a wide range of variations in electrolytic properties, their use in the development of high energy-density batteries is relevant and attractive.

Here we report some of the excess properties of 1,2-dimethoxyethane (DME) + water and tetrahydrofuran (THF) + water mixtures at several temperatures. Although both DME and THF have been reported to give good cell performance[2,3], it appears that their binary mixtures with water have not been studied. We thus carried out measurements on the viscosities and densities over the entire mole fraction range of these systems at 25, 35 and 45°C. From the experimental results, the relevant excess functions have been evaluated since their study may lead to conclusions concerning the deviation of the systems from an ideal mixture behavior.

Experimental

The purification of 1,2-dimethoxyethane (Fluka, purum) has been described earlier [4] . The solvent was shaken well with $FeSO_4$ (A.R., BDH) for 1-2 hours, decanted and distilled. The distillate was refluxed for 12 hours and distilled over metallic sodium (b.p. = 83.5°C, density = 0.8626 gm/c.c., viscosity = 0.0042P)

Tetrahydrofuran (Merck, India) was kept several days over KOH, refluxed for 24 hours and distilled over $LiAlH_4$. The boiling point (66°C), density (0.8807 gcm^{-3}) and viscosity (= 0.0046 P) compared well with the literature values [5] . All solutions were prepared by weight with deionized distilled water.

The densities were measured with an Ostwald-Sprengal type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 25, 35 and 45°C with doubly distilled water. The temperature control had an accuracy of ± 0.01°C; the reproductibility of density measurement was ± 3×10^{-5} gcm^{-3} .

The kinematic viscosities were measured by means of a suspended Ubbelohde-type viscometer with a flow time of water of about 539 s at 25°C. Temperature control during viscosity measurements was ± 0.01°C. The precision of the viscosity measurements was ± 0.05%. The kinematic viscosities were converted into the absolute viscosities were converted into the absolute viscosities by multiplying the former with density.

Results and treatment of results

The experimental results of densities and viscosities at various mole fractions of organic solvents and the three different temperatures are reported in table 1.

The excess functions have been calculated by the following equations :

$$V^E = V - (V_1 X_1 + V_2 X_2) \qquad (1)$$

$$\eta^E = \eta - (\eta_1 X_1 + \eta_2 X_2) \qquad (2)$$

$$G^{*E} = RT\left[\ln \eta V - (X_1 \ln \eta_1 V_1 + X_2 \ln \eta_2 V_2)\right] \qquad (3)$$

where X_1 and X_2 are the mole fractions of DME (or THF) and water respectively ; V, V_1 and V_2 are the molar volumes and η η_1 and η_2 are the measured co-efficients of viscosity of the mixture, DME (or THF) and water respectively. The molar volume

V is defined by

$$V = (M_1 X_1 + M_2 X_2)/\rho \qquad (4)$$

where M_1 and M_2 are the molecular weights of pure substances and ρ is the density of the mixture.

The excess functions at 25, 35 and 45°C are presented in table 2.

Graphical representations of V^E and η^E as a function of X_1 are given in fugures 1-4. The excess funtions Y^E were fitted to the Redlich-Kister [6] equation :

$$Y^E = x_1(1-x_1) \sum_{J=0}^{n} A_J (1-2x_1)^J \qquad (5)$$

where ^{E}is V^E / (cm³ mol^{-1}) or η^E/cp or G^{*E} / (J mol^{-1}) and A_0, A_1, A_2, ...etc. are adjustable parameters. These parameters were evaluated by fitting $Y^E / x_1 (1-x_1)$ to equation 5 by the method of least-squares. The values of these parameters along with the standard deviation $\sigma (Y^E)$ of Y^E as defined by

$$\sigma(Y^E) = \left[\sum (Y^E_{obs} - Y^E_{cal}) / (N-M) \right]^{0.5} \qquad (6)$$

are recorded in table 3. In equation 6, N is the number of parameters.

Discussion

It is well-known [7] that the sign and magnitude of V^E give a good estimate of the strength of the unlike interactions in the binary mixtures. Large positive V^E values are taken as indicative of weak intermolecular interactions whereas large negative values of V^E are usually found when these interactions are strong and intermolecular association " complexes " are believed to be present.

The systems DME + H_2O and THF + H_2O show that the V^E values are negative over the entire mole fraction range and over the entire range of temperatures studied. This implies that geometrical factors allowing the molecular species to form a more dense structure within the mixture may be important in both cases. The dense packing may be due to (i) different molecualr sizes (molar volumes of DME, THF and H_2O at 25°C are 104.65, 81.75 and 18.05 cm^3 respectively) leading to interstitial accommodation in the mexture, and (ii) formation of the possible hydrogen-bond interactions between unlike molecules.

The values of the quantity η^E, which refer to the deviations from a rectilinear dependence [8] of viscosity of the mixture on mole fraction, can be discussed from the viewpoint of intermolecular interactions [8,9]. For systems where dispersion and dipolar forces are operating, the values of η^E are found to be negative, whereas the existence of charge-transfer and hydrogen-bond interactions leading to the formation of complex species between the two components of the binary system tends to make the values of ^{E} positive. For systems where all types of intermolecular forces are operating, the values of η^{E} will be due to the contributions from all types of interactions. The systems DME + H_2O and THF + H_2O show positive deviation of η^{E} from ideality over the entire mole fraction range and over the whole range of studied temperatures. In order to explain this positive deviation it may be assumed that the hydrogen-bonding interactions between the unlike molecules are taking place leading to the formation of new species.

Another thermodynamic function, which has been investigated is the excess molar free energy of activation of flow (G^{*E}). The values of G^{*E} were calculated from equation 3, which results from the Eyring equation for viscosity flow modified for a binary mixture. The values of G^{*E} are always found to positive (table 2). According to Reed and Taylor [10] and Meyers et al [11], the G^{*E} parameters may be considered as a reliable measure to detect the nature of interactions between unlike molecules. Positive values of G^{*E} can be seen in binary systems where specific interaction between molecules take place. In the present systems the G^{*E} values are found to be positive at all compositions over the entire range of temperatures (table 2). This is obviously an indication of the presence of specific interaction between DME (or THF) and water molecules. In fact, mixtures where a strong specific interaction between unlike molecules is predominant are characterised by distinct maxima in the viscosity vs. composition vurves, by positive excess viscosities and by positive values of G^{*E} [8,12-15].

REFERENCES

1. Barthel, J.; Gores, H.J.; Scheemer, G. p Watcher, R. Non-aqueous Electrolyte Solutions in Chemistry and Modern Technology, Topics in Current Chemistry, Vol 3, Springer, Berlin, 1982.

2. Ikeda, H.; Saito, T.; Tamura, H. Denki Kagaku 1977, 45, 314.

3. Jasinski, R. Adv. Electrochem. Eng. 1971, 8, 253.

4. Nandi, D.; Das, S.; Hazra, D.K. Ind. J. Chem. 1988, 27A, 574.

5. Physical Chemistry of Organic Solvent Systems, Covington, A.K.; Dickinson, T. editors. Plenum : New York. 1973, P. 5.

6 Redlich, O.; Kister, A.T. Ind. Eng. Chem. 1948, 40,345.

7. Prigogine, I. The Molecular Theory of Solutions, North-Holland : Amsterdam 1971.

8. Fort, R.J.; Moore, W,R, Trans. Faraday. Soc. 1966, 62, 1112.

9. Nigam, R.K.,; Singh, P.P. Ind. J. Chem. 1971, 9, 691.

10. Reed, T.M.; Taylor, T.E. J. Phys. Chem. 1959, 63,58.

11. Meyer, R.; Meyer, M.; Metzer, J.; Peneloux, A. J. Chem. Phys. 1971, 62,405.

12. Assarsson, P.; Eirich, F.R. J. Phys. Chem. 1968, 72, 2710.

13. Westmeir, S.Z. Phys. Chem. (Leipzig). 1976, 257, 950.

14. Solimo, H.N.; Riggio, R.; Davolio, F.; Katz, M. Can.

J. Chem. 1975, 53, 1258.

15. Jannelli, L.; Rakshit, D.; Sacco, A.Z. Naturforsch 1974, 29A, 355.

TABLE - 1

Experimental density (ρ), Kinematic Viscosity (ν) and absolute Viscosity (η) data for the tetrahydrofuran + water and 1,2-dimethoxyethane + water mixtures at 25, 35 and 45°C.

x_1	ρ gcm^{-3}	ν St	η cP
	THF + H_2O mixtures at 25°C		
0.0000	0.99707	0.8929	0.8903
0.0271	0.99281	1.2101	1.2014
0.0587	0.98668	1.5101	1.4900
0.0967	0.97833	1.7169	1.6797
0.1427	0.96997	1.7857	1.7321
0.1998	0.95898	1.7494	1.6776
0.2726	0.94628	1.5750	1.4904
0.3682	0.93219	1.3228	1.2237
0.4500	0.92169	1.1114	1.0244
0.4998	0.91592	1.0085	0.9237
0.6000	0.90552	0.8369	0.7578
0.6921	0.89112	0.7366	0.6564
0.7500	0.88399	0.6879	0.6081
0.8000	0.88069	0.6576	0.5791
0.9000	0.87535	0.5895	0.5161
1.0000	0.88072	0.5257	0.4630

Contd...

X_1	ρ / gcm^{-3}	ν / St	η / cP
	At 35°C		
0.0000	0.99406	0.7268	0.7225
0.0587	0.98309	1.1526	1.1331
0.0967	0.97434	1.3001	1.2667
0.1427	0.96334	1.3736	1.3231
0.1998	0.95124	1.3596	1.2933
0.2726	0.93810	1.2677	1.1893
0.3682	0.92315	1.0717	0.9893
0.4500	0.91308	0.9329	0.8518
0.4998	0.90768	0.8637	0.7840
0.6000	0.89674	0.7283	0.6531
0.6921	0.88849	0.6439	0.5722
0.7500	0.88380	0.6098	0.5389
0.8000	0.88069	0.5810	0.5117
0.9000	0.87535	0.5394	0.4722
1.0000	0.87033	0.4914	0.4277
	At 45°C		
0.0000	0.99017	0.6044	0.5985
0.0271	0.98579	0.7632	0.7523
0.0587	0.97730	0.9175	0.8967
0.0967	0.96878	1.0287	0.9966

Contd...

X_1	ρ / gcm^{-3}	ν / St	η / cP
0.1427	0.95852	1.0904	1.0452
0.1998	0.94496	1.0959	1.0357
0.2726	0.92913	1.0323	0.9591
0.3682	0.91520	0.9074	0.8304
0.4500	0.90406	0.7902	0.7144
0.4998	0.89732	0.7371	0.6614
0.6000	0.88630	0.6365	0.5641
0.6921	0.87759	0.5766	0.5060
0.7500	0.87384	0.5410	0.4728
0.8000	0.87051	0.5197	0.4524
0.9000	0.86547	0.4877	0.4221
1.0000	0.86140	0.4529	0.3902

DME + H_2O mixtures

At 25°C

0.0000	0.99707	0.8929	0.8903
0.0399	0.99672	1.5073	1.5024
0.1251	0.97498	2.1233	2.0702
0.1800	0.96322	2.0973	2.0202
0.2525	0.94775	1.7922	1.6986
0.3124	0.93511	1.5106	1.4126
0.3552	0.92650	1.3379	1.2396

Contd...

X_1	$\frac{\rho}{\mathrm{gcm^{-3}}}$	$\frac{\nu}{\mathrm{St}}$	$\frac{\eta}{\mathrm{cP}}$
0.4198	0.91565	1.1098	1.0162
0.4648	0.90909	0.9842	0.8948
0.5088	0.90310	0.8859	0.8001
0.5499	0.89817	0.8122	0.7295
0.5955	0.89289	0.7506	0.6703
0.6622	0.88583	0.6775	0.6002
0.7199	0.88031	0.6339	0.5580
0.7550	0.87725	0.6158	0.5402
0.8051	0.87250	0.5756	0.5022
0.8584	0.86936	0.5450	0.4738
0.8999	0.86680	0.5307	0.4600
0.9511	0.86397	0.5104	0.4410
1.0000	0.86132	0.4918	0.4236

At 35°C

0.0000	0.99406	0.7268	0.7225
0.0399	0.98681	1.2161	1.2001
0.1251	0.96948	1.5309	1.4842
0.1800	0.95734	1.5539	1.4876
0.2525	0.94100	1.4371	1.3523
0.3124	0.92726	1.2780	1.1850
0.3552	0.91832	1.1720	1.0763

Contd...

X_1	ρ / gcm^{-3}	ν / St	η / cP
0.4198	0.90163	1.0352	0.9334
0.5088	0.89315	0.8824	0.7881
0.5499	0.88812	0.8241	0.7319
0.5955	0.88290	0.7675	0.6776
0.6622	0.87666	0.6855	0.6010
0.7199	0.87084	0.6248	0.5441
0.7550	0.86787	0.5907	0.5127
0.8051	0.86398	0.5440	0.4700
0.8584	0.86025	0.5050	0.4344
0.8999	0.85776	0.4817	0.4132
1.0000	0.85129	0.4519	0.3847
		At 45°C	
0.0000	0.99017	0.6044	0.5985
0.0399	0.98254	0.9772	0.9601
0.1251	0.96576	1.1825	1.1420
0.1800	0.94861	1.2148	1.1524
0.2525	0.92902	1.1841	1.1001
0.3124	0.91525	1.1099	1.0159
0.3552	0.90810	1.0353	0.9402
0.4198	0.89556	0.9313	0.8341
0.4648	0.88852	0.8663	0.7697

Contd...

X_1	ρ / gcm^{-3}	ν / St	η / cP
0.5088	0.88284	0.7972	0.7038
0.5499	0.87776	0.7455	0.6544
0.5955	0.87243	0.6879	0.6002
0.6622	0.86598	0.6119	0.5299
0.7199	0.86049	0.5369	0.4620
0.7550	0.85766	0.5319	0.4562
0.8051	0.85373	0.4945	0.4222
0.8584	0.85005	0.4703	0.3998
0.8999	0.84632	0.4629	0.3918
0.9511	0.84401	0.4473	0.3776
1.0000	0.84076	0.4158	0.3496

TABLE - 2

Excess molar volume V^E, excess viscosities η^E, and excess molar free energies of activation of flow G^{*E} for the tetrahydrofuran + water and 1,2-dimethoxyethane + water mixtures at 25, 35 and 45°C.

X_1	V^E / $cm^3\ mol^{-1}$	η^E / cP	G^{*E} / $J mol^{-1}$
	THF + H_2O mixtures		
	At 25°C		
0.0000	0.0000	0.0000	0.0000
0.0271	-0.1752	0.3222	899.54
0.0587	-0.3370	0.6248	1579.42
0.0967	-0.4773	0.8307	2046.13
0.1427	-0.6425	0.9028	2297.33
0.1998	-0.7607	0.8727	2407.20
0.2726	-0.8410	0.7365	2336.06
0.3682	-0.8712	0.4908	2020.35
0.4500	-0.8258	0.3265	1708.55
0.4998	-0.7719	0.2469	1515.09
0.6000	-0.6150	0.1235	1122.50
0.6921	-0.4382	0.0618	845.00
0.7500	-0.3373	0.0378	689.22
0.8000	-0.2499	0.0310	583.50
0.9000	-0.1008	0.0105	311.09
1.0000	0.0000	0.0000	0.00
	At 35°C		
0.0000	0.0000	0.0000	0.0000
0.0587	-0.3676	0.4279	1446.78
0.0967	-0.5239	0.5727	1895.37

Contd...

X_1	V^E $cm^3\ mol^{-1}$	η^E cP	G^{*E} $Jmol^{-1}$
0.1427	-0.6420	0.6427	2184.74
0.1998	-0.7552	0.6297	2297.82
0.2726	-0.8433	0.5472	2261.05
0.3682	-0.8912	0.3753	1962.29
0.4500	-0.8800	0.2620	1682.49
0.4998	-0.8413	0.2088	1514.89
0.6000	-0.6850	0.1075	1115.02
0.6921	-0.5090	0.0537	804.68
0.7500	-0.3820	0.0375	657.99
0.8000	-0.2844	0.2050	557.04
0.9000	-0.1008	0.0150	295.08
1.0000	0.0000	0.0000	0.00

At 45°C

0.0000	0.0000	0.0000	0.0000
0.0271	-0.2112	0.1594	744.33
0.0587	-0.3572	0.3104	1362.22
0.9067	-0.5342	0.4182	1798.85
0.1427	-0.6366	0.4804	2088.25
0.1998	-0.7282	0.4788	2235.67
0.2726	-0.7944	0.4175	2204.55
0.3682	-0.8268	0.3088	1973.55

Contd...

X_1	V^E / $cm^3 mol^{-1}$	η^E / cP	G^{*E} / $J mol^{-1}$
0.4500	-0.7867	0.2098	1662.37
0.4998	-0.7331	0.1672	1496.39
0.6000	-0.5599	0.0908	1118.28
0.6921	-0.3610	0.0492	838.58
0.7500	-0.2722	0.0307	647.35
0.8000	-0.2009	0.0208	515.29
0.9000	-0.0857	0.0113	280.48
1.0000	0.0000	0.0000	0.00

DME + H_2O Mixtures

At 25°C

X_1	V^E / $cm^3 mol^{-1}$	η^E / cP	G^{*E} / $J mol^{-1}$
0.0000	0.0000	0.0000	0.0000
0.0399	-0.5161	0.6307	1564.18
0.1251	-1.1678	1.2383	2837.81
0.1800	-1.4718	1.2139	3007.99
0.2525	-1.7065	0.9261	2822.62
0.3124	-1.7562	0.6681	2527.78
0.4198	-1.6741	0.3218	1927.28
0.4648	-1.6197	0.2214	1678.02
0.5088	-1.5395	0.1473	1454.79
0.5499	-1.4652	0.0958	1266.99
0.5955	-1.3503	0.0579	1094.79

Contd...

X_1	$\frac{V^E}{cm^3 mol^{-1}}$	$\frac{\eta^E}{cP}$	$\frac{G^{*E}}{Jmol^{-1}}$
0.6622	-1.1507	0.0189	861.45
0.7199	-0.9537	0.0037	703.41
0.7550	-0.8299	0.0023	631.66
0.8051	-0.5767	-0.0124	459.14
0.8584	-0.4548	-0.0159	312.12
0.8999	-0.3235	-0.0103	233.07
0.9511	-0.1691	-0.0054	116.04
1.0000	0.0000	0.0000	0.00
		At 35°C	
0.0000	0.0000	0.0000	0.0000
0.0399	-0.4523	0.4911	1581.62
0.1251	-1.2121	0.8040	2583.61
0.1800	-1.5409	0.8259	2812.12
0.2525	-1.7846	0.7151	2800.48
0.3552	-1.7810	0.4738	2456.32
0.4198	-1.4034	0.3527	2210.57
0.5088	-1.5188	0.2375	1862.41
0.5499	-1.4412	0.1952	1703.10
0.5955	-1.3342	0.1563	1523.71
0.6622	-1.2090	0.1022	1241.93
0.7199	-0.9927	0.0648	993.71

Contd...

X_1	$\frac{V^E}{cm^3 mol^{-1}}$	$\frac{\eta^E}{cP}$	$\frac{G^{*E}}{J mol^{-1}}$
0.7550	-0.8814	0.0452	839.31
0.8051	-0.7201	0.0195	607.15
0.8584	-0.5474	0.0019	386.38
0.8999	-0.4303	-0.0053	240.72
1.0000	0.0000	0.0000	0.00
At 45°C			
0.0000	0.0000	0.0000	0.0000
0.0399	-0.4815	0.3714	1513.31
0.1251	-1.3333	0.5746	2438.71
0.1800	-1.5400	0.5987	2691.93
0.2525	-1.6762	0.5644	2799.50
0.3124	-1.7014	0.4952	2730.57
0.3552	-1.7632	0.4301	2600.70
0.4198	-1.6384	0.3401	2378.01
0.4648	-1.5641	0.2869	2211.35
0.5088	-1.5131	0.2319	2005.86
0.5499	-1.4360	0.1928	1833.90
0.5955	-1.3240	0.1499	1619.04
0.6622	-1.1858	0.0962	1292.15
0.7199	-1.0014	0.0427	920.08
0.7550	-0.9060	0.0456	874.70

Contd...

X_1	$\frac{V^E}{cm^3 mol^{-1}}$	$\frac{\eta^E}{cP}$	$\frac{G^{*E}}{Jmol^{-1}}$
0.8051	-0.7444	0.0241	647.01
0.8584	-0.5809	0.0150	470.46
0.9511	-0.2385	0.0158	247.74

TABLE - 3

Co-efficients of equation (5) for V^E, η^E and G^{*E} and the standard deviations at 25, 35 and 45°C

Property	Temp	A_o	A_1	A_2	A_3	A_4	$\sigma(Y^E)$
				THF + H_2O mixtures			
V^E	25°C	-3.0987	-2.4670	0.4568	-0.5104	-1.3891	0.007
	35°C	-3.3537	-1.9084	1.1675	-1.6748	-2.2468	0.007
	45°C	-2.9849	-2.4096	1.8817	-1.0677	-4.1027	0.015
η^E	25°C	0.8998	3.0181	5.3546	4.1088	0.6734	0.018
	35°C	0.7980	2.2080	3.0296	2.6549	1.3706	0.005
	45°C	0.6278	1.8412	2.6750	1.5727	0.1063	0.007
G^{*E}	25°C	6271.375	6338.125	3213.125	9407.625	12797.500	64.607
	35°C	6082.981	6718.774	4262.000	7297.203	9053.375	39.790
	45°C	6109.094	6641.321	3470.250	6620.500	8741.875	37.602

Contd.....

Property	Temp	A_o	A_1	A_2	A_3	A_4	$\sigma(Y^E)$
DME + H_2O mixtures							
V^E	25°C	-6.3777	-3.7491	0.5055	-2.4391	-4.3239	0.004
	35°C	-6.2389	-4.7654	-4.0398	0.8724	2.1055	0.003
	45°C	-6.0239	-4.2878	-4.6114	-0.0255	1.3714	0.004
η^E	25°C	0.5510	3.4974	7.9450	6.7510	1.3038	0.003
	35°C	1.1471	2.4952	2.2485	4.8606	4.7835	0.007
	45°C	1.0716	1.6478	0.0322	3.9231	5.2636	0.004
G^{*E}	25°C	6146.399	8037.004	8752.344	14595.240	11231.940	61.393
	35°C	7914.293	5779.680	-20.957	16395.450	20122.500	12.655
	45°C	8630.488	6350.203	-3753.469	13470.870	23839.500	14.264

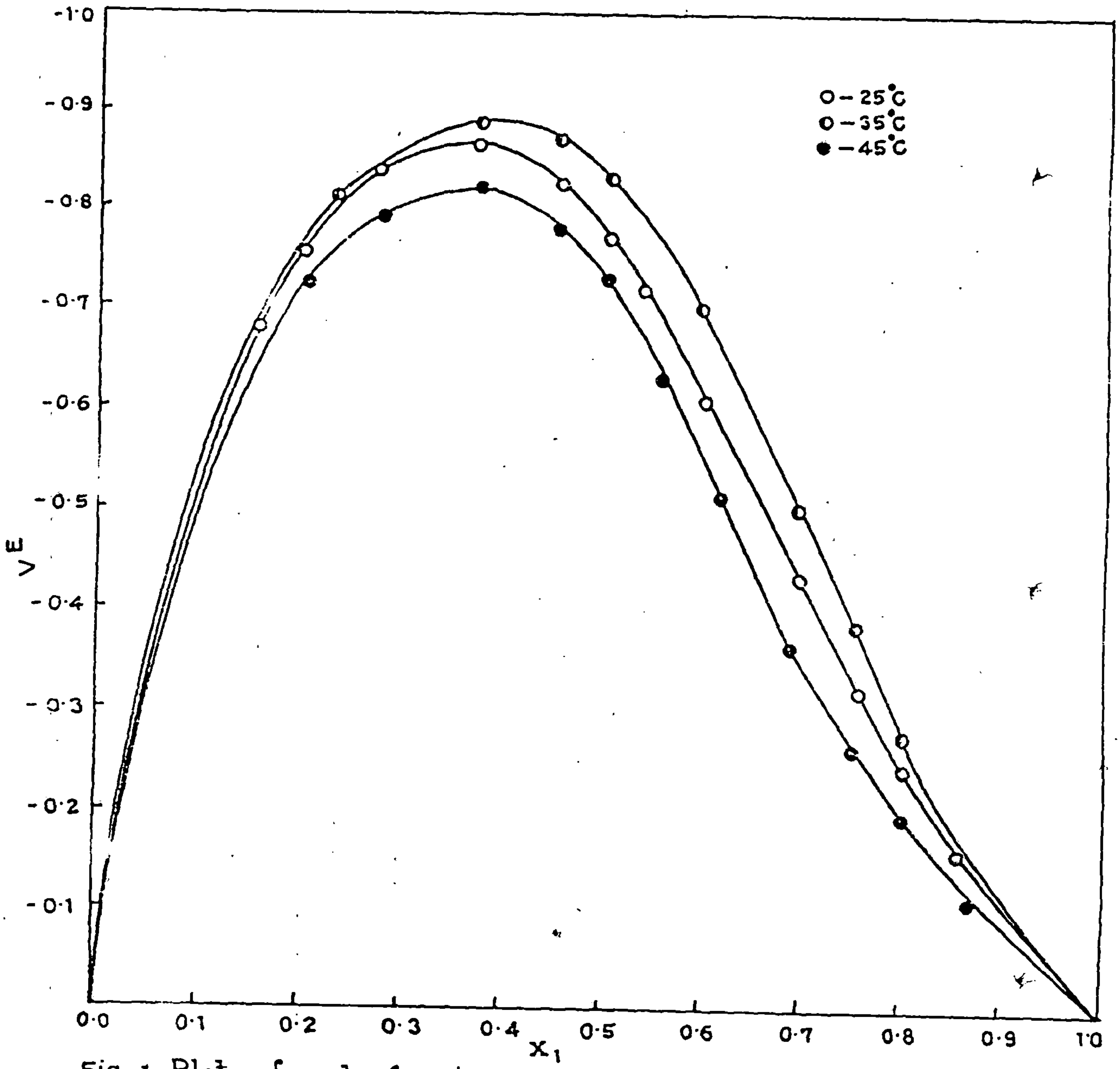

Fig. 1. Plots of mole-fractions vs excess molar volumes of THF+H_2O mixtures at different temperatures.

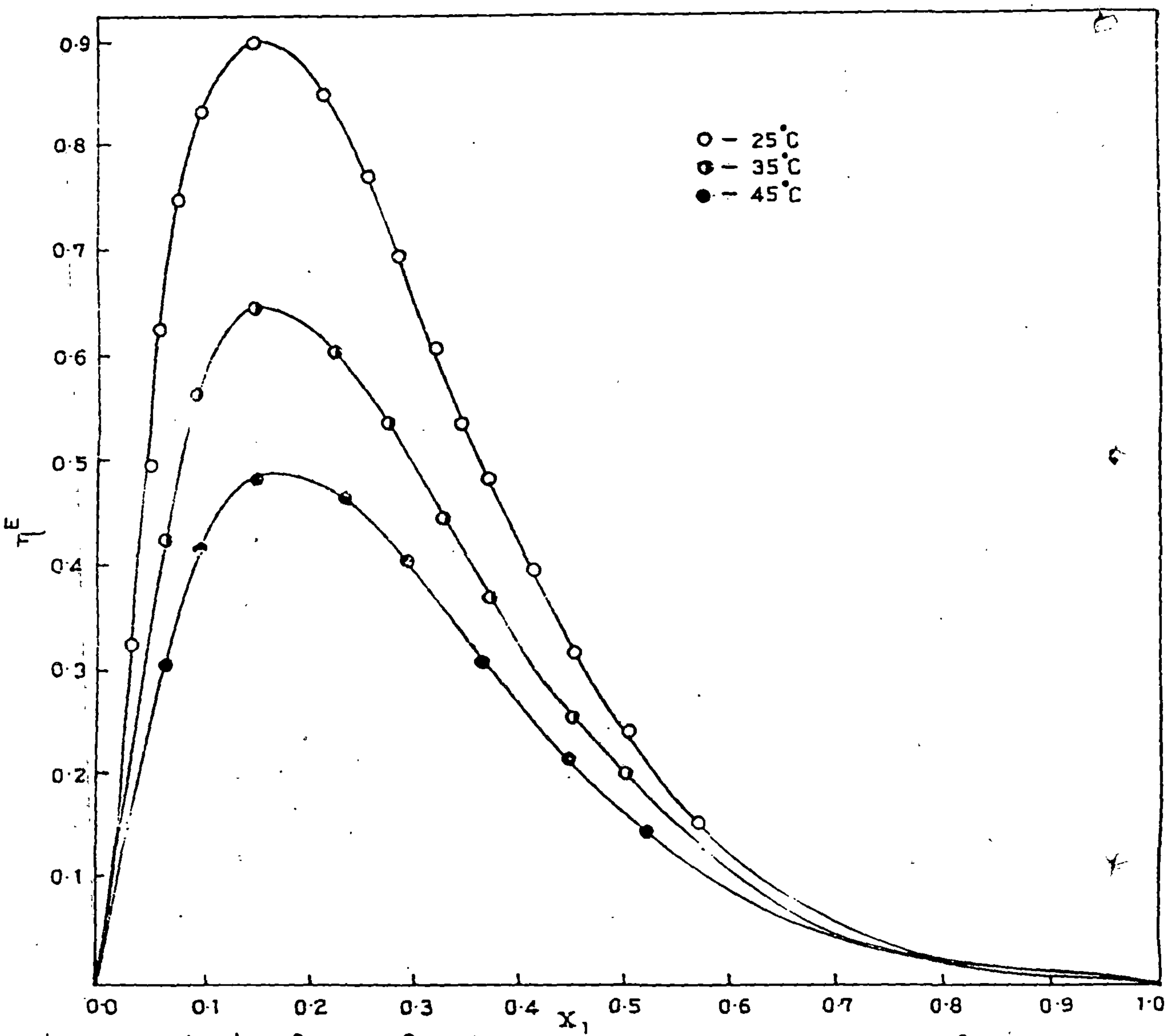

Fig. 2. Plots of mole-fractions vs excess viseosities of THF+ H_2O muixtures at different temperatures.

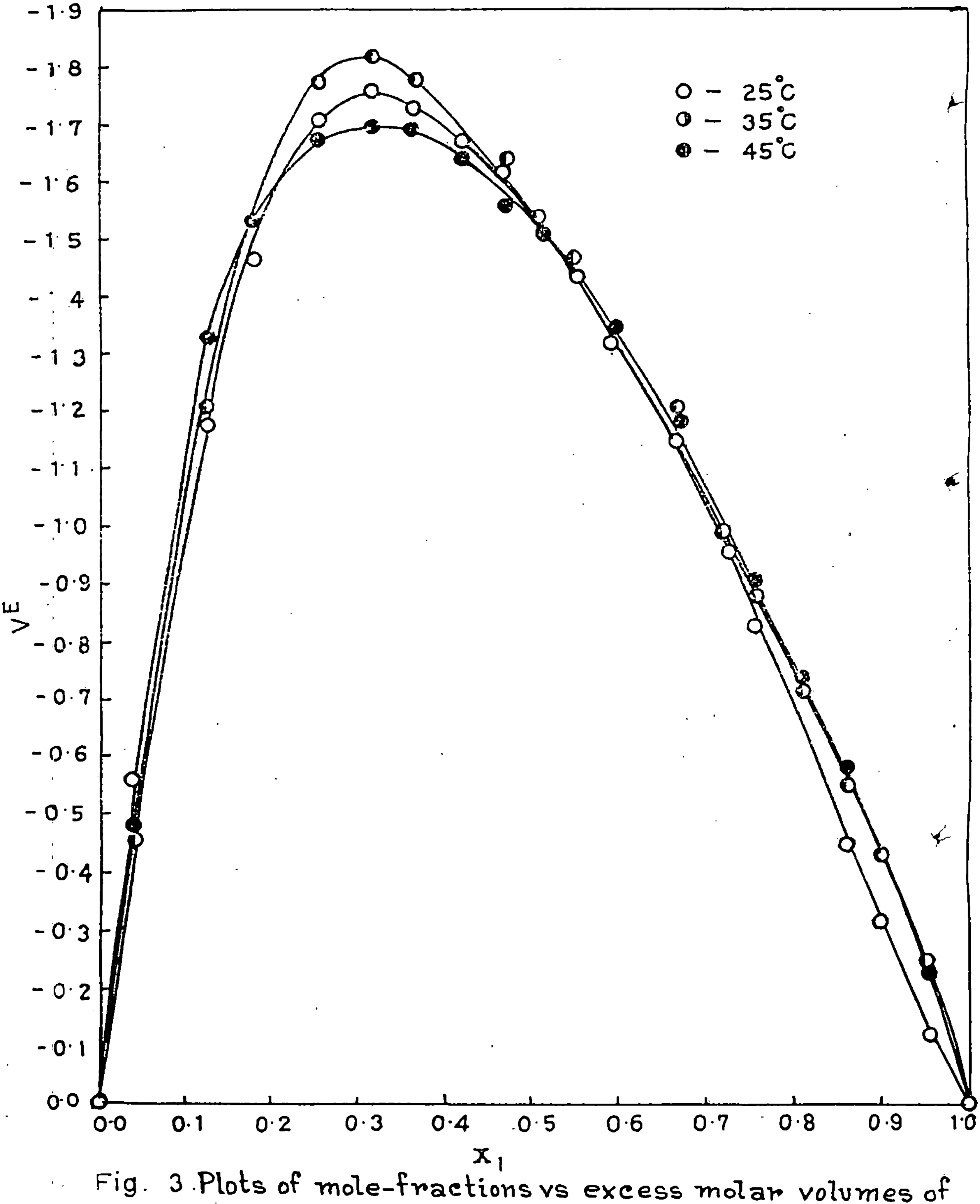

Fig. 3 Plots of mole-fractions vs excess molar volumes of DME + H_2O mixtures at different temperatures.

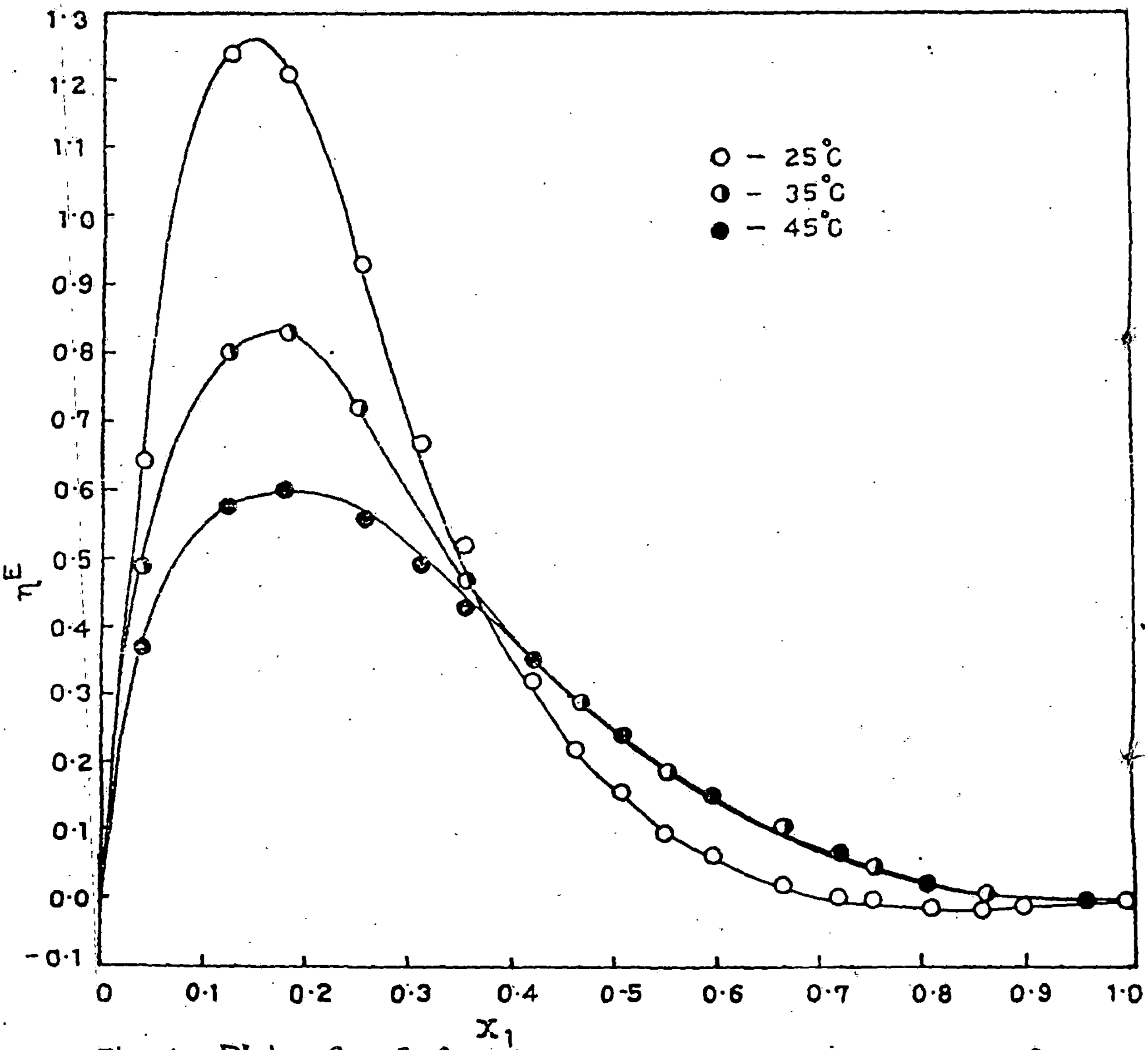

Fig. 4. Plots of molefractions vs excess viscosities of DME+H_2O mixtures at different temperatures.