

Excess molar volumes and viscosities of binary mixtures of some polyethers with 1-propanol at 288·15, 298·15, and 308·15 K

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Abstract. Excess molar volumes (V_m^E) and viscosities (\mathbf{h}) have been measured as a function of composition for binary liquid mixtures of 1-propanol, C_3H_7OH , with diethylene glycol diethyl ether (*bis*(2-ethoxyethyl)ether), $C_2H_5(OC_2H_4)_2OC_2H_5$, and diethylene glycol dibutyl ether (*bis*(2-butoxyethyl)ether), $C_4H_9(OC_2H_4)_2OC_4H_9$, at 288·15, 298·15, and 308·15 K and at atmospheric pressure. The excess volume results included the following mixing quantities at all range of concentrations and at equimolar concentrations: \mathbf{a} volume expansivity; $(\partial V_m^E/\partial T)_P$, and $(\mathbf{H}^E/\mathbf{P})_T$ at 298·15 K. The obtained results were then compared with the calculated values by using the Flory theory of liquid mixtures. The theory predicts the \mathbf{a} values rather well, while the calculated values of $(\partial V_m^E/\partial T)_P$ and $(\mathbf{H}^E/\mathbf{P})_T$ show variation with alkyl chain length of the polyether. The results are discussed in terms of order or disorder creation. From the viscosity data, deviations in viscosity ($\Delta\mathbf{h}$) have been calculated. These values are negative over the entire range of composition. The results for V_m^E and $\Delta\mathbf{h}$ are discussed in terms of interaction between components.

Keywords. Excess volumes; viscosity deviations; binary mixtures; polyethers; 1-propanol; Flory theory.

1. Introduction

The polyethers are important industrial solvents. Process design using these fluids requires accurate thermophysical property data. However, few such data have been published in the literature. Thus, study of physical data of binary mixtures containing polyethers has attracted considerable interest in the recent literature.^{1–6}

Binary mixtures containing alcohols and polyethers exhibit a particular challenge in order to describe their interactions behaviour occurring in the solutions. So, the treatment of this class of mixtures is a severe test for any theoretical model. The thermodynamic properties of the glyme–alkane,^{7,8} alkanol + alkane,⁹ polyether + alkanol¹⁰ mixtures have been well studied. It seems interesting, therefore, to investigate the mixing functions in order to analyze the order effects on this class of mixtures and to check the Flory theory.

Systematic studies on thermodynamic, transport, and acoustic properties of mixtures containing polyethers with dialkyl carbonate,¹¹ chloroalkanes,¹² and esters¹³ have been carried out in our laboratory. In our present investigation we have determined the excess molar volumes, V_m^E and viscosities, \mathbf{h} for binary solvent mixtures containing 1-propanol (C_3H_7OH) with diethylene glycol diethyl ether [$C_2H_5(OC_2H_4)_2OC_2H_5$], and diethylene glycol dibutyl ether [$C_4H_9(OC_2H_4)_2OC_4H_9$] at 288·15, 298·15, and 308·15 K over the complete composition range. Excess molar volumes for binary mixtures of 1-propanol (C_3H_7OH) with diethylene glycol dibutyl ether, ($C_4H_9(OC_2H_4)_2OC_4H_9$), at 298·15 K and also excess molar volumes and viscosities at 288·15, 298·15, and 308·15 K for 1-propanol (C_3H_7OH) with diethylene glycol dimethyl ether ($CH_3(OC_2H_4)_2OCH_3$) have been reported in our earlier papers.^{14–16} The present study was therefore undertaken to assess the effect of increasing alkyl group size in polyethers with a common polar head group. An attempt is also made to interpret the results by deriving the different mixing properties like \mathbf{a} , $(\partial V_m^E/\partial T)_P$, and $(\partial H^E/\partial P)_T$ at

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298.15 K. By using the Flory theory, the above thermodynamic mixing functions have been calculated and the results obtained from this theory are compared with experimental results.

2. Experimental

2.1 Materials

Materials are of the same origin and purity as used in the earlier studies.¹⁷ Prior to actual measurements, all liquids were dried over 0.4 nm molecular sieves (Fluka AG) and were partially degassed under vacuum. The densities and viscosities of the liquids were measured and compared at the working temperatures with the corresponding literature values^{1,6,18–23} as shown in table 1.

2.2 Apparatus and procedure

Densities (ρ) of pure solvents were measured with a single-arm pycnometer. That was calibrated at the working temperatures with doubly distilled water. The sensitivity of the pycnometer corresponded to a precision in density of $1 \times 10^{-3} \text{ kg m}^{-3}$. The reproducibility of the density measurements was found to be within $3 \times 10^{-3} \text{ kg m}^{-3}$.

Excess molar volumes, reproducible to $\pm 0.003 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$, were measured directly with a continuous dilution dilatometer as per Dickinson *et al*²⁴.

Each run covered just over half of the mole fraction range, giving an overlap between two runs. The details pertaining to calibration, experimental setup, and operational procedures have been described previously.^{11,25} The mole fraction of each mixture was obtained with an uncertainty of 1×10^{-4} from the measured mass of one of the components. All masses were corrected for buoyancy. All molar quantities were based upon the IUPAC table of atomic weights.²⁶

Kinematic viscosities $\nu (= \mathbf{h}/\rho)$ of the pure liquids and the mixtures were measured at 288.15, 298.15, and 308.15 K and atmospheric pressure using an Ubbelohde suspended-level viscometer.^{27,28} The details of the apparatus and procedures have been described previously.^{29,30} The viscometer was calibrated to determine the two constants A and B of the equation $\mathbf{h}/\rho = At - B/t$, obtained by measuring the flow time t with twice-distilled water and thrice-distilled benzene and cyclohexane. The flow-time measurements were made using an electronic stopwatch with a precision of $\pm 0.01 \text{ s}$. An average of four or five sets of flow times for each fluid was taken for the purpose of calculation of viscosity. Viscosities are reproducible to $\pm 0.003 \text{ mPa s}$. The performance of the viscometer was assessed by measuring and comparing the viscosities of the pure components with the values reported in the literature.^{21,31} A thermostatically controlled, well-stirred water bath whose temperature was controlled to $\pm 0.01 \text{ K}$ was used for all the measurements.

Table 1. Densities, ρ ; and viscosities, \mathbf{h} for pure components at various temperatures.

Component	T (K)	ρ (kg m^{-3})		\mathbf{h} (mPa s)	
		Exp.	Lit.	Exp.	Lit.
1-Propanol	288.15	807.34	807.4 ¹⁸	2.515	
	298.15	799.49	799.58 ⁶ 799.5 ¹⁹	1.938	1.943 ²¹
	308.15	791.29	791.4 ²⁰	1.505	
Diethylene glycol diethyl ether	288.15	912.42	911.7 ¹	1.511	1.498 ¹
	298.15	902.76	902.1 ¹ 902.81 ⁶ 903.3 ²²	1.239	1.238 ¹
	308.15	892.97	892.5 ¹	1.045	1.045 ¹
Diethylene glycol dibutyl ether	288.15	888.58		2.684	
	298.15	878.55	878.30 ⁶ 878.62 ²³	2.122	
	308.15	872.94		1.708	

3. Experimental results

Results obtained experimentally for excess molar volumes and viscosities of all binary mixtures as a function of mole fraction and temperature are reported in tables 2 and 3.

The densities of the liquid mixtures were calculated from the excess molar volumes and densities of pure liquids according to the equation:

$$r = (x_1 M_1 + x_2 M_2) / (V_m^E + x_1 V_1 + x_2 V_2), \quad (1)$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 are the molar masses, and V_1 and V_2 are the molar volumes of polyether (1) + 1-propanol (2) respectively. The plots of excess molar volume (V_m^E) against mole fraction of polyether are given in figure 1.

The viscosity deviations, Δh from linear dependence on mole fraction average has been calculated from the following relationship:

$$\Delta h = h - (h_1 x_1 + h_2 x_2), \quad (2)$$

Table 2. Excess molar volumes, V_m^E , for (polyether + 1-propanol) systems at various temperatures.

<i>Diethylene glycol diethyl ether (1) + 1-propanol (2)</i>						<i>Diethylene glycol dibutyl ether (1) + 1-propanol (2)</i>					
x_1	$V_m^E \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	x_1	$V_m^E \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	x_1	$V_m^E \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	x_1	$V_m^E \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	x_1	$V_m^E \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	x_1	$V_m^E \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)
288-15 K						288-15 K					
0-0169	-0-029	0-2638	-0-307	0-4532	-0-353	0-0102	-0-029	0-1431	-0-249	0-3896	-0-387
0-0375	-0-067	0-2706	-0-310	0-5214	-0-342	0-0215	-0-057	0-1687	-0-270	0-4297	-0-389
0-0645	-0-117	0-3010	-0-322	0-5842	-0-325	0-0325	-0-077	0-1736	-0-282	0-4777	-0-392
0-0924	-0-156	0-3095	-0-322	0-6351	-0-311	0-0463	-0-100	0-2009	-0-307	0-5316	-0-377
0-1232	-0-196	0-3295	-0-330	0-7113	-0-273	0-0598	-0-125	0-2094	-0-312	0-5930	-0-353
0-1549	-0-223	0-3307	-0-332	0-7825	-0-224	0-0698	-0-143	0-2380	-0-326	0-6719	-0-316
0-1895	-0-259	0-3522	-0-339	0-8442	-0-172	0-0836	-0-170	0-2392	-0-331	0-7622	-0-255
0-2197	-0-285	0-3796	-0-346	0-9060	-0-111	0-0977	-0-190	0-2728	-0-354	0-8717	-0-161
0-2437	-0-300	0-4128	-0-350	0-9847	-0-015	0-1089	-0-206	0-3138	-0-373	0-9622	-0-057
298-15 K						308-15 K					
0-0035	-0-009	0-2682	-0-305	0-4213	-0-332	0-0035	-0-003	0-1560	-0-232	0-3782	-0-360
0-0200	-0-045	0-2704	-0-307	0-4675	-0-328	0-0091	-0-018	0-1815	-0-264	0-4263	-0-360
0-0484	-0-095	0-2901	-0-312	0-5341	-0-319	0-0171	-0-038	0-1881	-0-267	0-4670	-0-355
0-0738	-0-136	0-3011	-0-313	0-5978	-0-302	0-0320	-0-066	0-2027	-0-283	0-5530	-0-332
0-1015	-0-173	0-3153	-0-318	0-6690	-0-267	0-0455	-0-090	0-2115	-0-290	0-6076	-0-310
0-1370	-0-214	0-3167	-0-319	0-7578	-0-222	0-0574	-0-110	0-2239	-0-299	0-6630	-0-279
0-1739	-0-252	0-3377	-0-322	0-8645	-0-133	0-0702	-0-130	0-2428	-0-307	0-7578	-0-212
0-1980	-0-269	0-3458	-0-323	0-9193	-0-087	0-0838	-0-150	0-2571	-0-321	0-8380	-0-159
0-2236	-0-287	0-3632	-0-326	0-9797	-0-028	0-0967	-0-174	0-2710	-0-326	0-9242	-0-080
0-2332	-0-289	0-3795	-0-328	0-9935	-0-010	0-1156	-0-199	0-2944	-0-339	0-9805	-0-019
0-2518	-0-301	0-3848	-0-329			0-1323	-0-213	0-3389	-0-351		
308-15 K											
0-0095	-0-025	0-2794	-0-300	0-4958	-0-312						
0-0264	-0-056	0-2858	-0-302	0-5479	-0-301						
0-0485	-0-091	0-3188	-0-315	0-6003	-0-288						
0-0708	-0-126	0-3203	-0-315	0-6707	-0-256						
0-1035	-0-171	0-3504	-0-320	0-7494	-0-209						
0-1324	-0-196	0-3529	-0-320	0-8031	-0-171						
0-1623	-0-225	0-3809	-0-322	0-8775	-0-109						
0-1908	-0-252	0-3949	-0-322	0-9764	-0-027						
0-2151	-0-263	0-4052	-0-321								
0-2399	-0-280	0-4494	-0-320								

Table 3. Densities, \mathbf{r} , and viscosities, \mathbf{h} for (polyether + 1-propanol) systems at various temperatures.

x_1	\mathbf{r} (kg m ⁻³)	\mathbf{h} (mPa s)	x_1	\mathbf{r} (kg m ⁻³)	\mathbf{h} (mPa s)	x_1	\mathbf{r} (kg m ⁻³)	\mathbf{h} (mPa s)	x_1	\mathbf{r} (kg m ⁻³)	\mathbf{h} (mPa s)
<i>Diethylene glycol diethyl ether (1) + 1-propanol (2)</i>						<i>Diethylene glycol dibutyl ether (1) + 1-propanol (2)</i>					
288.15 K						288.15 K					
0.0207	812.7	2.396	0.4501	879.3	1.555	0.0054	808.9	2.497	0.4445	868.4	2.417
0.0317	815.4	2.318	0.5111	884.8	1.533	0.0510	820.3	2.417	0.5169	872.7	2.447
0.0445	818.4	2.273	0.5882	890.9	1.515	0.0882	828.1	2.374	0.5763	875.8	2.481
0.0674	823.6	2.179	0.6345	894.2	1.508	0.1358	836.5	2.332	0.6474	878.9	2.516
0.1211	834.7	2.036	0.6918	897.9	1.500	0.1840	843.7	2.322	0.7182	881.5	2.550
0.1790	845.1	1.852	0.7718	902.5	1.497	0.2405	850.8	2.322	0.7618	883.0	2.566
0.2503	856.1	1.722	0.8763	907.6	1.499	0.2877	855.8	2.337	0.8296	884.9	2.604
0.3201	865.3	1.643	0.9169	909.4	1.503	0.3031	857.3	2.346	0.8733	886.0	2.624
0.3859	872.8	1.588	0.9613	911.1	1.508	0.3878	864.4	2.385	0.9294	887.3	2.652
298.15 K						298.15 K					
0.0207	804.7	1.849	0.4501	870.1	1.270	0.0054	800.9	1.927	0.4445	858.8	1.901
0.0317	807.3	1.810	0.5111	875.5	1.255	0.0510	811.9	1.875	0.5169	863.1	1.933
0.0445	810.3	1.764	0.5882	881.5	1.240	0.0882	819.5	1.854	0.5763	866.0	1.956
0.0674	815.4	1.705	0.6345	884.8	1.236	0.1358	827.7	1.835	0.6474	869.0	1.983
0.1211	826.2	1.592	0.6918	888.4	1.233	0.1840	834.7	1.828	0.7182	871.6	2.015
0.1790	836.4	1.485	0.7718	893.0	1.233	0.2405	841.6	1.832	0.7618	873.1	2.026
0.2503	847.2	1.390	0.8763	898.1	1.235	0.2877	846.5	1.844	0.8296	875.1	2.056
0.3201	856.3	1.326	0.9169	899.8	1.224	0.3031	847.9	1.855	0.8733	876.1	2.075
0.3859	863.7	1.293	0.9613	901.4	1.238	0.3878	855.0	1.883	0.9294	877.3	2.092
308.15 K						308.15 K					
0.0207	796.4	1.447	0.4501	860.7	1.057	0.0054	792.8	1.498	0.4445	852.3	1.535
0.0317	799.0	1.420	0.5111	866.0	1.046	0.0510	804.1	1.475	0.5169	856.7	1.558
0.0445	801.9	1.394	0.5882	872.0	1.040	0.0882	811.8	1.462	0.5763	859.8	1.579
0.0674	806.9	1.349	0.6345	875.2	1.037	0.1358	820.2	1.455	0.6474	863.0	1.603
0.1211	817.5	1.268	0.6918	878.8	1.033	0.1840	827.4	1.458	0.7182	865.7	1.623
0.1790	827.5	1.194	0.7718	883.3	1.037	0.2405	834.5	1.469	0.7618	867.1	1.635
0.2503	838.1	1.137	0.8763	888.3	1.042	0.2877	839.5	1.479	0.8296	869.2	1.657
0.3201	847.1	1.099	0.9169	890.0	1.043	0.3031	841.1	1.486	0.8733	870.3	1.672
0.3859	854.4	1.071	0.9613	891.6	1.045	0.3878	848.3	1.513	0.9294	871.6	1.688

where \mathbf{h} , \mathbf{h}_1 , and \mathbf{h}_2 are the viscosities of the mixtures and components 1 and 2 respectively. The variations of $\Delta\mathbf{h}$ with mole fraction of polyether at 298.15 K are shown in figure 2. Data on derived densities, and viscosities for the different binary mixtures at different temperatures are given in table 3.

The values of V_m^E , and $\Delta\mathbf{h}$ for each mixture were correlated to the Redlich–Kister polynomial equation:³²

$$Y(x) = x_1 x_2 \sum_{i=1}^n a_i (x_1 - x_2)^{i-1}. \quad (3)$$

Values of the coefficients a_i and standard deviations \mathbf{s} are summarized in table 4. $Y(x)$ represents V_m^E , and $\Delta\mathbf{h}$. For mixtures, $\mathbf{s}(V_m^E) \leq 0.003$ for the precision attainable with the dilatometer used. There are no literature values of either V_m^E or \mathbf{h} for these mixtures available for comparison.

The values of volume or thermal expansion coefficients \mathbf{a} for the liquids and their mixtures were calculated for our systems by adding the contributions of the expansivities of each component in the mixtures:

$$\mathbf{a} = (1/V)[\sum(M_i x_i / \mathbf{r}_i) \mathbf{a}_i + (\partial V_m^E / \partial T)_{p,x}], \quad (4)$$

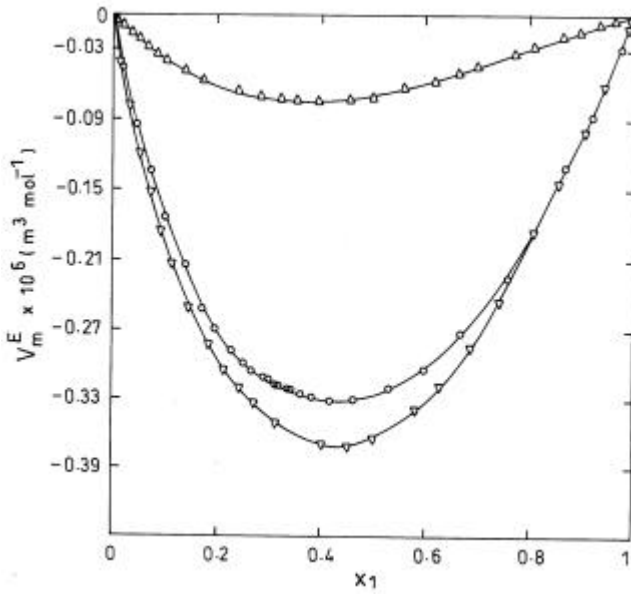


Figure 1. Experimental excess molar volumes V_m^E for $x_2\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + x_1\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$, Δ , from ref. [14]; $+x_1\text{C}_2\text{H}_5\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_2\text{H}_5$, \circ ; $+x_1\text{C}_4\text{H}_9\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_4\text{H}_9$, ∇ , from ref. [16], at 298.15 K. Continuous curves were drawn from (3) for experimental data.

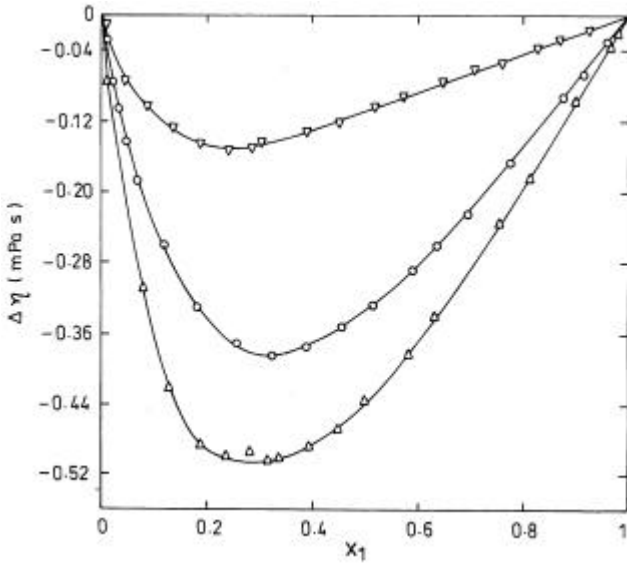


Figure 2. Experimental viscosity deviations Δh for $x_2\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + x_1\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_3$, Δ , from ref. [15]; $+x_1\text{C}_2\text{H}_5\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_2\text{H}_5$, \circ ; $+x_1\text{C}_4\text{H}_9\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_4\text{H}_9$, ∇ at 298.15 K. Continuous curves were drawn from (3) for experimental data.

where V is the molar volume of the mixtures; r_i and a_i are the density and the expansivity of pure component i at any particular temperature. In figure 3, a plots are shown for different mixtures at 298.15 K.

The a values increase for diethylene glycol dimethyl ether and diethylene glycol diethyl ether and slowly decrease for diethylene glycol dibutyl ether over the whole composition range.

4. Theoretical model

The Flory model^{33,34} has been commonly employed to analyse the molar volume of the mixture and the excess molar volume parting from the equation of the state in function of the reduced variables:

$$\tilde{P}\tilde{v}/\tilde{T} = [\tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1)] - 1/(\tilde{v}\tilde{T}), \quad (5)$$

where

$$\tilde{v} = V/V^* = [1 + (4/3)aT]/(1 + aT)]^3, \quad (6)$$

$$\tilde{P} = P/P^* = P/[aT\tilde{v}^2]/k_T], \quad (7)$$

$$\tilde{T} = T/T^* = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3}. \quad (8)$$

Theoretical values of dV_m^E/dT^{35} were calculated from the Flory theory using

$$T(dV_m^E/dT) = \left[\sum_{i=1}^2 x_i V_i^* [\tilde{T}(d\tilde{v}/d\tilde{T})] - \left(\sum_{i=1}^2 x_i V_i^* [\tilde{T}(d\tilde{v}/d\tilde{T})] \right)_i \right], \quad (9)$$

where

$$\tilde{T}(d\tilde{v}/d\tilde{T}) = \tilde{v}(1 - \tilde{v}^{-1/3})/[(4/3)\tilde{v}^{-1/3} - 1]. \quad (10)$$

In the present study the value of the reduced volume for the liquids and their mixtures \tilde{v} was determined from a values of the mixtures using the (6). Table 5 shows the data^{4,14,36-38} used in the application of the Flory model.

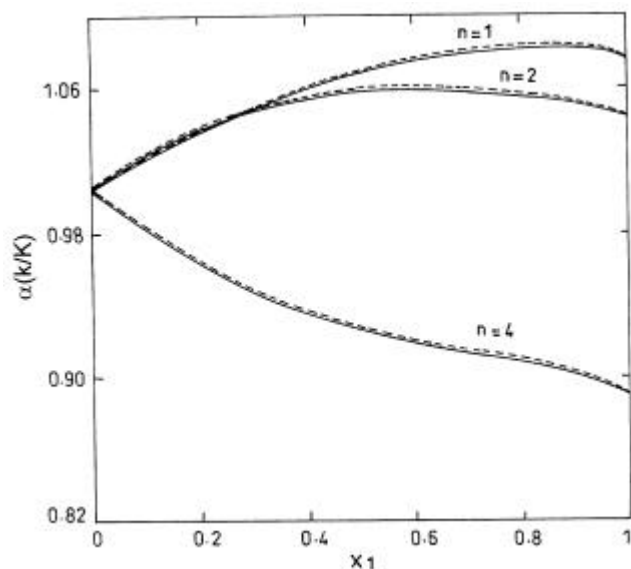
The excess function $(\partial V_m^E/\partial T)_p$ was computed by analytical differentiation of (3) at 298.15 K for each mixture. From $(\partial V_m^E/\partial T)_p$ and V_m^E of this work we have also obtained $(\partial H^E/\partial P)_T$ at zero pressure according to the equation:

$$(\partial H^E/\partial P)_T = V_m^E - T(\partial V_m^E/\partial T)_p. \quad (11)$$

Values of $(\partial V_m^E/\partial T)_p$, and $(\partial H^E/\partial P)_T$ for equimolar mixtures are reported in table 6. The values obtained for $(\partial V_m^E/\partial T)_p$ are positive for all the systems, and are

Table 4. Smoothing coefficients a_i from (3) and standard deviations \mathbf{s} of (polyether + 1-propanol) systems at various temperatures.

$Y(x)$	$T(K)$	a_1	a_2	a_3	a_4	a_5	\mathbf{s}
<i>Diethylene glycol diethyl ether (1) + 1-propanol (2)</i>							
$V_m^E \times 10^6 (\text{m}^3 \text{mol}^{-1})$	288.15	-1.3854	0.2411	-0.2851	0.1519		0.003
$\Delta h (\text{mPa s})$	288.15	-1.9008	1.3202	-0.9775	0.5228		0.014
$V_m^E \times 10^6 (\text{m}^3 \text{mol}^{-1})$	298.15	-1.2951	0.3152	-0.3935	0.2538		0.002
$\Delta h (\text{mPa s})$	298.15	-1.3441	0.9268	-0.3232	0.3520	-0.5944	0.008
$V_m^E \times 10^6 (\text{m}^3 \text{mol}^{-1})$	308.15	-1.2577	0.3700	-0.2497	0.1973		0.003
$\Delta h (\text{mPa s})$	308.15	-0.9048	0.5981	-0.4261	0.3375		0.003
<i>Diethylene glycol dibutyl ether (1) + 1-propanol (2)</i>							
$V_m^E \times 10^6 (\text{m}^3 \text{mol}^{-1})$	288.15	-1.5380	0.3927	-0.1930	0.0406	-0.3486	0.003
$\Delta h (\text{mPa s})$	288.15	-0.6272	0.6919	-0.7807	0.4749		0.003
$\Delta h (\text{mPa s})$	298.15	-0.4139	0.4357	-0.4824	0.2977		0.003
$V_m^E \times 10^6 (\text{m}^3 \text{mol}^{-1})$	308.15	-1.3988	0.5006	-0.0559	-0.0102	-0.2511	0.003
$\Delta h (\text{mPa s})$	308.15	-0.2135	0.2781	-0.3187	0.1868		0.001

**Figure 3.** Isobaric thermal expansivities α for $x_2\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + x_1\text{C}_n\text{H}_{2n+1}\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{C}_n\text{H}_{2n+1}$: $n=1$, ref. [14]; $n=2$, $n=4$ at 298.15 K. Continuous curves were drawn for experimental data; and (-----), Flory model.

in agreement with the values of V_m^E of figure 1. The values of $(\partial H^E/\partial P)_T$ are negative at equimolar concentration, for all polyether systems. The $(\partial V_m^E/\partial T)_p$ and $(H^E/P)_T$ have similar variation with the alkyl group size (n) in polyether but with opposite sign.

5. Model prediction

The calculated equimolar values of $(\partial V_m^E/\partial T)_p$, and $(\partial H^E/\partial P)_T$ from the application of Flory theory at 298.15 K show that the absolute values for both excess functions are substantially greater than those obtained from the experimental data. In table 6, we see again a correct prediction for the behaviour of $(\partial V_m^E/\partial T)_p$ and $(\partial H^E/\partial P)_T$ with ' n ', including the minimum and maximum respectively, but deviations between experimental and theoretical values are slightly higher in the diethylene glycol dimethyl ether-1-propanol system.

The V_m^E values for mole fraction ($x_1 = 0.5$) are represented in figure 4 with the chain length of the polyether. The results obtained reproduce the tendency of V_m^E to increase with temperature and to decrease with the lengthening of the polyether chain. It is argued^{7,10} that two atoms of oxygen separated by two methylene groups in polyethers make more rigid complexes due to the anomeric effect. The Flory theory, which does not explicitly consider order, predicts positive values of $(\partial V_m^E/\partial T)_p$. This result reflects the theoretical origin of the positive $(\partial V_m^E/\partial T)_p$ as a free-volume rather than an order effect. Further, destruction of order during mixing³⁵ contributes negatively to $(\partial V_m^E/\partial T)_p$. For this reason it can be expected that orientational order becomes less important due to experimental positive value of $(\partial V_m^E/\partial T)_p$. The values of α^E (not shown) have the same sign as

Table 5. Flory and related parameters of pure components at 298.15 K.

Component	\mathbf{a} (kK^{-1})	\mathbf{r} (kg m^{-3})	u (m s^{-1})	$C_{p,m}$ ($\text{J K}^{-1} \text{mol}^{-1}$)	\mathbf{k}_T (T Pa^{-1})	$V^* \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	T^* (K^{-1})	\tilde{v}	\tilde{T}
1-Propanol	1.004	799.49	1204.6 ³⁶	144.10 ³⁷	1019	60.21	5222	1.2485	0.0571
Diethylene glycol dimethyl ether	1.045 ¹⁴	938.97 ¹⁴	1280.1 ³⁶	279.58 ⁴	816	113.69	5105	1.2569	0.0584
Diethylene glycol diethyl ether	1.077	902.76	1239.8 ³⁸	347.42 ^a	900	142.25	5028	1.2633	0.0593
Diethylene glycol dibutyl ether	0.890	878.55	1269.0 ³⁸	479.62 ^a	829	202.92	5594	1.2247	0.0533

^aCalculated from group additivity

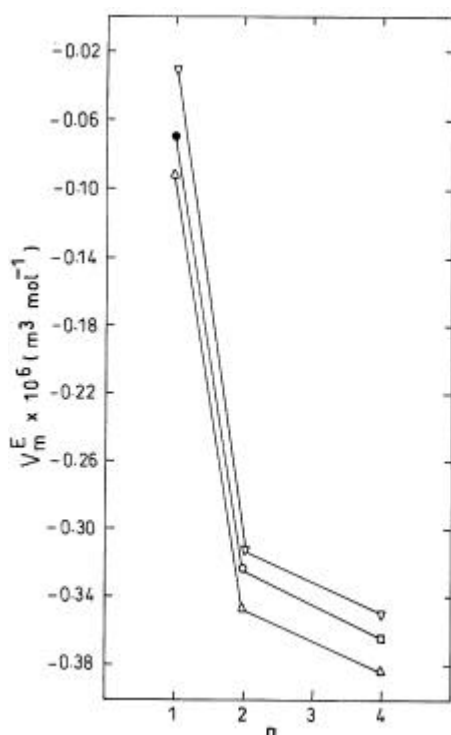


Figure 4. Excess molar volume V_m^E at $x_1 = 0.5$ for $x_2 \text{ CH}_3\text{CH}_2\text{CH}_2\text{OH} + x_1 \text{C}_n\text{H}_{2n+1}\text{O}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_n\text{H}_{2n+1}$: Δ , 288.15 K, this work; \circ , $n = 2$, this work; \bullet , $n = 1$, ref. [14]; \square , $n = 4$, ref. [16]) at 298.15 K; ∇ , 308.15 K, this work.

$(\partial V_m^E / \partial T)_p$ for all the systems. Furthermore, the magnitude of $(\partial V_m^E / \partial T)_p$ and \mathbf{a}^E are largely dependent on the size and type of component molecules.

The mixing parameters $(\partial V_m^E / \partial T)_p$ and $(\partial H^E / \partial P)_T$ are good indicators of order or non-randomness in the solution.^{39–41} Randomness in solution implies a negative contribution to the $(\partial V_m^E / \partial T)_p$. Here, $(\partial V_m^E / \partial T)_p$ is positive for each of the polyether mixtures with values that are higher with lower chain length of polyether. Deviations between experimental and theo-

retical values of $(\partial V_m^E / \partial T)_p$ and $(\partial H^E / \partial P)_T$ are much higher for diethylene glycol dimethyl ether–1-propanol system than for diethylene glycol diethyl ether or diethylene glycol dibutyl ether. In general, the predictions of Flory's theory are not good, the values of $(\partial V_m^E / \partial T)_p$ for diethylene glycol dimethyl ether + 1-propanol is significantly more positive than predicted and, correspondingly, $(\partial H^E / \partial P)_T$ is much more negative.

6. Results and discussion

Figure 1 shows V_m^E data for three mixtures at 298.15 K. We have not reported the experimental data at 288.15 or 308.15 K as the curves are similar in nature. For each of the mixtures studied, the V_m^E values are negative over the whole mole fraction range and increase with increased temperature. The magnitude of V_m^E decreases at each temperature with increase of the alkyl chain end length in the molecule of the diethylene glycol dimethyl ether, and this becomes less negative with the rise in temperature. This behaviour is consistent with that of the V_m^E results of the mixtures of glymes¹⁴ with 1-propanol: a marked increase in V_m^E with all three temperatures is evident here and also V_m^E decreases in magnitude in the negative direction with increase in the polar head group of the glymes. This behaviour is obvious as the polarity of the polyether increases by increasing the alkyl chain end length, resulting in larger association between the polyether and alcohol molecule. This is very important with diethylene glycol dibutyl ether. It is suggested¹⁰ that intermolecular self-association of the polyethers is relatively weaker than that of 1-propanol. This may be due to the possible existence of dipole–dipole association in polyethers; which has no significant influence on the self-associated 1-propanol on mixing. Table 3 shows

Table 6. Equimolar values of the excess functions at 298.15 K.

$(\partial V_m^E/\partial T)_p \times 10^3$ ($\text{m}^3 \text{mol}^{-1} \text{K}^{-1}$)		$(\partial H^E/\partial P)_T \times 10^5$ ($\text{J mol}^{-1} \text{bar}^{-1}$)	
Exp.	Theor.	Exp.	Theor.
<i>Diethylene glycol dimethyl ether (1) + 1-propanol (2)*</i>			
2.915	3.433	-0.937	-1.092
<i>Diethylene glycol diethyl ether (1) + 1-propanol (2)</i>			
1.600	1.876	-0.801	-0.883
<i>Diethylene glycol dibutyl ether (1) + 1-propanol (2)</i>			
1.740	2.045	-0.883	-0.961

*From ref. [14]

that the viscosities of all these mixtures decrease with increasing temperatures. At any particular temperature, as x_1 increases, the h of diethylene glycol dimethyl ether and diethylene glycol diethyl ether decreases, whereas for diethylene glycol dibutyl ether it decreases and then increases. A further comparison of data at different temperature shows that the temperature coefficients $(\partial h/\partial T)_p$ decreases with increasing temperatures. The presence of minima for the lower range of x_1 gives an indication of specific interaction between diethylene glycol dibutyl ether and 1-propanol.

The deviations in viscosity (Δh) presented in figure 2 are negative over the entire composition range for all the systems at 298.15 K. This happens at all three temperatures. It can be observed^{42,43} that the magnitude of h , and Δh increase at each temperature as the alkyl group of the polyether increased. The positive Δh values are an indication of specific interactions,⁴⁴⁻⁴⁶ as corroborated by the negative V_m^E values shown in figure 1. In fact, we observe negative deviations in viscosity which regularly increase as the size or viscosity of the polyether is increased.^{42,43} This reveals that the strength of specific interaction is not the only factor influencing the viscosity deviation of liquid mixtures. The molecular size and shape of the components also play an equally important role.

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