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Temperature Dependence of the Volumetric Properties of Binary Mixtures Containing Polyethers and 1-Propanol

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Excess molar volumes (V_m^E) were measured at 288.15, 298.15, and 308.15 K and atmospheric pressure as a function of composition with a continuous dilution dilatometer for the binary mixtures of 1-propanol [$CH_3CH_2CH_2OH$] with glymes [$CH_3O(CH_2CH_2O)_mCH_3$, $m = 1, 2, 3,$ and 4]. With these results and other thermodynamic data from the literature, the following mixing quantities have been reported over the complete range of concentration or at equimolar concentration: α, volume expansivity; α^E, excess volume expansivity; $(\partial V_m^E/\partial T)_P$, and $(\partial H^E/\partial P)_T$ at 298.15 K. The Prigogine–Flory–Patterson theory (PFP) of liquid mixtures has been applied to estimate interaction, free-volume, and internal-pressure contributions to V_m^E and to estimate the different mixing quantities for the mixtures. The calculated values using the PFP theory were then compared at 298.15 K with the experimentally obtained results. The PFP theory predicts excess volume V_m^E values rather well, while the calculated value of $(\partial V_m^E/\partial T)_P$ and $(\partial H^E/\partial P)_T$ by using the Flory theory show general variation with the chain length of the glyme. The $(\partial V_m^E/\partial T)_P$ and $(\partial H^E/\partial P)_T$ show deviations between theoretical and experimental values that are slightly larger in systems with lower glyme.

KEY WORDS: binary mixtures; excess volume; polyethers; 1-propanol; temperature.

1. INTRODUCTION

As part of our systematic studies on thermodynamic, transport, and acoustic properties of mixtures containing polyethers, we have recently reported excess molar volumes, speeds of sound, and viscosities of binary mixtures of polyethers with dialkyl carbonates [1], chloroalkanes [2],

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and esters [3]. In this paper, we present the excess molar volumes V_m^E for mixtures containing 1-propanol ($CH_3CH_2CH_2OH$) with glymes [$CH_3O(CH_2CH_2O)_mCH_3$ [$m = 1$, monoglyme; $m = 4$, tetraglyme] at 288.15, 298.15, and 308.15 K and [$m = 2$, diglyme; $m = 3$, triglyme] at 288.15 and 308.15 K over the complete composition range. The excess molar volumes at 298.15 K for 1-propanol with diglyme and triglyme have been reported in our earlier paper [4]. From these results, the mixing properties like α, α^E, $(\partial V_m^E/\partial T)_P$, and $(\partial H^E/\partial P)_T$ are reported at 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

1-Propanol (SRL, Bombay, GC 99.5 mol%), monoglyme (Acros, USA, 99 mol%), and diglyme (Merck-Schuchardt, FRG, GC > 99 mol%) were dried and fractionally distilled [5, 6]. Triglyme (Acros, USA, 99 mol%) and tetraglyme (Acros, USA, 99 mol%) were used without further purification. Prior to measurements, however, all liquids were

Table I. Observed and Literature Values of ρ of Pure Liquid Components at Different Temperatures

		ρ (kg·m^{-3})	
Component	T (K)	Exptl.	Lit.
1-Propanol	288.15	807.34	807.4 [7]
	298.15	799.49	799.58 [8], 799.5 [9]
	308.15	791.29	791.4 [10]
Monoglyme	288.15	872.32	872.4 [11], 872.18 [12]
	298.15	862.60	862.62 [13]
	308.15	850.31	850.24 [14]
Diglyme	288.15	948.96	948.64 [12]
	298.15	938.97	938.97 [15], 939.05 [16], 939.9 [17]
	308.15	929.34	
Triglyme	288.15	990.42	990.31 [12]
	298.15	980.71	980.67 [12], 980.65 [8]
	308.15	970.86	971.18 [12]
Tetraglyme	288.15	1015.37	1014.96 [12]
	298.15	1006.28	1006.27 [18], 1006.2 [19]
	308.15	997.51	996.42 [12], 997.61 [14]

degassed and stored over molecular sieve. The purities of the liquids were checked by measuring and comparing the densities with their corresponding literature values [7–19] as shown in Table I. Densities (ρ) of pure solvents are measured with a single-arm pycnometer. The pycnometer was calibrated at the working temperatures with doubly distilled water. The sensitivity of the pycnometer corresponded to a precision in density of 1×10^{-3} kg·m^{-3}. The reproducibility of the density measurements was found to be within 3×10^{-2} kg·m^{-3}.

The excess molar volumes were measured using a continuous–dilution dilatometer similar to that described by Dickinson et al. [20]. The details pertaining to calibration, experimental setup, and operational procedures have been described previously [1, 21]. The measured excess molar volumes were reproducible to ± 0.003 cm^3·mol^{-1}. Each run covered just half of the mole fraction range, giving an overlap between the two runs. 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 [22]. All measurements were carried out in a well-stirred water bath at a temperature controlled to ± 0.01 K. The uncertainty in temperature of our controlling bath is ± 0.01 K and V_m^E values is ± 0.003 cm^3·mol^{-1}.

3. RESULTS AND DISCUSSION

Table II gives the experimental results of the excess molar volumes for all of the mixtures as a function of the mole fraction at atmospheric pressure and at 288.15, 298.15, and 308.15 K.

The excess molar volumes of the mixtures V_m^E were fitted to the Redlich–Kister polynomial equation [23]:

$$V_m^E = x_1 x_2 \sum_{i=1}^{n} A_i (x_1 - x_2)^{i-1} \tag{1}$$

Values of the coefficients A_i and standard deviations σ are summarized in Table III. For all mixtures, $(\sigma / V_m^E) < 0.003$, in accord with the precision attainable with the dilatometer used. Figure 1 shows the values found for experimental excess molar volumes together with the fitted curves calculated from Eq. (1).

The excess molar volumes, represented in the complete composition range in Fig. 1 and shown in Table II are negative for the four systems.

Table II. Excess Molar Volume (V_m^E) for Binary Mixtures at Various Temperatures

x_1	V_m^E ($cm^3 \cdot mol^{-1}$)	x_1	V_m^E ($cm^3 \cdot mol^{-1}$)	x_1	V_m^E ($cm^3 \cdot mol^{-1}$)
x_1 monoglyme + x_2 1-propanol					
288.15 K					
0.0360	−0.021	0.3577	−0.085	0.5308	−0.091
0.0872	−0.039	0.3959	−0.086	0.6012	−0.086
0.1482	−0.055	0.4055	−0.088	0.6993	−0.073
0.2062	−0.066	0.4413	−0.090	0.8008	−0.052
0.2576	−0.072	0.4500	−0.091	0.8999	−0.030
0.3024	−0.077	0.4760	−0.091	0.9602	−0.010
0.3253	−0.079	0.5028	−0.091		
298.15 K					
0.0073	−0.005	0.2947	−0.056	0.5037	−0.071
0.0267	−0.012	0.3222	−0.060	0.5231	−0.071
0.0349	−0.015	0.3310	−0.061	0.5325	−0.071
0.0560	−0.020	0.3401	−0.062	0.5600	−0.070
0.0917	−0.026	0.3633	−0.064	0.5868	−0.070
0.1067	−0.031	0.3863	−0.064	0.6512	−0.064
0.1268	−0.034	0.4126	−0.067	0.7317	−0.057
0.1643	−0.039	0.4282	−0.068	0.8269	−0.043
0.1944	−0.046	0.4616	−0.069	0.8964	−0.030
0.2356	−0.051	0.4830	−0.070	0.9689	−0.010
0.2598	−0.054				
308.15 K					
0.0262	−0.015	0.3473	−0.063	0.5100	−0.066
0.0558	−0.027	0.3598	−0.064	0.5378	−0.065
0.0977	−0.037	0.3849	−0.065	0.5447	−0.065
0.1693	−0.045	0.3955	−0.066	0.6074	−0.062
0.2254	−0.053	0.4076	−0.066	0.6717	−0.056
0.2826	−0.056	0.4434	−0.067	0.7441	−0.048
0.2958	−0.059	0.4557	−0.067	0.8270	−0.037
0.3145	−0.059	0.4840	−0.067	0.9115	−0.024
0.3380	−0.061	0.4903	−0.067	0.9697	−0.008
x_1 diglyme + x_2 1-propanol					
288.15 K					
0.0257	−0.015	0.2672	−0.085	0.4509	−0.092
0.0587	−0.033	0.2905	−0.087	0.4761	−0.091
0.0856	−0.043	0.2973	−0.088	0.5518	−0.087
0.1278	−0.056	0.3253	−0.089	0.6182	−0.081
0.1702	−0.070	0.3386	−0.090	0.7025	−0.069
0.2137	−0.079	0.3660	−0.093	0.8408	−0.046
0.2270	−0.081	0.3926	−0.094	0.9283	−0.020
0.2447	−0.083	0.4128	−0.094		
0.2589	−0.084	0.4169	−0.093		

Table II. *(Continued)*

x_1	V_m^E (cm^3·mol^{-1})	x_1	V_m^E (cm^3·mol^{-1})	x_1	V_m^E (cm^3·mol^{-1})
308.15 K					
0.0146	−0.007	0.2960	−0.043	0.5139	−0.029
0.0435	−0.013	0.3393	−0.041	0.5760	−0.027
0.0729	−0.020	0.3777	−0.040	0.6535	−0.025
0.1113	−0.026	0.4106	−0.038	0.7082	−0.021
0.1556	−0.032	0.4164	−0.037	0.7833	−0.017
0.1949	−0.037	0.4403	−0.036	0.9168	−0.004
0.2236	−0.041	0.4634	−0.033		
0.2721	−0.042	0.4624	−0.031		
x_1 triglyme + x_2 1-propanol					
288.15 K					
0.0282	−0.031	0.2660	−0.149	0.4843	−0.159
0.0550	−0.057	0.2800	−0.149	0.5442	−0.153
0.0844	−0.079	0.3013	−0.153	0.5936	−0.146
0.1245	−0.107	0.3033	−0.154	0.6394	−0.136
0.1805	−0.130	0.3270	−0.156	0.7070	−0.118
0.2031	−0.136	0.3476	−0.157	0.7746	−0.087
0.2288	−0.143	0.3713	−0.159	0.8504	−0.055
0.2478	−0.147	0.4042	−0.160	0.9061	−0.031
0.2590	−0.147	0.4533	−0.161	0.9442	−0.018
308.15 K					
0.0097	−0.010	0.2097	−0.101	0.4073	−0.121
0.0269	−0.021	0.2150	−0.103	0.4542	−0.119
0.0549	−0.039	0.2282	−0.106	0.5271	−0.110
0.0872	−0.058	0.2496	−0.109	0.5912	−0.099
0.1189	−0.074	0.2500	−0.110	0.6700	−0.086
0.1507	−0.088	0.2812	−0.113	0.7588	−0.070
0.1673	−0.091	0.2884	−0.114	0.8599	−0.042
0.1789	−0.095	0.3162	−0.116	0.9458	−0.014
0.1915	−0.098	0.3574	−0.119		
x_1 tetraglyme + x_2 1-propanol					
288.15 K					
0.0035	−0.013	0.2255	−0.208	0.4369	−0.212
0.0150	−0.030	0.2560	−0.211	0.4641	−0.206
0.0372	−0.067	0.2656	−0.213	0.5671	−0.183
0.0558	−0.099	0.2850	−0.215	0.6384	−0.155
0.0839	−0.124	0.3034	−0.217	0.7671	−0.102
0.1076	−0.144	0.3255	−0.218	0.8837	−0.046
0.1477	−0.174	0.3473	−0.219	0.9782	−0.005
0.1766	−0.185	0.3582	−0.219		
0.1873	−0.196	0.3982	−0.217		

Table II. *(Continued)*

x_1	V_m^E ($cm^3 \cdot mol^{-1}$)	x_1	V_m^E ($cm^3 \cdot mol^{-1}$)	x_1	V_m^E ($cm^3 \cdot mol^{-1}$)
		298.15 K			
0.0128	−0.021	0.2083	−0.191	0.4107	−0.208
0.0233	−0.039	0.2172	−0.192	0.4523	−0.206
0.0385	−0.066	0.2318	−0.196	0.4987	−0.202
0.0587	−0.100	0.2419	−0.196	0.5625	−0.188
0.0833	−0.128	0.2626	−0.199	0.6171	−0.165
0.1063	−0.143	0.2776	−0.202	0.6844	−0.142
0.1326	−0.155	0.2878	−0.203	0.7847	−0.101
0.1602	−0.175	0.3107	−0.205	0.9291	−0.032
0.1831	−0.181	0.3410	−0.208		
0.1887	−0.185	0.3843	−0.209		
		308.15 K			
0.0049	−0.012	0.1985	−0.180	0.4244	−0.192
0.0130	−0.029	0.2261	−0.185	0.4637	−0.187
0.0275	−0.052	0.2510	−0.187	0.4969	−0.178
0.0398	−0.071	0.2745	−0.190	0.5453	−0.165
0.0622	−0.100	0.2945	−0.193	0.6204	−0.147
0.0905	−0.132	0.3117	−0.193	0.6737	−0.136
0.1221	−0.153	0.3237	−0.194	0.7565	−0.104
0.1446	−0.166	0.3414	−0.194	0.8763	−0.058
0.1679	−0.175	0.3834	−0.194	0.9809	−0.014

Table III. Fitting Coefficients A_i and Standard Deviations $\sigma[V_m^E(cm^3 \cdot mol^{-1})]$ of Eq. (1) for Binary Mixtures at Various Temperatures

T (K)	A_1	A_2	A_3	A_4	A_5	σ
			monoglyme + 1-propanol			
288.15	−0.3666	−0.0087	−0.0750	0.1836	−0.1963	0.001
298.15	−0.2824	−0.0251	0.0387	0.0482	−0.1672	0.001
308.15	−0.2682	0.0219	−0.0675	0.0892	−0.3018	0.001
			diglyme + 1-propanol			
288.15	−0.3619	0.0988	−0.1090	0.0542		0.001
308.15	−0.1286	0.1272	−0.0967	0.0114		0.002
			triglyme + 1-propanol			
288.15	−0.6309	0.1488	−0.0983	0.3932		0.001
308.15	−0.4517	0.1911	−0.1122	0.0851		0.001
			tetraglyme + 1-propanol			
288.15	−0.8020	0.4440	−0.1160	0.4123	−0.2977	0.003
298.15	−0.7975	0.3307	−0.0161	0.4743	−0.5152	0.003
308.15	−0.7162	0.3536	−0.1253	0.3891	−0.6138	0.002

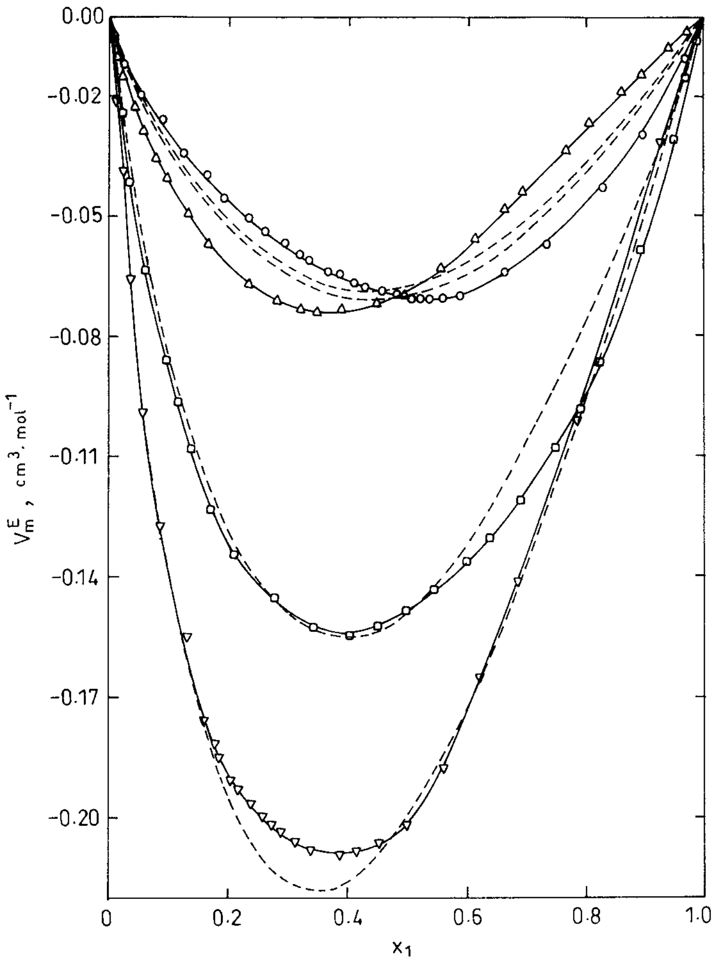

Fig. 1. Excess molar volumes for $x_1\,CH_3O(CH_2CH_2O)CH_3 + x_2\,CH_3CH_2CH_2OH$ at 298.15 K (○); $x_1\,CH_3O(CH_2CH_2O)_2CH_3 + x_2\,CH_3CH_2CH_2OH$ at 298.15 K (△); $x_1\,CH_3O(CH_2CH_2O)_3CH_3 + x_2\,CH_3CH_2CH_2OH$ at 298.15 K (□); and $x_1\,CH_3O(CH_2CH_2O)_4CH_3 + x_2\,CH_3CH_2CH_2OH$ at 298.15 K (▽). Continuous curves were calculated from Eq. (1) for experimental data and dotted curves from Flory theory.

Figure 2 shows how the V_m^E's at equimolar composition vary with the length of the glyme chain: the excess molar volumes increase from monoglyme to diglyme and then decrease. It can also be observed that, as the temperature increases, the excess molar volumes also increase, arranged in the sequence as diglyme > monoglyme > triglyme > tetraglyme.

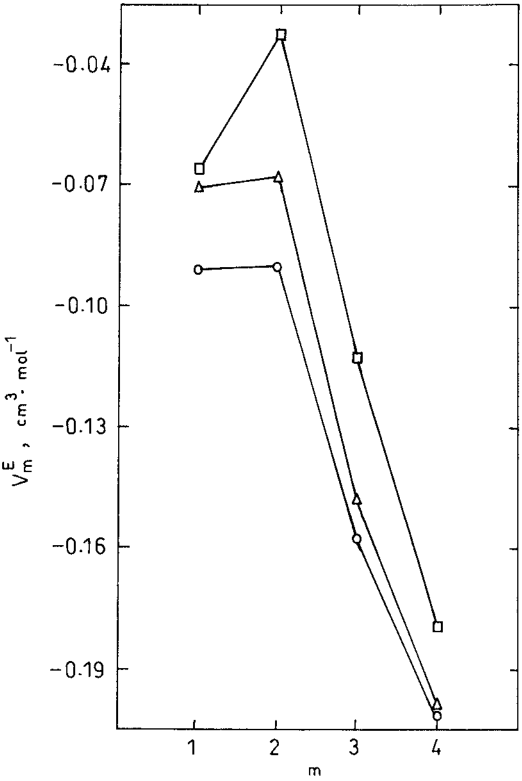

Fig. 2. Excess molar volume V_m^E at $x_1 = 0.5$ for $x_1\,CH_3O(CH_2CH_2O)_mCH_3 + x_2\,CH_3CH_2CH_2OH$, (○) 288.15 K, (△) 298.15 K, (□) 308.15 K.

The values of volume or thermal expansion coefficients α of the mixture at a particular composition were calculated for our systems by adding the contributions of the expansivities of each component in the mixtures:

$$\alpha = (1/V_m)\left[\sum (M_i x_i/\rho_i)\,\alpha_i + (\partial V_m^E/\partial T)_{p,x}\right] \tag{2}$$

where ρ_i and α_i are the density and the expansivity of pure component i at any particular temperature, and V_m $(= \sum x_i V_i)$ is the molar volume of the mixture. In Fig. 3, the α plots are shown for different mixtures at 298.15 K. A sharp increase in α is shown by the monoglyme-1-propanol system as the concentration of glyme increases. But the α values decrease for triglyme

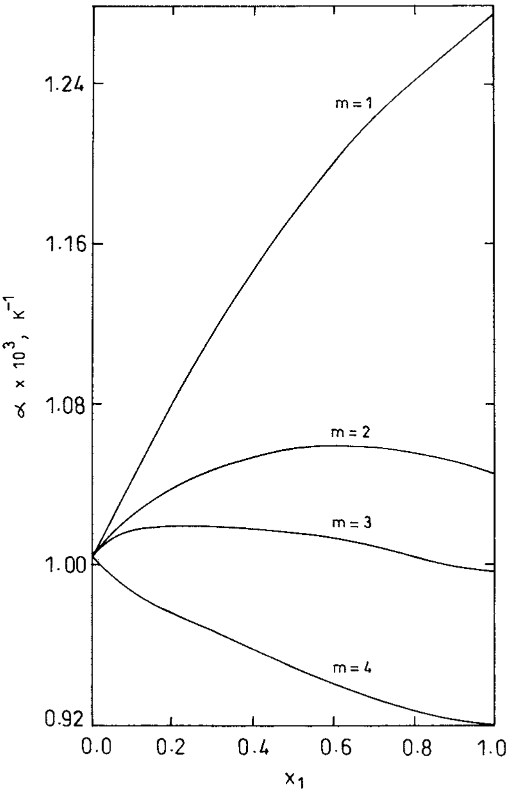

Fig. 3. Isobaric thermal expansivities α at 298.15 K for $x_1\,CH_3O(CH_2CH_2O)_mCH_3 + x_2\,CH_3CH_2CH_2OH$.

and tetraglyme and slowly increase for diglyme over the whole composition range.

4. THEORETICAL ANALYSIS

The Prigogine–Flory–Patterson [24–26] theory has been commonly employed to analyze excess thermodynamic functions. V_m^E can be separated into three factors: (i) an interaction contribution $V_m^E(H_m^E)$, (ii) a free volume contribution $V_m^E(f_v)$, and (iii) an internal pressure contribution $V_m^E(P^*)$. According to Patterson and Delmas [24], these can be expressed as

$$V_{\mathrm{m}}^{\mathrm{E}}(H_{\mathrm{m}}^{\mathrm{E}}) = \frac{V_{\mathrm{m}}(\tilde{v}^{1/3}-1)\,\tilde{v}^{2/3}}{[(4/3)\,\tilde{v}^{1/3}-1]}\psi_1\theta_2(\chi_{12}/P_1^*) \qquad \text{(interaction term)} \qquad (3)$$

$$V_{\mathrm{m}}^{\mathrm{E}}(f_{\mathrm{v}}) = -\frac{V_{\mathrm{m}}(\tilde{v}_1-\tilde{v}_2)^2\,[(14/9)\,\tilde{v}^{-1/3}-1]}{[(4/3)\,\tilde{v}^{1/3}-1]}\psi_1\psi_2 \qquad \text{(free volume term)} \qquad (4)$$

$$V_{\mathrm{m}}^{\mathrm{E}}(P^*) = \frac{V_{\mathrm{m}}(\tilde{v}_1-\tilde{v}_2)^2\,(P_1^*-P_2^*)}{P_1^*\psi_2+P_2^*\psi_1}\psi_1\psi_2 \qquad \text{(internal pressure term)} \qquad (5)$$

$$V_{\mathrm{m}}^{\mathrm{E}} = V_{\mathrm{m}}^{\mathrm{E}}(H_{\mathrm{m}}^{\mathrm{E}}) + V_{\mathrm{m}}^{\mathrm{E}}(f_{\mathrm{v}}) + V_{\mathrm{m}}^{\mathrm{E}}(P^*) \qquad (6)$$

ψ represents the contact energy fraction given by:

$$\psi_1 = 1-\psi_2 = \frac{\varphi_1 P_1^*}{\varphi_1 P_1^* + \varphi_2 P_2^*} \qquad (7)$$

Basically this theory has been formulated by Flory et al. [27]; it contains the relevant ideas conceived by Prigogine et al. [26, 28] and was later extended by Patterson et al. [29]. According to Flory's statistical theory, the reduced equation of state is given by

$$\tilde{P}\tilde{v}/\tilde{T} = [\tilde{v}^{1/3}/(\tilde{v}^{1/3}-1)] - 1/(\tilde{v}T) \qquad (8)$$

where

$$\tilde{v} = V/V^* = [(1+(4/3\alpha T))/(1+\alpha T)]^3 \qquad (9)$$

$$\tilde{P} = P/P^* = P/[(\alpha T\tilde{v}^2)/\kappa_T] \qquad (10)$$

$$\tilde{T} = T/T^* = (\tilde{v}^{1/3}-1)/\tilde{v}^{4/3} \qquad (11)$$

The parameter χ_{12} was obtained by employing the Marquardt algorithm [30] in an optimization procedure, using all experimental $V_{\mathrm{m}}^{\mathrm{E}}$ data at 298.15 K over the complete concentration range. The resulting χ_{12} was used to calculate $V_{\mathrm{m}}^{\mathrm{E}}$. Much better fits of $V_{\mathrm{m}}^{\mathrm{E}}$ were obtained when χ_{12} was treated as an adjustable parameter. The various parameters involved in Flory's theory for the pure components are given in Table IV along with the literature [5, 12, 31–33] values. The values of the contact interaction parameter χ_{12} together with the terms $V_{\mathrm{m}}^{\mathrm{E}}(f_{\mathrm{v}})$, $V_{\mathrm{m}}^{\mathrm{E}}(P^*)$, and $V_{\mathrm{m}}^{\mathrm{E}}(H_{\mathrm{m}}^{\mathrm{E}})$ for each mixture are given in Table V.

Table IV. Flory and Related Parameters of Pure Components at 298.15 K

Component	$\alpha \times 10^3$ (K^{-1})	u $(m \cdot s^{-1})$	$C_{p,m}$ $(J \cdot K^{-1} \cdot mol^{-1})$	κ_T (TPa^{-1})	V^*_m $(cm^3 \cdot mol^{-1})$	$P^* \times 10^{-6}$ $(J \cdot cm^{-3})$	T^* (K^{-1})	$\tilde{v}$	$\tilde{T}$
1-Propanol	1.004	1204.6[31]	144.10[33]	1019	60.21	458	5222	1.2485	0.0571
Monoglyme	1.276	1165.3[32]	193.3[5]	1116	80.26	578	4615	1.3017	0.0646
Diglyme	1.045	1280.1[31]	279.58[12]	816	113.69	603	5105	1.2569	0.0584
Triglyme	0.997	1341.5[32]	367.60[a]	713	145.73	648	5240	1.2471	0.0569
Tetraglyme	0.922	1382.4[31]	458.42[12]	642	179.37	649	5481	1.2315	0.0544

[a] Calculated from group additivity.

Theoretical dV^E_m/dT [34] values at 298.15 K were calculated from the Flory theory using

$$T(dV^E_m/dT) = \left[\sum_{i=1}^{2} x_i V^*_i [\tilde{T}(d\tilde{v}/d\tilde{T})] - \left(\sum_{i=1}^{2} x_i V^*_i [\tilde{T}(d\tilde{v}/d\tilde{T})]_i \right) \right] \tag{12}$$

where

$$\tilde{T}(d\tilde{v}/d\tilde{T}) = \tilde{v}(1 - \tilde{v}^{-1/3}) / [(4/3)\, \tilde{v}^{-1/3} - 1] \tag{13}$$

In Table V, the interaction term $V^E_m(H^E_m)$, which is proportional to χ_{12}, is negative for all the systems. The free volume term $V^E_m(f_v)$ is proportional to $-(\tilde{v}_1 - \tilde{v}_2)^2$, and it decreases from monoglyme to triglyme and then increases as the difference between the reduced volume v of two components in the mixture increases. The internal pressure term $V^E_m(P^*)$ is proportional to $(\tilde{v}_1 - \tilde{v}_2)^2 (P^*_1 - P^*_2)$. $V^E_m(P^*)$ may be positive or negative depending upon the relative cohesive energy of the expanded and less expanded component. The $V^E_m(P^*)$ term is positive for monoglyme and diglyme and negative for triglyme and tetraglyme. The V^E_m values have been

Table V. Calculated Values of Three Contributions to the Excess Molar Volume from the Prigogine–Flory–Patterson Theory for Glymes + 1-Propanol Mixtures at 298.15 K

1-Propanol +	$\chi_{12} \times 10^{-2}$ $(J \cdot cm^{-3})$	Calculated contribution $V^E_m(H^E_m)$	$V^E_m(f_v) \times 10^2$	$V^E_m(P^*)$
monoglyme	−0.1387	−0.2097	6.8848	0.2079
diglyme	−0.0733	−0.1169	0.1987	4.5230
triglyme	−0.0845	−0.1431	0.0062	−1.0590
tetraglyme	−0.0414	−6.9080	0.8074	−0.1222

calculated, theoretically, over the entire range of composition. They have been compared with the experimental results at 298.15 K as in Fig. 1, which demonstrate that the PFP theory is quite successful in predicting the trend of dependence on composition of V_m^E for the present mixtures.

The excess function $(\partial V_\mathrm{m}^\mathrm{E}/\partial T)_p$ was computed by analytical differentiation of Eq. (1) at 298.15 K for each mixture. From $(\partial V_\mathrm{m}^\mathrm{E}/\partial T)_p$ and V_m^E of this work, we have also obtained $(\partial H^\mathrm{E}/\partial P)_p$ at zero pressure according to the equation,

$$(\partial H^\mathrm{E}/\partial P)_T = V_\mathrm{m}^\mathrm{E} - T(\partial V_\mathrm{m}^\mathrm{E}/\partial T)_p \tag{14}$$

Equimolar mixture values of $(\partial V_\mathrm{m}^\mathrm{E}/\partial T)_p$, $(\partial H^\mathrm{E}/\partial P)_T$, and α^E are reported in Table VI. The values obtained for $(\partial V_\mathrm{m}^\mathrm{E}/\partial T)_p$, shown in Fig. 4, are positive for all the systems, and are in agreement with the values of V_m^E of Fig. 2. The values of $(\partial H^\mathrm{E}/\partial P)_T$, shown in Fig. 5, are negative over all ranges of concentration, for all glyme systems. The curves of $(\partial V_\mathrm{m}^\mathrm{E}/\partial T)_p$ and $(\partial H^\mathrm{E}/\partial P)_T$ have similar variation with m but with opposite sign.

The calculation made from the application of the Flory theory (Fig. 4) for $(\partial V_\mathrm{m}^\mathrm{E}/\partial T)_p$ shows that the absolute values are substantially greater than those obtained from the experimental data. The maximum deviation in $(\partial V_\mathrm{m}^\mathrm{E}/\partial T)_p$ between experimental and theoretical values in the diglyme–1-propanol system can be explained by the correlation of molecular orientations proposed by Patterson et al. [35] that are present in

Table VI. Equimolar Values of the Excess Functions at 298.15 K

$(\partial V_\mathrm{m}^\mathrm{E}/\partial T)_p$ ($\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}$)		$(\partial H_\mathrm{m}^\mathrm{E}/\partial P)_T \times 10$ ($\mathrm{J \cdot mol^{-1} \cdot bar^{-1}}$)		
Exptl.	Theor.	Exptl.	Theor.	$\alpha^\mathrm{E} \times 10^5$ ($\mathrm{K^{-1}}$)
		monoglyme + 1-propanol		
1.230	1.671	−0.437	−0.569	1.38
		diglyme + 1-propanol		
2.915	3.433	−0.937	−1.092	2.71
		triglyme + 1-propanol		
2.240	2.431	−0.816	−0.873	1.69
		tetraglyme + 1-propano		
1.075	1.368	−0.520	−0.608	0.72

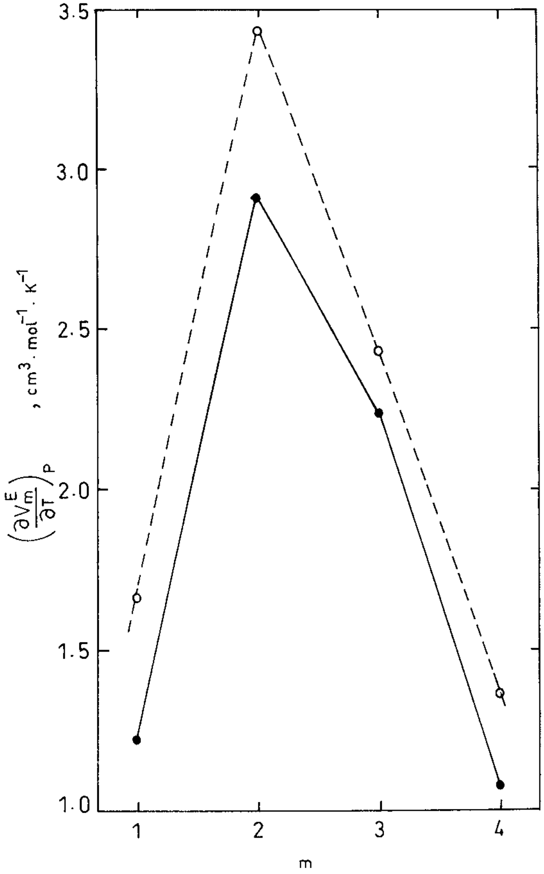

Fig. 4. Values of $(\partial V_m^E/\partial T)_p$ for 1-propanol with glymes at equimolar composition: ●, experimental values; ○, theoretical values at 298.15 K.

diglyme. The correlations of molecular orientations (CMO) increase initially and then decrease with the length of the glyme chain, and when the pure glymes are mixed, the CMO are destroyed, causing a negative contribution to $(\partial H^E/\partial P)_T$ and positive to $(\partial V_m^E/\partial T)_p$. This is very important with the diglyme + 1-propanol system. The values of α^E have the same sign as $(\partial V_m^E/\partial T)_p$ for all these mixtures. Furthermore, the magnitudes of $(\partial V_m^E/\partial T)_p$ and α^E are largely dependent on the size and type of component molecule.

The mixing quantities $(\partial V_m^E/\partial T)_p$ and $(\partial H^E/\partial P)_T$ are good indicators of order [36–38]. The deviations between experimental and calculated

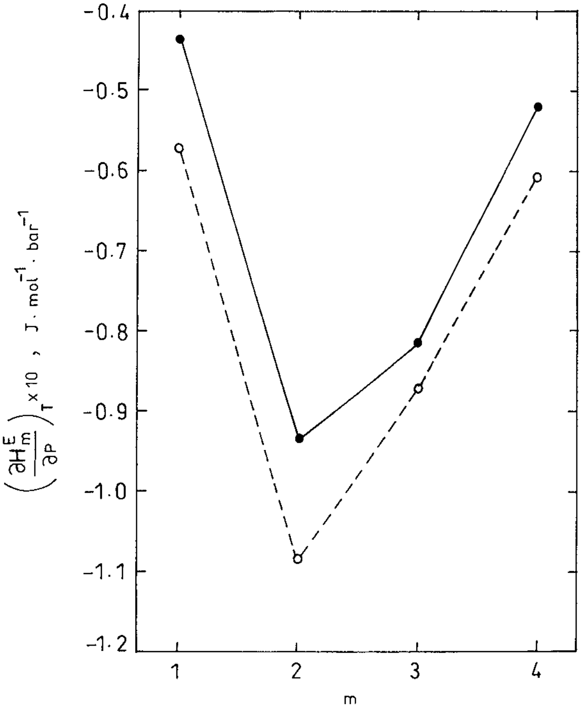

Fig. 5. Values of $(\partial H_m^E/\partial P)_T$ for 1-propanol with glymes at equimolar composition: ●, experimental values; ○, theoretical values at 298.15 K.

values of $(\partial V_m^E/\partial T)_p$ and $(\partial H^E/\partial P)_T$ are much larger for the diglyme—1-propanol system than for monoglyme, triglyme, or tetraglyme. It means that the diglyme + 1-propanol system acts to break the correlations of molecular orientations. This is expected to be larger than for other glyme + 1-propanol systems. In general, the predictions of Flory's theory are not good; $(\partial V_m^E/\partial T)_p$ for diglyme + 1-propanol is strikingly more positive than predicted and, correspondingly, $(\partial H^E/\partial P)_T$ is much more negative. Both of these discrepancies are expected in view of the orientational order in diglyme. Indeed, this order decreases with an increase of temperature. In this case, the thermal expansion coefficient of the ordered component is expected to be increased (Fig. 3) compared with that of the solution, and α^E becomes positive and $(\partial H^E/\partial P)_T$ negative compared with Flory's theory which ignores orientational order. An analysis of the results shows that orientational order has a small but important effect on α. We again conclude that a nonrigid linear molecule, like diglyme, acts to break the order when mixed with 1-propanol.

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