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Excess Molar Volumes and Viscosities of Mixtures of Diethylene Glycol Dibutyl Ether with Dialkyl Carbonates at 298.15, 308.15, and 318.15 K

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Excess molar volumes, V_m^E, and viscosities, η, were measured as a function of composition for the binary mixtures of diethylene glycol dibutyl ether + dimethyl carbonate, + diethyl carbonate, and + propylene carbonate at temperatures of 298.15, 308.15, and 318.15 K and atmospheric pressure over the whole range of mixture compositions. From the experimental results, deviations in the viscosity, $\Delta \ln \eta$, and excess free energies of activation of viscous flow, ΔG^{*E}, were calculated. The experimental results were correlated using the Redlich–Kister equation. The experimental and calculated quantities were used to analyze the mixing behavior of the components. Furthermore, activation enthalpies, ΔH^*, and entropies, ΔS^*, of viscous flow were evaluated and their variation with concentration is discussed.

KEY WORDS: binary mixtures; dialkyl carbonates; excess volume; polyethers; temperature; viscosity.

1. INTRODUCTION

This is a part of our systematic research program concerning the experimental study of several thermodynamic and transport properties of mixtures of polyethers with esters of carbonic acids [1–4]. In a continuation of these investigations, the present paper reports the experimental excess molar volumes, V_m^E, and viscosities, η, at 298.15, 308.15, and 318.15 K and atmospheric pressure for binary mixtures of diethylene glycol dibutyl ether

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with dimethyl carbonate, with diethyl carbonate, and with propylene carbonate over the complete composition range. Our primary interest was to compare the excess molar volumes of three types of systems (diethylene glycol dimethyl ether + dialkyl carbonates [1], diethylene glycol diethyl ether + dialkyl carbonates [2], and diethylene glycol dibutyl ether + dialkyl carbonates). We were also interested in comparing the excess molar volumes of diethylene glycol dibutyl ether + dialkyl carbonates with those of our previous results for triethylene glycol dimethyl ether + dialkyl carbonates [3], tetraethylene glycol dimethyl ether + dialkyl carbonates [4], and *n*-alkoxyethanols + dialkyl carbonates [5]. To our knowledge, data for the systems in this study are not available in the literature.

2. EXPERIMENTAL

Dimethyl carbonate (Sisco-Chem, Bombay; extrapure, 99 mol%), diethyl carbonate (Sisco-Chem; pure, 99 mol%), and propylene carbonate (Merck-Schuchardt, FRG; $GC_{min} > 99$ mol%) were the same as those used in earlier studies [5]. Diethylene glycol dibutyl ether (Merck-Schuchardt; GC > 98 mol%) was dried over $FeSO_4$ (A.R., BDH) and then fractionally distilled under reduced nitrogen gas pressure. Prior to actual measurements, all liquids were stored in contact with 4 Å molecular sieves to reduce the water content and were partially degassed under vacuum. The purity of the liquids was checked by measuring and comparing the density and viscosity at 298.15 ± 0.01 K and atmospheric pressure with the corresponding literature values as shown in Table I. The densities of the pure components

Table I. Comparison of Experimental Data with Literature Data for Pure Liquids at 298.15 K

	$\rho \times 10^{-3}$ (kg · m^3)		η (mPa · s)	
Component	Exptl.	Lit.	Exptl.	Lit.
Diethylene glycol dibutyl ether	0.8785	0.87830[6]	2.160	
Dimethyl carbonate	1.0632	1.06331[8] 1.06339[9]	0.589	
Diethyl carbonate	0.9690	0.96925[8] 0.96905[9] 0.96926[10]	0.749	
Propylene carbonate	1.1988	1.1978[11] 1.19957[12] 1.1998[13] 1.19883[15]	2.550	2.530[7] 2.51[14] 2.4711[15]

were measured with a bicapillary pycnometer that gave an uncertainty of 5 parts in 10^5.

The measurements of excess molar volumes were carried out with a continuous dilution dilatometer similar to that described by Dickinson et al. [16]. Details of its calibration, experimental setup, and operational procedures have been reported previously [17, 18]. The dilatometer was clamped vertically into the water bath. Readings of the reference marks and those of liquid levels filling the dilatometer were performed with a cathetometer that could be read to within an uncertainty of 0.001 cm. Before the start of experimental measurements on diethylene glycol dibutyl ether + dialkyl carbonates, the mixture benzene + cyclohexane was used to check the performance of the dilatometer. The overall uncertainty of the excess molar volume measurements is dependent on the uncertainty in the measurement of the capillary diameter, in the measurements of the difference in the heights (initial and final levels of mercury), in the measurement of the weight of the syringe (before and after the injection of component 1), and in the measurement of the difference in cathetometer readings of the tube (before and after the addition of component 2) and the change in height of the mercury level in the capillary; these uncertainties are of the order of 2×10^{-5}, 3×10^{-3}, 1×10^{-4}, and 2×10^{-5}, respectively. Thus, the excess molar volumes are accurate to within $\pm 0.003 \times 10^{-6}\ \mathrm{m}^3 \cdot \mathrm{mol}^{-1}$. Each run covered just over half of the mole fraction range, giving an overlap between two runs.

The kinematic viscosities ($\nu = \eta/\rho$) of the pure liquids and their mixtures were measured at 298.15, 308.15, and 318.15 K and atmospheric pressure using an Ubbelohde suspended-level viscometer [19]. The viscometer was calibrated so as to determine the two constants A and B in the equation $\eta/\rho = At - (B/t)$, obtained by measuring the flow time with triply distilled water and twice-distilled ethyl acetate [2, 20, 21]. The details of the apparatus and procedure have been reported previously [22, 23]. The viscometer is filled with a pure liquid or liquid mixtures, and its limbs are closed with Teflon caps, taking precaution to minimize the evaporation losses. The flow time measurements were made using an electronic stopwatch with a precision of ± 0.01 s. An average of four or five sets of flow times for each liquid was taken for determination of the viscosity. The caps of the limbs were removed during the measurements of flow time. The measured values of kinematic viscosities were converted to dynamic viscosities (η) after multiplication by the density. The overall uncertainty of the viscosity measurements is dependent on the equilibrium stability of the viscometer, the time of flow, and the change of concentration, which are of the order of 1×10^{-2}, 1×10^{-2}, and 3×10^{-4}, respectively. The reproducibility of the viscosity results was found to be within $\pm 0.003\ \mathrm{mPa} \cdot \mathrm{s}$. The mole fraction of each mixture was obtained to an uncertainty of 10^{-4} from the measured apparent masses of the components. All apparent masses were corrected for buoyancy. All molar quantities were based on the relative atomic mass table of 1986 issued by IUPAC [24]. All the measurements were carried out in a thermostat-controlled, well-stirred water bath, whose temperature was controlled to ± 0.01 K.

3. RESULTS AND DISCUSSION

The experimental results on the excess molar volumes and viscosities of the different binary mixtures as a function of the mole fractions at atmospheric pressure and at 298.15, 308.15, and 318.15 K are reported in Tables II and III. The measured viscosities were fitted to a polynomial of the type

$$\eta = \sum_{i=0}^{n} a_i x_1^i \tag{1}$$

by the method of least squares, with each point weighted equally. The values of the coefficients a_i and standard deviations σ are summarized in Table IVa. From the experimental values of the excess molar volume, the densities of the liquid mixtures were calculated using the following equation:

$$\rho = (x_1 M_1 + x_2 M_2)/(V_m^E + x_1 V_1^0 + x_2 V_2^0) \tag{2}$$

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

x_1	$V_m^E \times 10^6$ $(m^3 \cdot mol^{-1})$	x_1	$V_m^E \times 10^6$ $(m^3 \cdot mol^{-1})$	x_1	$V_m^E \times 10^6$ $(m^3 \cdot mol^{-1})$
Diethylene glycol dibutyl ether (1) + dimethyl carbonate (2)					
298.15 K					
0.0033	0.006	0.2293	0.188	0.4659	0.208
0.0105	0.017	0.2529	0.194	0.5180	0.200
0.0180	0.025	0.2670	0.199	0.5884	0.184
0.0380	0.049	0.2876	0.206	0.6654	0.162
0.0717	0.084	0.2913	0.205	0.7326	0.140
0.1030	0.117	0.3024	0.210	0.7720	0.120
0.1297	0.142	0.3154	0.207	0.8304	0.087
0.1610	0.159	0.3399	0.212	0.8764	0.066
0.1832	0.169	0.3801	0.213	0.9220	0.046
0.2009	0.178	0.4159	0.212		

Table II. *(Continued)*

x_1	$V_m^E \times 10^6$ ($m^3 \cdot mol^{-1}$)	x_1	$V_m^E \times 10^6$ ($m^3 \cdot mol^{-1}$)	x_1	$V_m^E \times 10^6$ ($m^3 \cdot mol^{-1}$)
308.15 K					
0.0177	0.028	0.2465	0.214	0.5098	0.220
0.0572	0.078	0.2558	0.216	0.5920	0.197
0.0839	0.109	0.2815	0.221	0.6502	0.175
0.1163	0.142	0.2936	0.226	0.6947	0.158
0.1447	0.165	0.3195	0.230	0.7440	0.137
0.1717	0.180	0.3474	0.231	0.8121	0.102
0.1924	0.191	0.3594	0.233	0.8475	0.081
0.1987	0.196	0.4126	0.234	0.9162	0.056
0.2173	0.200	0.4763	0.229	0.9396	0.035
318.15 K					
0.0035	0.004	0.2012	0.218	0.3652	0.259
0.0149	0.024	0.2250	0.226	0.4165	0.256
0.0336	0.059	0.2304	0.229	0.5059	0.240
0.0504	0.083	0.2516	0.241	0.6092	0.210
0.0707	0.110	0.2695	0.244	0.6971	0.167
0.0933	0.135	0.2777	0.245	0.7768	0.132
0.1237	0.162	0.3026	0.251	0.8958	0.068
0.1559	0.193	0.3189	0.256	0.9636	0.023
0.1902	0.214	0.3630	0.255		
Diethylene glycol dibutyl ether (1) + diethyl carbonate (2)					
298.15 K					
0.0076	−0.004	0.3400	−0.028	0.6456	−0.027
0.0150	−0.006	0.3574	−0.028	0.6959	−0.025
0.0266	−0.007	0.3833	−0.029	0.7398	−0.023
0.0517	−0.009	0.3911	−0.029	0.7836	−0.019
0.0957	−0.010	0.3967	−0.028	0.8071	−0.018
0.1379	−0.016	0.4133	−0.030	0.8487	−0.013
0.1771	−0.019	0.4376	−0.028	0.8952	−0.008
0.2161	−0.022	0.4573	−0.030	0.9034	−0.008
0.2475	−0.024	0.4824	−0.028	0.9589	−0.003
0.2582	−0.024	0.5280	−0.030	0.9709	−0.002
0.2842	−0.026	0.5441	−0.028		
0.3070	−0.026	0.6159	−0.029		
308.15 K					
0.0154	−0.005	0.2638	−0.036	0.5705	−0.042
0.0293	−0.008	0.2846	−0.038	0.6633	−0.041
0.0597	−0.012	0.3206	−0.040	0.7369	−0.034
0.0998	−0.018	0.3457	−0.040	0.8036	−0.026
0.1521	−0.025	0.3706	−0.041	0.8891	−0.016
0.2056	−0.030	0.4322	−0.043	0.9411	−0.008
0.2420	−0.034	0.4964	−0.044		

Table II. *(Continued)*

x_1	$V_{\mathrm{m}}^{\mathrm{E}} \times 10^6$ $(\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$	x_1	$V_{\mathrm{m}}^{\mathrm{E}} \times 10^6$ $(\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$	x_1	$V_{\mathrm{m}}^{\mathrm{E}} \times 10^6$ $(\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$
318.15 K					
0.0236	−0.005	0.4055	−0.054	0.6626	−0.052
0.0477	−0.011	0.4107	−0.056	0.6912	−0.048
0.0913	−0.022	0.4310	−0.056	0.7370	−0.044
0.1448	−0.029	0.4727	−0.060	0.8025	−0.036
0.2030	−0.037	0.4789	−0.059	0.8400	−0.030
0.2565	−0.044	0.5170	−0.057	0.9107	−0.019
0.3047	−0.049	0.5291	−0.060	0.9734	−0.005
0.3397	−0.050	0.5702	−0.057		
0.3551	−0.052	0.6262	−0.054		
Diethylene glycol dibutyl ether (1) + propylene carbonate (2)					
298.15 K					
0.0035	−0.009	0.1920	−0.398	0.3887	−0.604
0.0093	−0.025	0.2076	−0.424	0.4656	−0.632
0.0188	−0.052	0.2088	−0.425	0.5609	−0.646
0.0385	−0.105	0.2403	−0.463	0.6816	−0.586
0.0624	−0.157	0.2420	−0.468	0.7333	−0.540
0.1041	−0.252	0.2726	−0.500	0.8418	−0.397
0.1293	−0.298	0.2809	−0.510	0.8935	−0.289
0.1598	−0.355	0.2941	−0.526	0.9359	−0.187
0.1735	−0.368	0.3134	−0.550	0.9762	−0.074
0.1795	−0.385	0.3224	−0.552		
308.15 K					
0.0139	−0.035	0.2360	−0.497	0.5562	−0.726
0.0279	−0.073	0.2663	−0.537	0.5986	−0.715
0.0541	−0.137	0.2758	−0.550	0.6537	−0.682
0.1035	−0.250	0.2885	−0.565	0.7214	−0.618
0.1433	−0.329	0.3189	−0.607	0.7896	−0.521
0.1763	−0.393	0.3394	−0.625	0.8584	−0.386
0.1883	−0.416	0.3857	−0.670	0.9188	−0.243
0.2031	−0.445	0.4497	−0.708	0.9638	−0.115
0.2314	−0.492	0.5051	−0.722		
318.15 K					
0.0219	−0.067	0.2462	−0.555	0.5523	−0.790
0.0446	−0.133	0.2842	−0.609	0.6206	−0.771
0.0735	−0.206	0.3024	−0.631	0.6959	−0.713
0.1031	−0.284	0.3323	−0.674	0.7706	0.623
0.1251	−0.333	0.3529	−0.685	0.8875	−0.380
0.1716	−0.430	0.3678	−0.706	0.9798	−0.080
0.2141	−0.505	0.4194	−0.746		
0.2441	−0.553	0.4815	−0.775		

where x_1 and x_2 are the mole fractions, M_1 and M_2 are the molar masses, and V_1^0 and V_2^0 are the molar volumes of pure components 1 and 2, respectively.

The deviations in viscosity $\Delta \ln \eta$ from linear dependence on the mole fraction average were calculated from the following relation:

$$\Delta \ln \eta = \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \tag{3}$$

where η is the dynamic viscosity of the mixtures and η_1 and η_2 are the viscosities of components 1 and 2.

On the basis of the theory of reaction rate [25], the excess energies of activation ΔG^{*E} for viscous flow can be calculated from the expression

$$\Delta G^{*E} = RT[\ln \eta V - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2] \tag{4}$$

where V is the molar volume of the mixture and RT is the usual energy term. Data for derived densities, viscosities, and energies of activation for viscous flow for the different binary mixtures at different temperatures are given in Table III.

The values of V_m^E, $\Delta \ln \eta$, and ΔG^{*E} for each mixture were fitted to the Redlich–Kister polynomial equation [26]:

$$Y(x) = x_1 x_2 \sum_{i=0}^{n} a_i (x_1 - x_2)^i \tag{5}$$

In each case, the optimum number of coefficients a_i was determined from an examination of the variation of the standard deviation:

$$\sigma(Y(x)) = \left[\sum (Y(x)_{\text{cal.}} - Y(x)_{\text{obs.}})^2 / (k - n) \right]^{1/2} \tag{6}$$

where k is the total number of experimental values and n is the number of parameters.

The values of coefficients a_i and standard deviations σ are summarized in Table IVb. $Y(x)$ stands for V_m^E, $\Delta \ln \eta$, or ΔG^{*E}. For all the mixtures $\sigma(V_m^E) \leqslant 0.003$, which is consistent with the precision attainable with the dilatometer.

From Figs. 1 and 2, it can be seen that mixtures containing dimethyl carbonate have positive V_m^E values, while those with propylene carbonate or diethyl carbonate have negative V_m^E values. The negative values of V_m^E can be explained by considering the chemical or specific interaction which may have resulted from differences in molecular and free volumes [28] and possible dipole–dipole interactions leading to weak complex formation.

Table III. Viscosities on Mixing for the Binary Mixtures Diethylene Glycol Dibutyl Ether (1) + Dimethyl Carbonate, + Diethyl Carbonate, or + Propylene Carbonate (2) at Temperatures of 298.15, 308.15, and 318.15 K

	ρ (kg · m^3)			η (mPa · s)			ΔG^{*E} (J · mol^{-1})		
x_1	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
				Diethylene glycol dibutyl ether (1) + dimethyl carbonate (2)					
0.0000	1.0632	1.0508	1.0377	0.589	0.520	0.472			
0.0176	1.0539	1.0418	1.0290	0.616	0.546	0.488	89	105	74
0.0289	1.0482	1.0364	1.0236	0.635	0.562	0.498	152	167	122
0.0543	1.0362	1.0249	1.0125	0.678	0.599	0.523	279	300	223
0.0894	1.0214	1.0107	0.9986	0.743	0.650	0.560	446	456	360
0.1574	0.9970	0.9873	0.9758	0.862	0.747	0.634	677	683	581
0.2414	0.9730	0.9642	0.9532	1.012	0.867	0.726	873	870	768
0.3274	0.9535	0.9452	0.9347	1.169	0.991	0.820	989	981	878
0.3389	0.9512	0.9430	0.9326	1.189	1.005	0.830	998	984	881
0.4400	0.9332	0.9257	0.9157	1.367	1.131	0.947	1026	979	947
0.5417	0.9187	0.9117	0.9020	1.518	1.266	1.043	936	929	886
0.6360	0.9076	0.9010	0.8915	1.653	1.377	1.125	802	808	771
0.7193	0.8993	0.8929	0.8837	1.745	1.451	1.182	620	631	609
0.8605	0.8876	0.8817	0.8727	1.934	1.606	1.289	309	637	316
0.9421	0.8820	0.8763	0.8675	2.047	1.677	1.351	112	115	125
1.0000	0.8785	0.8729	0.8642	2.160	1.762	1.408			
				Diethylene glycol dibutyl ether (1) + diethyl carbonate (2)					
0.0000	0.9690	0.9577	0.9438	0.749	0.658	0.578			
0.0131	0.9666	0.9555	0.9417	0.771	0.675	0.587	47	43	19
0.0338	0.9630	0.9521	0.9386	0.806	0.699	0.603	118	94	58
0.0756	0.9561	0.9457	0.9326	0.864	0.751	0.638	210	203	139
0.1533	0.9447	0.9351	0.9227	0.976	0.842	0.707	348	340	268

0.2472	0.9328	0.9240	0.9123	1.118	0.949	0.792	473	446	384
0.3392	0.9229	0.9147	0.9036	1.245	1.056	0.871	518	508	441
0.4137	0.9158	0.9080	0.8973	1.359	1.140	0.940	547	522	473
0.4250	0.9146	0.9071	0.8964	1.379	1.153	0.950	553	524	475
0.4831	0.9098	0.9024	0.8921	1.457	1.220	1.002	535	520	477
0.6085	0.9003	0.8935	0.8837	1.630	1.357	1.105	469	461	425
0.7927	0.8890	0.8827	0.8735	1.892	1.556	1.255	304	296	276
0.8959	0.8830	0.8776	0.8686	2.018	1.656	1.328	153	153	141
0.9540	0.8810	0.8749	0.8661	2.116	1.734	1.383	90	98	84
1.0000	0.8785	0.8729	0.8642	2.160	1.762	1.408			
Diethylene glycol dibutyl ether (1) + propylene carbonate (2)									
0.0000	1.1988	1.1897	1.1780	2.550	2.046	1.703			
0.0070	1.1927	1.1837	1.1721	2.562	2.064	1.704	28	46	19
0.0158	1.1852	1.1763	1.1648	2.574	2.086	1.721	60	93	67
0.0590	1.1515	1.1431	1.1322	2.676	2.174	1.735	247	290	188
0.1317	1.1043	1.0966	1.0863	2.748	2.244	1.768	439	497	375
0.2166	1.0604	1.0532	1.0434	2.735	2.263	1.773	536	628	505
0.3183	1.0188	1.0122	1.0027	2.700	2.187	1.729	596	629	541
0.3560	1.0057	0.9993	0.9898	2.674	2.161	1.712	596	621	544
0.3871	0.9957	0.9894	0.9800	2.649	2.141	1.695	590	613	538
0.4126	0.9879	0.9817	0.9723	2.635	2.129	1.686	588	610	537
0.4929	0.9660	0.9600	0.9507	2.579	2.086	1.649	560	579	511
0.5658	0.9488	0.9428	0.9337	2.534	2.051	1.623	526	543	485
0.5869	0.9442	0.9383	0.9292	2.526	2.045	1.620	519	535	482
0.6616	0.9292	0.9233	0.9144	2.487	2.013	1.595	476	487	441
0.7058	0.9211	0.9153	0.9064	2.475	1.999	1.584	456	460	418
0.7480	0.9139	0.9081	0.8992	2.469	1.992	1.566	441	439	380
0.8266	0.9016	0.8958	0.8871	2.402	1.954	1.537	347	359	309
0.9183	0.8888	0.8831	0.8744	2.323	1.899	1.489	224	240	189
1.0000	0.8785	0.8729	0.8642	2.160	1.762	1.408			

Table IVa. Fitting Coefficients a_i and Standard Deviations σ of Eq. (1) for Binary Mixtures at Various Temperatures

η (mPa · s)	a_0	a_1	a_2	a_3	a_4	σ
			Diethylene glycol dibutyl ether (1) + dimethyl carbonate (2)			
298.15 K	0.590	1.518	1.732	−3.501	1.798	0.003
308.15 K	0.520	1.460	0.070	−0.529	0.206	0.003
318.15 K	0.473	0.858	1.302	−2.344	1.108	0.002
			Diethylene glycol dibutyl ether (1) + diethyl carbonate (2)			
298.15 K	0.753	1.483	−0.062			0.003
308.15 K	0.659	1.216	−0.149	0.055		0.002
318.15 K	0.570	0.903	−0.007	−0.053		0.003
			Diethylene glycol dibutyl ether (1) + propylene carbonate (2)			
298.15 K	2.543	2.673	−10.787	14.493	−6.756	0.007
308.15 K	2.049	2.675	−11.011	15.022	−6.974	0.006
318.15 K	1.698	1.081	−4.850	6.493	−3.010	0.006

The positive values of V_m^E may be due to nonrandomness in the mixture diethylene glycol dibutyl ether + dimethyl carbonate. The binary mixtures with propylene carbonate or diethyl carbonate show V_m^E values that decrease with an increase in temperature, while for the mixtures with dimethyl carbonate, V_m^E increases with increasing temperature. The V_m^E values decrease on passing from diethyl carbonate to dimethyl carbonate in diethylene glycol dibutyl ether mixtures. These results and those of Pal et al. [1, 2] show that, for mixtures of polyethers with diethyl carbonate or propylene carbonate, V_m^E decreases in the sequence diethylene glycol dimethyl ether < diethylene glycol dibutyl ether < diethylene glycol diethyl ether, while for mixtures of polyethers with dimethyl carbonate, V_m^E becomes more positive and varies in the sequence diethylene glycol diethyl ether < diethylene glycol dimethyl ether < diethylene glycol dibutyl ether. In all cases, the magnitude of V_m^E increases with an increase in temperature. Again, the V_m^E for mixtures of diethylene glycol dibutyl ether at each temperature decreases in the sequence dimethyl carbonate > diethyl carbonate > propylene carbonate. However, the V_m^E here is more negative for the mixture with propylene carbonate. The more significant decrease in V_m^E for the diethylene glycol dibutyl ether + propylene carbonate system indicates a possible dipole–dipole interaction between the unlike molecules. Similar variations in V_m^E occur in mixtures of triethylene glycol dimethyl ether [3], tetraethylene glycol dimethyl ether [4], *n*-alkoxyethanols [5], or branched ether [27] with dialkyl carbonates.

Table IVb. Fitting Coefficients a_i and Standard Deviations $\sigma\,[Y(x)]$ of Eq. (5) for Binary Mixtures at Various Temperatures

$Y(x)$	a_0	a_1	a_2	a_3	a_4	$\sigma\,[Y(x)]$
Diethylene glycol dibutyl ether (1) + dimethyl carbonate (2)						
298.15 K						
$V_m^E \times 10^6$ $(m^3 \cdot mol^{-1})$	0.815	−0.318	0.198	−0.148		0.002
$\Delta \ln [\eta\ (mPa \cdot s)]$	1.027	−0.509	−0.152	−0.058		0.003
ΔG^{*E} $(J \cdot mol^{-1})$	3923	−1709	−167	−239		8
308.15 K						
$V_m^E \times 10^6$ $(m^3 \cdot mol^{-1})$	0.889	−0.413	0.092	−0.090	0.195	0.002
$\Delta \ln [\eta\ (mPa \cdot s)]$	0.955	−0.415	0.026	−0.151		0.003
ΔG^{*E} $(J \cdot mol^{-1})$	3846	−1485	270	−594		11
318.15 K						
$V_m^E \times 10^6$ $(m^3 \cdot mol^{-1})$	0.968	−0.472	0.164	−0.110	0.180	0.002
$\Delta \ln [\eta\ (mPa \cdot s)]$	0.835	−0.259	−0.223			0.003
ΔG^{*E} $(J \cdot mol^{-1})$	3658	−1188	−365			9
Diethylene glycol dibutyl ether (1) + diethyl carbonate (2)						
298.15 K						
$V_m^E \times 10^6$ $(m^3 \cdot mol^{-1})$	−0.119	−0.003	−0.005	0.059		0.001
$\Delta \ln [\eta\ (mPa \cdot s)]$	0.612	−0.205	−0.013	0.003	0.223	0.003
ΔG^{*E} $(J \cdot mol^{-1})$	2114	−685	331			12
308.15 K						
$V_m^E \times 10^6$ $(m^3 \cdot mol^{-1})$	−0.173	0.004	−0.045			0.002
$\Delta \ln [\eta\ (mPa \cdot s)]$	0.559	−0.178	−0.009	−0.006	0.219	0.003
ΔG^{*E} $(J \cdot mol^{-1})$	2058	−591	−1	−36	575	9
318.15 K						
$V_m^E \times 10^6$ $(m^3 \cdot mol^{-1})$	−0.232	−0.009	0.006	0.037		0.001
$\Delta \ln [\eta\ (mPa \cdot s)]$	0.471	−0.108	−0.053	0.114		0.003
ΔG^{*E} $(J \cdot mol^{-1})$	1882	−434	−89	−313		8
Diethylene glycol dibutyl ether (1) + propylene carbonate (2)						
298.15 K						
$V_m^E \times 10^6$ $(m^3 \cdot mol^{-1})$	−2.562	−0.266	−0.464	0.046		0.003
$\Delta \ln [\eta\ (mPa \cdot s)]$	0.366	−0.145	0.672	0.044		0.003
ΔG^{*E} $(J \cdot mol^{-1})$	2237	−703	1787	−116		14
308.15 K						
$V_m^E \times 10^6$ $(m^3 \cdot mol^{-1})$	−2.897	−0.352	−0.102	0.023		0.002
$\Delta \ln [\eta\ (mPa \cdot s)]$	0.368	−0.206	0.705	−0.073	0.284	0.003
ΔG^{*E} $(J \cdot mol^{-1})$	2289	−957	1960	−268	789	9
318.15 K						
$V_m^E \times 10^6$ $(m^3 \cdot mol^{-1})$	−3.123	−0.487	−0.483			0.003
$\Delta \ln [\eta\ (mPa \cdot s)]$	0.251	−0.116	0.453	0.098		0.003
ΔG^{*E} $(J \cdot mol^{-1})$	2039	−757	1606	171	−434	8

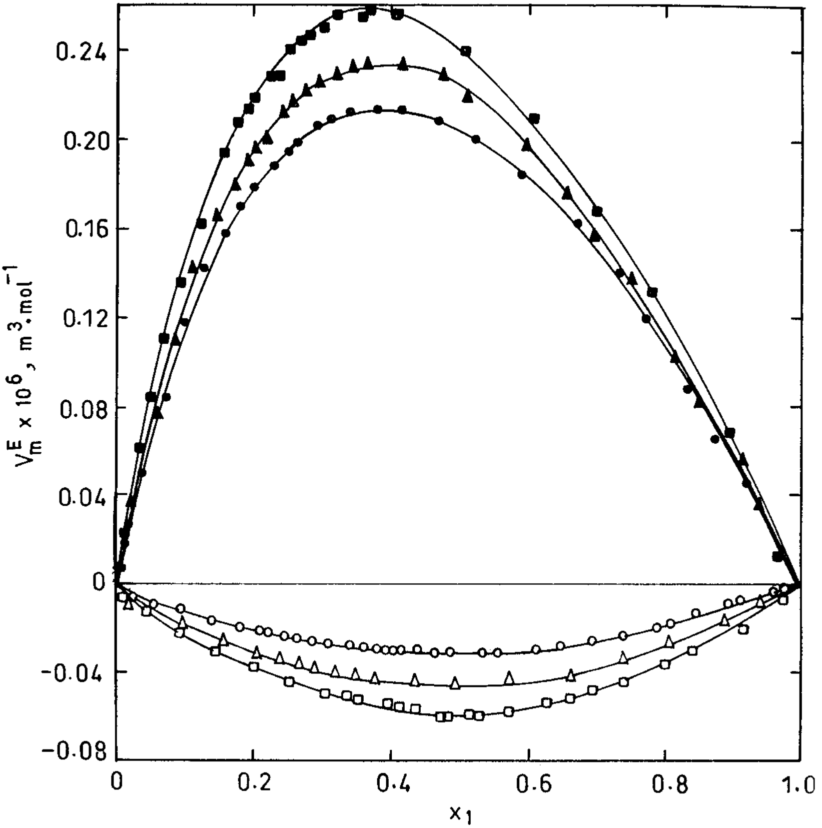

Fig. 1. Excess molar volume, V_m^E for x_1 diethylene glycol dibutyl ether $+ x_2$ dimethyl carbonate, (●) 298.15 K, (▲) 308.15 K, and (■) 318.15 K, or $+x_2$ diethyl carbonate, (○) 298.15 K, (△) 308.15 K, and (□) 318.15 K. The solid curves were drawn from Eq. (5).

The temperature coefficient $(\partial V_m^E/\partial T)_p$ is highly positive for mixtures with dimethyl carbonate and negative for mixtures with diethyl carbonate or propylene carbonate over the whole composition range. Again, $(\partial V_m^E/\partial T)_p$ increases in a positive direction on passing from propylene carbonate to dimethyl carbonate. The highly temperature-dependent behavior of diethylene glycol dibutyl ether + dimethyl carbonate is due to the nonrandom character of the mixture, while diethylene glycol dibutyl ether + diethyl carbonate shows less temperature-dependent behavior. The value of V_m^E decreases from dimethyl carbonate to diethyl carbonate. This suggests that the polar groups are diluted, their interactions are weakened, and, hence, their energies of mixing with diethylene glycol dibutyl ether are decreased, i.e.,

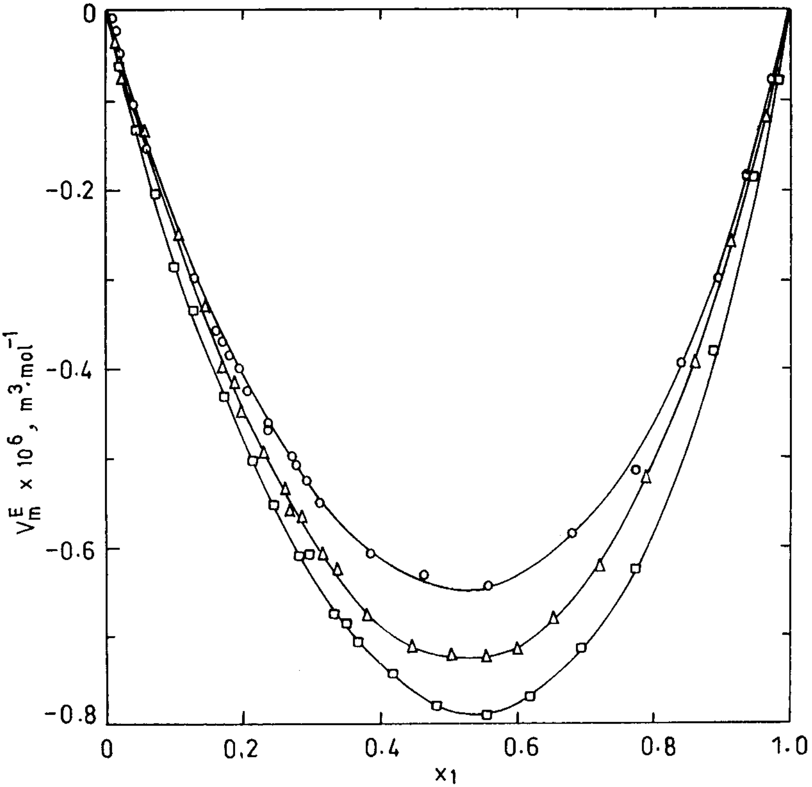

Fig. 2. Excess molar volume, V_m^E for x_1 diethylene glycol dibutyl ether + x_2 propylene carbonate: (○) 298.15 K; (△) 308.15 K; (□) 318.15 K. The solid curves were drawn from Eq. (5).

the mixing process is favored. Thus, a more nonrandom character of the dimethyl carbonate with respect to the diethyl carbonate is present in diethylene glycol dibutyl ether mixtures.

We determined the dynamic viscosity η and calculated $\Delta \ln \eta$ and ΔG^{*E} at 298.15, 308.15, and 318.15 K. Only η, $\Delta \ln \eta$, and ΔG^{*E} are shown at 298.15 K in Figs. 3–5, since for the other temperatures the curves are similar. Table III shows that viscosities of all these mixtures decrease with increasing temperature. The absolute values of η for mixtures of diethylene glycol dibutyl ether molecule at all temperatures vary in the sequence dimethyl carbonate < diethyl carbonate < propylene carbonate. At any particular temperature, as x_1 increases, the η of dimethyl carbonate and diethyl carbonate increases, whereas for propylene carbonate it increases up to $x_1 < 0.2$ and then decreases. A further comparison of data at different

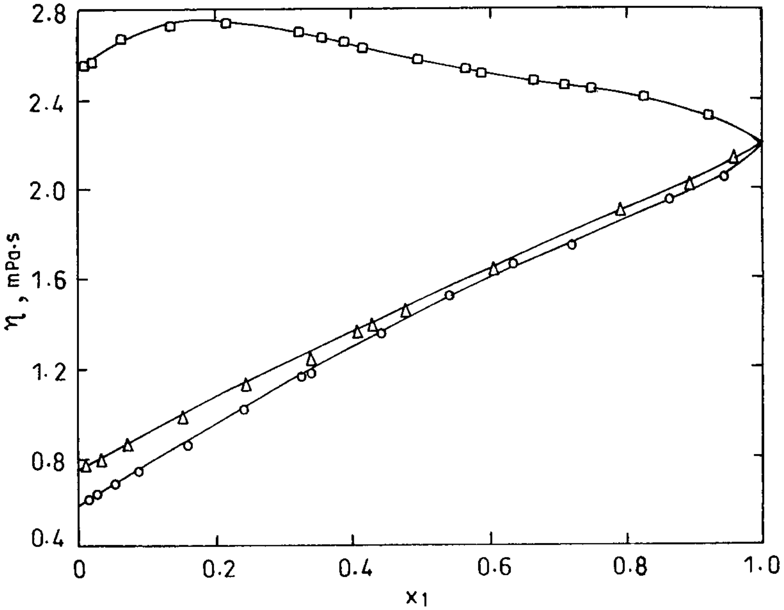

Fig. 3. Viscosity, η, for x_1 diethylene glycol dibutyl ether $+x_2$ dimethyl carbonate (○), $+x_2$ diethyl carbonate (△), or $+x_2$ propylene carbonate (□) at 298.15 K. The solid curves were drawn from Eq. (1).

temperatures reveals that the temperature coefficient $(\partial\eta/\partial T)_p$ decreases for the three mixtures with increasing temperatures. The presence of maxima for the lower range of x_1 gives an indication of specific interactions between diethylene glycol dibutyl ether and propylene carbonate.

The $\Delta \ln \eta$-versus-composition plot in Fig. 4 shows that deviations in viscosity ($\Delta \ln \eta$) are positive over the entire composition range for all systems at 298.15 K. In fact, large positive deviations over the entire range of composition for diethylene glycol dibutyl ether + dimethyl carbonate and smaller positive deviations for diethylene glycol dibutyl ether + diethyl carbonate or + propylene carbonate are observed. This reveals that the strength of the specific interactions is not the only factor influencing the viscosity deviations of liquid mixtures. The molecular size and shape of the components are equally important factors. The excess energies of activation ΔG^{*E} for viscous flow presented in Fig. 5 are positive for all the mixtures at 298.15 K over the entire composition range. The increasing positive values of ΔG^{*E} in the sequence diethyl carbonate < propylene carbonate < dimethyl carbonate suggests that they are attributed to the large size and cohesive energy difference between the two unlike components.

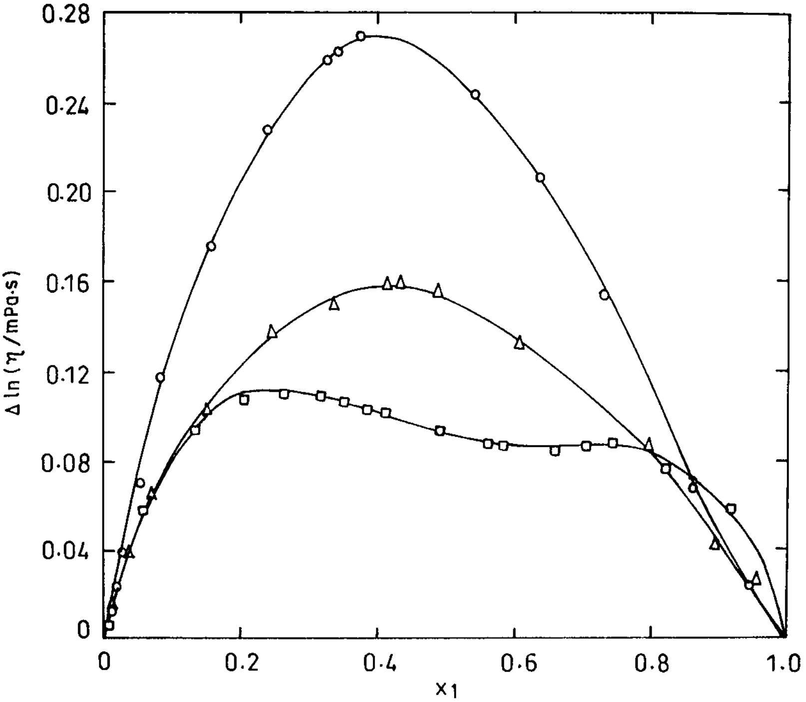

Fig. 4. Viscosity deviations, $\Delta \ln \eta$, as a function of mole fraction of diethylene glycol dibutyl ether at 298.15 K. The symbols are the same as in Fig. 3. The solid curves were drawn from Eq. (5).

The values of the cubic expansion coefficient α of the mixture at a particular composition can be obtained by adding the contributions of the expansivities of each component in the mixtures:

$$\alpha = (1/V)\left[\sum (M_i x_i/\rho)\,\alpha_i + (\partial V_{\mathrm{m}}^{\mathrm{E}}/\partial T)_{p,\,x}\right] \tag{7}$$

where ρ is the density of the mixture at each composition and α_i is the expansivity of the pure components at any particular temperature. In Fig. 6, the α plots are shown for different mixtures at 298.15 K. A sharp decrease in α is shown for the diethylene glycol dibutyl ether + dimethyl carbonate or diethyl carbonate mixtures as the concentration of diethylene glycol dibutyl ether increases. But with propylene carbonate, the α value decreases slowly over the entire composition range.

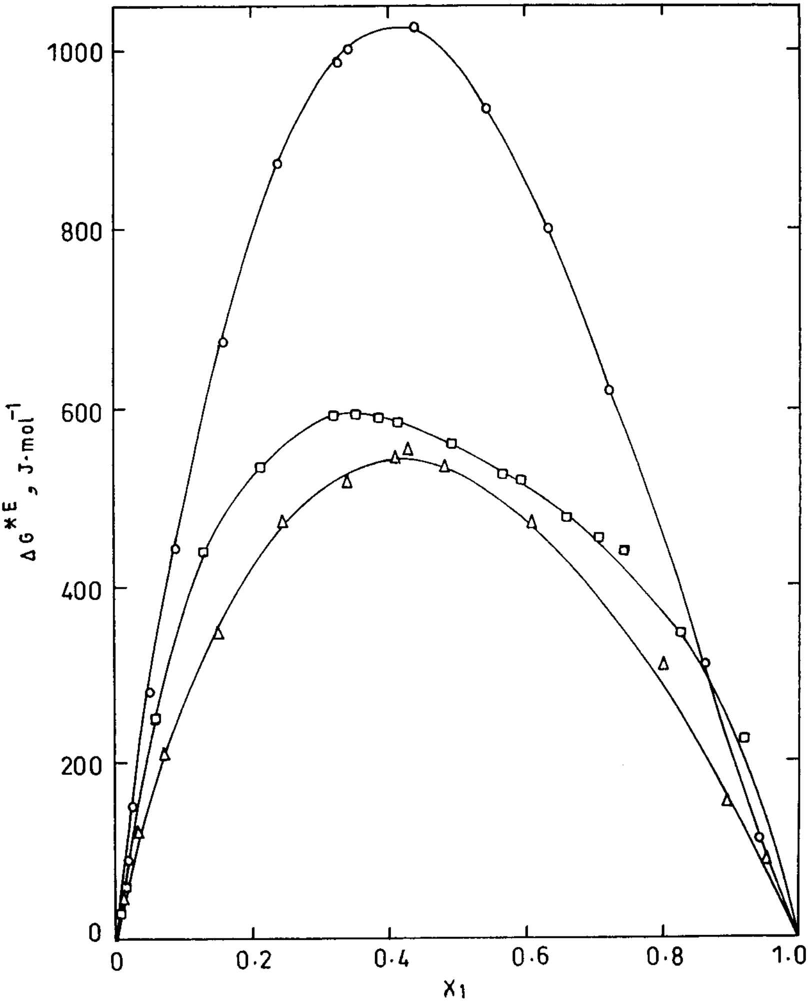

Fig. 5. Excess free energy of activation for viscous flow, $\Delta G^{*\mathrm{E}}$, as a function of mole fraction of diethylene glycol dibutyl ether at 298.15 K. The symbols are the same as in Fig. 3. The solid curves were drawn from Eq. (5).

Furthermore, it is useful to discuss the activation parameter of viscous flow, which is defined by the viscosity equation proposed by Erying and co-workers [29]:

$$\eta = (hN/V)\exp(\Delta G^{*}/RT) \tag{8}$$

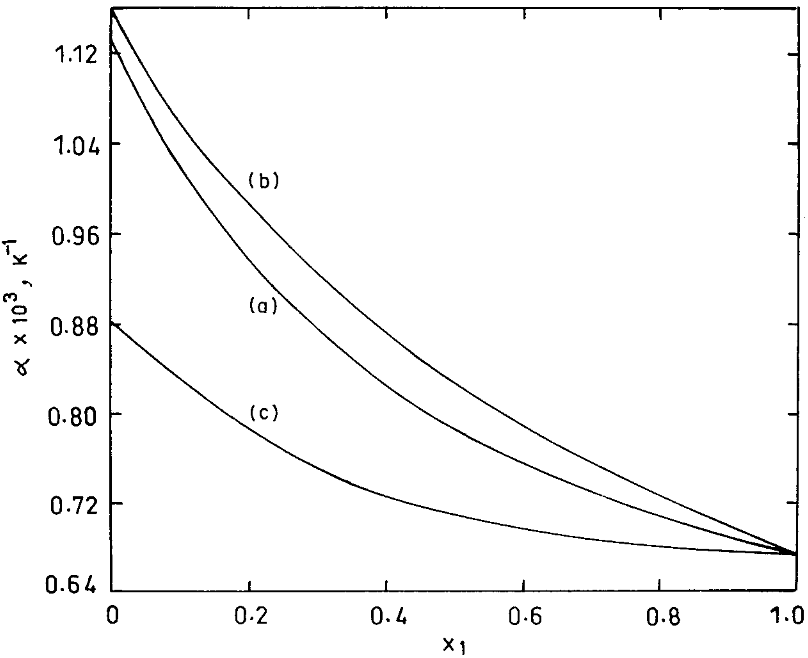

Fig. 6. Isobaric thermal expansivities, α, for x_1 diethylene glycol dibutyl ether $+x_2$ dimethyl carbonate (a), $+x_2$ diethyl carbonate (b), or $+x_2$ propylene carbonate (c) at 298.15 K.

combined with

$$\Delta G^* = \Delta H^* - T\,\Delta S^* \tag{9}$$

yields the equation

$$R\ln(\eta V) = [R\ln hN - \Delta S^*] + \Delta H^*/T \tag{10}$$

where h is Planck's constant, N is the Avogadro number, ΔH^* is the enthalpy of activation for viscous flow, and ΔS^* is the entropy. A plot of $R\ln(\eta V)$ versus $1/T$ for each binary mixture was found to be linear, indicating that the ΔH^* values are constant in the temperature range 298.15 to 318.15 K. The values of ΔS^* and ΔH^* vary considerably with the mixture composition. It was found that the values of ΔH^* are positive and increase with the mole fraction of diethylene glycol dibutyl ether in every mixture. This indicates that the formation of activation species necessary for viscous flow is quite easy in the dialkyl carbonate-rich region and becomes difficult as the diethylene glycol dibutyl ether concentration increases. The negative values of ΔS^* are found to decrease as the mole fraction of diethylene glycol dibutyl ether in the mixture increases. This suggests that in the initial state, during viscous flow, the liquid is more structured as a result of the formation of the activated species. The high negative values of ΔS^* of diethylene glycol dibutyl ether + dimethyl carbonate compared to those for diethylene glycol dibutyl ether + diethyl carbonate or propylene carbonate are indicative of the formation of molecular complexes in solution. Thus, nonrandomness increases on passing from propylene carbonate to dimethyl carbonate in diethylene glycol dibutyl ether mixtures; this results in lower viscosities and higher positive excess volumes for the dimethyl carbonate mixture. The absolute value of η for diethylene glycol dibutyl ether + dimethyl carbonate supports the conclusion drawn from ΔH^* and ΔS^*.

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