

# High-Pressure Measurements of the Viscosity and Density of Two Polyethers and Two Dialkyl Carbonates

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The viscosity and density of four pure liquid compounds (dimethyl carbonate, diethyl carbonate, triethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether) were measured at several temperatures between 283.15 and 353.15 K. The density measurements were performed up to 60 MPa with an uncertainty of  $1 \times 10^{-4} \text{ g} \cdot \text{cm}^{-3}$ . The viscosity at atmospheric pressure was measured with an Ubbelohde-type glass capillary tube viscometer with an uncertainty of  $\pm 1\%$ . At pressures up to 100 MPa the viscosity was determined with a falling ball viscometer with an uncertainty of  $\pm 2\%$ . The density (410 experimental values) and viscosity data (184 experimental values) were fitted to several correlation equations.

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**KEY WORDS:** density; dialkyl carbonates; high pressure; internal pressure; isobaric thermal expansion coefficients; isothermal compressibilities; polyethylene glycol dimethyl ethers; viscosity.

## 1. INTRODUCTION

For many industrial processes, knowledge of the dynamic viscosity as a function of temperature and pressure is of major importance. It so happens that among all the thermophysical properties, viscosity is often the most strongly influenced by pressure and temperature. A study of viscosity as a function of both pressure and temperature is also of fundamental interest. While there are abundant data describing the variations of viscosity with

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temperature at atmospheric pressure, studies versus pressure are less frequent. To test their models, theoreticians need experimental data on various chemical species. This paper is of both fundamental and practical interest.

Polyalkylene glycol dimethyl ethers,  $\text{CH}_3\text{O}-((\text{CH}_2)_2\text{O})_n-\text{CH}_3$ , are good candidates as absorbents for several refrigerants in absorption refrigeration systems and have also been selected as lubricants for HFC refrigerants in automobile air-conditioners. On the other hand, carbonate-based lubricants have been also proposed for use with HFCs. Viscosity is one of the fundamental properties required to determine the reliability of fluids for use as lubricants in refrigeration compressors and, also, as absorbents for absorption systems.

The formation of an elasto-hydrodynamic film as a separating rubbing surface is important in preventing the wear and failure of compressor elements. The properties of the lubricant that determine the film thickness in elasto-hydrodynamic contact are normally the dynamic viscosity,  $\eta$ , and also derived quantities such as  $(\partial\eta/\partial p)_T$  and  $(\partial\eta/\partial T)_p$ . The latter coefficient is involved in the determination of the viscosity index, which is an empirical number indicating the rate of change in viscosity of an oil over a given temperature range. Higher numbers indicate a small change, while lower numbers indicate a relatively large change. The higher the number the better. Therefore, it is necessary to have viscosity data on lubricant candidates as a function of pressure and temperature.

In this paper we report new viscosity data for triethylene glycol dimethyl ether (TriEGDME), for tetraethylene glycol dimethyl ether (TEGDME), and for dimethyl and diethyl carbonate  $[(\text{CH}_3-(\text{CH}_2)_{n-1}-\text{O})_2\text{CO}]$ , with  $n = 1, 2$  at temperatures from 283.15 to 353.15 K and at pressures up to 100 MPa. Moreover, there are few data in the literature concerning these chemical species, so the data we provide should be interesting to test the more-or-less generality of the models developed in the literature.

Another equally important quantity which is often required to determine (and model) the viscosity is the density  $\rho$ . If the density is known along various isotherms and isobars, the isothermal compressibility coefficient, the thermal expansion coefficient, and the internal pressure of the fluids can be determined. We, therefore, also present the measured densities  $\rho$  (up to 60 MPa) as a function of pressure and temperature.

## 2. EXPERIMENTAL

### 2.1. Experimental Apparatus

We used an Anton Paar DMA 60/512P vibrating tube densimeter to determine the density as a function of pressure and temperature. The DMA

512P density measuring cell is designed to perform measurements over a broad range of temperature (from 263.15 to 423.15 K) and pressure (from vacuum to 70 MPa).

The calibration parameters of this apparatus were determined using vacuum and water, more details of this calibration have been described by Lagourette et al. [1]. The uncertainty of the temperature and pressure for measurements of density is estimated as  $\pm 0.05$  K and  $\pm 0.05$  MPa, respectively. The uncertainty of the density is less than  $1 \times 10^{-4} \text{ g} \cdot \text{cm}^{-3}$ . This error is comparable with that obtained by other authors for similar experimental apparatus [2, 3].

At atmospheric pressure the kinematic viscosities,  $\nu$ , were measured with a Ubbelohde-type glass capillary-tube viscometer with a Schott-Geräte automatic measuring unit (Model AVS 350) in a thermostated bath (Bioblock Scientific), which regulates the temperature to within an uncertainty of  $\pm 0.01$  K. After multiplication by the density at atmospheric pressure, the dynamic viscosity,  $\eta$ , is obtained with a relative uncertainty better than 1%.

A falling body viscometer, of the type designed by Ducoulombier et al. [4], was used to measure the viscosity of the compressed liquids. In this apparatus, a stainless-steel cylinder falls through a fluid of unknown viscosity under given conditions of temperature and pressure. The viscosity is a function of the falling time, of the density difference between the cylinder and the fluid, and of one constant obtained by calibrating the viscometer with a substance of known viscosity and density. We have used toluene [5] as a calibrating fluid except for the 283.15 K isotherm, for which we have used water [6]. Decane [7, 8] has been used to verify the calibration.

For the high-pressure viscosity measurements, the temperature has an uncertainty of  $\pm 0.5$  K, whereas the pressure is determined with an uncertainty of less than  $\pm 0.05$  MPa. Each measurement of the fall time was repeated six times at thermal and mechanical equilibrium, and they are reproducible to better than 1%. The final value is an average of these measurements. The total uncertainty of the viscosity values obtained was estimated to be within 2%, which is comparable to that estimated by other authors for similar devices as discussed in previous papers [9, 10]. The interested reader will find comparative curves for heptane and methylcyclohexane [11], for water and 2-propanol [12], and for 2,2,4,4,6,8,8-heptamethylnonane [13] which plot the experimental values obtained at this laboratory and those obtained by other authors with other techniques.

A very important factor for the correct interpretation of the viscosity measurements is the equation employed to extrapolate the experimental values of density from 60 to 100 MPa. In this work we obtained the

extrapolated values of density by using a modified Tait equation, due to Hogenboom et al. [14]:

$$\frac{1}{\rho(p, T)} = \frac{1}{\rho(0.1, T)} - A \ln \left( 1 + \frac{p - 0.1}{B} \right) \quad (1)$$

The  $A$  and  $B$  values for the different pure fluids were determined by correlating  $(T, p, \rho)$  data between 0.1 and 60 MPa. The interested reader will find, for example, in Ref. 15, how reliable Eq. (1) is to extrapolate the density.

## 2.2. Materials

Dimethyl carbonate (Fluka; puriss; mole fraction purity,  $>0.99$ ; molar mass,  $90.08 \text{ g} \cdot \text{mol}^{-1}$ ), diethyl carbonate (Fluka; puriss; mole fraction purity,  $>0.995$ ; molar mass,  $118.13 \text{ g} \cdot \text{mol}^{-1}$ ), triethylene glycol dimethyl ether (TriEGDME) and tetraethylene glycol dimethyl ether (TEGDME) (Aldrich; mole fraction,  $>0.99$ ; molar mass, 178.23 and  $222.28 \text{ g} \cdot \text{mol}^{-1}$ , respectively) were subjected to no further purification other than drying with 0.4-nm Union Carbide molecular sieves.

## 3. RESULTS AND DISCUSSION

### 3.1. Density

#### 3.1.1. Density Representation

The measured densities of dimethyl carbonate, diethyl carbonate, TriEGDME, and TEGDME are reported along isotherms between 283.15 and 353.15 K at pressures to 60 MPa in Table I.

There are several experimental density data at 0.1 MPa for dialkyl carbonates. In a recent paper López et al. [16] determined the experimental densities of dimethyl carbonate and diethyl carbonate at different temperatures up to 323.15 K. The deviations between our data and their density values are less than 0.05 and 0.01 %, respectively. For dimethyl carbonate, our values differ from CRC data [17] at 293.15 K by 0.004% and from Comelli and Francesconi [18] data at 313.15 K by 0.04%. Other authors, Pardo et al. [19] and Francesconi and Comelli [20], have also published density values of dialkyl carbonates at 0.1 MPa but not at the same temperatures. To our knowledge, there are no density values for these liquid dialkyl carbonates at higher pressures.

In the case of TriEGDME, our data agree within 0.01% with those of Tovar et al. [21] at several temperatures and at atmospheric pressure. For TEGDME there are some literature density data at 0.1 MPa due to Tovar et al. [21] and Esteve et al. [22]. In this case the average deviations from our experimental values are 0.01 and 0.1%, respectively. At 1 MPa the deviations between our data and those of Conesa et al. [23] (measured with an Anton Paar DMA 602 densimeter) are less than 0.05% for TriEGDME and 0.04% for TEGDME. Svejda et al. [24] have published density values (measured with an Anton Paar DMA 512 densimeter) for TEGDME at 293.15 K and at pressures up to 10 MPa. Our average deviation from these data is 0.01%. In previous work, Comuñas et al. [25] reported density values of TriEGDME and TEGDME between 278.15 and 328.15 K at pressures up to 12 MPa, also obtained with an Anton Paar DMA 60/512P; the average deviations with this set of data are less than 0.04 and 0.03%, respectively. To our knowledge, there are no other density values at higher pressures for these two polyethers.

Following previous work, Comuñas et al. [25] represented the  $(T, p, \rho)$  relation for the compressed liquid surface for both dialkyl carbonates and polyethers by the following modified Tait equation:

$$\rho(T, p) = \frac{\rho(T, p_{\text{ref}})}{1 - C \ln[(B(T) + p)/(B(T) + p_{\text{ref}})]} \quad (2)$$

where  $\rho(T, p_{\text{ref}})$ , the density at the reference pressure ( $p_{\text{ref}} = 0.1$  MPa), is given by

$$\rho(T, p_{\text{ref}}) = A_0 + A_1 T + A_2 T^2 + A_3 T^3 \quad (3)$$

Parameter  $C$  was assumed to be temperature independent, and for  $B(T)$ , we used the following polynomial form:

$$B(T) = B_0 + B_1 T + B_2 T^2 \quad (4)$$

The standard deviation  $\sigma$ , the absolute average deviation AAD, and the maximum deviation DMAX from the Tait correlation of two alkyl carbonates and polyethers are listed in Table II.

The numerical calculation shows that the function  $B(T)$  decreases with an increase in temperature. The dependence of  $B(T)$  on the polyether size agrees with the results of Comuñas et al. [25] for four polyalkylene glycol dimethyl ethers. The diminution of  $B(T)$  when the number of  $\text{CH}_2$  groups increases for the organic carbonates has also been observed for other polar compounds such as 2-alkanones [26–28] and alkyl alcanoates [29].

**Table I.** Experimental Densities,  $\rho$  ( $\text{g} \cdot \text{cm}^{-3}$ ), Versus Temperature  $T$  and Pressure  $p$ 

$p$ (MPa)	$\rho$ at $T$ (K)							
	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15
Dimethyl carbonate								
0.1	1.0828	1.0694	1.0562	1.0430	1.0294	1.0158	1.0020	0.9881
5	1.0871	1.0739	1.0611	1.0481	1.0351	1.0216	1.0083	0.9949
10	1.0911	1.0783	1.0657	1.0530	1.0401	1.0274	1.0145	1.0014
15	1.0951	1.0824	1.0702	1.0578	1.0453	1.0328	1.0203	1.0075
20	1.0989	1.0865	1.0745	1.0624	1.0501	1.0379	1.0257	1.0135
25	1.1026	1.0904	1.0786	1.0668	1.0548	1.0428	1.0310	1.0189
30	1.1063	1.0943	1.0827	1.0710	1.0593	1.0476	1.0359	1.0243
35		1.0980	1.0866	1.0752	1.0636	1.0522	1.0408	1.0293
40		1.1015	1.0903	1.0791	1.0678	1.0567	1.0454	1.0342
45		1.1050	1.0940	1.0829	1.0718	1.0609	1.0498	1.0389
50		1.1084	1.0975	1.0867	1.0758	1.0650	1.0541	1.0434
55		1.1118	1.1010	1.0902	1.0796	1.0690	1.0584	1.0477
60		1.1150	1.1044	1.0938	1.0833	1.0730	1.0624	1.0520
Diethyl carbonate								
0.1	0.9861	0.9747	0.9634	0.9522	0.9407	0.9291	0.9174	0.9056
5	0.9901	0.9792	0.9680	0.9572	0.9460	0.9347	0.9235	0.9122
10	0.9942	0.9834	0.9726	0.9619	0.9510	0.9402	0.9294	0.9184
15	0.9980	0.9875	0.9769	0.9665	0.9559	0.9454	0.9348	0.9242
20	1.0017	0.9914	0.9811	0.9709	0.9606	0.9502	0.9400	0.9297
25	1.0052	0.9952	0.9850	0.9751	0.9650	0.9550	0.9450	0.9350
30	1.0087	0.9988	0.9890	0.9792	0.9693	0.9595	0.9498	0.9400
35	1.0121	1.0024	0.9926	0.9830	0.9734	0.9638	0.9543	0.9448
40	1.0154	1.0058	0.9962	0.9869	0.9773	0.9680	0.9586	0.9493
45	1.0186	1.0091	0.9997	0.9905	0.9812	0.9720	0.9628	0.9537
50	1.0218	1.0123	1.0030	0.9940	0.9849	0.9758	0.9669	0.9579
55	1.0247	1.0154	1.0063	0.9974	0.9885	0.9796	0.9708	0.9619
60	1.0276	1.0185	1.0095	1.0007	0.9919	0.9832	0.9745	0.9659
TriEGDME								
0.1	0.9950	0.9854	0.9758	0.9663	0.9567	0.9471	0.9375	0.9279
5	0.9980	0.9887	0.9792	0.9699	0.9605	0.9510	0.9417	0.9324
10	1.0010	0.9919	0.9826	0.9735	0.9642	0.9550	0.9460	0.9368
15	1.0041	0.9949	0.9858	0.9769	0.9678	0.9589	0.9499	0.9411
20	1.0068	0.9980	0.9890	0.9802	0.9713	0.9625	0.9538	0.9451
25	1.0096	1.0010	0.9920	0.9834	0.9747	0.9661	0.9576	0.9489
30	1.0123	1.0038	0.9950	0.9865	0.9779	0.9695	0.9613	0.9527
35	1.0151	1.0065	0.9979	0.9895	0.9811	0.9728	0.9646	0.9563
40	1.0176	1.0092	1.0007	0.9924	0.9843	0.9760	0.9679	0.9598
45	1.0202	1.0119	1.0035	0.9953	0.9873	0.9792	0.9711	0.9631
50	1.0226	1.0145	1.0061	0.9982	0.9901	0.9822	0.9743	0.9664
55	1.0251	1.0170	1.0089	1.0008	0.9931	0.9851	0.9775	0.9695
60	1.0275	1.0194	1.0113	1.0035	0.9958	0.9880	0.9804	0.9728

Table I. (Continued)

$p$ (MPa)	$\rho$ at $T$ (K)							
	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15
TEGDME								
0.1	1.0206	1.0112	1.0019	0.9927	0.9833	0.9741	0.9648	0.9556
5	1.0235	1.0144	1.0052	0.9959	0.9869	0.9778	0.9686	0.9597
10	1.0263	1.0173	1.0082	0.9993	0.9904	0.9815	0.9727	0.9639
15	1.0292	1.0202	1.0113	1.0025	0.9938	0.9851	0.9764	0.9677
20	1.0318	1.0231	1.0143	1.0057	0.9971	0.9884	0.9799	0.9714
25	1.0345	1.0258	1.0172	1.0087	1.0003	0.9918	0.9835	0.9751
30	1.0371	1.0285	1.0201	1.0117	1.0034	0.9950	0.9868	0.9787
35	1.0397	1.0311	1.0228	1.0145	1.0063	0.9982	0.9901	0.9821
40	1.0421	1.0338	1.0254	1.0173	1.0092	1.0013	0.9932	0.9854
45	1.0446	1.0362	1.0281	1.0201	1.0122	1.0042	0.9963	0.9885
50	1.0470	1.0387	1.0307	1.0228	1.0149	1.0070	0.9993	0.9916
55	1.0493	1.0411	1.0332	1.0253	1.0176	1.0100	1.0022	0.9946
60	1.0515	1.0435	1.0356	1.0279	1.0203	1.0128	1.0050	0.9976

### 3.1.2. Derived Properties

From Eq. (2) it is easy to obtain several derived functions by differentiation: the isothermal compressibility,  $\kappa_T$  [ $\kappa_T = (1/\rho)(\partial\rho/\partial p)_T$ ], the isobaric thermal expansion coefficient,  $\alpha_p$  [ $\alpha_p = -(1/\rho)(\partial\rho/\partial T)_p$ ], and, finally, the internal pressure  $\pi$  [ $\pi = T(\alpha_p/\kappa_T) - p$ ], which is used to evaluate intermolecular interactions ( $\pi$  corresponds to the  $a/V^2$  term in the Van der Waals equation).

Table III summarizes the isobaric thermal expansion coefficient, isothermal compressibility, and internal pressure of four liquids. To reduce the amount of tabulated data, we present them only for three temperatures. The interested reader will be supplied with detailed results for each temperature upon request. The estimated uncertainties are  $\pm 0.02 \times 10^{-3} \text{ K}^{-1}$

Table II. Results for Density Correlation of Eq. (2)

Parameter	TriEGDME	TEGDME	Dimethyl carbonate	Diethyl carbonate
$\sigma$ ( $\text{g} \cdot \text{cm}^{-3}$ )	$1 \times 10^{-4}$	$5 \times 10^{-5}$	$1 \times 10^{-4}$	$5 \times 10^{-5}$
AAD (%)	$6 \times 10^{-3}$	$4 \times 10^{-3}$	$5 \times 10^{-3}$	$4 \times 10^{-3}$
DMAX (%)	$2 \times 10^{-2}$	$2 \times 10^{-2}$	$2 \times 10^{-2}$	$2 \times 10^{-2}$
Bias (%)	$5 \times 10^{-4}$	$3 \times 10^{-4}$	$-3 \times 10^{-5}$	$1 \times 10^{-4}$

**Table III.** Isobaric Thermal Expansion Coefficients,  $\alpha_p$ , Isothermal Compressibilities,  $\kappa_T$ , and Internal Pressures,  $\pi$ , of the Pure Liquids

	P (MPa)												
	0.1	5	10	15	20	25	30	35	40	45	50	55	60
Dimethyl carbonate													
$\alpha_p$ ( $10^{-4} \text{ K}^{-1}$ )	12.41	12.09	11.79	11.50	11.24	11.00	10.78	10.56	10.37	10.18	10.00	9.84	9.68
$\kappa_T$ ( $10^{-4} \text{ MPa}^{-1}$ )		8.28	7.95	7.65	7.37	7.11	6.87	6.64	6.43	6.24	6.05	5.88	
$\pi$ (MPa)		423	424	426	427	429	430	431	432	434	435	436	
							293.15 K						
$\alpha_p$ ( $10^{-4} \text{ K}^{-1}$ )	12.83	12.43	12.06	11.72	11.41	11.13	10.86	10.62	10.39	10.18	9.98	9.80	9.62
$\kappa_T$ ( $10^{-4} \text{ MPa}^{-1}$ )		9.69	9.24	8.83	8.46	8.12	7.81	7.52	7.25	7.00	6.77	6.56	
$\pi$ (MPa)		397	399	401	402	404	406	407	409	410	411	413	
							313.15 K						
$\alpha_p$ ( $10^{-4} \text{ K}^{-1}$ )	13.46	12.97	12.52	12.12	11.75	11.42	11.11	10.84	10.58	10.34	10.12	9.91	9.72
$\kappa_T$ ( $10^{-4} \text{ MPa}^{-1}$ )		11.41	10.79	10.24	9.75	9.30	8.89	8.52	8.19	7.87	7.59	7.32	
$\pi$ (MPa)		374	376	379	382	384	386	388	391	392	394	396	
							333.15 K						
Diethyl carbonate													
$\alpha_p$ ( $10^{-4} \text{ K}^{-1}$ )	11.57	11.24	10.93	10.65	10.39	10.15	9.93	9.72	9.53	9.35	9.18	9.02	8.87
$\kappa_T$ ( $10^{-4} \text{ MPa}^{-1}$ )		8.84	8.46	8.10	7.78	7.48	7.21	6.95	6.72	6.50	6.29	6.10	
$\pi$ (MPa)		368	369	370	372	373	374	375	376	377	377	378	
							293.15 K						
$\alpha_p$ ( $10^{-4} \text{ K}^{-1}$ )	11.97	11.57	11.20	10.86	10.55	10.27	10.02	9.78	9.56	9.36	9.17	8.99	8.82
$\kappa_T$ ( $10^{-4} \text{ MPa}^{-1}$ )		10.27	9.75	9.28	8.86	8.48	8.13	7.81	7.51	7.24	6.99	6.75	
$\pi$ (MPa)		348	350	351	353	354	356	357	358	360	361	362	
							313.15 K						
$\alpha_p$ ( $10^{-4} \text{ K}^{-1}$ )	12.50	12.00	11.55	11.15	10.79	10.47	10.17	9.91	9.66	9.43	9.22	9.02	8.84
$\kappa_T$ ( $10^{-4} \text{ MPa}^{-1}$ )		12.00	11.30	10.68	10.13	9.63	9.18	8.78	8.41	8.07	7.76	7.48	
$\pi$ (MPa)		328	331	333	335	337	339	341	343	344	346	347	
							333.15 K						



## TriEGDME

$\alpha_p$ ( $10^{-4} \text{ K}^{-1}$ )	9.69	9.49	9.29	9.10	8.93	8.77	293.15 K		8.33	8.20	8.07	7.96	7.84
$\kappa_T$ ( $10^{-4} \text{ MPa}^{-1}$ )		6.56	6.34	6.14	5.95	5.77	8.61	8.47	5.30	5.16	5.02	4.90	
$\pi$ (MPa)		419	419	420	420	420	421	421	421	421	421	421	421
$\alpha_p$ ( $10^{-4} \text{ K}^{-1}$ )	9.92	9.68	9.45	9.23	9.03	8.85	313.15 K		8.36	8.22	8.08	7.95	7.83
$\kappa_T$ ( $10^{-4} \text{ MPa}^{-1}$ )		7.44	7.16	6.91	6.67	6.44	8.68	8.51	5.86	5.69	5.53	5.38	
$\pi$ (MPa)		402	403	404	404	405	406	406	407	407	407	408	408
$\alpha_p$ ( $10^{-4} \text{ K}^{-1}$ )	10.13	9.85	9.58	9.34	9.12	8.91	333.15 K		8.37	8.21	8.06	7.92	7.79
$\kappa_T$ ( $10^{-4} \text{ MPa}^{-1}$ )		8.47	8.11	7.78	7.48	7.20	8.72	8.54	6.48	6.28	6.08	5.90	
$\pi$ (MPa)		382	384	385	386	387	388	389	390	391	392	392	392

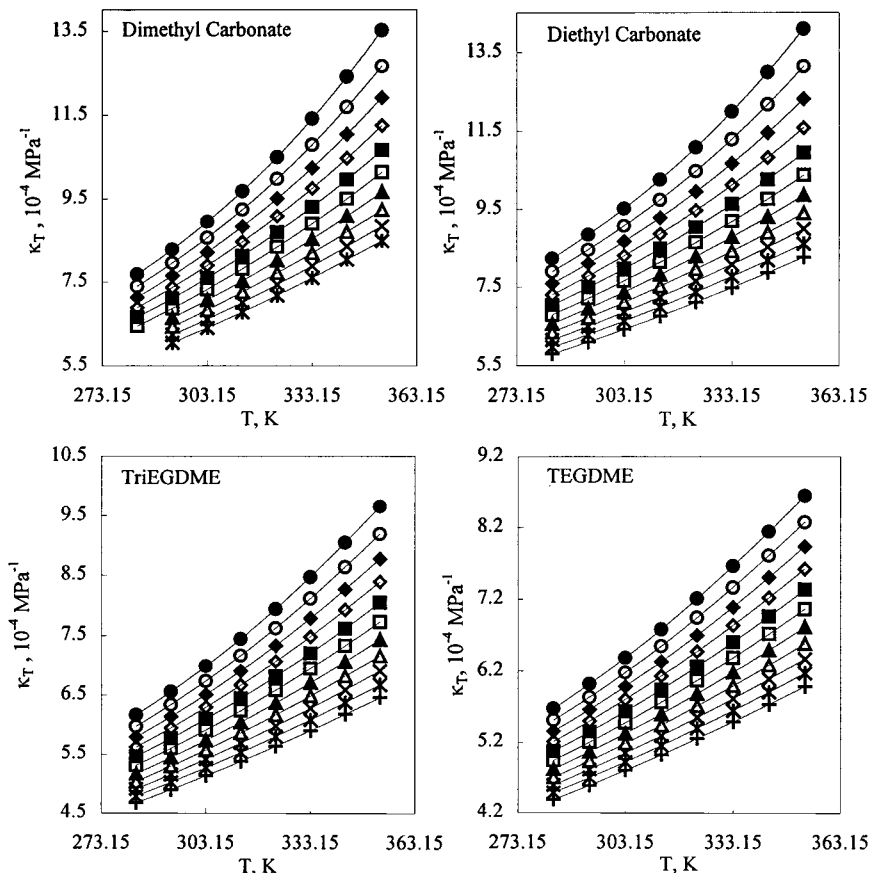
## TEGDME

$\alpha_p$ ( $10^{-4} \text{ K}^{-1}$ )	9.23	9.05	8.88	8.72	8.57	8.42	293.15 K		8.03	7.91	7.80	7.70	7.59
$\kappa_T$ ( $10^{-4} \text{ MPa}^{-1}$ )		6.02	5.84	5.66	5.50	5.35	8.28	8.15	4.94	4.82	4.70	4.59	
$\pi$ (MPa)		436	436	436	437	437	437	437	437	437	437	437	437
$\alpha_p$ ( $10^{-4} \text{ K}^{-1}$ )	9.34	9.13	8.94	8.75	8.58	8.42	313.15 K		7.98	7.86	7.73	7.62	7.51
$\kappa_T$ ( $10^{-4} \text{ MPa}^{-1}$ )		6.78	6.55	6.33	6.13	5.94	8.26	8.12	5.44	5.30	5.16	5.02	
$\pi$ (MPa)		417	417	418	418	418	419	419	419	420	420	420	420
$\alpha_p$ ( $10^{-4} \text{ K}^{-1}$ )	9.50	9.26	9.04	8.83	8.64	8.46	333.15 K		7.98	7.84	7.71	7.59	7.47
$\kappa_T$ ( $10^{-4} \text{ MPa}^{-1}$ )		7.66	7.36	7.09	6.84	6.61	8.29	8.13	5.99	5.82	5.65	5.49	
$\pi$ (MPa)		398	399	400	401	402	402	403	404	404	405	405	405

and  $\pm 0.05 \times 10^{-4} \text{ MPa}^{-1}$ , respectively, for the first two properties and 1% for the last one.

For dimethyl carbonate and diethyl carbonate at 0.1 MPa, we compared the isobaric thermal expansion coefficient values obtained in this work with those obtained by López et al. [16] in a more accurate densimeter (Anton Paar DMA 602, with an uncertainty of  $10^{-5} \text{ g} \cdot \text{cm}^{-3}$ ). Those data agree with ours to 0.7 and 0.5%, respectively.

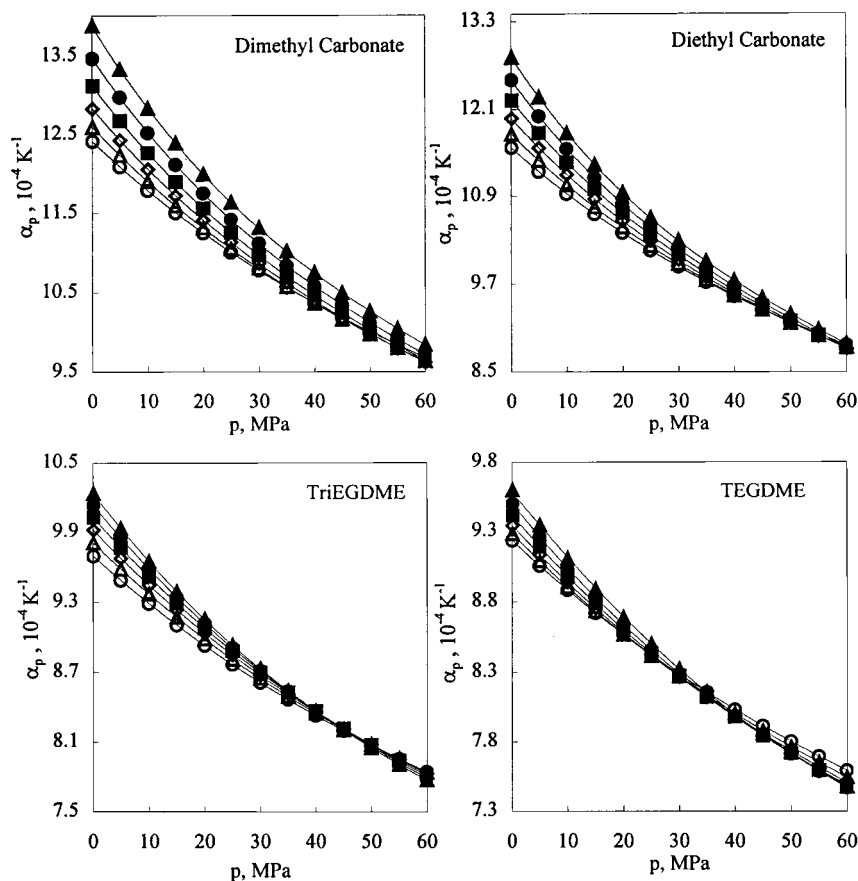
In the case of TriEGDME and TEGDME we calculated the average deviation from recently published values [25] for the isobaric thermal expansion coefficient, the isothermal compressibility, and the internal



**Fig. 1.** Temperature and pressure dependence of the isothermal compressibility,  $\kappa_T$ : (●) 5 MPa; (○) 10 MPa; (◆) 15 MPa; (◇) 20 MPa; (■) 25 MPa; (□) 30 MPa; (▲) 35 MPa; (△) 40 MPa; (×) 45 MPa; (\*) 50 MPa; (+) 55 MPa.

pressure up to 12 MPa. For the first property the average deviation from the present values is 0.3% for TriEGDME and 0.8% for TEGDME, whereas it is 2% for the isothermal compressibilities for both polyethers and 2% for TriEGDME and 3% for TEGDME for the internal pressure. We also analyzed the differences from the isothermal compressibilities calculated from the Svejda et al. [24] density values at 293.15 K, which agree with the present values to 0.9%.

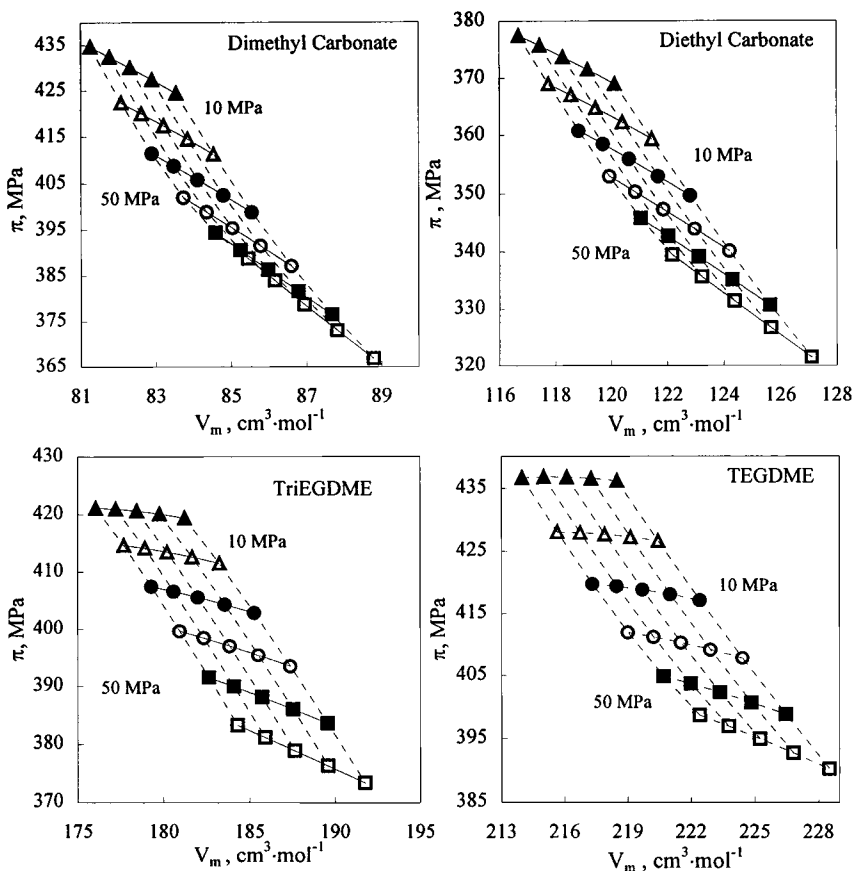
The pressure and temperature variation of isothermal compressibilities is shown in Fig. 1. This property decreases with an increase in pressure and a decrease in temperature for the two dialkyl carbonates and polyethers.



**Fig. 2.** Variation of the isobaric thermal expansion coefficient,  $\alpha_p$  with pressure at different temperatures: (○) 293.15 K; (△) 303.15 K; (◇) 313.15 K; (■) 323.15 K; (●) 333.15 K; (▲) 343.15 K.

The diethyl carbonate isothermal compressibilities are the highest of the four liquids studied.

The dependence on the pressure of the isobaric thermal expansion coefficient  $\alpha_p$  is shown in Fig. 2. This property has an intersection point of isotherms, which is related to the minimum of isobaric heat capacity. Several authors have reported similar behavior for many compounds such as hexane [30, 31] and 2,2,4-trimethylpentane [32]. At the pressure of the crossing point,  $\alpha_p$  is independent of temperature. As a consequence of this crossing, the shape of the specific volume isobars will be different at lower and at higher pressures. In our pressure interval we can observe clearly the



**Fig. 3.** Variation of the internal pressure,  $\pi$ , with molar volume at different temperatures and pressures: ( $\blacktriangle$ ) 293.15 K; ( $\triangle$ ) 303.15 K; ( $\bullet$ ) 313.15 K; ( $\circ$ ) 323.15 K; ( $\blacksquare$ ) 333.15 K; ( $\square$ ) 343.15 K; (---) isobars from 10 to 50 MPa at 10-MPa intervals.

intersection point for TEGDME, whereas this point is less apparent for the dialkyl carbonates.

The internal pressure is a significant factor in the determination of the behavior of liquids because it is a measure of cohesive forces acting in a liquid. This property is sensitive to changes in temperature and external pressure as shown in Fig. 3, where the internal pressure,  $\pi$ , is plotted against the molar volume of the liquid. For the four liquids, at a constant volume, the internal pressure decreases with temperature. For the polyethers, Table III shows that, at a given temperature,  $\pi$  is larger for TEGDME than for TriEGDME. This means that the introduction of a polar group increases the internal pressure. Similar behavior has been found by Gibson and Loeffler [33] for several aromatic compounds. On the contrary, for the dialkyl carbonates this variation is the inverse; the internal pressure for dimethyl carbonate is higher than that for diethyl carbonate. Thus, the insertion of methylene groups reduces the internal pressure. This fact is also obtained for 2-alkanones (from 2-butanone to 2-hexanone) and ethyl alkanoates compounds as can be deduced from the  $pvT$  data of Malhotra and Woolf [27–29].

### 3.2. Dynamic Viscosity

The experimental dynamic viscosity values at different pressures and temperatures are listed in Table IV. To our knowledge there are no literature viscosities for these fluids at pressures different from the atmospheric value. Several authors have published experimental measurements at atmospheric pressure and at different temperatures. At atmospheric pressure, our experimental values agree with published measurements of Pal and Kumar [34] at 298.15, 308.15, and 318.15 K, with an average deviation of 0.3% for dimethyl carbonate and of 1% for diethyl carbonate. Conesa et al. [23] have published viscosities of TriEGDME and TEGDME at temperatures from 283.15 to 423.15 K at 10-K intervals. The average deviation of our measurements from their values is 0.9% for TriEGDME and 0.8% for TEGDME. The present values at 343.15 and 353.15 K are between those of Conesa et al. [23] and those of Herraiz et al. [35]. These deviations are consistent with the uncertainty of the experimental apparatus at 0.1 MPa.

The behavior of the viscosity on an isobar as a function of temperature,  $\eta(T)$ , is described using the following modification of Andrade's equation [36]:

$$\eta(T) = A \exp\left(\frac{B}{T - C}\right) \quad (5)$$

**Table IV.** Viscosity  $\eta$  (mPa · s) Versus Temperature  $T$  and Pressure  $p$ 

$p$ (MPa)	$\eta$ at $T$ (K)							
	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15
Dimethyl carbonate								
0.1		0.630	0.550	0.495	0.445	0.405	0.365	0.330
20		0.735	0.630	0.570	0.515	0.460	0.420	0.390
40		0.830	0.710	0.650	0.580	0.525	0.475	0.440
60		0.910	0.800	0.730	0.650	0.585	0.535	0.490
80			0.890	0.810	0.720	0.650	0.595	0.545
100			0.985	0.890	0.785	0.710	0.655	0.595
Diethyl carbonate								
0.1	0.935	0.810	0.710	0.625	0.560	0.495	0.445	0.405
20	1.130	0.965	0.840	0.735	0.665	0.585	0.540	0.485
40	1.315	1.115	0.975	0.860	0.780	0.685	0.625	0.560
60	1.500	1.260	1.110	0.990	0.900	0.790	0.720	0.640
80	1.705	1.425	1.250	1.130	1.015	0.895	0.825	0.730
100	1.925	1.605	1.395	1.270	1.125	1.005	0.935	0.825
TriEGDME								
0.1	2.740	2.185	1.785	1.485	1.260	1.080	0.945	0.835
20	3.230	2.570	2.090	1.755	1.490	1.300	1.145	1.000
40	3.795	3.005	2.430	2.040	1.725	1.505	1.315	1.150
60	4.390	3.450	2.800	2.350	1.980	1.715	1.505	1.310
80	5.085	3.930	3.210	2.680	2.245	1.925	1.700	1.480
100	5.865	4.435	3.655	3.045	2.515	2.130	1.910	1.655
TEGDME								
0.1	5.000	3.820	2.975	2.400	1.985	1.670	1.435	1.245
20	5.800	4.460	3.565	2.825	2.410	1.995	1.760	1.500
40	6.955	5.200	4.205	3.350	2.825	2.320	2.015	1.735
60	8.185	6.030	4.855	3.920	3.255	2.665	2.305	1.995
80	9.570	6.955	5.520	4.510	3.690	3.025	2.640	2.275
100	11.040	7.990	6.200	5.105	4.110	3.395	3.040	2.575

The constants  $A$ ,  $B$ , and  $C$  in Eq. (5) were determined for each isobar and for each liquid by fitting to our experimental data. The maximum deviations are lower than the experimental viscosity uncertainty, except for TriEGDME at 100 MPa and at 313.15 K, for which the deviation is just 2% (i.e., the experimental uncertainty).

The experimental data for viscosity on an isotherm,  $\eta(p)$ , were fitted for each isotherm to the following Tait-like equation:

$$\eta(p) = A \exp \left[ B \ln \left( \frac{C+p}{C+0.1} \right) \right] \quad (6)$$

On the basis of the experimental data, we determined for each isotherm and for each liquid the constants  $A$ ,  $B$ , and  $C$ . Using this equation the average absolute deviations of the correlations are  $\leq 1\%$  (the maximum deviation is  $1\%$  for TEGDME at  $T = 343.15$  K and at  $20$  MPa).

We also looked for an empirical representation of  $\eta(p, T)$  to be able to interpolate over the entire  $[p, T]$  range. For this purpose, we used the Table Curve 3D software (Jandel Scientific) with a Marquardt–Levenberg-type algorithm for the  $\eta(p, T)$  representation. For fitting we utilized the following polynomial equation with five parameters:

$$\eta(p, T) = \frac{a + bp + cT}{1 + dp + eT} \quad (7)$$

An average absolute deviation of  $0.6\%$  for dimethyl carbonate,  $0.7\%$  for TriEGDME,  $0.9\%$  for diethyl carbonate, and  $1.1\%$  for TEGDME, and a maximum deviation of  $1.8\%$  for dimethyl carbonate,  $2.3\%$  for TriEGDME,  $2.7\%$  for diethyl carbonate, and  $2.9\%$  for TEGDME were obtained.

Assael et al. [37] suggested the following empirical procedure, with five adjustable parameters, to correlate the viscosity as a function of reduced density and reduced temperature:

$$\eta(\rho_r, T_r) = h_0 \exp \left( \frac{h_1}{T_r} + \frac{h_2}{T_r^4} \right) \frac{\rho_r}{1 - \rho_r(h_3 + h_4 T_r^2)} \quad (8)$$

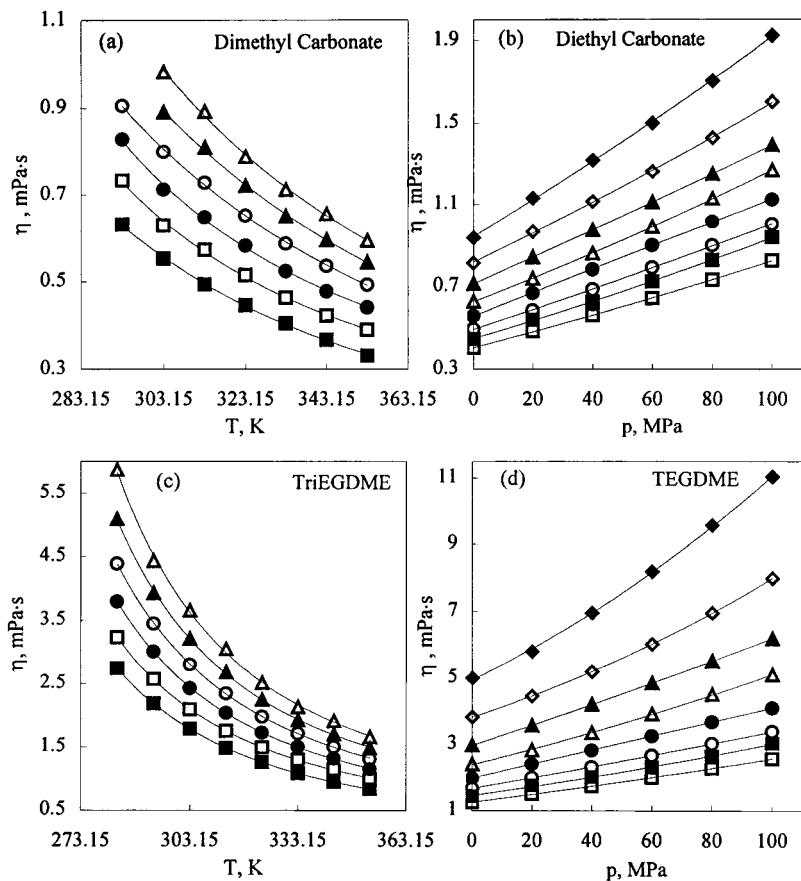
where  $\rho_r = \rho/\rho_c$  and  $T_r = T/T_c$ , with  $\rho_c$  and  $T_c$  the critical density and critical temperature. The values of  $h_i$  were determined by fitting our experimental values, obtaining an average absolute deviation of  $2.1\%$  for TEGDME,  $1.6\%$  for TriEGDME,  $1.5\%$  for diethyl carbonate, and  $0.8\%$  for dimethyl carbonate. The maximum deviations are  $5.9$ ,  $4.4$ ,  $5$ , and  $2.4\%$ , respectively.

Following the Tait-like equation, we propose the following fitting procedure of the viscosity as a function of temperature and pressure:

$$\eta(p, T) = \eta_0(T) \exp \left[ D \ln \left( \frac{E(T) + p}{E(T) + 0.1} \right) \right] \quad (9)$$

where  $\eta_0(T)$  is the temperature dependence of the viscosity at the reference pressure and is given by Eq. (5). Therefore, from Eqs. (5) and (9) one obtains the following equation:

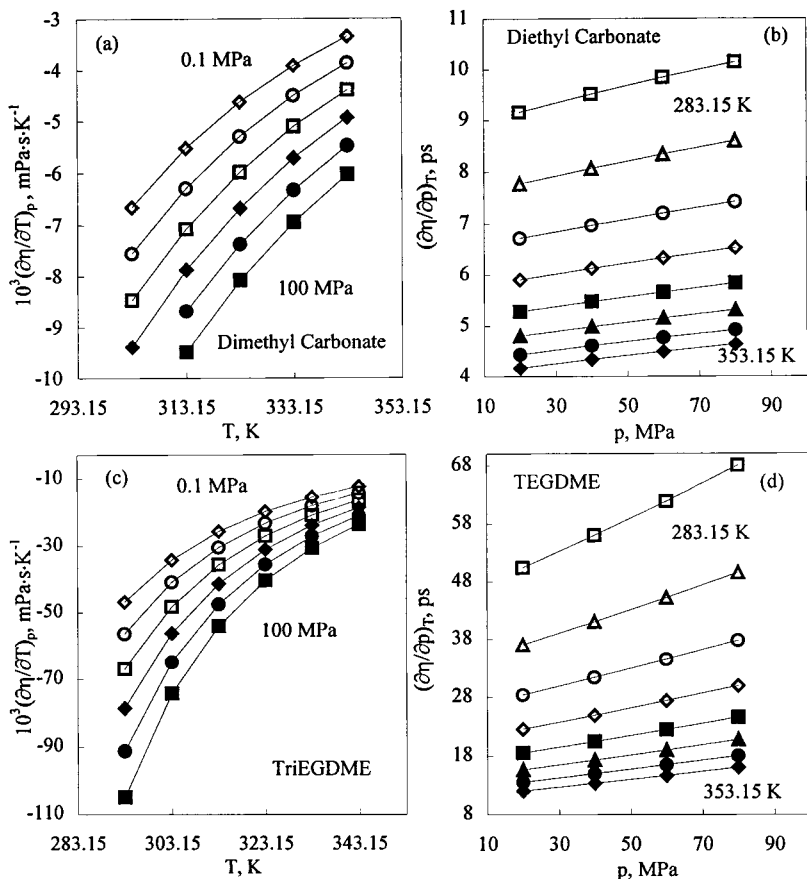
$$\eta(p, T) = A \exp \left[ \frac{B}{T - C} \right] \exp \left[ D \ln \left( \frac{p + E(T)}{0.1 + E(T)} \right) \right] \quad (10)$$



**Fig. 4.** Experimental liquid dynamic viscosity,  $\eta$ , versus pressure and temperature. (a, c) (■) 0.1 MPa; (□) 20 MPa; (●) 40 MPa; (○) 60 MPa; (▲) 80 MPa; (△) 100 MPa; (—) Andrade's correlation. (b, d) (◆) 283.15 K; (◇) 293.15 K; (▲) 303.15 K; (△) 313.15 K; (●) 323.15 K; (○) 333.15 K; (■) 343.15 K; (□) 353.15 K; (—) Tait-like correlation.



where  $D$  is assumed to be temperature independent and  $E(T)$  is a second-order polynomial similar to Eq. (4). Using this equation (involving seven parameters) we obtained an average absolute deviation of 1.3% for TEGDME, 0.9% for TriEGDME, 1% for diethyl carbonate, and 0.6% for dimethyl carbonate. The maximum deviations are 4, 3.2, 2.6, and 1.7%, respectively. These deviations are smaller than those obtained with the Assael et al. correlation [37], but the parameter number is seven for Eq. (10) instead of five for Eq. (8).



**Fig. 5.** Pressure-viscosity coefficient  $(\partial\eta/\partial p)_T$ , in picoseconds, and temperature-viscosity coefficient  $(\partial\eta/\partial T)_p$  as a function of temperature and pressure. (a, c) (◇) 0.1 MPa; (○) 20 MPa; (□) 40 MPa; (◆) 60 MPa; (●) 80 MPa; (■) 100 MPa. (b, d) (□) 283.15 K; (△) 293.15 K; (○) 303.15 K; (◇) 313.15 K; (■) 323.15 K; (▲) 333.15 K; (●) 343.15 K; (◆) 353.15 K.

Typical plots of  $\eta$  as a function of pressure and temperature are shown in Fig. 4. From Eq. (9) it is easy to obtain by differentiation the temperature coefficient  $(\partial\eta/\partial T)_p$  and pressure coefficient  $(\partial\eta/\partial p)_T$  of viscosity. The  $(\partial\eta/\partial T)_p$  values are less than zero, becoming more negative when the pressure increases or the temperature decreases as can be seen in Fig. 5. On the contrary, the pressure viscosity coefficient is positive, increasing when either the pressure increases or the temperature decreases. Figure 6 shows that the  $(\partial\eta/\partial p)_T$  values increase linearly in proportion to the logarithm of the dynamic viscosity.

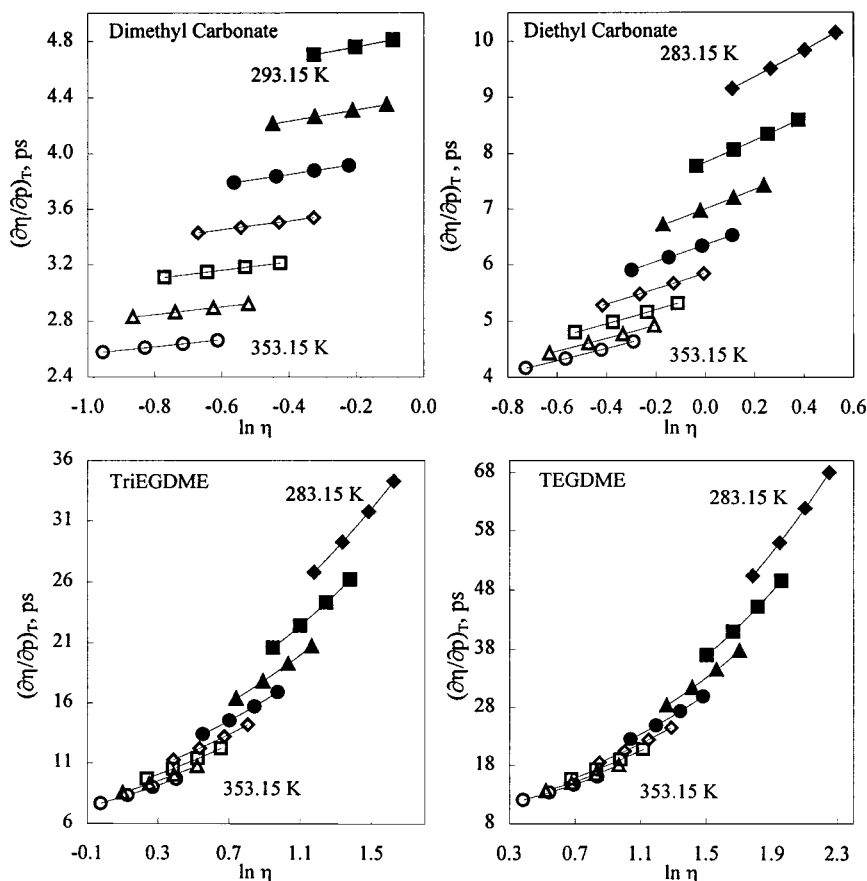


Fig. 6. Pressure-viscosity coefficient  $(\partial\eta/\partial p)_T$ , in picoseconds, versus the logarithm of dynamic viscosity  $\ln \eta$  at ( $\blacklozenge$ ) 283.15 K, ( $\blacksquare$ ) 293.15 K, ( $\blacktriangle$ ) 303.15 K, ( $\bullet$ ) 313.15 K, ( $\diamond$ ) 323.15 K, ( $\square$ ) 333.15 K, ( $\triangle$ ) 343.15 K, and ( $\circ$ ) 353.15 K.

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