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Investigation of Volumetric Properties of Some Glycol Ethers Using a Simple Equation of State

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In this work, a simple equation of state (EoS) has been used to predict the density and other thermodynamic properties such as the isobaric expansion coefficient, α_P, the isothermal compressibility, κ_T, and the internal pressure, P_i, of six glycol ethers including diethylene glycol monobutyl ether (DEGBE), propylene glycol propyl ether (PGPE), diethylene glycol monomethyl ether (DEGME), diethylene glycol monoethyl ether (DEGEE), triethylene glycol dimethyl ether (TriEGDME), and tetraethylene glycol dimethyl ether (TEGDME) at different temperatures and pressures. A comparison with literature experimental data has been made. Additionally, statistical parameters between experimental and calculated densities for the GMA EoS and four other EoSs (Soave–Redlich–Kwong, Peng–Robinson, Soave–Redlich–Kwong with volume translation, and Patel–Teja) indicate the superiority of the GMA EoS.

KEY WORDS: density; glycol ethers; GMA equation of state; internal pressure; isobaric expansion coefficient; isothermal compressibility.

1. INTRODUCTION

Glycol ethers are miscible over a wide range of solvents including water. Their primary use is as a component of liquid cleaners. Their use has increased because of their fast evaporation rate and excellent ability to solubilize organic soils. The cleaning of exhaust air and gas streams from industrial production plants with the simultaneous recovery of useful materials is taking on increasing importance. It is not only required by legal regulations but also conserves resources by recycling useful materials. Thus, the use of glycol ethers as scrubbing liquids has been suggested

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because of their favorable properties [1, 2]. Moreover, glycol ethers are widely used as detergents by forming stable homogeneous solutions with high fractions of water and oil [3, 4]. In addition, lubricants, hydraulic fluids, greases, etc. contain glycol ethers, and the compatibility of certain oil additives is improved and turbidity is corrected by the addition of glycol ether-type compounds. Due to their mild odor, glycol ethers are used as solvents for many resins, waxes, fats, and dyestuffs. The ability of the product to improve penetration makes it attractive for non-grain-raising wood stains, spirit-type dyes, and textile dye pastes [5]. Among the different glycol ethers, polyalkylene glycol dimethyl ethers 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 [6].

Equations of state are required for the calculation of thermodynamic properties needed in process engineering. A new equation of state (EoS) for liquids has been recently introduced by Goharshadi et al. [7] (Goharshadi-Morsali-Abbaspour, "GMA EoS"), which has been found to be valid for polar, nonpolar, and hydrogen-bonded fluids [7, 8]. The EoS has also been applied to liquid mixtures [9].

In the present work, we used the GMA EoS to accurately reproduce and predict the volumetric and thermodynamic properties of six glycol ethers at various temperatures and pressures and compared the results with experimental data. Furthermore, we examined the capability of some equations of state to predict the volumetric behavior of these glycol ethers compared with the GMA EoS.

2. THEORETICAL BASIS OF GMA EOS

The average potential energy is approximately equal to the summation of the contributions from the nearest neighbors only, assuming single inverse powers for the effective repulsion and attraction;

$$U = \frac{N}{2} Z(\rho) \left[\frac{C_n}{\bar{r}^n} - \frac{C_m}{\bar{r}^m} \right], \tag{1}$$

where U is the total potential energy among N molecules, $Z(\rho)$ is the average number of nearest neighbors, which is proportional to density, ρ, for liquids, C_n and C_m are temperature parameters, and $\bar{r}$ is the average distance between nearest neighbors. U can be written as

$$\frac{U}{N} = \frac{K_n}{V^{(n/3)+1}} + \frac{K_m}{V^{(m/3)+1}}, \tag{2}$$

where K_n and K_m are the potential parameters. The internal pressure is

$$P_i = \left(\frac{\partial E}{\partial V}\right)_T \approx \left[\frac{\partial\,(U/N)}{\partial V}\right]_T \tag{3}$$

Carrying out the differentiation, the internal pressure can be written as

$$P_i = \left(\frac{m}{3}+1\right) K_m \rho^{\frac{m}{3}+2} - \left(\frac{n}{3}+1\right) K_n \rho^{\frac{n}{3}+2} \tag{4}$$

Equation (4) shows that $P_i V_m^{\frac{m}{3}+2}$ versus $\rho^{\frac{n}{3}-\frac{m}{3}}$ must be linear for all isotherms of a liquid, where $\mathrm{V}_m (V_m = 1/\rho)$ is the molar density. Using experimental data, it has been found that the best near-linearity relation results when $m=6$ and $n=9$ or $P_i V_m^4$ versus ρ is linear for all isotherms of a liquid [7], namely,

$$P_i V_m^4 = a(T) + b(T)\rho, \tag{5}$$

where a and b are temperature parameters. It has been assumed that $a(T)$ and $b(T)$ have linear relations with temperature. It has been shown that this assumption works well [7]. Hence, $a(T)$ and $b(T)$ are defined as

$$a(T) = A_1 + A_2 T \tag{6}$$

$$b\,(T) = B_1 + B_2 T \tag{7}$$

where A_1, A_2, B_1, and B_2 are constants.

Comparing Eqs. (5)–(7) with Eq. (4) gives

$$\left(\frac{m}{3}+1\right) K_m = A_1 + A_2 T \tag{8}$$

$$-\left(\frac{n}{3}+1\right) K_n = B_1 + B_2 T \tag{9}$$

Therefore, K_n and K_m are temperature-dependent parameters. These equations can predict the temperature dependence of the potential parameters.

Using the well-known thermodynamic equation of state

$$P_i = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{10}$$

or

$$d\left(\frac{P}{T}\right) = \frac{P_i}{T^2}\,dT \tag{11}$$

and Eqs. (5)–(7),

$$d\left(\frac{P}{T}\right)=\left(\frac{A_1+A_2T}{T^2}\rho^4+\frac{B_1+B_2T}{T^2}\rho^5\right)dT \tag{12}$$

a new EoS results:

$$\frac{P}{T}=\left(-\frac{A_1}{T}+A_2\ln T\right)\rho^4+\left(-\frac{B_1}{T}+B_2\ln T\right)\rho^5+g\left(\rho\right) \tag{13}$$

$g(\rho)$ has been arbitrarily chosen as the following function:

$$g(\rho)=x\rho+y\rho^4+w\rho^5 \tag{14}$$

since as $\rho\to 0$ the pressure also goes to zero. Experimental data show this choice works well and the parameters x, y, and w are $\frac{R}{2}$, $\frac{R}{2}A_0$, and $\frac{R}{2}B_0$, respectively (A_0 and B_0 are constants).

Inserting Eq. (14) into Eq. (13) and re-arranging gives the GMA EoS [7], that is,

$$(2Z-1)V_m^3=A(T)+B(T)\rho \tag{15}$$

This equation is restricted to the liquid phase, and the intercept and the slope both depend on temperature via the equations,

$$A(T)=A_0-\frac{2A_1}{RT}+\frac{2A_2\ln T}{R} \tag{16}$$

$$B(T)=B_0-\frac{2B_1}{RT}+\frac{2B_2\ln T}{R} \tag{17}$$

where A_0-A_2 and B_0-B_2 are constants. To use this equation of state for a liquid, the A and B parameters must be known. To find these parameters, we may plot $(2Z-1)V_m^3$ against ρ for different isotherms. The slope and intercept of the straight lines can be fitted with Eqs. (16) and (17) from which A_0-A_2 and B_0-B_2 can be found.

3. RESULTS AND DISCUSSION

3.1. Experimental Test of GMA EoS

Table I summarizes the formulas, molar masses, M_w, and temperature and pressure ranges of the glycol ethers that have been studied, including propylene glycol propyl ether (PGPE), CH_3–$(CH_2)_2$–O–CH_2–$CH(CH_3)OH$; diethylene glycol monomethyl ether (DEGME), CH_3–O–$(CH_2)_2$–O–$(CH_2)_2$–OH; diethylene glycol monoethyl ether (DEGEE),

Table I. Formula, Molar Mass, M_w, and Temperature and Pressure Ranges of the Glycol Ethers Studied

Compound	Formula	M_w ($g \cdot mol^{-1}$)	ΔT (K)	ΔP (MPa)	Ref
PGPE	$C_6H_{14}O_2$	118.17	283.15–353.15	0.1–25	10
DEGME	$C_5H_{12}O_3$	120.15	283.15–353.15	0.1–25	5
DEGEE	$C_6H_{14}O_3$	134.17	283.15–353.15	0.1–25	5
DEGBE	$C_8H_{18}O_3$	162.23	283.15–353.15	0.1–25	10
TriEGDME	$C_8H_{18}O_4$	178.23	283.15–353.15	0.1–60	6
TEGDME	$C_{10}H_{22}O_5$	222.28	283.15–353.15	0.1–60	6

CH_3–CH_2–O–$(CH_2)_2$–O–$(CH_2)_2$–OH; diethylene glycol monobutyl ether (DEGBE), CH_3–$(CH_2)_3$–O–$(CH_2)_2$–O–$(CH_2)_2$–OH; triethylene glycol dimethyl ether (TriEGDME), CH_3–O–$[(CH_2)_2O]_3$–CH_3; and tetraethylene glycol dimethyl ether (TEGDME), CH_3–O–$[(CH_2)_2O]_4$–CH_3. We have used the experimental PVT data of some glycol ethers at various temperatures and pressures to examine the linearity of $(2Z-1)V_m^3$ versus ρ (Eq. (15)). Figure 1 shows the results for tetraethylene glycol dimethyl ether (TEGDME) at different temperatures. As the figure shows, the linearity holds very well for (TEGDME), and both the slope and the intercept depend on the temperature. As Fig. 1 and the values of R^2 in Table II show, the linearity of $(2Z-1)\,V_m^3$ versus ρ holds well for all glycol ethers at different temperatures. Table III shows the values of the constants of Eqs. (16) and (17) for the tested glycol ethers. The ranges of pressure and temperature in this table are the same as in Table I.

Liquid densities can be calculated from equations of state. The densities of six glycol ethers at different temperatures and pressures have been calculated using the GMA EoS by Eq. (15).

The percent deviation between the experimental density data and those calculated with the GMA EoS are presented in Fig. 2 for the glycol ethers studied. Also, the ability of this EoS to reproduce and predict density at different temperatures and pressures for these compounds may be evaluated using statistical parameters [11, 12], namely, the absolute average deviation (AAD), the average percent deviation (bias), the standard deviation (SD), and the root-mean-square deviation (RMSD). The AAD is defined as follows:

$$\mathrm{AAD} = \frac{1}{N}\sum_{i=1}^{N} 100 \left| \frac{\rho_{\exp} - \rho_{\mathrm{cal}}}{\rho_{\exp}} \right| \tag{18}$$

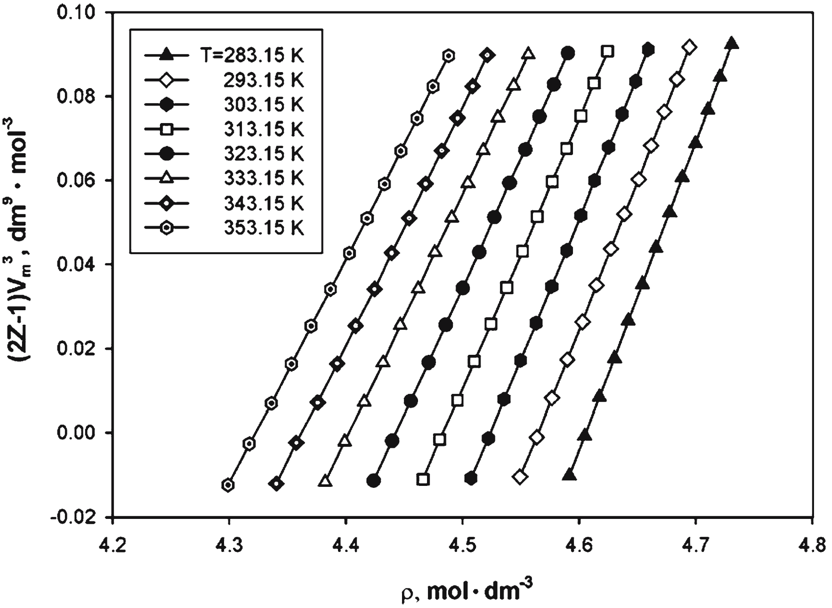

Fig. 1. Isotherms of $(2Z-1)V_m^3$ versus ρ for tetraethylene glycol dimethyl ether (TEGDME) [6].

The statistical parameters between experimental and calculated densities, and the number of points for the glycol ethers studied, are listed in Table IV. This table shows that the GMA EoS can reproduce experimental densities of these compounds with a good accuracy.

We assessed the performance of the GMA EoS compared with other EoSs, (Soave–Redlich–Kwong (SRK) [13], Peng–Robinson (PR) [14], Soave–Redlich–Kwong with volume translation (SRK-VT) [15], and Patel–Teja (PT) [16]) and found that the GMA EoS gives much higher accuracies. The AAD and bias between the experimental density data and those predicted using these EoSs for pure glycol ethers are presented in Table V.

3.2. Derived Properties

The isobaric expansion coefficient, $\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, the isothermal compressibility, $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$, and the internal pressure, $P_i = \left(\frac{\partial U}{\partial V}\right)_T$ of the glycol ethers have been calculated at different temperatures and pressures. The functions used for calculating these properties using the GMA EoS

Table II. Intercept (A), Slope (B), and Square of Correlation Coefficient (R^2) of Eq. (15) for the Glycol Ethers Studied

T (K)	$A(T)$ ($\mathrm{dm^9 \cdot mol^{-3}}$)	$B(T)$ ($\mathrm{dm^{12} \cdot mol^{-4}}$)	R^2	T (K)	$A(T)$ ($\mathrm{dm^9 \cdot mol^{-3}}$)	$B(T)$ ($\mathrm{dm^{12} \cdot mol^{-4}}$)	R^2
	PGPE				DEGBE		
283.15	−0.339675	0.0445444	0.9997	283.15	−1.13731	0.191276	0.9993
293.15	−0.318747	0.0422015	0.9998	293.15	−1.08277	0.183645	0.9999
303.15	−0.303208	0.040551	0.9999	303.15	−1.0207	0.174593	0.9999
313.15	−0.282608	0.0381792	0.9998	313.15	−0.970172	0.167379	0.9998
323.15	−0.271324	0.0370463	0.9999	323.15	−0.923144	0.160697	0.9999
333.15	−0.258484	0.0356781	0.9998	333.15	−0.87941	0.154455	0.9998
343.15	−0.240716	0.0335673	0.9998	343.15	−0.826549	0.1464	1.0000
353.15	−0.226637	0.031955	0.9998	353.15	−0.783284	0.139999	0.9998
	DEGME				TriEGDME		
283.15	−0.301107	0.0349894	0.9992	283.15	−1.42055	0.253445	0.9999
293.15	−0.282234	0.0330697	0.9991	293.15	−1.33925	0.241148	0.9999
303.15	−0.27602	0.0326163	0.9994	303.15	−1.26638	0.230192	0.9999
313.15	−0.256457	0.0305456	0.9999	313.15	−1.19611	0.219458	0.9998
323.15	−0.236646	0.0284114	0.9996	323.15	−1.1346	0.210169	1.0000
333.15	−0.23138	0.0280318	0.9998	333.15	−1.06624	0.199419	0.9998
343.15	−0.217911	0.0266193	0.9999	343.15	−1.00903	0.190526	0.9996
353.15	−0.208894	0.0257507	0.9999	353.15	−0.964442	0.183882	0.9998
	DEGEE				TEGDME		
283.15	−0.485805	0.0650034	0.9998	283.15	−3.38732	0.735473	0.9999
293.15	−0.457561	0.061779	0.9998	293.15	−3.21988	0.705325	0.9995
303.15	−0.429491	0.0584829	0.9997	303.15	−3.03997	0.67194	0.9997
313.15	−0.413755	0.056834	0.9999	313.15	−2.83142	0.6316	0.9998
323.15	−0.386413	0.0535428	0.9999	323.15	−2.68516	0.604364	0.9999
333.15	−0.372135	0.0520297	0.9997	333.15	−2.54833	0.578821	0.9999
343.15	−0.352378	0.0497049	0.9998	343.15	−2.39235	0.548454	0.9993
353.15	−0.336525	0.0479091	0.9998	353.15	−2.29383	0.530665	0.9997

are given as Eqs. (19)–(21)

$$\alpha_P = \frac{(2B_1 + 2B_2 T)\,\rho^5 + (2A_1 + 2A_2 T)\,\rho^4 + 2P}{5\rho^5\left(RT^2 B_0 - 2B_1 T + 2T^2 B_2 \ln T\right) + 4\rho^4\left(A_0 RT^2 - 2A_1 T + 2A_2 T^2 lnT\right) + RT^2\rho} \tag{19}$$

$$\kappa_T = \frac{2}{\rho RT + 4\rho^4\,(RTA_0 - 2A_1 + 2TA_2 \ln T) + 5\rho^5\,(B_0 RT - 2B_1 + 2B_2 T \ln T)} \tag{20}$$

$$P_i = (B_1 + B_2 T)\,\rho^5 + (A_1 + A_2 T)\,\rho^4 \tag{21}$$

Table III. The Values of the Constants of the GMA EoS (Eqs. (16) and (17)) for the Glycol Ethers Studied

Compound	A_0 (10^{-9} $m^9 \cdot mol^{-3}$)	A_1 (10^{-7} $m^{12} \cdot Pa$ mol^{-4})	A_2 (10^{-7} $m^{12} \cdot Pa \cdot mol^{-4} \cdot K^{-1}$)	B_0 (10^{-12} $m^{12} \cdot mol^{-4}$)	B_1 (10^{-10} $m^{15} \cdot Pa \cdot mol^{-5}$)	B_2 (10^{-10} $m^{15} \cdot Pa \cdot mol^{-5} \cdot K^{-1}$)
PGPE	−0.727342	4.742678745	0.005829075	0.175592	−0.354305154	−0.001187681
DEGME	0.841779	6.86724108	−0.004122539	−0.0610487	−0.654294029	0.00029826
DEGEE	4.33379	16.70291963	−0.025034672	−0.49339	−1.925144603	0.002906751
DEGBE	−5.58234	8.889434768	0.038289502	1.27157	−0.437246759	−0.008227975
TriEGDME	7.53159	40.20383483	−0.040774599	−0.90596	−5.738916278	0.004948287
TEGDME	15.0048	91.36657635	−0.078386135	−1.86457	−15.52278735	0.009459499

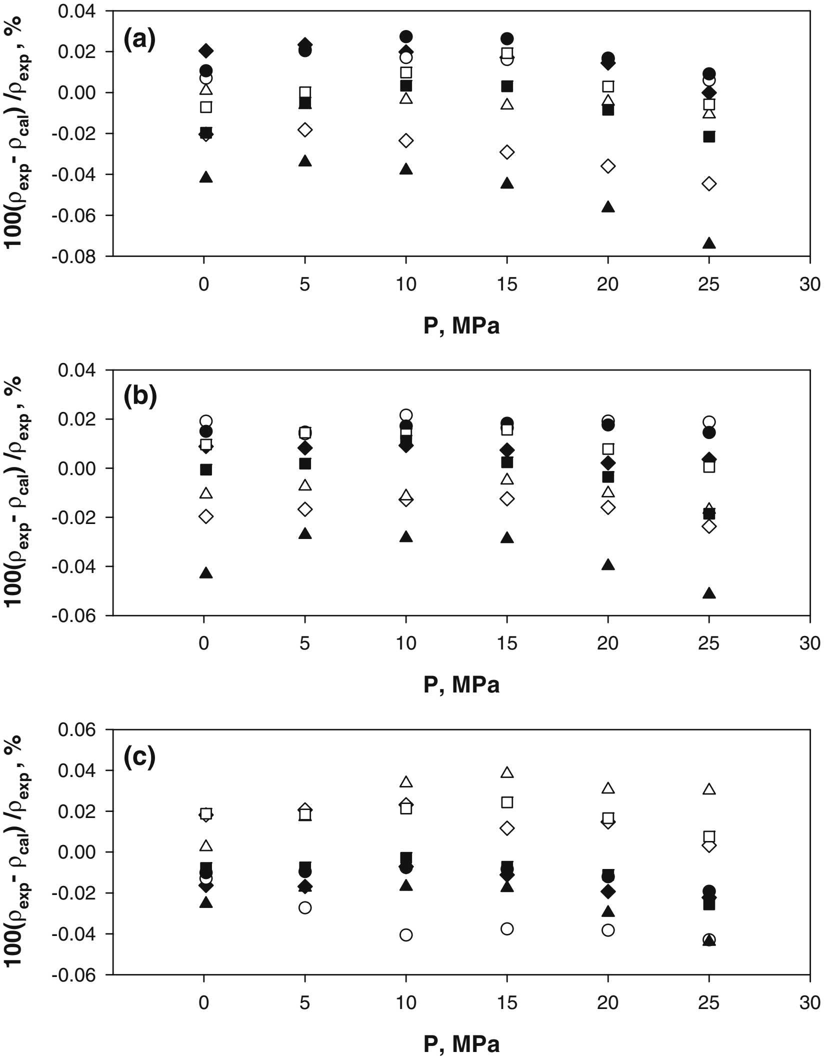

Fig. 2. Percent deviations between the experimental density data and those calculated with the GMA EoS for (a) PGPE [10], (b) DEGBE [10], (c) DEGME [5], (d) DEGEE [5], (e) TriEGDME [6], and (f) TEGDME [6] at different temperatures: ◊ 283.15 K; ♦ 293.15 K; ○ 303.15 K; ● 313.15 K; △ 323.15 K; ▲ 333.15 K; □ 343.15 K; ■ 353.15 K.

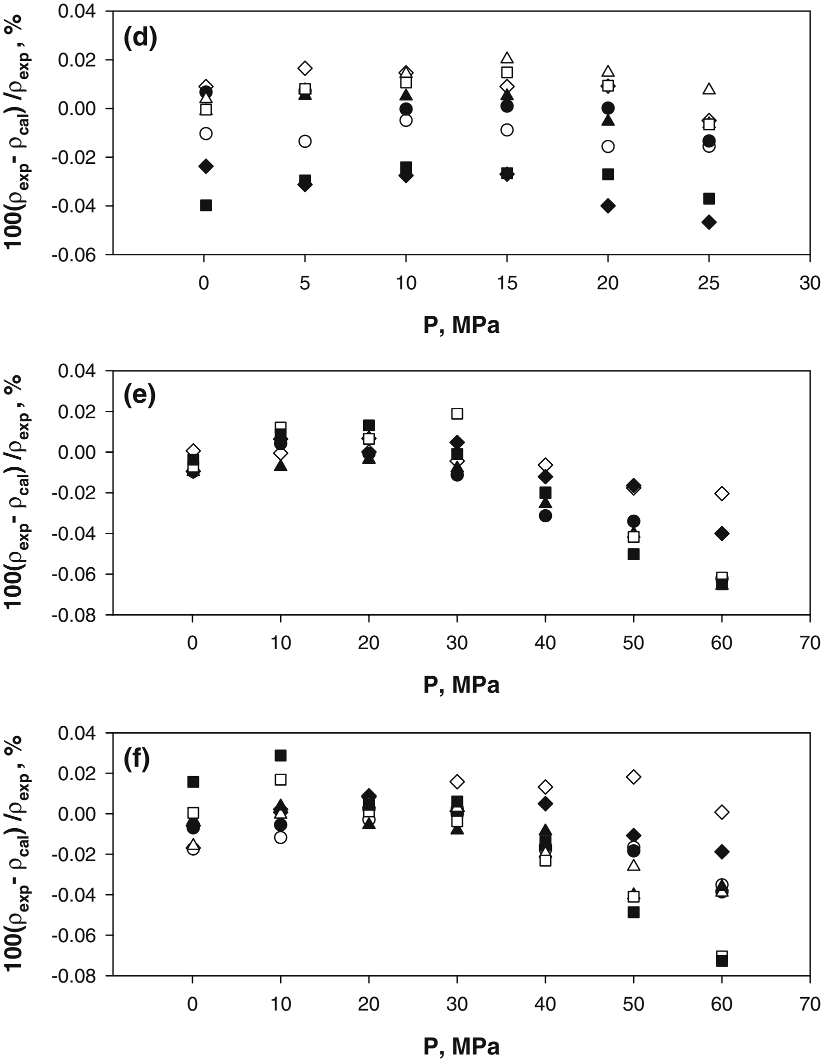

Fig. 2. Continued

The statistical parameters corresponding to calculations of α_P, κ_T, and P_i and the number of points have been given in Table VI. The values of the statistical parameters show that the GMA EoS can predict these thermophysical properties very well in comparison with experimental data.

Table IV. Statistical Parameters between Experimental and Calculated Densities, and the Number of Points for the Glycol Ethers Studied

Parameter	PGPE	DEGBE	DEGME	DEGEE	TriEGDME	TEGDME
Bias (%)	−0.005	−0.002	−0.004	−0.006	−0.014	−0.008
AAD (%)	0.018	0.015	0.018	0.014	0.018	0.015
RMSD (%)	0.023	0.018	0.021	0.018	0.026	0.021
σ ($\mathrm{mol \cdot L^{-1}}$)	0.002	0.001	0.002	0.001	0.001	0.001
NP	72	72	72	72	78	104

Table V. AAD and Bias between Experimental Density Data and Those Predicted Using Several EoSs

	PR	SRK	SRK-VT	PT	GMA
			PGPE		
AAD (%)	6.2	16.4	2.8	1.7	0.018
Bias (%)	6.2	16.4	−2.8	1.7	−0.005
			DEGBE		
AAD (%)	1.1	11.5	19.6	8.5	0.015
Bias (%)	1	11.5	−19.6	−8.5	−0.002
			DEGME		
AAD (%)	8.4	18.3	3.1	2.9	0.018
Bias (%)	8.4	18.3	−3.1	2.9	−0.004
			DEGEE		
AAD (%)	8.3	18.2	6.3	1.5	0.014
Bias (%)	8.3	18.2	−6.3	1.5	−0.006

Table VI. Statistical Parameters (in %) of the Isobaric Expansion Coefficient (α_P), Isothermal Compressibility (κ_T), and Internal Pressure (P_i) for Some Glycol Ethers

	Derived Property								
	$\boldsymbol{\alpha_P}$			κ_T			$\boldsymbol{P_i}$		
Compound	Bias	AAD	NP	Bias	AAD	NP	Bias	AAD	NP
PGPE	−0.12	0.68	22	0.17	1.01	22	−0.29	1.17	22
DEGBE	−0.18	0.81	22	0.57	1.1	22	−0.77	1.48	22
TriEGDME	0.27	0.43	40	−1.36	1.7	34	1.74	2.10	34
TEGDME	0.4	0.68	40	−0.86	1.46	34	1.38	2.03	34

4. CONCLUSION

We have developed a new equation of state called the GMA EoS and applied it to the glycol ethers. We found that it calculates thermodynamic properties for these compounds successfully and accurately. The capability of this EoS to predict densities has been demonstrated and compared with several other EoSs. It can also predict other volumetric and dynamic properties of the glycol ethers at any temperature and pressure.

In general, the GMA EoS provide a simple procedure for prediction of thermodynamic properties of glycol ethers. This is a significant benefit in practical applications.

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