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Calculation of thermodynamic properties of lubricant + refrigerant mixtures using GMA equation of state

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Abstract

In this work, we have used a simple equation of state (EoS) to calculate the density of five lubricant/refrigerant mixtures including octane/dimethyl carbonate, TriEGDME/HFC-134a, TEGDME/HFC-134a, heptane/TEGDME, and decane/dimethyl carbonate at different temperatures, pressures, and compositions. The excess molar volumes of these mixtures have been calculated using this equation of state. Also, we have computed other thermodynamic properties such as isobaric expansion coefficient, isothermal compressibility, and internal pressure, for octane/dimethyl carbonate system for which the corresponding experimental values are available. A wide comparison with experimental data has been made for each thermodynamic property. The values of statistical parameters between experimental and calculated properties show the ability of this equation of state in reproducing and calculating of different thermodynamic properties for studied mixtures.

Keywords: Excess molar volume; GMA equation of state; Internal pressure; Isobaric expansion coefficient; Isothermal compressibility; Lubricant; Refrigerant

1. Introduction

IUPAC and the Thermophysical Properties Division of NIST have identified the knowledge of the properties of mixtures of lubricants with replacement HFC refrigerants as a high priority research area, and there is a need to develop methods to predict compatibility regimes and properties [1]. The polyol esters (POEs) and the polyalkylene glycols (PAGs) have been proposed as refrigerant oils. The optimal applications of POE and PAG lubricant/refrigerant mixtures require the study of their physical properties such as density.

In the last few years new oils based on carbonate molecules have been proposed [2–4] as candidates for stationary air conditioners because of their thermal stability, lubricity, and miscibility with refrigerants. Dialkyl carbonates have been proposed as alternative lubricants in low environmental impact air conditioners because of their miscibility with HFC's, favorable viscosity, and thermal stability [5–7]. Besides their intrinsic interest, thermodynamic properties of the dialkyl carbonate + n-alkane mixtures allow us to obtain parameters for molecular models that are useful to predict thermophysical properties for HFC's + carbonate systems [8,9].

Experimental densities for the compressed liquid phase have been reported for dimethyl carbonate, octane, and nine of their mixtures over the wide composition, temperature, and pressure ranges by Lugo et al. [10]. Comunas et al. [11] reported 1017 PVT measurements of HFC-134a and TEGDME system. Experimental densities in the compressed liquid phase were reported for HFC-134a, TriEGDME, and six of their mixtures by Comunas et al. [12]. From the experimental results, they analyzed the volumetric behavior of HFC-134a + TriEGDME. For each composition, the experimental values were correlated using a Tait-type equation. Furthermore, the isothermal compressibilities, isobaric expansion coefficients, and internal pressures have been calculated using the Tait correlations. Marsh and Kandil [13] summarized some recent work on measurements on mixtures of HFC refrigerants with synthetic lubricant oils. Acevedo et al. [14] reported 885 experimental density values for tetraethylene glycol dimethyl ether (TEGDME), heptane, and nine of their mixtures in the compressed liquid phase. The isothermal compressibility, the isobaric expansion coefficient, the internal pressure, and the excess molar volume have been

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Nomenclature

P	pressure	MPa
P_i	internal pressure	MPa
T	temperature	K
V_m^E	excess molar volume	$cm^3\,mol^{-1}$
x	mole fraction	
Z	compression factor	

Greek letters

α_P	isobaric expansion coefficient	K^{-1}
κ_T	isothermal compressibility	MPa^{-1}
ρ	molar density	$mol\,m^{-3}$

determined from the density data. Density data of the dimethyl carbonate + decane system reported for a wide temperature and pressure ranges over the whole composition range by Troncoso et al. [15]. Data were correlated through a temperature-dependent Tait equation to derive isothermal compressibilities and isobaric expansion coefficients. Excess quantities for molar volume, isothermal compressibility, and isobaric thermal expansion coefficients were also given.

Equations of state are required for the calculations of thermodynamic properties needed in process engineering. A new equation of state (EoS) for liquids has been recently introduced by Goharshadi et al. [16] (Goharshadi–Morsali–Abbaspour "GMA EoS") which has been found to be valid for a wide range of fluids including polar, nonpolar, refrigerants, and hydrogen-bonded fluids [16–18]. The EoS has been also applied for liquid mixtures properly [19–21].

In this work, we have used the GMA EoS to reproduce and calculate accurately the volumetric and thermodynamic properties such as density, isobaric expansion coefficient, α_P, isothermal compressibility, κ_T, and internal pressure, P_i, of five lubricant/refrigerant mixtures at various temperatures, pressures, and compositions. In addition, the excess molar volumes for these mixtures were calculated. A wide comparison with corresponding experimental data has been made in each case.

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

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

Eq. (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 V_m ($V_m = 1/\rho$) is the molar volume. 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 [16], 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 a linear relation with temperature. It has been proved that this assumption works well [16]. 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),

$$d\left(\frac{P}{T}\right) = \left(\frac{A_1 + A_2 T}{T^2}\rho^4 + \frac{B_1 + B_2 T}{T^2}\rho^5\right)dT \tag{12}$$

a new EoS results

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

$g(\rho)$has been arbitrary 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) in Eq. (13) and arranging gives GMA EoS [16], that is

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

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 to 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

We have used the experimental PVT data of some lubricant/refrigerant mixtures at various temperatures, pressures, and compositions to examine the linearity of $(2Z-1)V_m^3$ versus ρ (Eq. (15)). As an example, Fig. 1 shows the results for TriEGDME + HFC-134a ($x_{\text{HFC-134a}} = 0.6015$) at different temperatures. As Fig. 1 and the maximum and minimum values of *Rsqr* in Table 1 show the linearity of $(2Z-1)V_m^3$ versus ρ holds well for all studied mixtures at different temperatures. Table 2 shows the values of the constants of Eqs. (16) and (17) for tested mixtures.

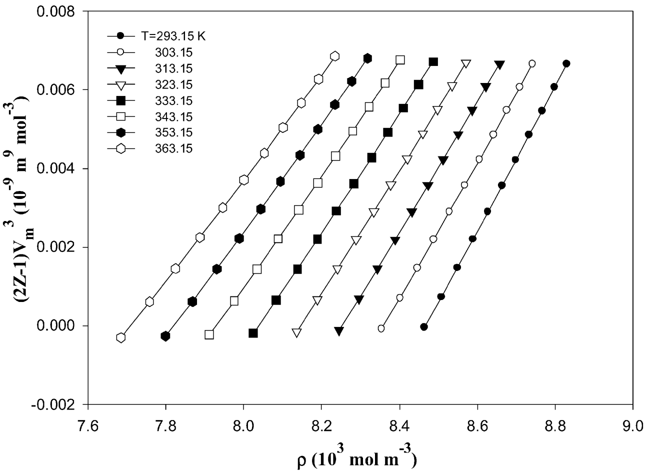

Fig. 1. Isotherms of $(2Z-1)V_m^3$ versus ρ for a mixture of TriEGDME + HFC-134a ($x_{\text{HFC-134a}} = 0.6015$) [12].

Liquid densities can be calculated from equations of state and it provides a reasonable test for the equation of state. The density of five lubricant/refrigerant mixtures at different temperatures and pressures has been calculated using GMA EoS by the following equation:

$$B(T)\rho^5 + A(T)\rho^4 + \rho - \frac{2P}{RT} = 0 \tag{18}$$

Table 1

The minimum and maximum values of square of correlation coefficient (*Rsqr*) of Eq. (15) and pressure range of the data for lubricant/refrigerant mixtures

X	$Rsqr_{\text{min}}$–$Rsqr_{\text{max}}$	ΔP [MPa]	NP
octane $(1-x)$ + dimethyl carbonate (x) [10]			
0.00000	0.9997–0.9999	0.1–25	81
0.10449	0.9998–1.0000	0.1–25	81
0.22037	0.9998–1.0000	0.1–25	81
0.32926	0.9998–1.0000	0.1–25	81
0.3996	0.9998–0.9999	0.1–25	81
0.5016	0.9998–1.0000	0.1–25	81
0.60277	0.9999–1.0000	0.1–25	81
0.69048	0.9999–1.0000	0.1–25	81
0.80821	0.9999–1.0000	0.1–25	81
0.90164	0.9999–1.0000	0.1–25	81
1.00000	1.0000–1.0000	0.1–25	81
TriEGDME $(1-x)$ + HFC-134a (x) [12]			
0.0000	0.9996–0.9999	0.1–50	117
0.2013	0.9998–1.0000	10–50	99
0.3517	0.9998–1.0000	10–50	99
0.4596	0.9995–0.9999	10–50	99
0.6015	0.9995–0.9999	10–50	99
0.7784	0.9990–0.9998	10–50	99
0.9295	0.9989–0.9997	10–50	99
1.0000	0.9992–0.9997	10–50	99
TEGDME $(1-x)$ + HFC-134a (x) [11]			
0.0000	0.9998–1.0000	10–60	99
0.1114	0.9995–1.0000	10–60	98
0.2896	0.9997–1.0000	10–60	55
0.3648	0.9998–1.0000	10–60	99
0.5702	0.9993–0.9999	10–60	99
0.6931	0.9994–0.9998	10–60	99
0.7288	0.9992–0.9998	10–60	55
0.8727	0.9986–0.9996	10–60	99
0.9290	0.9988–0.9996	10–60	99
1.0000	0.9993–0.9988	10–60	99
heptane $(1-x)$ + TEGDME (x) [14]			
0.0000	0.9997–0.9999	0.1–25	81
0.10504	0.9995–0.9998	0.1–25	81
0.40213	0.9995–0.9999	0.1–25	81
0.59095	0.9997–0.9999	0.1–25	81
0.69827	0.9995–1.0000	0.1–25	81
0.80114	0.9995–0.9998	0.1–25	81
0.90199	0.9996–1.0000	0.1–25	81
1.0000	0.9996–1.0000	0.1–25	81
decane $(1-x)$ + dimethyl carbonate (x) [15]			
0.0000	0.9999–1.0000	0.1–40	35
0.0676	0.9998–1.0000	0.1–40	34
0.2934	0.9999–1.0000	0.1–40	33
0.5476	0.9998–1.0000	0.1–40	34
0.7101	1.0000–1.0000	0.1–40	34
0.9062	0.9999–1.0000	0.1–40	33
1.0000	0.9999–1.0000	0.1–40	35

Table 2
Values of constants of GMA EoS, correlation coefficient of Eqs. (16) and (17), the number of calculated density, and the AAD in density for lubricant/refrigerant mixtures

x	A_0 [L^3 mol^{-3}]	A_1 [L^4 atm mol^{-4}]	A_2 [L^4 atm mol^{-4} K^{-1}]	*Rsqr*	B_0 [L^4 mol^{-4}]	B_1 [L^5 atm mol^{-5}]	B_2 [L^5 atm mol^{-5} K^{-1}]	*Rsqr*	*NP*	*AAD*
octane $(1-x)$ + dimethyl carbonate (x)										
0.00000	2.0914	14.0959	−0.0102086	0.9997	−0.155366	−1.69168	0.000681236	0.9995	81	0.013
0.10449	3.33534	14.7051	−0.0181931	0.9999	−0.372634	−1.80588	0.00205743	0.9998	81	0.013
0.22037	1.18106	8.88566	−0.00553223	0.9997	−0.0580755	−0.929265	0.000199998	0.9996	81	0.011
0.32926	1.75778	8.61353	−0.00939616	0.9997	−0.158482	−0.910887	0.000853369	0.9995	81	0.011
0.39960	0.899168	6.24319	−0.00436075	0.9997	−0.0476315	−0.592925	0.000199714	0.9995	81	0.013
0.50160	0.3211	4.21941	−0.00107788	0.9996	0.0123778	−0.351099	−0.000141084	0.9994	81	0.011
0.60277	−0.10233	2.61809	0.00128881	0.9996	0.051826	−0.173322	−0.000360632	0.9995	81	0.010
0.69048	−0.194458	1.91139	0.0017216	0.9996	0.0501287	−0.111866	−0.000339334	0.9994	81	0.034
0.80821	0.762673	3.18079	−0.00421888	0.9999	−0.0557288	−0.250056	0.000313658	0.9998	81	0.011
0.90164	0.284317	1.86523	−0.00141717	0.9998	−0.0125986	−0.12558	5.97E–05	0.9997	81	0.007
1.00000	0.237733	1.43335	−0.00122233	0.9999	−0.0114444	−0.0901187	5.90E–05	0.9998	81	0.005
TriEGDME $(1-x)$ + HFC-134a (x)										
0.0000	0.133164	25.0326	0.00442114	0.9985	0.490579	−2.90266	−0.00354884	0.9978	117	0.021
0.2030	3.12842	19.9658	−0.0158958	0.9997	−0.256581	−2.39269	0.00125728	0.9995	99	0.015
0.3517	1.73591	12.0212	−0.00848994	0.9997	−0.101288	−1.25919	0.000431082	0.9995	99	0.018
0.4596	−0.59409	4.50852	0.00493278	0.9990	0.182617	−0.279885	−0.00121334	0.9985	99	0.023
0.6015	1.03478	5.20941	−0.0054478	0.9998	−0.0738172	−0.461072	0.000386492	0.9997	99	0.036
0.7784	0.292338	1.86449	−0.00141304	1.0000	−0.0104107	−0.126957	4.12E–05	0.9999	99	0.057
0.9295	−0.0424086	0.423027	0.000407207	0.9992	0.0113386	−0.0121125	−7.60E–05	0.9983	99	0.073
1.0000	0.0569684	0.418082	−0.00024646	1.0000	−0.000979334	−0.0206703	1.48E–06	0.9999	99	0.096
TEGDME $(1-x)$ + HFC-134a (x)										
0.0000	20.2148	98.9135	−0.109833	0.9998	−2.88029	−16.9791	0.0156959	0.9998	99	0.010
0.1114	22.5293	86.9225	−0.126914	0.9995	−3.67241	−14.7595	0.0209897	0.9992	98	0.011
0.2896	8.20568	39.2958	−0.0443912	0.9997	−1.00093	−5.53814	0.00545487	0.9996	55	0.016
0.3648	7.03322	31.1365	−0.038536	0.9999	−0.842336	−4.15401	0.00466444	0.9998	99	0.015
0.5702	2.01585	10.551	−0.0106216	0.9969	−0.15684	−1.07627	0.000816714	0.9948	99	0.029
0.6931	2.38167	8.22858	−0.0134491	0.9991	−0.230341	−0.815306	0.0013173	0.9987	99	0.040
0.7288	0.15553	3.07741	−0.00020759	1.0000	0.0272788	−0.215423	−0.00021859	1.0000	55	0.047
0.8727	0.0988832	1.16649	−0.000320968	1.0000	0.00532017	−0.0654183	−4.82E–05	1.0000	99	0.069
0.9290	0.00588971	0.612866	0.000144053	0.9999	0.00849575	−0.0257166	−6.08E–05	0.9999	99	0.077
1.0000	0.0452766	0.396211	−0.000175455	0.9999	0.00016502	−0.0184879	−5.46E–06	0.9999	99	0.085
heptane $(1-x)$ + TEGDME (x)										
0.00000	1.55273	9.09467	−0.00787303	0.9991	−0.107618	−0.962393	0.000506697	0.9987	81	0.012
0.10504	5.24363	18.1098	−0.0298794	0.9979	−0.669354	−2.33383	0.00387433	0.9968	81	0.012
0.40213	−6.06138	4.8242	0.0404012	0.9996	1.37396	0.170901	−0.00871977	0.9994	81	0.009
0.50997	3.68503	28.317	−0.0177536	0.9972	−0.263976	−3.84651	0.00109074	0.9959	81	0.007
0.59095	6.80383	37.8971	−0.0361936	0.9966	−0.822409	−5.59223	0.00443986	0.9947	81	0.006
0.69827	12.0749	55.4671	−0.0663244	0.9984	−1.63444	−8.63168	0.00907104	0.9975	81	0.006
0.80114	−14.6248	12.0427	0.0973861	0.9958	4.02846	0.623435	−0.025554	0.9938	81	0.006
0.90199	23.3037	93.0594	−0.131268	0.9981	−3.99737	−16.5411	0.0229313	0.9973	81	0.004
1.00000	6.30945	72.5193	−0.0248311	0.9996	−0.0422313	−11.6498	−0.00169375	0.9995	81	0.004
decane $(1-x)$ + dimethyl carbonate (x)										
0.0000	−0.317728	21.2263	0.00648127	0.9992	0.43774	−2.75881	−0.00316017	0.9987	35	0.006
0.0676	3.00226	24.9766	−0.0140433	0.9992	−0.220885	−3.48658	0.000875674	0.9988	34	0.008
0.2934	3.22228	17.1635	−0.0171401	0.9994	−0.354274	−2.19351	0.00191936	0.9991	33	0.011
0.5476	−0.500452	4.09401	0.00407782	0.9997	0.143662	−0.289719	−0.000943364	0.9995	34	0.008
0.7101	4.917	12.374	−0.0292462	0.9998	−0.553632	−1.34417	0.00332668	0.9997	34	0.006
0.9062	−0.347948	0.864809	0.00247622	0.9995	0.050028	−0.025686	−0.000324435	0.9992	33	0.008
1.0000	−0.143269	0.730671	0.00110462	0.9998	0.02071	−0.0305947	−0.00013725	0.9997	35	0.008

As Eq. (18) shows the GMA EoS is a fifth-order polynomial in density and hence it has five roots. Only one or two roots have physical significance since they correspond to the vapor and liquid roots. An important part of the practical use of equations of state is the reliable computation of a desired root which is a nontrivial task and that is a function of a number of algorithmic issues, including the numerical method used to solve the equations and initial estimate of the root [22]. To explain the numerical aspects associated with the GMA EoS, consider octane + dimethyl carbonate

Table 3
Density roots of the GMA EoS for octane + dimethyl carbonate ($x_{\text{dimethyl carbonate}} = 0.50160$) at 0.1 MPa and 278.15 K

Root	Value
1(liquid)	8.1834
2	1.8412
3 (vapor)	0.0865
4	0.9259 + 1.39001i
5	0.9259 − 1.39001i

($x_{\text{dimethyl carbonate}} = 0.50160$) at 0.1 MPa and 278.15 K. The five density roots of the GMA EoS for these conditions are shown in Table 3. Note that only roots 1 and 3 have physical significance since they correspond to the liquid and vapor roots, respectively.

The ability of this EoS to reproduce and calculate different thermodynamic properties for these compounds at different temperatures and pressures may be evaluated using the statistical parameters [23,24] namely, the absolute average deviation (AAD) and the average percent deviation (bias). *AAD* is defined as follows:

$$AAD = \frac{1}{N}\sum_{i=1}^{N} 100\left|\frac{Y_{\text{exp}} - Y_{\text{cal}}}{Y_{\text{exp}}}\right| \tag{19}$$

where Y is a property of interest.

The AAD characterizes the fact that the calculated values are more or less close to experimental points. The bias characterizes the quality of the distribution of the calculated data on either side of the experimental points [25]. The statistical parameters between experimental and calculated densities and the number of points for lubricant/refrigerant studied mixtures have been listed in Table 2. Also, the accuracy of calculating density from measurements at other temperatures for TEGDME $(1 - x)$ + HFC-134a (x) [11] has been given in Table 4. These tables show the fact that GMA EoS can calculate and reproduce the experimental density of these compounds with a good accuracy.

3.2. Derived properties

Isobaric expansion coefficient, $\alpha_P = \frac{1}{V}(\frac{\partial V}{\partial T})_P$, isothermal compressibility, $\kappa_T = -\frac{1}{V}(\frac{\partial V}{\partial P})_T$, and internal pressure,

Table 4
Accuracy of calculating binary mixture densities from measurements at other temperatures for TEGDME $(1 - x)$ + HFC-134a (x) [11]

T [K]	$x = 0.2896$			$x = 0.7288$		
	P [MPa]	ρ_{cal} [10^3 mol m^{-3}]	$\%(\rho_{\text{exp}}-\rho_{\text{cal}})/\rho_{\text{exp}}$	P [MPa]	ρ_{cal} [10^3 mol m^{-3}]	$\%(\rho_{\text{exp}}-\rho_{\text{cal}})/\rho_{\text{exp}}$
313.15	10	5.5253	−0.004	10	8.4086	0.004
	15	5.5459	−0.001	15	8.4638	0.019
	20	5.5660	0.003	20	8.5163	0.013
	25	5.5855	−0.003	25	8.5665	0.008
	30	5.6045	0.001	30	8.6145	0.003
	35	5.6230	−0.006	35	8.6606	−0.006
	40	5.6410	−0.014	40	8.7049	−0.021
	45	5.6587	−0.014	45	8.7476	−0.042
	50	5.6759	−0.026	50	8.7889	−0.055
	55	5.6928	−0.032	55	8.8288	−0.078
	60	5.7092	−0.031	60	8.8675	−0.087
353.15	10	5.3067	0.004	10	7.9209	−0.036
	15	5.3323	0.013	15	7.9967	0.010
	20	5.3570	0.019	20	8.0674	0.018
	25	5.3809	0.021	25	8.1336	0.007
	30	5.4040	0.018	30	8.1961	−0.012
	35	5.4264	0.009	35	8.2552	−0.036
	40	5.4481	0.002	40	8.3115	−0.060
	45	5.4692	−0.022	45	8.3651	−0.089
	50	5.4897	−0.036	50	8.4165	−0.089
	55	5.5096	−0.030	55	8.4657	−0.126
	60	5.5290	−0.053	60	8.5130	−0.158
373.15	10	5.1991	−0.042	10	7.6596	0.039
	15	5.2276	−0.015	15	7.7501	0.077
	20	5.2550	−0.008	20	7.8332	0.087
	25	5.2813	−0.011	25	7.9102	0.071
	30	5.3066	−0.006	30	7.9821	0.045
	35	5.3311	−0.024	35	8.0495	0.009
	40	5.3547	−0.027	40	8.1132	−0.044
	45	5.3776	−0.046	45	8.1736	−0.073
	50	5.3998	−0.062	50	8.2310	−0.130
	55	5.4214	−0.056	55	8.2858	−0.172
	60	5.4423	−0.078	60	8.3382	−0.221

$P_i = (\frac{\partial U}{\partial V})_T$ for octane $(1-x)$ + dimethyl carbonate (x) [10] have been calculated at different temperatures, pressures, and compositions. The functions used for calculating these properties using GMA EoS are given as Eqs. (20)–(22), respectively.

$$\begin{aligned}\alpha_P = {} & \big[(2B_1 + 2B_2T)\rho^5 + (2A_1 + 2A_2T)\rho^4 + 2P\big] \\ & \times \big[5\rho^5\big(RT^2B_0 - 2B_1T + 2T^2B_2\ln T\big) \\ & + 4\rho^4\big(A_0RT^2 - 2A_1T + 2A_2T^2\ln T\big) \\ & + RT^2\rho\big]^{-1} \end{aligned} \tag{20}$$

$$\begin{aligned}\kappa_T = {} & 2\big[\rho RT + 4\rho^4(RTA_0 - 2A_1 + 2TA_2\ln T) \\ & + 5\rho^5(B_0RT - 2B_1 + 2B_2T\ln T)\big]^{-1} \end{aligned} \tag{21}$$

$$P_i = (B_1 + B_2T)\rho^5 + (A_1 + A_2T)\rho^4 \tag{22}$$

The statistical parameters correspond to calculations of α_P, κ_T, and P_i and the number of points for this mixture have been given in Table 5. The values of statistical parameters show GMA EoS can calculate these thermophysical properties very well in accord to corresponding experimental data.

Table 5
The statistical parameters of isobaric expansion coefficient (α_P), isothermal compressibility (K_T), and internal pressure (P_i) for octane $(1-x)$ + dimethyl carbonate (x) [10]

x	Derived property								
	α_P			κ_T			P_i		
	bias	*AAD*	*NP*	*bias*	*AAD*	*NP*	*bias*	*AAD*	*NP*
0.00000	0.18	0.44	63	0.33	1.50	63	−0.231	1.632	49
0.10449	0.20	0.33	63	0.14	1.30	63	0.080	1.343	49
0.22037	0.14	0.22	63	0.18	1.26	63	−0.109	1.295	49
0.32926	0.20	0.44	63	0.26	1.29	63	−0.033	1.332	49
0.39960	0.05	0.41	63	0.40	1.34	63	−0.419	1.464	49
0.50160	2.91	2.93	63	0.49	1.31	63	−0.457	1.358	49
0.60277	0.08	0.24	62	0.46	1.25	63	−0.430	1.300	49
0.69048	0.04	0.24	63	0.77	1.40	63	−0.539	1.239	49
0.80821	0.19	0.83	63	0.54	1.11	63	−0.348	1.269	49
0.90164	0.13	0.35	63	0.46	0.98	63	−0.344	0.984	49
1.00000	0.00	0.45	54	0.33	0.67	56	−0.304	0.791	42

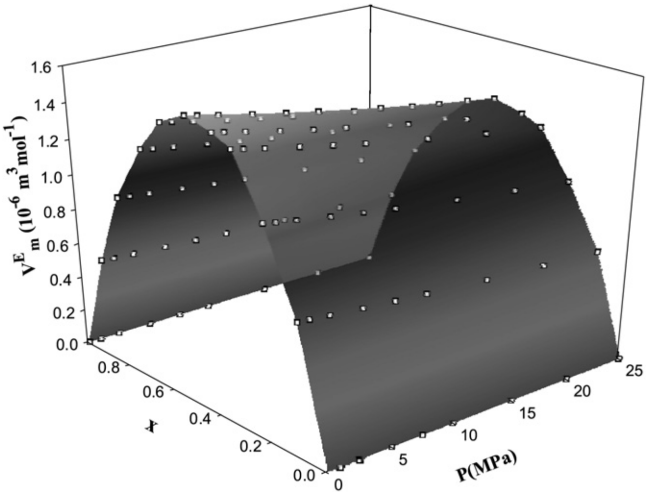

Fig. 2. The three-dimensional surface of calculated V_m^E versus pressure and mole fraction at 323.15 K for the octane $(1-x)$ + dimethyl carbonate (x) mixture [10].

3.3. Excess molar volumes

Excess molar volumes reflect interaction between the molecules of a mixture. From a practical point of view, the excess molar volumes are useful for the design of mixing, storage, and process equipment. The values of V_m^E are calculated from the following equation:

$$\begin{aligned}V_m^E = {} & \big[\big(xM_1 + (1-x)M_2\big)/\rho\big] \\ & - \big[(xM_1/\rho_1) + \big((1-x)M_2/\rho_2\big)\big] \end{aligned} \tag{23}$$

where ρ, ρ_i, and x are the density of liquid mixture and the density of pure components and mole fraction, respectively. M_i stands for molar mass of pure component i $(i = 1, 2)$. Fig. 2 shows the three-dimensional surface of calculated V_m^E versus pressure and mole fraction at 323.15 K for the octane $(1-x)$ + dimethyl carbonate (x) mixture.

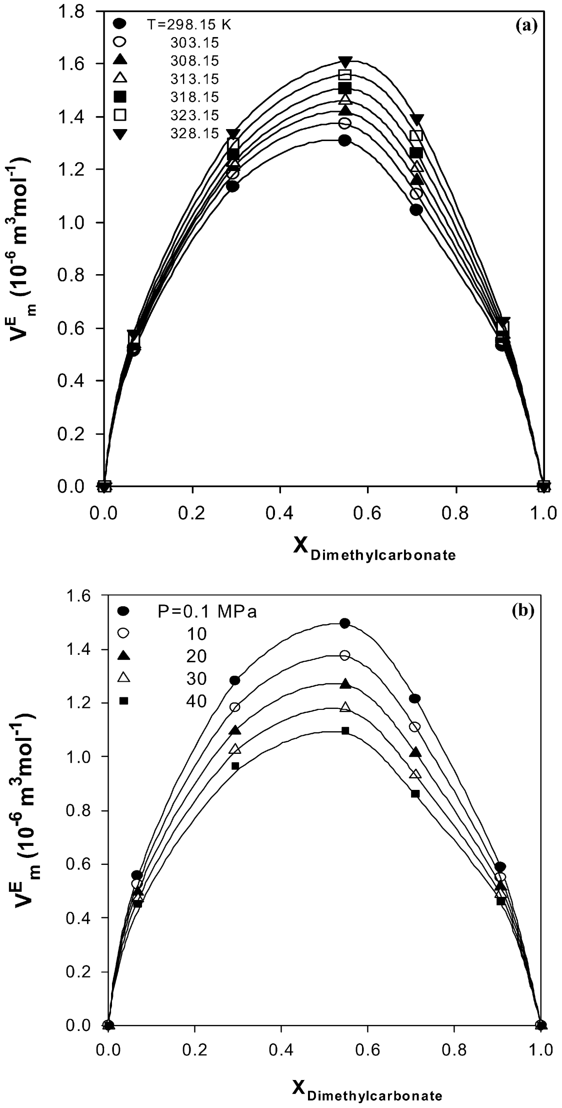

Fig. 3. Experimental (symbols) and calculated (solid lines) excess molar volumes for the decane $(1-x)$ + dimethyl carbonate (x) system [15] versus mole fractions (a) at 10 MPa for different temperatures and (b) at 303.15 K for different pressures.

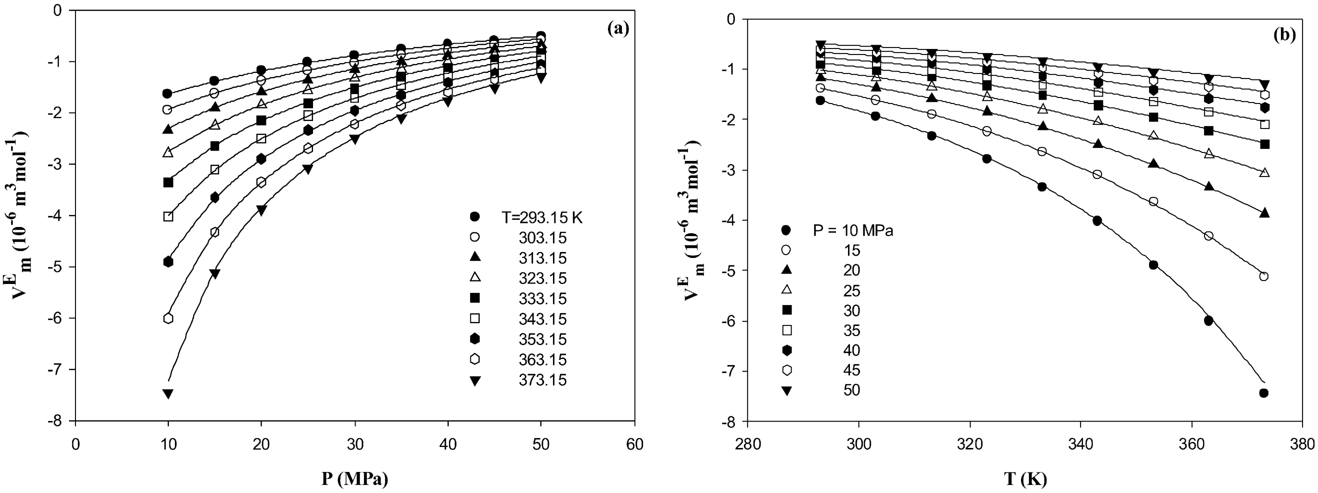

Fig. 4. Experimental (symbols) and calculated (solid lines) excess molar volumes at $x = 0.4596$ for the TriEGDME $(1 - x)$ + HFC-134a (x) system (a) versus pressures for different temperatures and (b) versus temperatures for different pressures.

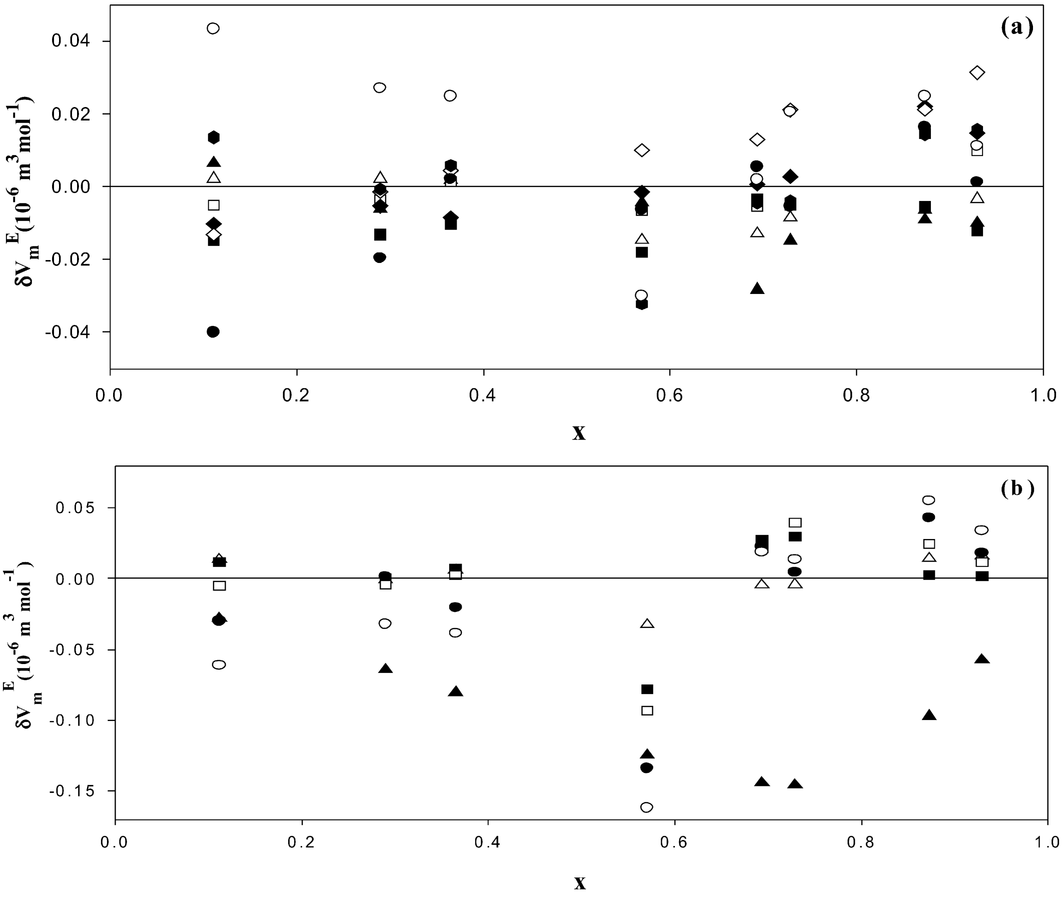

Fig. 5. Deviation of experimental excess molar volumes, V^E_m, from the calculated values with GMA EoS for TEGDME $(1 - x)$ + HFC-134a (x) [10] (a) at 20 MPa for different temperatures: ▲ 293.15 K; △ 303.15 K; ■ 313.15 K; □ 323.15 K; ◆ 333.15 K; ◇ 343.15 K; ⬢ 353.15 K; ○ 363.15 K; ● 373.15 K, and (b) at 353.15 K for different pressures: ▲ 10 MPa; △ 20 MPa; ■ 30 MPa; □ 40 MPa; ● 50 MPa; ○ 60 MPa.

Fig. 3 shows the calculated and experimental excess molar volumes for the decane $(1 - x)$ + dimethyl carbonate (x) [15] system versus mole fractions at 10 MPa for different temperatures and at 303.15 K for different pressures.

The calculated and experimental excess molar volumes for the TriEGDME $(1 - x)$ + HFC-134a (x) [12] mixture at $x = 0.4596$ versus pressure at different temperatures and versus temperature at different pressures have been represented in Figs. 4(a) and 4(b), respectively. It can be seen easily that the excess molar volumes increase when the pressure decreases for different isotherms and when the temperature increases for different isobars.

Table 6
The statistical parameters of excess molar volume for lubricant/refrigerant mixtures

x	*bias*	*AAD*
octane $(1-x)$ − dimethyl carbonate (x)		
0.10449	0.105	1.574
0.22037	−0.040	0.656
0.32926	0.006	0.401
0.39960	0.249	0.516
0.50160	0.154	0.556
0.60277	0.104	0.334
0.69048	−0.042	0.484
0.80821	0.113	0.721
0.90164	0.034	0.553
TriEGDME $(1-x)$ + HFC-134a (x)		
0.2030	3.433	3.861
0.3517	2.707	2.867
0.4596	2.043	2.164
0.6015	1.328	1.397
0.7784	0.662	0.794
0.9295	3.199	5.148
TEGDME $(1-x)$HFC-134a (x)		
0.1114	1.180	3.810
0.2896	1.731	2.203
0.3648	1.477	1.785
0.5702	1.856	2.026
0.6931	0.571	1.335
0.7288	−0.363	1.120
0.8727	−0.363	1.933
0.929	−1.530	1.991
heptane $(1-x)$ + TEGDME (x)		
0.10504	0.2502	2.9219
0.40213	0.1572	2.0055
0.50997	0.1317	1.9659
0.59095	−3.1137	1.9297
0.69827	−0.3634	2.1928
0.80114	−0.5356	4.2500
decane $(1-x)$ + dimethyl carbonate (x)		
0.0676	2.664	2.979
0.2934	1.377	1.454
0.5476	0.435	0.508
0.7101	0.192	0.277
0.9062	0.204	0.379

Fig. 5 shows the deviation of calculated excess molar volumes from corresponding experimental data against mole fraction for TEGDME $(1-x)$ + HFC-134a (x) at 20 MPa for different temperatures and at 353.15 K for different pressures.

To assess the performance of GMA EoS in calculation of excess molar volumes, we compare our results with two different correlations that have been introduced by Lugo et al. [26] for octane $(1-x)$ + dimethyl carbonate (x) system. The AAD and bias for the first correlation (consists of 67 parameters) are 1.2 and 0.2, and for the second correlation (consists of 11 parameters) are 1.8 and 0.2, and for our work are 0.644 and 0.076, respectively. Hence, GMA EoS has superior ability to calculate the excess molar volumes of this system than those of Lugos' correlations.

The calculated values of V_m^E have been also compared with the corresponding experimental data using statistical parameters (bias and AAD) for investigated liquid mixtures and the results have been shown in Table 6.

4. Conclusion

We have used a new equation of state called GMA EoS to the lubricant/refrigerant mixtures and found it is applied for these compounds successfully. The capability of this EoS to calculate density has been demonstrated. It can also calculate other volumetric and thermophysical properties of these mixtures at any temperature and pressure.

The results support that GMA equation of state is capable of calculating the excess molar volume of lubricant/refrigerant mixtures.

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