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Prediction of thermodynamic properties of polymeric liquids using a new equation of state

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Abstract

In this paper, we have used a simple equation of state (EoS) to predict the density for polymeric liquid mixtures at different temperatures, pressures, and compositions. The excess molar volumes of these mixtures have been also calculated using this equation of state. Also, we have computed isothermal compressibility. 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 predicting different thermodynamic properties for studied polymeric mixtures.

Keywords: Equation of state; Polymeric liquids; Specific volume

1. Introduction

Polymeric liquids are widely used for industrial and academic purposes. Poly(ethylene glycol)s (PEGs), are frequently used in the pharmaceutical and cosmetic fields as solvents, carriers, humectants, lubricants, binders, bases, and coupling agents and also for extraction, separation, and purification of biological materials [1].

During the last decade, aqueous solutions of PEGs have received considerable attention both experimentally [2–6] and theoretically [7–10]. Aqueous solutions of a closely related polymer, poly(propylene glycol) (PPG) have also been studied. The higher hydrophobicity of PPG makes it soluble in a broad range of solvents, ranging from *n*-hexane (where it shows an upper consolute temperature) to water (where it shows a lower consolute temperature) [11].

Predicting the thermodynamic properties of hydrogen-bonded systems (such as PEG systems) is a challenging problem that has received considerable attention. Both activity coefficient models and equations of state (EoSs) have been developed for hydrogen-bonded fluids [12]. Different theoretical EoSs have been tested against extensive pressure–volume–temperature (PVT) data of pure polymers [13,14], polymer–solvent, and blend systems [15–17].

The purpose of this study is to report the results of simultaneous calculations of volumetric and thermodynamic properties such as molar density, ρ_m, specific volume, V, excess volume, V^E, and isothermal compressibility, κ_T, for polymer melts, solutions, and blends using a new EoS derived by Goharshadi, Morsali, and Abbaspour 'the GMA EoS' [18]. A wide comparison with experimental data was made. The accuracy of the equation of state in prediction of thermodynamic properties of polymer melts and mixtures has been determined by the statistical parameters and compared with other ones calculated by the the Flory–Orwoll–Vrij (FOV), the Schotte, and the Ihm–Song–Mason (ISM) equations of state.

1.1. Theoretical basis

A general EoS for liquids has been recently derived by Goharshadi et al. (the GMA EoS) [18], which has been found to be valid for polar, nonpolar, and hydrogen-bonded pure fluids and non-polymeric liquid mixtures [18–21]. The equation of state is based on the average potential energy and that is

$$(2Z-1)V_m^3 = A(T) + B(T)\rho_m \quad (1)$$

where Z, V_m, and ρ_m are compressibility factor, molar volume, and molar density, respectively. The intercept and the slope of this equation both depend on temperature via the equations

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

$$B(T) = B_0 - \frac{2B_1}{RT} + \frac{2B_2 \ln\ T}{R} \quad (3)$$

where A_0-A_2 and B_0-B_2 are constants. To use the GMA EoS for a liquid, the A and B parameters must be known. To find these parameters, one may plot $(2Z-1)V_m^3$ against ρ_m for different isotherms. The slope and intercept of the straight lines can be fitted to Eqs. (2) and (3) and from which A_0 to A_2 and B_0 to B_2 can be found, respectively.

The functions used for calculating density and isothermal compressibility using Eq. (1) are given as Eqs. (4) and (5), respectively. The constants A_0-A_2 and B_0-B_2 can be used to calculate these properties of liquid polymer systems at any temperature and pressure.

$$\left(\frac{B_0RT}{2} - B_1 + TB_2 \ln\ T\right)\rho_m^5 + \left(\frac{A_0RT}{2} - A_1 + A_2T \ln\ T\right)\rho_m^4 + \frac{\rho_m RT}{2} - P = 0 \quad (4)$$

$$\kappa_T = \frac{2}{\rho_m RT + 4\rho_m^4(RTA_0 - 2A_1 + 2TA_2 \ln\ T) + 5\rho_m^5(B_0RT - 2B_1 + 2B_2T \ln\ T)} \quad (5)$$

2. Results and discussion

Experimental PVT data of some polymer melts, and binary polymer solutions and blends [22–27] at various temperatures and pressures have been used to examine the linearity of $(2Z-1)V_m^3$ versus ρ_m (Eq. (1)). This regularity has also been studied for ternary polymeric mixtures [28]. In some cases, i.e. PEG-200+PPG-400 and water+PPG-400 [24,25] the experimental densities were calculated using a generalized Tait equation of the form

$$\rho = \frac{\rho_0}{1 - B_4 \ln\ \left(\frac{B+P}{B+P_0}\right)} \quad (6)$$

where

$$\rho_0 = B_1 + B_2T + B_3T^2 \quad (7)$$

$$B = B_5 \exp(-B_6T) \quad (8)$$

where B_1 to B_6 are constants, which are independent of temperature and pressure. The value of P_0 is 0.1 MPa and ρ_0 is the density at P_0. As a sample, Fig. 1 depicts the isotherms of $(2Z-1)V_m^3$ against molar density for PEG-200(1)+PPG-400(2) ($x_1=0.6$). As the figure shows the linearity holds very well and the slope and the intercept both depend on temperature. The results for binary and ternary mixtures have been summarized in Tables 1 and 2, respectively, including the intercept, slope, and the square of the correlation coefficient (R^2) of Eq. (1) at each temperature and the pressure range of the experimental data. Considering the values of R^2 of the different polymer blends, solutions, and pure substances, it seems that this linearity is a universal feature for all these liquids. Tables 3 and 4 show the values of the constants of Eqs. (2) and (3). The ranges of pressure and temperature of these tables are the same as Tables 1 and 2.

A more sensitive test for the EoS is to calculate density at different temperatures, pressures, and compositions and compare with the corresponding experimental data. Hence, the density of the binary and ternary polymer mixtures and their pure components in the wide ranges of temperature, pressure, and composition has been calculated using Eq. (4) and the results have been changed to specific volumes (in $cm^3\ g^{-1}$) via this equation

$$V = \frac{1000}{\rho_m M_w} \quad (9)$$

which M_w is the molecular weight of the compound.

The accuracy in prediction of specific volume can be described by the average absolute deviation, AAD. The AAD characterizes that the experimental points are more or less close to calculated values. Tables 5–7 show the values of AAD of calculated specific volumes for the pure polymer melts and solvents, the binary solutions and blends, and the ternary mixtures, respectively. The ranges of pressure and temperature of these tables are the same as Tables 1 and 2.

To assess and compare the performance of the GMA EoS in prediction of specific volume of these polymeric mixtures and their pure components, the corresponding values of AAD obtained by the Flory–Orwoll–Vrij (FOV) [29], the Schotte [30], and the Ihm–Song–Mason (ISM) [31,32] EoSs have been calculated. The lower values of AAD obtained by the GMA EoS for binary and ternary mixtures support the ability of this EoS in prediction of specific volume of these liquid systems.

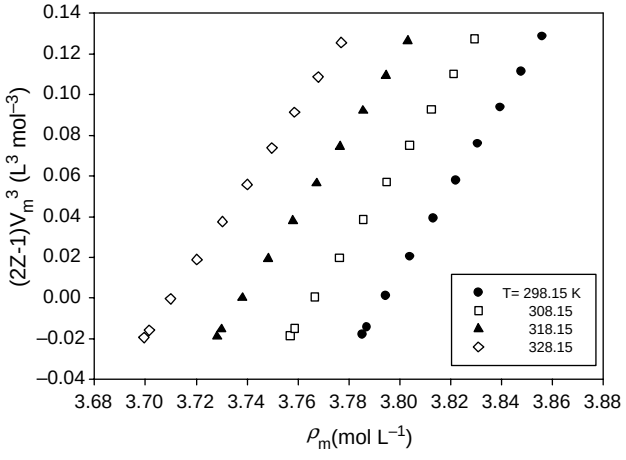

Fig. 1. The isotherms of $(2Z-1)V_m^3$ versus molar density for PEG-200(1)+PPG-400(2) ($x_1=0.6$) [25].

Table 1
The intercept (A), slope (B), the square of correlation coefficient (R2) of Eq. (1), and pressure range of the data for binary polymeric mixtures

X_1	T (K)	B (L^4 mol^{-4})	A (L^3 mol^{-3})	R^2	ΔP (MPa)	X_1	T (K)	B (L^4 mol^{-4})	A (L^3 mol^{-3})	R^2	ΔP (MPa)
	PEG–200(1) + 1–octanol(2)[a]					0.8	298.15	0.289595	−1.66072	0.999707	0.1–30
0.0	298.15	0.103319	−0.65545	0.999915	0.1–30		318.15	0.266766	−1.50827	0.999884	
	318.15	0.092212	−0.57583	0.999484			328.15	0.255226	−1.43226	0.999834	
	328.15	0.089367	−0.55341	0.999575			338.15	0.247646	−1.37981	0.999837	
	338.15	0.08632	−0.5301	0.999789		0.9	298.15	0.326245	−1.85064	0.999658	0.1–30
0.1	298.15	0.116729	−0.7302	0.999847	0.1–30		318.15	0.307442	−1.71964	0.999905	
	318.15	0.106696	−0.65705	0.999931			328.15	0.289702	−1.60884	0.999723	
	328.15	0.102047	−0.62327	0.99958			338.15	0.282928	−1.56022	0.999913	
	338.15	0.09895	−0.59944	0.999826		1.0	298.15	0.370921	−2.08283	0.999715	0.1–30
0.2	298.15	0.133246	−0.8221	0.999836	0.1–30		318.15	0.337466	−1.86874	0.999873	
	318.15	0.121847	−0.7403	0.999944			328.15	0.326342	−1.79448	0.999754	
	328.15	0.117228	−0.70633	0.999542			338.15	0.315133	−1.72061	0.999373	
	338.15	0.112651	−0.67352	0.999546		PEGME-350(1) + PEG-200(2)[b]					
0.3	298.15	0.153139	−0.93241	0.99984	0.1–30	0.1	298.15	0.531654	−2.76226	0.999591	0.1–30
	318.15	0.140036	−0.83985	0.999779			318.15	0.483876	−2.4792	0.999582	
	328.15	0.13431	−0.79883	0.999902			328.15	0.464018	−2.36024	0.999574	
	338.15	0.128729	−0.75981	0.999512			338.15	0.454823	−2.29694	0.999867	
0.4	298.15	0.172868	−1.03944	0.999901	0.1–30	0.2	298.15	0.739655	−3.57561	0.999791	0.1–30
	318.15	0.15896	−0.94173	0.999847			318.15	0.676215	−3.22216	0.999924	
	328.15	0.152843	−0.89812	0.999909			328.15	0.653248	−3.09029	0.999768	
	338.15	0.146155	−0.85239	0.999508			338.15	0.640255	−3.00706	0.999528	
0.5	298.15	0.195222	−1.15941	0.999479	0.1–30	0.3	298.15	1.03531	−4.67907	0.999777	0.1–30
	318.15	0.181466	−1.06208	0.999776			318.15	0.9264	−4.12628	0.99966	
	328.15	0.172877	−1.00373	0.997382			328.15	0.904895	−4.00124	0.999706	
	338.15	0.165936	−0.95628	0.999237			338.15	0.866896	−3.80489	0.999732	
0.6	298.15	0.225341	−1.32248	0.999747	0.1–30	0.4	298.15	1.38958	−5.89619	0.999394	0.1–30
	318.15	0.180772	−1.04513	0.980608			318.15	1.263	−5.28112	0.99984	
	328.15	0.197542	−1.13376	0.999588			328.15	1.21848	−5.05598	0.999604	
	338.15	0.191837	−1.09312	0.999808			338.15	1.1521	−4.74552	0.999823	
0.7	298.15	0.252209	−1.46299	0.999415	0.1–30	0.5	298.15	1.84376	−7.37224	0.999585	0.1–30
	318.15	0.235877	−1.34883	0.99992			318.15	1.66191	−6.54555	0.999436	
	328.15	0.223743	−1.26971	0.999568			328.15	1.60384	−6.26942	0.999907	
	338.15	0.215978	−1.21692	0.99957			338.15	1.55018	−6.01443	0.999363	
						0.2839	298.15	6.21989	−18.5672	0.999793	0.1–40
							308.15	5.90177	−17.4805	0.999924	
							318.15	5.63634	−16.5649	0.999863	
							328.15	5.37638	−15.6759	0.999735	
0.58	298.15	2.26979	−8.67483	0.999251	0.1–30	0.39598	298.15	4.29297	−13.8443	0.999876	0.1–40
	318.15	2.07581	−7.81496	0.999468			308.15	4.13713	−13.2416	0.999897	
	328.15	1.98068	−7.40067	0.999703			318.15	3.98956	−12.6715	0.999892	
	338.15	1.92653	−7.14372	0.999543			328.15	3.86857	−12.1924	0.999912	
0.7	298.15	3.07375	−11.0185	0.999466	0.1–30	0.60723	298.15	2.07049	−7.85551	0.999943	0.1–40
	318.15	2.78706	−9.8399	0.999709			308.15	2.00699	−7.55886	0.99988	
	328.15	2.68972	−9.42265	0.999713			318.15	1.93507	−7.23352	0.999839	
	338.15	2.59954	−9.03732	0.999136			328.15	1.87129	−6.94247	0.999869	
0.8	298.15	3.83928	−13.0849	0.999704	0.1–30	0.80381	298.15	0.92853	−4.20762	0.999826	0.1–40
	318.15	3.52236	−11.8208	0.999939			308.15	0.893696	−4.02133	0.999757	
	328.15	3.42219	−11.3974	0.999259			318.15	0.861479	−3.84861	0.999743	
	338.15	3.30116	−10.9082	0.999335			328.15	0.839145	−3.72177	0.999944	
0.9	298.15	4.84175	−15.7265	0.999834	0.1–30	0.88454	298.15	0.65237	−3.21375	0.99988	0.1–40
	318.15	4.44651	−14.2219	0.999509			308.15	0.63034	−3.08346	0.999934	
	328.15	4.20097	−13.3317	0.99966			318.15	0.609501	−2.9605	0.999935	
	338.15	4.14777	−13.0619	0.999592			328.15	0.588768	−2.8395	0.999858	
1.0	298.15	6.15894	−19.1072	0.999735	0.1–30	1.00000	298.15	0.364399	−2.04933	0.999987	0.1–40
	318.15	5.43504	−16.6027	0.999686			308.15	0.351854	−1.96492	0.999913	
	328.15	5.29023	−16.0309	0.999774			318.15	0.345162	−1.91406	0.999986	
	338.15	5.09031	−15.3079	0.999732			328.15	0.333167	−1.83459	0.999911	
	PEG-200(1) + PPG-400(2)[c]					Water(1) + PPG-400(2)[d]					
0.00000	298.15	13.1202	−33.002	0.999701	0.1–40	0.20105	298.15	6.4771	−20.0663	0.999739	0.1–40
	308.15	12.5483	−31.3122	0.999718			308.15	6.31579	−19.5795	0.999569	
	318.15	12.0685	−29.8764	0.999472			318.15	6.20119	−19.2064	0.999965	
	328.15	11.6269	−28.5511	0.999666			328.15	6.19109	−19.1302	0.999921	

Table 1 (*continued*)

X_1	T (K)	B (L^4 mol^{-4})	A (L^3 mol^{-3})	R^2	ΔP (MPa)	X_1	T (K)	B (L^4 mol^{-4})	A (L^3 mol^{-3})	R^2	ΔP (MPa)
0.13477	298.15	9.45101	−25.6901	0.999753	0.1–40	0.37701	298.15	1.48624	−5.88177	0.999986	0.1–40
	308.15	9.04112	−24.3849	0.999747			308.15	1.41916	−5.57178	0.999922	
	318.15	8.72766	−23.3555	0.999902			318.15	1.36649	−5.32217	0.999945	
	328.15	8.3913	−22.2781	0.999889			328.15	1.31313	−5.0727	0.999961	
0.61406	298.15	0.169398	−1.04511	0.999839	0.1–40	0.8	298.15	26.4777	−58.4786	0.999937	0.1–50
	308.15	0.16327	−0.99948	0.999923			318.15	24.0713	−52.3174	0.999868	
	318.15	0.156333	−0.94948	0.999712			348.15	21.1901	−44.9325	0.999867	
	328.15	0.152016	−0.91583	0.999847		0.9	298.15	30.3208	−64.765	0.999909	0.1–50
0.85537	298.15	0.0032	−0.04515	0.999882	0.1–40		318.15	27.6989	−58.2317	0.99987	
	308.15	0.003062	−0.04288	0.999923			348.15	24.4466	−50.1466	0.999853	
	318.15	0.002955	−0.04105	0.99983		1.0	298.15	35.2304	−72.8249	0.99995	0.1–50
	328.15	0.002848	−0.03925	0.999897			318.15	32.051	−65.22	0.999888	
1.00000	298.15	3.76E×06	−0.00021	0.999976	0.1–40		348.15	27.9872	−55.5816	0.999758	
	308.15	3.67E×06	−0.00021	0.999973			PEG-200(1)+ Anisole(2)[f]				
	318.15	3.61E×-06	−0.00021	0.999977		0.0	298.15	0.01845	−0.18315	0.999083	10–50
	328.15	3.61E×06	−0.00021	0.999966			318.15	0.017047	−0.16661	0.999835	
	PPG-425(1)+ PEGME-350(2)[e]						338.15	0.016734	−0.16099	0.996337	
0.0	298.15	7.55512	−22.4199	0.999915	0.1–50	0.1	298.15	0.030315	−0.25941	0.999543	10–50
	318.15	6.75406	−19.7321	0.999604			318.15	0.027846	−0.23416	0.99998	
	348.15	6.07456	−17.338	0.99993			338.15	0.028307	−0.23406	0.996089	
0.1	298.15	9.12054	−25.8483	0.999983	0.1–50	0.2	298.15	0.045188	−0.36209	0.997819	10–50
	318.15	8.14531	−22.7194	0.999516			318.15	0.040631	−0.32013	0.999565	
	348.15	7.32677	−19.9571	0.99994			338.15	0.039145	−0.3031	0.998856	
0.2	298.15	10.7522	−29.1742	0.999838	0.1–50	0.3	298.15	0.066144	−0.49876	0.999787	10–50
	318.15	9.89436	−26.4219	0.999702			318.15	0.0649	−0.4822	0.983357	
	348.15	8.73062	−22.7642	0.999963			338.15	0.05764	−0.42084	0.981155	
0.3	298.15	12.6341	−32.9944	0.999986	0.1–50	0.4	298.15	0.089754	−0.6384	0.999089	10–50
	318.15	11.571	−29.7344	0.999602			318.15	0.084954	−0.59497	0.999975	
	348.15	10.1847	−25.547	0.999917			338.15	0.075884	−0.52273	0.994366	
0.4	298.15	15.1447	−38.142	0.999905	0.1–50	0.5	298.15	0.125815	−0.84756	0.999294	10–50
	318.15	13.7397	−34.0494	0.999588			318.15	0.116348	−0.77147	0.999878	
	348.15	12.1088	−29.2973	0.999909			338.15	0.113517	−0.74078	0.997355	
0.5	298.15	17.5053	−42.5982	0.999927	0.1–50	0.6	298.15	0.165757	−1.05981	0.999869	10–50
	318.15	15.7558	−37.7339	0.999798			318.15	0.158156	−0.99557	0.999512	
	348.15	13.9563	−32.6288	0.999844			338.15	0.161343	−1.00048	0.989908	
0.6	298.15	20.0266	−47.1506	0.999962	0.1–50	0.7	298.15	0.205946	−1.25336	0.998873	10–50
	318.15	18.0463	−41.8202	0.999807			318.15	0.207387	−1.24504	0.997922	
	348.15	15.9658	−36.1176	0.999883			338.15	0.200503	−1.18556	0.99929	
0.7	298.15	23.0188	−52.4982	0.999937	0.1–50	0.8	298.15	0.283548	−1.65096	0.999752	10–50
	318.15	20.8061	−46.7016	0.999801			318.15	0.270585	−1.55283	0.999956	
	348.15	18.4907	−40.49	0.999819			338.15	0.259627	−1.46861	0.994008	
0.9	298.15	0.382159	−2.12184	0.9993	10–50	1.0	298.15	0.473244	−2.52853	0.999465	10–50
	318.15	0.337079	−1.84371	0.998882			318.15	0.454459	−2.3966	0.999808	
	338.15	0.405408	−2.19616	0.99675			338.15	0.421821	−2.19282	0.993999	

[a] Data sources: Lee et al. [22,23].
[b] Data source: Lee et al. [22].
[c] Data source: Colin et al. [25].
[d] Data source: Colin et al. [24].
[e] Data source: Lee et al. [27].
[f] Data source: Lee et al. [26].

Isothermal compressibility, κ_T, and excess volume, V^E, are other thermodynamic properties investigated in this study. The values of κ_T have been calculated using Eq. (5) and compared with the corresponding pseudo-experimental values calculated based on the Tait equation. The results are tabulated in Table 8. The constants of the Tait equation for each mixture have been gathered from the references of Table 1.

The excess volume is related to the molecular interactions in a mixture. By definition, the excess volume of a binary system is calculated via the following equation

$$V^E = V_m - x_1 V_1^\circ - x_2 V_2^\circ \quad (11)$$

with

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho_m} \quad (12)$$

Table 2
The intercept (A), slope (B), the square of correlation coefficient (R^2) of Eq. (1), and pressure range of the data for ternary polymeric mixtures of PEG-200(1)+PEGME-350(2)+anisole(3)

x_1, x_2	T (K)	B (L^4 mol^{-4})	A (L^3 mol^{-3})	R^2	ΔP (MPa)
0.2, 0.2	298.15	0.286915	−1.61872	0.99993	0.1–50
	318.15	0.261502	−1.45199	0.999488	
	348.15	0.229972	−1.246	0.999863	
0.2, 0.6	298.15	2.68966	−9.98782	0.999899	0.1–50
	318.15	2.41041	−8.81632	0.999686	
	348.15	2.0903	−7.45948	0.999659	
0.6, 0.2	298.15	1.16045	−5.09561	0.99997	0.1–50
	318.15	1.02757	−4.44534	0.999519	
	348.15	0.927176	−3.9213	0.999859	
0.35, 0.325	298.15	1.06229	−4.68953	0.999931	0.1–50
	318.15	0.952868	−4.14207	0.999486	
	348.15	0.85163	−3.616	0.999886	

Data source: Lee et al. [28].

Table 3
The values of constants and the square of the correlation coefficients of Eqs. (2) and (3) for binary mixtures

x_1	A_0 (L^3 mol^{-3})	A_1 (L^4 atm mol^{-4})	A_2 (L^4 atm mol^{-4} K^{-1})	B_0 (L^4 mol^{-4})	B_1 (L^5 atm mol^{-5})	B_2 (L^5 atm mol^{-5} K^{-1})
	PEG-200(1)+1-octanol(2)					
0.0	40.0619	89.2086	−0.240693	−6.35321	−13.8946	0.0383143
0.1	16.6121	44.8683	−0.0984721	−2.6309	−6.85289	0.015752
0.2	8.88077	31.5992	−0.0512691	−1.33471	−4.61501	0.00785402
0.3	2.89271	22.3938	−0.0143622	−0.350488	−3.09326	0.00180569
0.4	−5.30418	8.0251	0.0354343	1.40596	0.0572098	−0.00884611
0.5	−28.4905	−34.7568	0.17635	4.96699	6.60907	−0.0304709
0.6	416.949	822.687	−2.52767	−71.6557	−140.863	0.434692
0.7	−38.8611	−50.1707	0.239766	6.98494	9.73894	−0.0427487
0.8	21.965	70.2016	−0.128809	−3.69248	−11.3629	0.021987
0.9	−8.7116	12.8522	0.0569343	1.35577	−1.92553	−0.00854016
1.0	66.6365	163.685	−0.398494	−11.655	−27.9819	0.0701268
	PEGME-350(1)+PEG-200(2)					
0.1	142.632	320.913	−0.858089	−27.6172	−60.9758	0.166809
0.2	187.007	416.714	−1.1271	−38.6384	−84.5283	0.233806
0.3	234.053	534.219	−1.40462	−51.0183	−114.539	0.30741
0.4	−31.8625	48.877	0.215775	6.73468	−10.0457	−0.044406
0.5	338.045	782.783	−2.02657	−82.5888	−187.998	0.497334
0.6	228.362	591.294	−1.35887	−57.9662	−146.289	0.347656
0.7	406.098	975.055	−2.42969	−111.009	−260.776	0.668003
0.8	289.673	770.708	−1.72646	−82.3444	−212.274	0.495646
0.9	620.907	1465	−3.72217	−189.289	−436.466	1.14106
1.0	1432.69	3120.81	−8.61728	−456.601	−982.281	2.7541
	PEG-200(1)+PPG-400(2)					
0.00000	−8.33334	11.611	0.0521067	1.27202	−1.67643	−0.00752609
0.13477	301.45	1004.11	−1.76457	−102.364	−331.065	0.610266
0.2839	266.878	868.003	−1.5445	−78.9297	−256.737	0.462021
0.39598	176.611	549.581	−1.04799	−54.6745	−160.321	0.33026
0.60723	−111.344	−92.8975	0.690524	29.7627	29.961	−0.181771
0.80381	127.23	305.249	−0.766817	−28.339	−65.8464	0.171999
0.88454	−20.8185	8.7586	0.131931	4.56506	0.26472	−0.0280201
1.00000	600.674	1706.55	−3.55852	−226.239	−623.38	1.35667
	Water(1)+PPG(2)					
0.20105	1203.95	2435.72	−7.38051	−452.444	−905.755	2.77156
0.37701	92.2481	277.382	−0.543336	−22.1775	−64.3974	0.132491
0.61406	−4.99771	7.34401	0.0327926	0.702584	−0.991677	−0.00442427
0.85537	0.749271	2.17316	−0.00444128	−0.0512678	−0.142999	0.000308035
1.00000	0.0124196	0.0250714	−0.000762238	−0.00025755	−0.000514735	0.00000157874
	PPG-425(1)+PEGME-350(2)					
0.0	1082.49	2516.88	−6.47495	−355.89	−814.21	2.1379
0.1	1285.18	2976.45	−7.68865	−442.075	−1007.63	2.65594
0.2	−107.967	305.483	0.747222	59.0943	−50.5666	−0.377883
0.3	19.1816	634.968	−0.00193592	16.4603	−167.944	−0.126416

Table 3 (*continued*)

x_1	A_0 (L^3 mol^{-3})	A_1 (L^4 atm mol^{-4})	A_2 (L^4 atm mol^{-4} K^{-1})	B_0 (L^4 mol^{-4})	B_1 (L^5 atm mol^{-5})	B_2 (L^5 atm mol^{-5} K^{-1})
0.4	533.82	1747.86	−3.08984	−181.721	−601	1.06386
0.5	1182.1	3100.28	−6.99412	−459.702	−1184	2.73942
0.6	1186.21	3193.32	−7.00171	−476.384	−1258.07	2.83411
0.7	1278.45	3453.31	−7.55141	−540.939	−1423.15	3.22334
0.8	570.946	2196.49	−3.23953	−222.514	−863.811	1.28451
0.9	347.619	1850.36	−1.88036	−127.507	−728.18	0.70787
1.0	179.26	1725.98	−0.799254	−35.7944	−657.074	0.124655
	PEG-200(1)+anisole(2)					
0.0	16.2773	33.6234	−0.0987401	−1.67553	−3.41094	0.0101905
0.1	40.2539	80.2112	−0.244522	−4.78131	−9.43902	0.0290925
0.2	36.4138	75.947	−0.220119	−4.60887	−9.4873	0.0279293
0.3	−84.8153	−155.549	0.515604	11.1956	20.6871	−0.0679665
0.4	−61.3373	−106.788	0.374235	8.76445	15.4932	−0.0533468
0.5	66.2191	138.431	−0.401462	−10.0034	−20.5739	0.0608303
0.6	111.3	221.502	−0.678724	−17.844	−35.0597	0.109051
0.7	−95.4494	−175.452	0.57503	14.9804	27.9716	−0.0899258
0.8	4.07458	26.913	−0.0253872	−0.775777	−4.12396	0.00520064
0.9	1083.5	2083.72	−6.59103	−195.844	−375.778	1.19183
1.0	−158.637	−271.311	0.964439	29.2541	50.9323	−0.177271

Table 4
The values of constants and the square of the correlation coefficients of Eqs. (2) and (3) for ternary mixtures of PEG-200(1)+PEGME-350(2)+anisole(3)

x_1, x_2	A_0 (L^3 mol^{-3})	A_1 (L^4 atm mol^{-4})	A_2 (L^4 atm mol^{-4} K^{-1})	B_0 (L^4 mol^{-4})	B_1 (L^5 atm mol^{-5})	B_2 (L^5 atm mol^{-5} K^{-1})
0.2, 0.2	9.24847	47.8653	−0.0500786	−1.23603	−7.04515	0.00681955
0.2, 0.6	157.188	506.801	−0.905507	−40.4906	−127.058	0.236149
0.6, 0.2	317.58	712.84	−1.90399	−71.491	−158.269	0.430001
0.35, 0.325	181.801	440.26	−1.08377	−40.1339	−95.3578	0.240523

where V_m is the molar volume of mixture. x_i, V_i°, and M_i stand for the mole fraction, molar volume, and molecular weight, respectively, for component i. A comparison between experimental and calculated values of excess molar volumes has been shown in Table 8. As an example, Fig. 2 shows the variation of excess molar volume with composition for PPG-425 (1)+PEGME-350 (2) at 0.1 MPa at different temperatures.

Table 5
Results of specific volume correlation with the equations of state for 'pure' compounds

Compound	AAD[a] (cm^3 g^{-1})			
	GMA EoS	FOV EoS	Schotte EoS	ISM EoS
PEG-200	0.00012[b]	0.00021[b]	0.00007[b]	
	0.00020[c]	0.00017[c]	0.00012[c]	
	0.00006[d]			0.01006[d]
PPG-400	0.00004			0.00750[d]
PPG-425	0.00014	0.00025[e]	0.00025[e]	
PEGME-350	0.00007[b]	0.00017[b]	0.00010[b]	
	0.00010[e]	0.00021[e]	0.00014[e]	
Anisole	0.00053	0.00029[c]	0.00032[c]	
1-Octanol	0.00031	0.00023[b]	0.00016[b]	

[a] $AAD = (1/n)\sum_{i=1}^{n} |V_{i,calc} - V_{i,exp}|$.
[b] Data source: Lee et al. [22].
[c] Data source: Lee et al. [26].
[d] Data source: Sabzi and Boushehri [33].
[e] Data source: Lee et al. [27].

Table 6
Results of specific volume correlation with the equations of state for polymer solutions and blends

Mixture (1)+(2)	AAD[a]			
	GMA EoS	FOV EoS	Schotte EoS	ISM EoS
PEG-200+1-octanol	0.019	0.040[b]	0.040[b]	0.421[c]
PEG-200+PPG-400	0.006	0.146[d]	0.115[d]	1.169[c]
PPG-425+PEGME-350	0.014	0.264[d]	0.255[d]	
PEG-200+anisole	0.042	0.150[e]	0.140[e]	
PEGME-350+PEG-200	0.012	0.020[b]	0.010[b]	
Water+PPG-400	0.011			

[a] $AAD = (100/n)\sum_{i=1}^{n} |V_{i,calc} - V_{i,exp}|/V_{i,exp}$.
[b] Data source: Lee et al. [22].
[c] Data source: Sabzi and Boushehri [34].
[d] Data source: Lee et al. [27].
[e] Data source: Lee et al. [26].

Table 7
Results of specific volume correlation with the equations of state for the ternary polymer solution, PEG-200(1)+PEGME-350(2)+anisole(3)

x_1, x_2	AAD[a]		
	GMA EoS	FOV EoS[b]	Schotte EoS[b]
0.2, 0.6	0.01	0.12	0.10
0.2, 0.2	0.01	0.13	0.12
0.6, 0.2	0.02	0.12	0.11
0.35, 0.325	0.02	0.12	0.13

[a] $AAD = (100/n)\sum_{i=1}^{n} |V_{i,calc} - V_{i,exp}|/V_{i,exp}$.
[b] Data Source: Lee et al. [28].

3. Conclusion

The excellent mutual agreement between calculated and experimental properties such as specific volume, isothermal compressibility, and excess volume supports the ability of the GMA EoS in predicting and reproducing the experimental thermodynamic properties of liquid mixtures.

In summary, the GMA EoS contains some important features:

Table 8
Results of excess volume and isothermal compressibility correlation with the GMA EoS for polymer solution and blends

Mixture (1)+(2)	κ_T AAD[a]	V^E AAD[b]×10² ($cm^3\ mol^{-1}$)
PEG-200+1-octanol	3.15	3.01
PEG-200+anisole	4.36	6.56
PPG-425+PEGME-350	2.23	2.86
PEGME-350+PEG-200	2.21	3.26
PEG-200+PPG-400	1.29	2.66
Water+PPG-400	1.36[c]	3.62

[a] $AAD = (100/n)\sum_{i=1}^{n} |\kappa_{i,calc} - \kappa_{i,exp}|/\kappa_{i,exp}$.
[b] $AAD\ (cm^3\ mol^{-1}) = (1/n)\sum_{i=1}^{n} |V^E_{i,calc} - V^E_{i,exp}|$.
[c] This value has been calculated for these compositions: $x_1 = 0.37701$, 0.61406, and 0.85537.

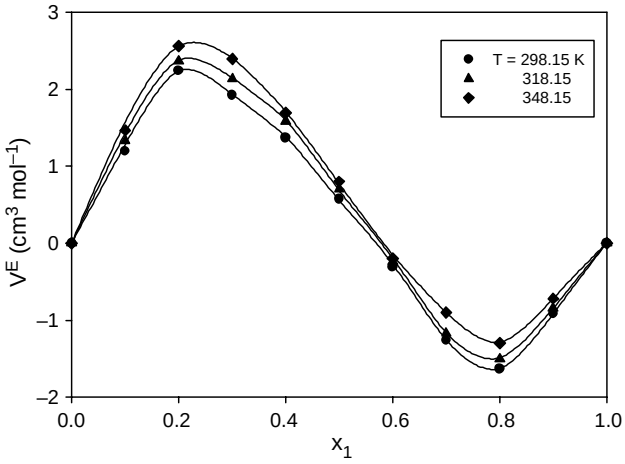

Fig. 2. The variation of excess molar volume with composition for PPG-425 (1)+PEGME-350(2) at 0.1 MPa at different temperatures. The solid lines show our calculated values and the symbols stand for experimental ones.

1. The form of the GMA EoS is very simple. Evaluation of its coefficients is very easy.
2. The GMA EoS can predict the thermodynamic properties of polymeric liquids of studied in any temperature, pressure, and composition.

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