



## Excess Thermodynamic Properties of Some Liquid Mixtures

Fluids

### Correlation of Data

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**property:** volumetric properties

**material:** multi-functional materials

**others:** liquids mixtures

The topic of this study, excess thermodynamic properties of the binary mixtures, is one of the most interesting phenomena in molecular physics. They provide us information to understand the observed properties of the mixtures from the point of view of microscopic interactions. Excess thermodynamic properties of mixtures provide insight into the molecular interactions between the various components and can be used for the development of molecular models describing the thermodynamic behavior of mixtures. From a practical point of view, the excess molar volumes are useful for the design of mixing and storage tanks and transport equipments.

A new equation of state (EoS) has been derived for liquids by Goharshadi et al. [1] Goharshadi-Morsali-Abbaspour "GMA EoS". It has been used to calculate the different thermodynamic and volumetric properties such as density, isobaric expansion coefficient, and isothermal compressibility for a wide range of fluids including polar, nonpolar, and hydrogen-bonded fluids [1-7].

In this work, we have calculated excess thermodynamic properties for some liquid mixtures at the extended ranges of temperature, pressure, and composition. The results have been compared with experimental data using statistical parameters.

### References

1. E. K. Goharshadi, A. Morsali, and M. Abbaspour, *Fluid Phase Equilib.* 230,170, 2005.
2. E. K. Goharshadi and A. R. Berenji, *J. Nucl. Mat.* 348, 40, 2006.
3. M. Moosavi and E. K. Goharshadi, *Int. J. Thermophys.* 27, 1515, 2006.
4. E. K. Goharshadi and F. Moosavi, *Int. J. Refrig.* 30, 377, 2007.
5. E. K. Goharshadi and M. Moosavi, *Ind. Eng. Chem. Res.* 44, 6973, 2005.
6. E. K. Goharshadi and M. Moosavi, *Thermochim. Acta* 64, 447, 2006.
7. A. R. Berenji and E. K. Goharshadi, *Polymer* 47, 4726, 2006.

**Prediction of volumetric and thermodynamic  
properties of two aromatic-alcohol mixtures  
using GMA equation of state**

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## **Abstract**

In this work, we have calculated the densities of two mixtures composed of 1-propanol + toluene and ethanol + toluene at different temperatures, pressures, and compositions using GMA equation of state. We have also calculated some thermodynamic properties of these mixtures such as isobaric thermal expansion coefficient, isothermal compressibility coefficient, internal pressure, and excess functions such as the excess volumes, excess Gibbs free energy, excess enthalpy, excess entropy, excess internal energy, and excess Helmholtz free energy. A wide comparison with the experimental data shows the ability of this equation of state to reproduce and predict different thermodynamic properties.

*Keywords:* Excess properties; GMA equation of state; Isobaric thermal expansion coefficient; Isothermal compressibility coefficient; Internal pressure; Tait equation

## **1. Introduction**

The ability of aromatic compounds to act as electron donors with their  $\pi$  electrons has been investigated by several researchers [1-4]. Because of this ability, weak intermolecular interactions, such as hydrogen bonding, can be formed in mixtures composed of aromatic compounds and polar or associating compounds. In the recent investigation using FTIR spectroscopy, Brinkley, and Gupta [4] found a clear evidence for the formation of hydrogen bonding between aromatic hydrocarbons and alcohols. They studied qualitatively the degree of hydrogen bonding formation by adding aromatic hydrocarbons to alkane + alcohol mixtures having a very low content of alcohol in order to avoid any influence of self-association of the alcohol [5].

In petroleum and gasoline fluids, aromatic hydrocarbons are important constituents. With the addition of polar compounds, such as ethanol, to these systems, and as a result of the ability of aromatic compounds to act as electron donors, intermolecular interactions

between the  $\pi$ -electrons of the aromatic hydrocarbons and the hydroxyl group of, e. g. ethanol can occur, resulting interesting and complex behaviors of the mixtures [1, 3, 4, 6].

The binary mixtures containing alcohols and aromatics have been studied with a considerable interest because these mixtures exhibit varying molecular interactions and are important from a practical point of view. Alcohols and aromatics are widely used in variety of industrial and consumer applications, such as perfumes, cosmetics, paints, varnishes, drugs, fuels, explosives, fats, waxes, resins, plastics, rubbers, detergents, DDT, etc. [7].

A new equation of state (EoS) has been recently introduced for liquids by Goharshadi et al. [8-12] (Goharshadi-Morsali-Abbaspour "GMA EoS"). It has been used to calculate different thermodynamic and volumetric properties for a wide range of fluids including polar, nonpolar, refrigerants, and hydrogen-bonded fluids [8-12]. The EoS has been also applied for liquid mixtures properly [13, 14].

It has been known that the GMA EoS can reproduce the different volumetric and thermodynamic properties for all these fluids within experimental errors [8-14].

The purpose of the present paper is to predict and reproduce some thermodynamic and volumetric properties such as isobaric thermal expansion coefficient, isothermal compressibility coefficient, internal pressure, and excess properties of two mixtures composed of ethanol + toluene and 1-propanol + toluene using a new equation of state called GMA equation of state at the extended ranges of temperature and pressure.

## 2. GMA EoS and derived properties

The GMA equation of state is based on the average potential energy and is given as:

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

where  $Z$ ,  $V_m$ , and  $\rho$  are compressibility factor, molar volume, and density, respectively.

The intercept and slope of this equation depend on temperature via the equations:

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

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

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

The density can be calculated based on the GMA EoS using the following equation:

$$B(T, x)\rho^5 + A(T, x)\rho^4 + \rho - \frac{2p}{RT} = 0 \quad (4)$$

Isobaric expansion coefficient,  $\alpha_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$ , isothermal compressibility coefficient,  $\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$ , and internal pressure,  $P_i = \left( \frac{\partial U}{\partial V} \right)_T$ , can be calculated using the GMA

EoS from the following equations:

$$\alpha_p = \frac{(2B_1 + 2B_2T)\rho^5 + (2A_1 + 2A_2T)\rho^4 + 2P}{5\rho^5(RT^2B_o - 2B_1T + 2T^2B_2 \ln T) + 4\rho^4(A_oRT^2 - 2A_1T + 2A_2T^2 \ln T) + RT^2\rho} \quad (5)$$

$$\kappa_T = \frac{2}{\rho RT + 4\rho^4(RTA_o - 2A_1 + 2TA_2 \ln T) + 5\rho^5(B_oRT - 2B_1 + 2B_2T \ln T)} \quad (6)$$

$$P_i = (B_1 + B_2T)\rho^5 + (A_1 + A_2T)\rho^4 \quad (7)$$

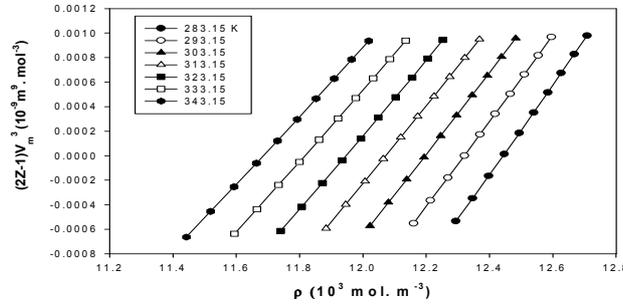
The values of the excess molar volume,  $V_m^E$ , can be calculated from the following equation:

$$V^E = [(xM_1 + (1-x)M_2)/\rho] - [(xM_1/\rho_1) + ((1-x)M_2/\rho_2)] \quad (8)$$

where  $\rho$  and  $\rho_i$  are the densities of liquid mixture and pure components, respectively.  $M_i$  stands for the molar masses of pure components  $i$  ( $i = 1, 2$ ).

### 3. Results and Discussions

We have tested the GMA EoS for two different mixtures of ethanol + toluene and 1-propanol + toluene. Figure 1 shows the typical isotherms of  $(2Z-1)V_m^3$  versus  $\rho$  (Eq. (1)) for ethanol + toluene.



**Fig. 1.** Isotherms of  $(2Z-1)V_m^3$  versus  $\rho$  for a mixture of ethanol (1) + toluene (2) ( $X_{\text{ethanol}} = 0.5$ ) [15].

Table 1 represents the minimum and maximum values of square of correlation coefficient ( $R^2$ ) of Eq. (1) and pressure and temperature ranges of the data for studied mixtures.

**Table 1** The minimum and maximum values of square of correlation coefficient ( $R^2$ ) of Eq. (1), pressure and temperature ranges

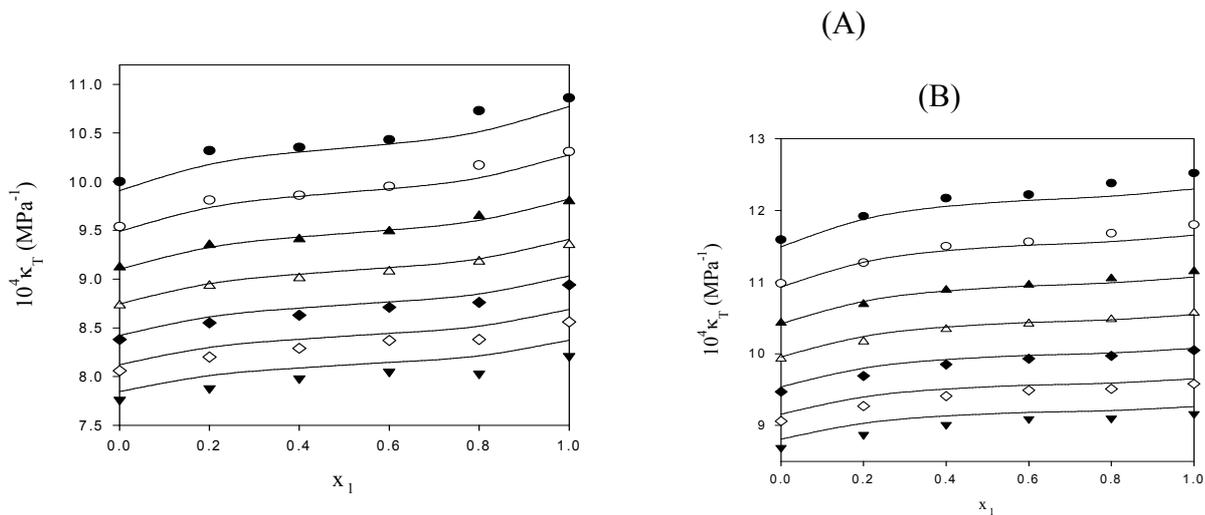
$x_1$	$R^2_{\min}-R^2_{\max}$	$\Delta P$ (MPa)	$\Delta T$ (K)	NP
<b><u>Ethanol (1) + Toluene (2) [15]</u></b>				
0.000	0.9999-1.0000	0.1-45	283.15-353.15	80
0.125	0.9998-0.9999	0.1-45	283.15-353.15	80
0.250	0.9997-0.9999	0.1-45	283.15-353.15	79
0.375	0.9998-0.9999	0.1-45	283.15-353.15	79
0.500	0.9998-0.9999	0.1-45	283.15-353.15	79
0.625	0.9998-0.9999	0.1-45	283.15-353.15	79
0.750	0.9999-1.0000	0.1-45	283.15-353.15	79
0.875	0.9998-1.0000	0.1-45	283.15-353.15	79
1.000	0.9959-0.9999	0.1-45	283.15-353.15	79
<b><u>1-Propanol (1) + Toluene (2) [5]</u></b>				
0.0	0.9999-1.0000	0.1-30	303.15-333.15	28
0.2	0.9999-1.0000	0.1-30	303.15-333.15	28
0.4	0.9999-1.0000	0.1-30	303.15-333.15	28
0.6	0.9998-1.0000	0.1-30	303.15-333.15	28
0.8	0.9997-1.0000	0.1-30	303.15-333.15	28
1.0	0.9999-1.0000	0.1-30	303.15-333.15	28

As Fig. 1 and the values of the square of correlation coefficient of this table show the linearity of  $(2Z-1)V_m^3$  versus  $\rho$  hold very well for these mixtures. Table 2 shows the values of the constants of Eqs. (2) and (3) for tested mixtures.

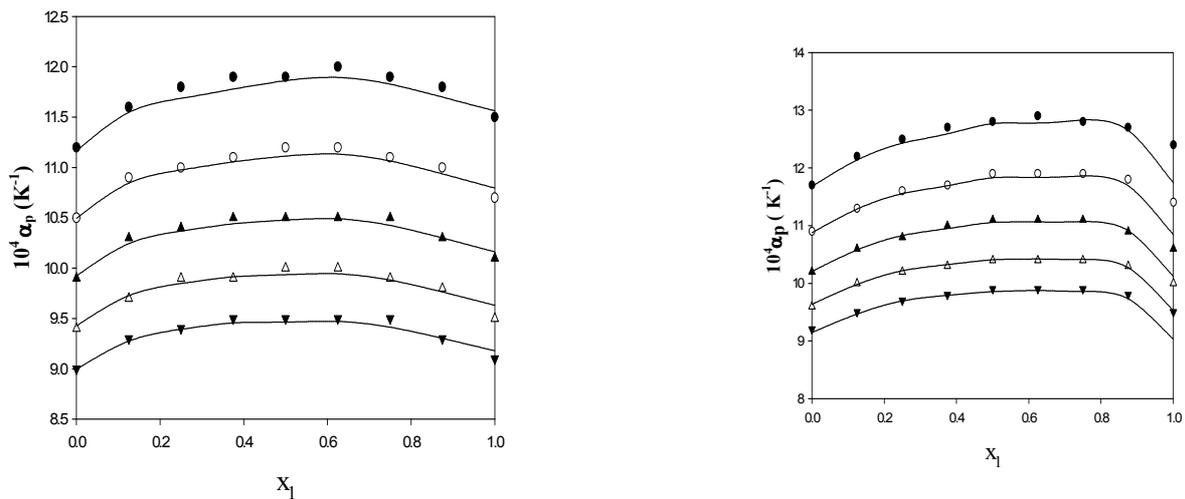
**Table 2** Values of constants of GMA EoS and correlation coefficient of Eqs. (2) and (3) for binary mixtures

$x_1$	$A_0$ ( $L^3 mol^{-3}$ )	$A_1$ ( $L^4 atmmol^{-4}$ )	$A_2$ ( $L^4 atmmol^{-4} K^{-1}$ )	$R^2$	$B_0$ ( $L^4 mol^{-4}$ )	$B_1$ ( $L^5 atmmol^{-5}$ )	$B_2$ ( $L^5 atmmol^{-5} K^{-1}$ )	$R^2$
<b><u>Ethanol (1) + Toluene (2) [15]</u></b>								
0.000	0.58852	3.56997	-0.00303	0.99983	-0.03747	-0.29219	0.00019	0.99976
0.125	0.24032	2.35438	-0.00104	0.99995	-0.00632	-0.17241	0.00001	0.99992
0.250	0.15573	1.73815	-0.00063	0.99989	-0.00473	-0.12303	0.00001	0.99982
0.375	0.03816	1.15419	0.00000	0.99970	0.00293	-0.07422	-0.00003	0.99956
0.500	0.01120	0.83241	0.00011	0.99992	0.00307	-0.05000	-0.00003	0.99988
0.625	0.05771	0.68300	-0.00023	0.99993	-0.00222	-0.04063	0.00001	0.99990
0.750	-0.04095	0.31423	0.00033	0.99978	0.00383	-0.01555	-0.00003	0.99967
0.875	-0.01356	0.23191	0.00013	0.99975	0.00128	-0.01124	-0.00001	0.99962
1.000	0.01426	0.18748	-0.00006	0.99942	0.00035	-0.00700	0.00000	0.99932
<b><u>1-Propanol(1) + Toluene (2) [5]</u></b>								
0.0	-0.97191	0.46076	0.00639	0.99996	0.12967	0.04056	-0.00082	0.99993
0.2	-1.32442	-0.75055	0.00842	0.99926	0.14768	0.13312	-0.00092	0.99887
0.4	-1.53275	-1.58892	0.00959	0.99977	0.15224	0.18618	-0.00094	0.99962
0.6	-0.79461	-0.50679	0.00504	0.99766	0.07336	0.06620	-0.00046	0.99652
0.8	-0.03411	0.66970	0.00036	1.00000	0.00392	-0.04257	-0.00003	0.99999
1.0	0.73137	1.90555	-0.00435	0.99879	-0.05538	-0.13789	0.00033	0.99822

Figures 2 and 3 show isothermal compressibility coefficient versus mole fraction for 1-propanol + toluene and isobaric thermal expansion coefficient versus mole fraction for ethanol + toluene at different temperature and pressure.



**Fig. 2.** Isothermal compressibility coefficient versus mole fraction for propanol (1) + toluene (2) at: (A) 313.15 K (B) 333.15 K for: 0.1 MPa(●); 5MPa(○); 10 MPa(▲); 15 MPa(△); 20 MPa(◆); 25 MPa(◇); and 30 MPa(▼). The points are experimental data [5].



**Fig. 3.** Isobaric thermal expansion coefficient versus mole fraction for ethanol (1) + toluene (2) at (A) 313.15 K and (B) 333.15 K for: 0.1 MPa(●); 10MPa(○); 20 MPa(▲); 30 MPa(△); and 40 MPa(▼). The points are experimental data [15].

#### 4. Conclusions

It has been shown that the GMA equation of state can predict and reproduce some volumetric and thermodynamic properties of two mixtures of composed of ethanol +

toluene and 1-propanol + toluene in wide ranges of temperature and pressure within experimental errors.

It seems to us the GMA EoS contains the following of particular interest:

- (1) The form of The GMA EoS is generalized and very simple. The evaluation of the coefficients is very easy.
- (2) It can predict the thermodynamic properties of the liquid mixtures of studied at any temperature, pressure, and composition.
- (3) The calculated volumetric properties of liquid mixtures of studied assuming the composition dependence of the parameters of the equation of state as quadratic functions of mole fraction are in an excellent agreement with experiment.
- (4) The statistical parameters in prediction of density of these mixtures based on the GMA EoS are much lower than those of computed based on Tait equation.

## References

- [1] L. H. Jones, R.M. Badger, J. Am. Chem. Soc. 73 (1951) 3132-3134.
- [2] M. Tamres, J. AnChem . Soc. 74 (1952) 3375-3378.
- [3] Y. Ioki, H. Kawana, K. Nishimoto, Bull. Chem. Soc. Jpn. 51 (1978) 963-966.
- [4] R. L. Brinkley, R.B. Gupta, AIChE J. 47 (2001) 948-953.
- [5] C. K. Zeberg-Mikkelsen, S. I. Andersen, J. Chem. Eng. Data. 50 (2005) 524-528.
- [6] M. J. Tamres, AnChem . Soc. 74 (1952) 3375-3378.
- [7] P. S. Šerbanović, M.L. Kijevčanin, I.R. Radović, B.D. Djordjević, Fluid Phase Equilib. 239 (2006) 69-82.
- [8] E. K. Goharshadi, A. Morsali, M. Abbaspour, Fluid Phase Equilib. 230 (2005) 170-175.
- [9] E. K. Goharshadi, A. R. Berenji, J. Nucl. Mat. 348 (2006) 40-44.
- [10] E. K. Goharshadi, F. Moosavi, Fluid Phase Equilib. 238 ( 2005) 112-119.

- [11] E. K. Goharshadi, F. Moosavi, *Int. J. Refrigeration* 30 (2007) 377-383.
- [12] A. R. Berenji, E. K. Goharshadi, *Polymer* 47 (2006) 4726-4733.
- [13] E. K. Goharshadi, M. Moosavi, *Ind. Eng. Chem. Res* 44 ( 2005) 6973-6980.
- [14] E. K. Goharshadi, M. Moosavi, M. Abareshi, *Int. J. Thermal Sciences* 46 (2007) 944–952.
- [15] C. K. Zeberg-Mikkelsen, L. Lugo, J. Carcia, J. Fernandez, *Fluid Phase Equilib.* 235 (2005) 139-151.