



## Compressed Liquid Densities for Binary Mixtures at Temperatures from 280-440K at Pressures up to 200 MPa

Zahra Sharafi<sup>a,\*</sup> and Maryam Mojahed Taghi<sup>a</sup>

<sup>a</sup>Department of Chemistry, Marvdasht Branch, Islamic Azad University, Marvdasht, Iran

### Abstract

A method for predicting liquid densities of binary mixtures from heat of vaporization and liquid density at boiling point temperature ( $\Delta H_{\text{vap}}$  and  $\rho_{nb}$ ) as scaling constants, is presented.  $B_2(T)$  follows a promising corresponding-states principle. Calculation of  $\alpha(T)$  and  $b(T)$ , the two other temperature-dependent constants of the equation of state, are made possible by scaling. As a result  $\Delta H_{\text{vap}}$  and  $\rho_{nb}$  are sufficient for determination of thermophysical properties of liquid mixtures. We applied the procedure to predict liquid densities of ( $x_1$  n-butane +  $x_2$  isobutane) at compressed state with temperature range from 280 to 440 K and pressures up to 200 MPa. The experimental liquid densities were correlated satisfactory with our procedure and the results are within 5%.

**Keywords:** Equation of State, Liquid Densities, Scaling Constants

### Introduction

Recent works on a statistical-mechanical theory for the equation of state of fluids [1-3] has yielded accurate results for both pure and binary molecular fluids. The applicability of an equation of state to a given system is reliable if in the first place, accurate input data are available. In practice, the input data may not be available for a given system or it may not be possible to measure these data accurately for some systems. The purpose of this paper is to present a method for predicting the equation of state of liquid mixtures from properties that are readily available at ordinary pressure and temperatures. In particular, we use the heat of vaporization and liquid density at the normal boiling point as two parameters that can correlate and predict the behavior of

high and low density of fluid mixtures [4]. From these two properties three temperature-dependent parameters are obtained,  $B_2(T)$ , the second virial coefficient,  $\alpha(T)$  which is the contribution of the repulsive side of the potential function to the second virial coefficient and  $b(T)$  which is analogue to the van der Waals covolume. In addition to  $B_2(T)$ ,  $\alpha(T)$  and  $b(T)$ , one temperature-independent constant that is characteristic of the particular substance is needed.

In this study, we measured ( $P, \rho, T, x$ ) property data for ( $x_1$  n-butane +  $x_2$  isobutane) with  $x_1 = (0.2625, 0.4913, \text{ and } 0.7508)$  over a wide range of temperatures from 280-440 K and pressures up 200 MPa using the ISM equation of state [4]. This mixture is simple however; the density data are essential numerical information not only for the industrial use, but also for the scientific research. The molar masses of the components

\*Corresponding Author

E-mail address: [zahra\\_sharafi@yahoo.com](mailto:zahra_sharafi@yahoo.com)

are the same, and the difference between the critical temperature is large (425.125 K for n-butane [5] and 407.885 for isobutene [6]). Our calculation results will be compared with the experimental measurements [7] and will show that the density of liquid mixtures for ( $x_1$  n-butane +  $x_2$  isobutane) can be predicted within 5% at any temperature and pressure.

### Theoretical method

An alternative to empirical representation of the  $PVT$  behavior is to develop theoretical model, starting from an understanding of the forces that exist between molecules. In principle, these forces could be calculated from quantum mechanics, however, since the true potential energy function is not known exactly, one usually assumes that those forces obey an empirical potential law such as the hard-sphere [8] or Lennard-Jones 12-6 potential. The use of statistical mechanics bridges the gap between quantum and continuum mechanics, allowing one to take statistical averages using molecular variable to obtain macroscopically observable quantities.

Here, we consider the statistical-mechanical equation of state derived by Song and Mason [9], which is based on the Week-Chandler-Anderson (WCA) [10], including the division of the intermolecular potential at its minimum into regions of attractive and repulsive forces, but differs in two significant respects. The first is that the second virial coefficient is treated by a perturbation theory. The second is choice of an algorithm for calculating the effective hard-sphere diameter as a function of temperature.

The derivation begins with the equation relating the pressure to the pair distribution function,  $g(r)$  [11]:

$$\frac{P}{\rho k T} = 1 - \frac{2\pi}{3} \frac{\rho}{RT} \int_0^\infty \frac{du}{dr} g(r) r^3 dr \quad (1)$$

where  $P$  is the pressure,  $\rho$  is the density,  $RT$  is the thermal energy per mole, and  $du/dr$  is the derivative of the intermolecular potential

function with respect to the distance  $r$ .

Upon applying the perturbation scheme of the WCA method to the potential function and working out a correction for attractive forces, the equation of states reads [12]:

$$\frac{P}{\rho k T} = 1 - \frac{(\alpha - B_2)\rho}{1 + 0.2 \lambda b \rho} + \frac{\alpha \rho}{1 - \lambda b \rho} \quad (2)$$

where, the new corresponding-state principle for  $G(b\rho)$  has the form:

$$G(b\rho)^{-1} = \alpha \rho \left[ Z - 1 + \frac{(\alpha - B_2)\rho}{1 + 0.2 \lambda b \rho} \right]^{-1} = 1 - \lambda b \rho \quad (3)$$

where  $Z = P/\rho RT$  is the compressibility factor and  $G(b\rho)$  is the average pair distribution function at contact for equivalent hard convex bodies that still have pairwise additivity of the intermolecular forces as in  $g(r)$ . The many-body nature of the system may be contained in  $G(b\rho)$  [12].

The parameters  $B_2(T)$ ,  $\alpha(T)$  and  $b(T)$  can be obtained by integration if the intermolecular potential is accurately known, but we do not have any potential model here. Song and Mason [13] showed that  $B_2(T)$  can be found experimentally and  $\alpha(T)$  and  $b(T)$  can be calculated from  $B_2(T)$  by means of simple two-constant scaling rules, because  $\alpha(T)$  and  $b(T)$ , depend only on the intermolecular repulsive forces and are insensitive to the details of the shape of the intermolecular potential.

$G(b\rho)^{-1}$  is a function of  $b\rho$  only and satisfies corresponding states, varying linearly with slope  $\lambda$  over the whole range of temperatures from the freezing line up to the critical point. The functional form of  $G(b\rho)^{-1}$  implies that, according to corresponding states, all the  $PVT$  data collapse to a single line. The value of  $\lambda$ , determined from  $PVT$  data by iteration, along with  $B_2(T)$ ,  $\alpha(T)$  and  $b(T)$ , characterizes the thermodynamic properties of particular systems.

### Extension to Mixtures

Ihm et al. [14] have extended the theory for pure cases to mixtures of any number of components as follows:

$$\frac{P}{\rho k T} = 1 + \rho \sum_{ij} x_i x_j (B_{ij} - \alpha_{ij}) F_{ij} + \rho \sum_{ij} x_i x_j G_{ij} \alpha_{ij} \quad (4)$$

where  $x_i$  and  $x_j$  are mole fractions, and summations run over all components of the mixture and subscripts  $ij$  refer to the  $i$ - $j$  interactions. The parameters  $F_{ij}$  and  $G_{ij}$  are defined as:

$$F_{ij} = \frac{1}{1 - \xi_3} - \left( \frac{d_i d_j}{d_j} \right) \frac{\frac{1}{6} \pi \rho \sum_k x_k d_k^2 (4\delta_k + 1)}{(1 - \xi_3) \left( 1 + \frac{2}{3} \pi \rho \sum_k x_k d_k^3 \delta_k \right)} \quad (5)$$

$$G_{ij} = \frac{1}{1 - \xi_3} - \left( \frac{d_i d_j}{d_j} \right) \frac{\frac{1}{6} \pi \rho \sum_k x_k d_k^2 (4\lambda_k + 1)}{(1 - \xi_3) \left( 1 - \frac{2}{3} \pi \rho \sum_k x_k d_k^3 \lambda_k \right)} \quad (6)$$

where  $\xi_3 = \frac{1}{6} \pi \rho \sum_k x_k d_k^3$  is packing fraction for the mixture and  $\delta_k = 0.2 \lambda_k$ ,  $\lambda$  is an adjustable parameter. The algorithm for calculation  $d_k$  is  $b_k = (2/3) \pi d_k^3$ .

$B_{ij}$ ,  $b_{ij}$  and  $\alpha_{ij}$  are well defined in terms of  $i$ - $j$  intermolecular potential and are evaluated in the same way as the corresponding quantities for single substances, either from the potential model or from experimental data on second virial coefficient. In the present work we have utilized a correlation to obtain the cross second virial coefficient required by the mixture version of the ISM EoS.

### Correlation procedure

The minimum input information needed for using Eq. (2) are the values of  $B_2(T)$ ,  $\alpha(T)$  and  $b(T)$ . If the intermolecular potential is not available, knowledge of experimental second virial coefficient data is sufficient to calculate values of the other two temperature-dependent parameters [12]. For the system n-butane + isobutene, neither the intermolecular potential

nor the experimental  $B_2$  values are available. In this case, there is several correlation schemes, usually based on the corresponding state principle, by which second virial coefficient can be calculated.

Sharafi and Boushehri [4] used the heat of vaporization and the liquid density at the normal boiling point as two scaling constants for correlating  $B_2$ . Their resulting correlation for the second virial coefficient is:

$$B_{\rho_{nb}} = 0.403891 - 0.076484(\Delta H_{vap}/RT)^2 - 0.0002504(\Delta H_{vap}/RT)^4 \quad (7)$$

Once the  $B_2(T)$  values are known, the parameter  $\alpha(T)$  and  $b(T)$  of the equation of state are derived from the second virial coefficient [4]:

$$\alpha_{\rho_{nb}} = a_1 \exp[-c_1(RT/\Delta H_{vap})] + a_2 \{1 - \exp[-c_2(\Delta H_{vap}/RT)^{1/4}]\} \quad (8)$$

$$b_{\rho_{nb}} = a_1 [1 - c_1(RT/\Delta H_{vap})] \exp[-c_1(RT/\Delta H_{vap})] + a_2 \{1 - [1 + 0.25c_2(\Delta H_{vap}/RT)^{1/4}] \exp[-c_2(\Delta H_{vap}/RT)^{1/4}]\} \quad (9)$$

$$a_1 = -0.1053, \quad a_2 = 2.9359, \quad c_1 = 5.7862, \quad c_2 = 0.7966$$

The correlations cover a wide range of temperatures.

To obtain cross second virial coefficient, we used the following simple combining rules for the heat of vaporization and the molar density:

$$(\Delta H_{vap})_j = (\Delta H_{vap})_i (\Delta H_{vap})_j^{1/2} \quad (10)$$

$$(\rho_{nb})_{ij}^{-1/3} = \frac{(\rho_{nb})_i^{-1/3} + (\rho_{nb})_j^{-1/3}}{2} \quad (11)$$

Once  $(\rho_{nb})_{ij}$  and  $(\Delta H_{vap})_{ij}$  are known, the values of  $(B_2)_{ij}$ ,  $\alpha_{ij}$  and  $b_{ij}$  follow from Eqs. (7)-(9) as was done for pure substances.

### Results and discussion

As already mentioned, the  $PVTx$  properties for system n-butane + isobutene, should be known accurately for the industrial use and

for the scientific research. In this respect, an EoS for the liquid mixtures has been developed based on the statistical-mechanical perturbation theory.

We employed the two-parameter macroscopic corresponding states correlation obtained in our previous work [4] in conjunction with simple combining rules for the heat of vaporization and molar liquid density at normal boiling point to predict the interact second virial coefficient as well as the ones for single substances. To obtain interaction second virial coefficient, we used combining rules for the heat of vaporization and the molar density given by Eqs (10) and (11). The values of  $\lambda_k$  that appear in Eqs (5) and (6) were found from the *PVT* data of dense pure components, and are listed in **Table 1**. It is a characteristic free constant that incorporate the inaccuracy associated with the temperature-dependent parameters. This method for determining  $\lambda$  makes the whole procedure self-correcting, because if the input values  $\Delta H_{\text{vap}}$  and liquid density  $\rho_{nb}$  at the normal boiling point are not accurate, the effects will be largely compensated by this adjustable parameter.

We carried out density,  $\rho$ , measurements of ( $x_1$  n-butane +  $x_2$  isobutane) with  $x_1 = (0.2625, 0.4913, \text{ and } 0.7508)$  over a wide range of temperatures from (280 to 440) K at pressures up to 200 MPa. The calculated results are given in **Table 2** for ( $x_1$  n-butane +  $x_2$  isobutane) with  $x_1 = 0.2625$ , in **Table 3** with  $x_1 = 0.4913$ , in **Table 4** with  $x_1 = 0.7508$ . The results with  $x_1 = 0.2625$  cover the density range  $\rho = (469 \text{ to } 706) \text{ kg.m}^{-3}$  at five temperature from (280 to

440) K and the pressures from  $P = (1 \text{ to } 200 \text{ MPa})$ . The results with  $x_1 = 0.4913$  cover the density range  $\rho = (532 \text{ to } 708) \text{ kg.m}^{-3}$  at the same as temperature and pressures in the Table 2. The results with  $x_1 = 0.7508$  cover the density range  $\rho = (541 \text{ to } 709) \text{ kg.m}^{-3}$  at five temperature from (280 to 440) K and the pressures from  $P = (1 \text{ to } 200 \text{ MPa})$ .

As the Tables show, agreement between calculated densities and literature values are quite good and all deviations are within 5%. No fitting was done for these systems other than combining rule by using of the parameters of the pure substances without proposing any mixing rule.

### Conclusion

Our procedure successfully predicts a statistical-mechanical equation of state for density of liquid mixtures over a wide range of temperatures and pressures. The ISM EoS accurately represents the effect of pressure on the liquid density for the system n-butane + isobutene. This indicates that the physical properties can be predicted from just two scaling constants, the heat of vaporization and the liquid density at normal boiling temperature, which can readily be measured. The present work demonstrated that the mixture version of the ISM EoS is able to provide reliable information on the *PVT* properties of ( $x_1$  n-butane +  $x_2$  isobutane) mixtures as well as pure systems without using any fitting parameter.

**Table 1.** The parameters for pure substances

substances	M. W. (g. mol <sup>-1</sup> )	T <sub>nb</sub> <sup>a</sup> (K)	$\Delta H_{\text{vap}} / R^a$ (K)	$\rho_{nb}^a$ (kg. m <sup>-3</sup> )	$\lambda$
n- butane	58.12	272.65	2691.4	602.0	0.390
isobutane	58.12	261.35	2565.6	595.0	0.389

<sup>a</sup> from Ref. [15]

**Table 2.** Comparisons between calculated liquid densities and experimental values [7] of compressed state for mixture {n-butane (1) + isobutane (2)} at  $x_1 = 0.2625$

P(MPa)	$\rho_{\text{exp}}$ (kg/m <sup>3</sup> )	$\rho_{\text{cal}}$ (kg/m <sup>3</sup> )	Dev% <sup>a</sup>
<b>T = 280 K</b>			
200	706.05	675.01	4.396
160	691.28	664.62	3.857
120	673.84	651.73	3.281
80	652.53	635.07	2.676
60	639.66	624.57	2.359
40	624.41	611.91	2.002
20	605.71	595.99	1.605
10	593.89	586.23	1.290
5	587.09	580.72	1.085
1	580.73	575.92	0.828
<b>T = 320K</b>			
200	685.47	661.60	3.482
160	669.26	648.10	3.162
120	649.73	631.00	2.883
80	625.51	608.14	2.777
60	610.30	593.17	2.807
40	591.82	574.26	2.967
20	567.26	548.69	3.274
10	550.53	531.53	3.451
5	540.14	521.00	3.544
1	530.15	511.23	3.569
<b>T = 360K</b>			
200	666.71	648.26	2.767
160	649.01	631.85	2.644
120	627.56	610.75	2.679
80	599.96	581.74	3.037
60	582.23	562.11	3.456
40	559.82	536.29	4.203
20	527.70	498.43	5.547
10	502.82	469.42	6.643
5	484.88	449.07	7.385
2	469.97	433.11	7.843
<b>T = 400 K</b>			
200	648.34	635.34	2.005
160	628.97	616.25	2.022
120	605.85	591.45	2.377
80	575.00	556.70	3.183
70	565.35	545.40	3.529
60	554.58	532.53	3.976
50	542.19	517.54	4.546
<b>T = 440 K</b>			
200	632.67	622.95	1.536
160	612.20	601.48	1.751
140	600.22	588.46	1.959
120	586.73	573.34	2.282
100	571.02	555.39	2.737
90	562.49	545.00	3.109
80	552.55	533.38	3.469
70	541.79	520.20	3.985
60	529.25	505.05	4.573

**Table 3.** The same as table 2. for  $x_1 = 0.4913$

P(MPa)	$\rho_{\text{exp}}$ (kg/m <sup>3</sup> )	$\rho_{\text{cal}}$ (kg/m <sup>3</sup> )	Dev% <sup>a</sup>
<b>T = 280 K</b>			
200	708.00	676.80	4.407
160	693.26	666.64	3.840
120	675.91	654.08	3.230
80	654.98	637.91	2.606
60	642.40	627.77	2.277
40	627.45	615.59	1.890
20	608.98	600.40	1.409
10	597.45	591.15	1.054
5	591.12	585.95	0.875
1	585.41	581.46	0.675
<b>T = 320 K</b>			
200	687.99	663.35	3.581
160	672.00	650.10	3.259
120	652.68	633.36	2.960
80	628.69	611.04	2.807
60	613.74	596.50	2.809
40	595.50	578.23	2.900
20	571.45	553.71	3.104
10	555.38	537.38	3.241
5	545.40	527.52	3.278
1	535.84	518.47	3.242
<b>T = 360 K</b>			
200	669.76	649.94	2.959
160	652.16	633.78	2.818
120	630.84	613.02	2.825
80	603.53	584.59	3.138
60	586.24	565.41	3.553
40	563.90	540.31	4.183
<b>T = 400 K</b>			
200	651.40	636.94	2.220
160	632.55	618.09	2.286
120	609.08	593.63	2.537
90	587.47	569.28	3.096
80	578.67	559.42	3.327
60	558.40	535.72	4.062
50	546.27	521.04	4.619
<b>T = 440 K</b>			
200	635.69	624.49	1.762
180	625.93	614.49	1.828
160	615.27	603.21	1.960
140	603.26	590.34	2.142
120	590.02	575.40	2.478
100	574.54	557.65	2.940
90	565.64	547.40	3.225
80	556.07	535.93	3.622
70	545.18	522.94	4.079
60	532.82	507.99	4.660

$$^a \text{Dev}\% = 100 \times \left( \frac{\rho_{\text{exp}} - \rho_{\text{cal}}}{\rho_{\text{exp}}} \right)$$

**Table 4.** The same as Table 2. for  $x_1 = 0.7508$ 

P(MPa)	$\rho_{\text{exp}}$ (kg/m <sup>3</sup> )	$\rho_{\text{cal}}$ (kg/m <sup>3</sup> )	Dev% <sup>a</sup>
<b>T = 280 K</b>			
200	709.43	678.82	4.315
160	694.86	668.93	3.732
120	677.69	656.74	3.091
80	656.95	641.11	2.411
60	644.70	631.36	2.069
40	612.32	605.30	1.146
20	601.36	596.59	0.793
10	594.99	591.72	0.550
5	590.90	588.60	0.389
1	589.56	587.53	0.344
<b>T = 320K</b>			
200	689.51	665.34	3.505
160	673.62	652.38	3.153
120	654.79	636.03	2.865
80	631.01	614.32	2.645
60	616.38	600.26	2.615
40	598.52	582.67	2.648
20	575.19	559.31	2.761
10	559.85	543.92	2.845
5	550.35	534.73	2.838
1	541.44	526.38	2.781
<b>T = 360K</b>			
200	672.02	651.87	2.998
180	663.57	644.36	2.895
140	644.56	626.49	2.803
120	633.40	615.62	2.807
90	613.96	595.75	2.966
80	606.56	587.83	3.088
60	589.35	569.17	3.424
40	567.64	544.88	4.010
30	554.09	529.29	4.476
<b>T = 400 K</b>			
200	653.90	638.78	2.312
160	634.89	620.18	2.317
140	623.93	609.01	2.391
120	611.77	596.10	2.561
100	598.02	580.91	2.861
90	590.11	572.18	3.038
80	581.70	562.52	3.297
70	572.18	551.66	3.586
60	561.67	539.34	3.976
50	549.67	525.02	4.485
<b>T = 440 K</b>			
200	637.80	626.22	1.816
160	617.59	605.18	2.009
140	605.80	592.47	2.200
120	592.51	577.73	2.494
100	577.23	560.22	2.947
90	568.41	550.13	3.216
80	558.93	538.83	3.596

$$^a \text{Dev}\% = 100 \times \left( \frac{\rho_{\text{exp}} - \rho_{\text{cal}}}{\rho_{\text{exp}}} \right)$$

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