Common Intersection Points of Binary Mixtures: Unlike Interactions Compared to Like Ones

Nahid Farzi

Department of Chemistry, Tarbiat Modares University, Tehran, Iran

Gholamabbas Parsafar*

Department of Chemistry, Isfahan University of Technology, Isfahan, Iran 84154

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In the present work the existence of a common compression factor point for binary mixtures has been investigated, both experimentally and theoretically. We found that the linear isotherm regularity (LIR) is able to predict the common compression factor point and the common bulk modulus point for binary mixtures, as well as pure dense fluids. An important conclusion deduced from this work is that a physical interpretation for such points may be given using LIR. The LIR along with the mean geometric approximation (MGA) have been used to relate the density at the common points of a mixture to those of its pure components. The numerical investigation shows that such a relation may be represented by a quadratic function in terms of the system composition for most mixtures. However, we have found that such a quadratic relation is generally valid for all investigated mixtures. An important result obtained from this work is that we may get information about the magnitude of interactions between unlike molecules, compared to those of like interactions. Such a result can be used to predict the deviation of a solution from ideality without having any vapor pressure data.

Introduction

An equation of state that has recently been derived for dense fluids is the linear isotherm regularity,[1,2] which has been abbreviated as the LIR. The LIR may be written as

$$(Z-1)v^2 = A + B\rho^2 \tag{1}$$

where $\rho = 1/v$ and Z are the molar density and compression factor, respectively, and A and B are temperature-dependent parameters, which for pure fluids are given as

$$A = A'' - \frac{A'}{RT} \tag{2a}$$

and

$$B = \frac{B'}{RT} \tag{2b}$$

where the constants A' and B' are related to the intermolecular attraction and repulsion, respectively, and the constant A'' is related to the nonideal contribution of the thermal pressure.

This equation of state has been found to be valid for nonpolar, polar, hydrogen-bonded, and quantum fluids.[1] Experimentally, the regularity holds for liquid isotherms from the vaporization line to the freezing line and for supercritical isotherm for densities greater than the Boyle density and for temperatures less than twice the Boyle temperature.

The LIR has been extended to mixtures. The composition dependencies of the LIR parameters for binary mixtures are obtained as[3]

$$B_{\text{mix}} = x_1{}^2 B_{11} + 2x_1x_2B_{12} + x_2{}^2 B_{22} \tag{3}$$

and

$$\left(\frac{A}{B}\right)_{\text{mix}} = x_1{}^2\left(\frac{A}{B}\right)_{11} + 2x_1x_2\left(\frac{A}{B}\right)_{12} + x_2{}^2\left(\frac{A}{B}\right)_{22} \tag{4}$$

The 11 and 22 subscripts on each parameter denote that parameter for the pure components, and the 12 subscript is for a hypothetical mixture with 12 interactions.

The LIR has also been found to be valid for different types of binary mixtures,[3] but the temperature dependencies of its parameters for a mixture are as follows:

$$A_{\text{mix}} = A''_{\text{mix}} - \frac{A'_{\text{mix}}}{RT} \tag{5a}$$

$$B_{\text{mix}} = B''_{\text{mix}} + \frac{B'_{\text{mix}}}{RT} \tag{5b}$$

Although the LIR is a simple equation of state, it is able to predict many empirically known regularities, along with some new ones.[4,5] Najafi et al.[4] have used LIR to investigate the existence of a common point for the isotherms of the compression factor and another common point for the isotherms of the bulk modulus, which was earlier found by Huang and O'Connell[6] for more than 250 different liquids. Such common points can be obtained from

$$\left(\frac{\partial Z}{\partial T}\right)_{\rho_{\text{OZ}}} = 0 \tag{6a}$$

and

$$\left(\frac{\partial B_{\text{r}}}{\partial T}\right)_{\rho_{\text{OB}}} = 0 \tag{6b}$$

where B_{r} is the reduced bulk modulus, which is given as $B_{\text{r}} = 1 + 3A\rho^2 + 5B\rho^4$ using LIR, and ρ_{OZ} and ρ_{OB} are the densities

* Corresponding author. E-mail: parsafar @ CC.IUT.AC.IR.

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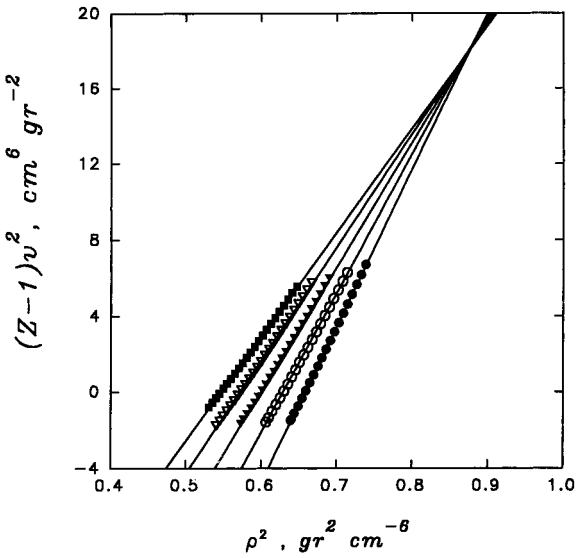

Figure 1. Searching for the common compression factor point for the $xCS_2 + (1 - x)Si(CH_3)_4$ mixture, using the experimental data for $x = 0.212$ and $T = 208.15$ K (●), 228.12 K (○), 248.35 K (▼), 268.22 K (▽), and 288.10 K (■).

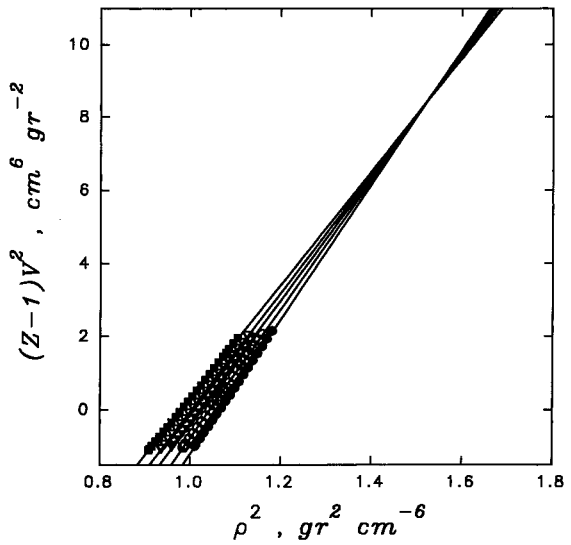

Figure 2. Same as Figure 1, except for $x = 0.699$ and $T = 257.96$ K (●), 267.86 K (○), 277.75 K (▼), 286.83 K (▽), and 297.99 K (■).

at the common compression factor and common bulk modulus, respectively. The LIR gives the densities of the common points for a pure dense fluid as

$$\rho_{OZ} = \left(\frac{A'}{B'}\right)^{1/2} \tag{7a}$$

and

$$\rho_{OB} = \left(0.6\frac{A'}{B'}\right)^{1/2} \tag{7b}$$

From eqs 7a and 7b, the relation between two densities is given as

$$\rho_{OB} = (0.6)^{1/2}\rho_{OZ} \tag{8}$$

The purpose of this work is the investigation of the following points for a binary mixture:

(1) The existence of such common points, using the experimental $p-v-T$ data.

(2) The ability of LIR to predict such common points.

(3) To find a relation among ρ_{OZ} (or ρ_{OB}) for a mixture with those of its pure components.

(4) Due to the fact that such common points are related to the intermolecular interactions, we may be able to predict the unlike interactions compared to those of like ones.

Common Intersection Points of Binary Mixtures

Since it has been observed that there is a common compression factor point and a common bulk modulus for isotherms of pure dense fluids, we may expect that such common points do exist for the mixtures, as well, which may be investigated by using the LIR.

We may plot Z (or B_r) versus ρ for different isotherms of a mixture to find its common point. However, according to the LIR, it is more convenient to plot $(Z - 1)v^2$ [or $(B_r - 1)v^2$] versus ρ^2, which is expected to be linear, as in the case of pure fluids.[4]

We have used the experimental $p-v-T$ data of Rubio et al.[7] and Baonza et al.[8,9] for the $xCS_2 + (1 - x)$ $Si(CH_3)_4$ mixture to plot $(Z - 1)v^2$ against ρ^2 to find the common compression point for each given composition, shown in Figures 1 and 2. As shown in these figures, the common point occurs at a density of 0.934 and 1.241 g cm^{-3} when the composition is $x = 0.212$ and $x = 0.699$, respectively. Also we have used the experimental data of Kabata et al.[10−12] for the $xCF_3CH_2OH + (1 - x)H_2O$ mixture to plot $(B_r - 1)v^2$ versus ρ^2 to find the common bulk modulus point for each given composition, shown in Figure 3. As shown in this figure the common point occurs at a density of 1.034, 1.229 and 1.304 gr cm^{-3} for the mixture with the composition of $x = 0.051$, $x = 0.301$, and $x = 0.653$, respectively. Such investigations have been done for 16 different binary mixtures, to find ρ_{OZ} and ρ_{OB} for some given system compositions. The results are summerized in columns 6 and 8 of Table 1, respectively. From Table 1 we may conclude that there is a common compression point and also a common bulk modulus point for each binary mixture, as expected, whose value depends on the system composition. The small inconsistencies in pure component from mixture to mixture are due to using different experimental reported $p-v-T$ data.

Common Intersection Points Investigation Using LIR

Due to the fact that the LIR is able to predict such common points for pure fluids,[4] we may expect that it is able to predict such points for binary mixtures as well.

Using LIR along with eq 6a, the density at the common compression point for binary mixtures is given as

$$(\rho_{OZ})_{mix} = \left(\frac{A'}{B'}\right)_{mix}^{1/2} \tag{9a}$$

To calculate $(\rho_{OZ})_{mix}$ for a mixture with a given composition, the A'_{mix} and B'_{mix} parameters of the mixture must be known. To find these parameters, we may plot $(Z - 1)v^2$ against ρ^2 for different isotherms. The slope and intercept of the straight lines can be used to plot B and A versus $1/T$, from which B' and A' can be found from the slope of B and A, respectively.

The LIR gives the following results for the density at the common bulk modulus point (see eq 6b).

$$(\rho_{OB})_{mix} = \left(0.6\left(\frac{A'}{B'}\right)_{mix}\right)^{1/2} \tag{9b}$$

By having A'_{mix} and B'_{mix} for a mixture, we may calculate ρ_{OZ} and ρ_{OB} for that mixture. The results for some binary mixtures at some given compositions are summarized in columns 5 and 7 of Table 1, respectively, which may be

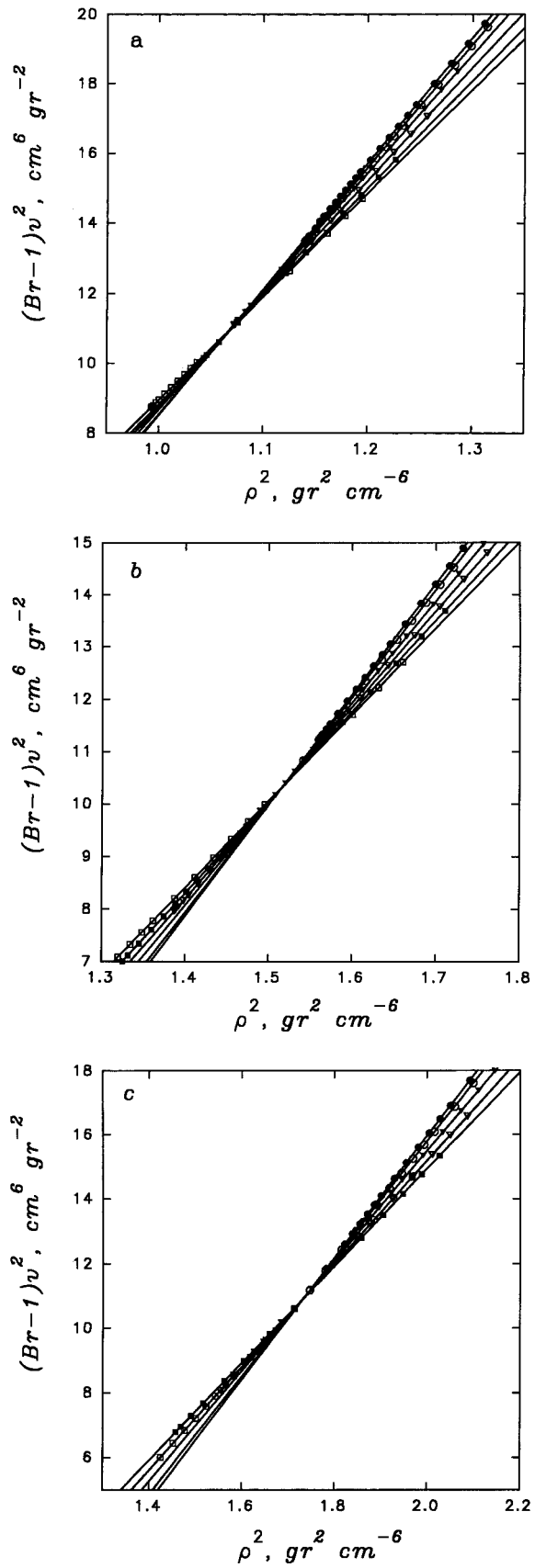

Figure 3. Searching for the common bulk modulus point for the $x$$CF_3$-$CH_2OH$ + $(1 - x)H_2O$ mixture at $T = 310$ K (●), 320 K (○), 340 K (▼), 360 K (▽), 380 K (■), and 400 K (□) and (a) $x = 0.0507$, (b) $x = 0.3013$, and (c) $x = 0.6532$.

compared with those obtained from experimental data given in the same table.

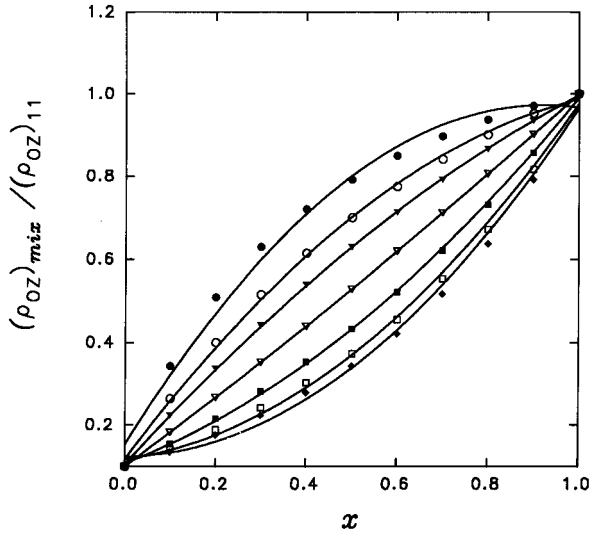

Figure 4. Quadratic dependency of the experimentally obtained $(\rho_{OZ})_{mix}$ in terms of system composition, when $\alpha = 0.1$ and $\beta = 0.3$ (●), 0.5 (○), 0.7 (▼), 1.1 (▽), 1.7 (■), 2.3 (□), and 2.7 (◆).

Dependencies of $(\rho_{OZ})_{mix}$ and $(\rho_{OB})_{mix}$ on Those of Pure Components and the System Composition

Using the LIR, the density at the common compression point for a binary mixture is given by eq 9a. Knowing the composition dependencies of A' and B' parameters,[3] ρ_{OZ} of a mixture may be given as

$$(\rho_{OZ})_{mix} = \left(\frac{x_1^2 A'_{11} + 2x_1x_2A'_{12} + x^2{}_2A'_{22}}{x_1^2 B'_{11} + 2x_1x_2B'_{12} + x^2{}_2B'_{22}}\right)^{1/2} \qquad (10)$$

The parameters A'_{11} (or A'_{22})and B'_{11} (or B'_{22}) are related to the attraction and repulsion for pure components, and A'_{12} and B'_{12} are for the hypothetical mixture with 12 interactions. However, it has been shown that the latter parameters may be related to those of pure components via the mean geometric approximations as[13]

$$A_{12} = \sqrt{A_{11}A_{22}} \qquad B_{12} = \sqrt{B_{11}B_{22}} \qquad (11)$$

Substitution of A_{12} and B_{12} from eq 11 into eq 10 gives the following result:

$$(\rho_{OZ})_{mix} = \frac{x_1(A'_{11})^{1/2} + x_2(A'_{22})^{1/2}}{x_1(B'_{11})^{1/2} + x_2(B'_{22})^{1/2}} \qquad (12)$$

This equation can be used to calculate $(\rho_{OZ})_{mix}$ for a mixture at any given composition. The results of such a calculation are given in the last column of Table 1, which may be compared with the experimental values given in the same table.

To relate $(\rho_{OZ})_{mix}$ of eq 12 to $(\rho_{OZ})_{22} = [(A'/B')_{22}]^{1/2}$ and $(\rho_{OZ})_{11} = [(A'/B')_{11}]^{1/2}$, eq 12 may be rearranged into

$$(\rho_{OZ})_{mix}\left(1 + \frac{x_2}{x_1}\left(\frac{B'_{22}}{B'_{11}}\right)^{1/2}\right) = (\rho_{OZ})_{11} + \frac{x_2}{x_1}\left(\frac{B'_{22}}{B'_{11}}\right)^{1/2}(\rho_{OZ})_{22} \qquad (13)$$

The $(\rho_{OZ})_{mix}$ given by eq 13 is a complicated function in terms of $(\rho_{OZ})_{11}$, $(\rho_{OZ})_{22}$, and the mixture composition. However, we have plotted $(\rho_{OZ})_{mix}$ given by eq 13 in terms of mixture composition, one sample of which is given in Figure 4. We have noticed that when the value of $\beta = (B'_{22}/B'_{11})^{1/2}$ is in the range of 0.37−2.7, regardless of the value of $\alpha = (\rho_{OZ})_{22}/(\rho_{OZ})_{11}$,

TABLE 1: Calculated and Experimental Densities at the Common Compression Factor, $(\rho_{OZ})_{mix}$, and Common Bulk Modulus, $(\rho_{OB})_{mix}$, Points and the Common Compression Point Density Given by the Mean Geometry Approximation (Eq 12) for Different Mixtures at Given Compositions

mixture	x	A'_{mix}/R, cm^6 g^{-2}	B'_{mix}/R, cm^{12} g^{-4}	$(\rho_{OZ})_{mix}$, g cm^{-3} cal	$(\rho_{OZ})_{mix}$, g cm^{-3} exp	$(\rho_{OZ})_{mix}$, g cm^{-3} cal	$(\rho_{OZ})_{mix}$, g cm^{-3} exp	$(\rho_{OZ})_{mix}$, mean g cm^{-3}
$xH_2O + (1-x)CH_3OH$[a]	0	6 179.517	6 101.833	1.006	1.007	0.779	0.780	1.006
	0.25	5 075.383	4 215.817	1.097	1.084	0.850	0.840	1.084
	0.5	5 084.808	4 337.793	1.083	1.082	0.839	0.838	1.083
	0.75	3 983.094	3 195.903	1.116	1.117	0.864	0.865	1.116
	1	1 439.904	885.1790	1.275	1.277	0.988	0.989	1.275
$xC_2H_5OH + (1-x)C_7H_{16}$[b]	0	30 127.57	42 645.15	0.841	0.837	0.651	0.648	0.841
	0.305	18 349.33	21 729.30	0.919	0.925	0.712	0.717	0.864
	0.573	24 325.16	35 839.57	0.824	0.827	0.638	0.641	0.892
	0.819	15 459.46	18 311.26	0.919	0.919	0.712	0.712	0.929
	1	10 083.19	10 757.99	0.967	0.968	0.749	0.749	0.968
$xCS_2 + (1-x)Si(CH_3)_4$[c]	0	25 510.92	35 625.48	0.846	0.840	0.655	0.651	0.846
	0.212	19 135.17	22 151.20	0.930	0.934	0.720	0.723	0.890
	0.485	12 479.62	10 527.77	1.089	1.076	0.843	0.833	0.982
	0.699	8 776.916	5 598.990	1.252	1.241	0.970	0.961	1.111
	1	4 967.982	1 951.500	1.596	1.587	1.236	1.229	1.596
$xn\text{-}C_{16}H_{34} + (1-x)n\text{-}C_6H_{14}$[d]	0	30 845.02	44 279.36	0.835	0.833	0.647	0.645	0.835
	0.2	31 092.23	37 417.70	0.916	0.915	0.710	0.709	0.876
	0.4	40 352.79	47 179.63	0.925	0.925	0.717	0.717	0.918
	0.6	40 669.21	41 971.40	0.984	0.982	0.762	0.761	0.963
	0.8	37 750.79	35 683.61	1.029	1.025	0.797	0.794	1.010
	1	39 469.25	35 198.18	1.059	1.057	0.820	0.819	1.059
$xCF_3CH_2OH + (1-x)H_2O$[e]	0	1 439.904	885.1790	1.275	1.276	0.988	0.988	1.275
	0.051	2 616.563	1 464.121	1.337	1.335	1.036	1.034	1.304
	0.301	3 234.029	1 279.975	1.590	1.587	1.232	1.229	1.433
	0.653	3 777.538	1 327.750	1.687	1.683	1.307	1.304	1.588
	1	4 363.727	1 480.790	1.716	1.720	1.329	1.332	1.717
$xCH_3CH_2F + (1-x)CHF_2CH_3$[f]	0	3 762.600	2 010.704	1.368	1.368	1.060	1.059	1.368
	0.248	3 242.140	1 697.650	1.382	1.432	1.070	1.109	1.434
	0.499	2 874.670	1 163.090	1.572	1.581	1.218	1.225	1.518
	0.751	2 566.240	913.6410	1.676	1.683	1.298	1.304	1.624
	1	2 359.150	759.4360	1.763	1.789	1.366	1.386	1.763
$xC_6H_6 + (1-x)C_6H_5NO_2$[g]	0	14 520.67	7 011.850	1.439	1.426	1.115	1.105	1.439
	0.2	12 999.04	6 694.670	1.394	1.387	1.080	1.074	1.340
	0.4	12 116.32	6 626.720	1.352	1.371	1.047	1.062	1.257
	0.6	11 483.74	6 767.490	1.303	1.295	1.009	1.003	1.185
	0.8	10 648.95	6 824.395	1.249	1.238	0.967	0.959	1.122
	1	6 328.320	14 350.62	1.067	1.061	0.826	0.822	1.067
$xC_6H_6 + (1-x)C_6H_5Cl$[h]	0	14 368.23	9 181.068	1.251	1.281	0.969	0.992	1.251
	0.25	15 407.40	9 958.152	1.244	1.241	0.964	0.961	1.197
	0.5	15 626.87	10 965.74	1.194	1.194	0.925	0.925	1.148
	0.75	14 974.38	11 333.68	1.149	1.149	0.890	0.890	1.104
	1	15 867.37	13 992.95	1.065	1.078	0.825	0.835	1.065
$xCH_3C_5H_9 + (1-x)C_7H_{16}$[i]	0	30 127.57	42 645.15	0.841	0.837	0.651	0.648	0.841
	0.353	29 420.77	40 487.46	0.852	0.855	0.660	0.662	0.863
	0.616	24 757.91	31 378.01	0.888	0.887	0.688	0.687	0.883
	0.881	22 974.11	28 528.19	0.939	0.897	0.727	0.695	0.906
	1	24 126.37	29 235.18	0.908	0.908	0.704	0.704	0.908
$xCH_3C_5H_9 + (1-x)C_2H_5OH$[j]	0	10 083.19	10 757.99	0.968	0.968	0.750	0.749	0.968
	0.186	12 910.27	14 349.90	0.949	0.946	0.735	0.733	0.955
	0.488	17 120.01	19 775.73	0.930	0.930	0.720	0.720	0.938
	0.699	22 213.66	27 128.20	0.905	0.911	0.701	0.705	0.928
	1	24 126.37	29 235.18	0.908	0.908	0.704	0.704	0.908
$xDCE$[q] $+ (1-x)TMP$[k,r]	0	34 951.68	50 163.14	0.835	0.849	0.647	0.658	0.835
	0.2	26 742.59	32 363.26	0.909	0.922	0.704	0.714	0.878
	0.4	21 152.21	21 228.97	0.998	0.985	0.773	0.763	0.939
	0.6	15 221.17	11 970.60	1.127	1.105	0.873	0.856	1.032
	0.8	11 215.14	6 715.571	1.292	1.307	1.001	1.012	1.189
	1	8 442.930	3 666.724	1.517	1.521	1.175	1.178	1.517
$xCH_3CN + (1-x)C_6H_6$[l]	0	13 731.88	11 013.22	1.117	1.116	0.865	0.864	1.117
	0.303	13 164.49	11 446.64	1.072	1.063	0.830	0.823	1.095
	0.483	12 428.11	11 047.50	1.061	1.061	0.822	0.822	1.081
	0.816	11 658.20	11 069.94	1.026	1.036	0.795	0.802	1.623
	1	8 893.832	8 273.690	1.037	1.037	0.803	0.803	1.037
$xC_6H_6 + (1-x)TMP$[m]	0	4 939.95	49 080.10	0.844	0.842	0.654	0.652	0.844
	0.249	27 461.00	33 450.91	0.906	0.906	0.702	0.702	0.884
	0.498	21 468.20	22 910.69	0.968	0.966	0.750	0.748	0.941
	0.756	13 869.29	11 110.41	1.117	1.109	0.865	0.859	1.033
	1	11 512.37	8 240.190	1.182	1.175	0.916	0.910	1.182

TABLE 1 (Continued)

mixture	x	A'_{mix}/R, cm^6 g^{-2}	B'_{mix}/R, cm^{12} g^{-4}	$(\rho_{OZ})_{mix}$, g cm^{-3} cal	$(\rho_{OZ})_{mix}$, g cm^{-3} exp	$(\rho_{OZ})_{mix}$, g cm^{-3} cal	$(\rho_{OZ})_{mix}$, g cm^{-3} exp	$(\rho_{OZ})_{mix}$, mean g cm^{-3}
xCH$_4$ + (1 − x)Ar[n]	0	813.9650	272.7130	1.728	1.727	1.339	1.338	1.727
	0.316	1 648.310	10 052.97	1.280	1.281	0.991	0.992	0.746
	0.522	2 895.810	2 861.579	1.006	1.014	0.779	0.785	0.645
	0.711	2 744.260	7 035.255	0.821	0.819	0.636	0.634	0.598
	1	10 621.85	34 278.84	0.557	0.526	0.431	0.407	0.557
xCH$_4$ + (1 − x)N$_2$[o]	0	1 970.183	1 931.92	1.010	1.009	0.782	0.782	1.010
	0.294	3 356.268	4 732.01	0.842	0.841	0.652	0.651	0.721
	0.497	4 369.728	7 425.68	0.767	0.764	0.594	0.592	0.644
	0.680	6 090.470	12 983.4	0.685	0.685	0.531	0.531	0.602
	1	10 621.85	34 278.8	0.557	0.526	0.431	0.407	0.557
xC$_6$F$_6$ + (1 − x)C$_6$H$_6$[p]	0	12 038.39	8 986.47	1.157	1.172	0.896	0.908	1.157
	0.250	6 746.471	2 868.66	1.534	1.494	1.188	1.157	1.255
	0.500	5 902.920	2 007.60	1.715	1.715	1.328	1.328	1.401
	0.874	7 147.660	2 028.01	1.877	1.879	1.454	1.455	1.838
	1	4 553.445	1 004.50	2.129	2.121	1.459	1.643	2.129

[a] Reference 22. [b,i,j] Reference 23. [c] References 7−9. [d] Reference 24. [e] References 10−12. [f] References 25 and 26. [g] Reference 27. [h] Reference 28. [k] Reference 16. [l] Reference 29. [m] Reference 30. [n] References 31 and 32. [o] Reference 32. [p] Reference 33. [q] DCE = 1,2-dichloroethane. [r] TMP = 2,2,4-trimethylpentane.

TABLE 2: Value of $\alpha = (\rho_{OZ})_{22}/(\rho_{OZ})_{11}$ and $\beta = (B'_{22}/B'_{11})^{1/2}$ for Given Mixture

mixture	$\alpha = (\rho_{OZ})_{22}/(\rho_{OZ})_{11}$	$\beta = (B'_{22}/B'_{11})^{1/2}$
xH$_2$O + (1 − x)CH$_3$OH	0.788	2.626
xC$_2$H$_5$OH + (1 − x)C$_7$H$_{16}$	0.864	1.991
xCS$_2$ + (1 − x)Si(CH$_3$)$_4$	0.529	4.273
xn-C$_{16}$H$_{34}$ + (1 − x)n-C$_6$H$_{14}$	0.788	1.122
xCF$_3$CH$_2$OH + (1 − x)H$_2$O	0.742	0.773
xCF$_3$CH$_2$F + (1 − x)CHF$_2$CH$_3$	0.765	1.627
xC$_6$H$_6$ + (1 − x)C$_6$H$_5$NO$_2$	1.344	0.699
xC$_6$H$_6$ + (1 − x)C$_6$H$_5$Cl	1.188	0.810
xCH$_3$C$_5$H$_9$ + (1 − x)C$_7$H$_{16}$	0.912	1.208
xCH$_3$C$_5$H$_9$ + (1 − x)C$_2$H$_5$OH	1.056	0.607
xDCE + (1 − x)TMP	1.742	3.699
xCH$_3$CN + (1 − x)C$_6$H$_6$	1.076	1.154
xC$_6$H$_6$ + (1 − x)TMP	0.717	2.440
xCH$_4$ + (1 − x)Ar	3.280	0.089
xCH$_4$ + (1 − x)N$_2$	1.918	0.237
xC$_6$F$_6$ + (1 − x)C$_6$H$_6$	0.552	2.991

$(\rho_{OZ})_{mix}$ fits well on a quadratic function as

$$(\rho_{OZ})_{mix} = x_1^2(\rho_{OZ})_{11} + 2x_1x_2(\rho_{OZ})_{12} + x_2^2(\rho_{OZ})_{22} \quad (14)$$

where $(\rho_{OZ})_{12}$ is the density at the common compression factor for a hypothetical pure fluid with 12 interactions.

The values of α and β are given in Table 2 for 16 different mixtures. Even though the values of β for most mixtures are in the range within which the quadratic relation (eq 14) is expected to be valid, its values are out of the range for some mixtures. However, we have found that the experimental $(\rho_{OZ})_{mix}$ fits well on a quadratic function in terms of the system composition, for all mixtures given in Table 3. Even for the CS_2 + Si(CH$_3$)$_4$ mixture with $\beta = 4.273$, which is not expected to give a quadratic behavior for $(\rho_{OZ})_{mix}$ according to eq 13, shows a very good quadratic fit, see Figure 5. The unability of eq 13 to predict such a quadratic fit for some mixtures is expected to be due to the unvalidity of the mean geometric approximation, eq 11, for such mixtures.

Conclusion and Discussion

We have experimentally investigated a common compression factor point for binary mixtures. The LIR can predict the densities at the common intersection points of both the compression factor and the bulk modulus for a binary mixture as well as those for a pure dense fluid. As discussed before, the average intermolecular separation at ρ_{OZ} is such that the attraction and repulsion forces exactly cancel out each other.[5]

We have obtained a quadratic relation, eq 14, among the ρ_{OZ}

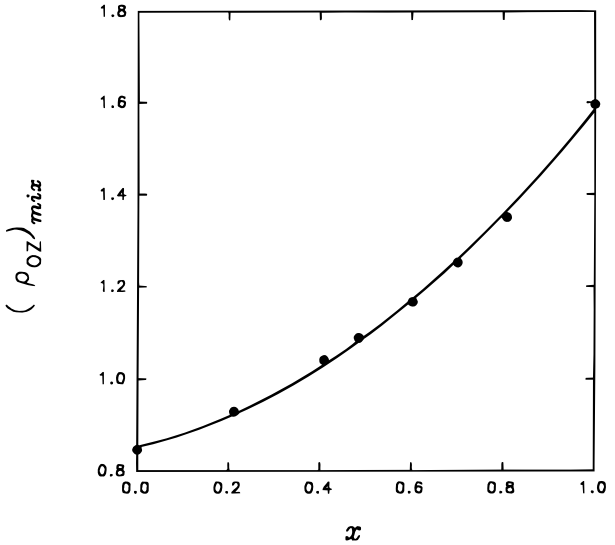

Figure 5. Excellent quadratic fit of experimentally obtained $(\rho_{OZ})_{mix}$ for the xCS$_2$ + (1 − x) Si(CH$_3$)$_4$ mixture. Note that eq 13 cannot predict such a quadratic behavior for this mixture.

TABLE 3: Coefficients of Eq 14 Obtained from the Quadratic Fit of the Experimentally Obtained $(\rho_{OZ})_{mix}$. The Arithmetic Mean of Density, $\rho_M = (\rho_{11} + \rho_{22})/2$, Is Given To Compare with ρ_{12}

mixture	ρ_{11}, g cm^{-3}	ρ_{22}, g cm^{-3}	ρ_{12}, g cm^{-3}	ρ_M, g cm^{-3}
xH$_2$O + (1 − x)CH$_3$OH	1.258	1.059	1.005	1.159
xC$_2$H$_5$OH + (1 − x)C$_7$H$_{16}$	0.957	0.860	0.832	0.909
xCS$_2$ + (1 − x)Si(CH$_3$)$_4$	1.584	0.853	0.967	1.219
n-C$_{16}$H$_{34}$ + (1 − x)n-C$_6$H$_{14}$	1.060	0.841	0.975	0.951
xCF$_3$CH$_2$OH + (1 − x)H$_2$O	1.704	1.291	1.845	1.498
xCF$_3$CH$_2$F + (1 − x)CHF$_2$CH$_3$	1.777	1.344	1.527	1.561
xC$_6$H$_6$ + (1 − x)C$_6$H$_5$NO$_2$	1.089	1.424	1.421	1.257
xC$_6$H$_6$ + (1 − x)C$_6$H$_5$Cl	1.066	1.253	1.244	1.160
xCH$_3$C$_5$H$_9$ + (1 − x)C$_7$H$_{16}$	0.916	0.829	0.842	0.873
xCH$_3$C$_5$H$_9$ + (1 − x)C$_2$H$_5$OH	0.908	0.961	0.914	0.935
xDCE + (1 − x)TMP	1.515	0.845	0.938	1.180
xCH$_3$CN + (1 − x)C$_6$H$_6$	1.035	1.118	1.021	1.077
xC$_6$H$_6$ + (1 − x)TMP	1.194	0.839	0.963	1.017
xCH$_4$ + (1 − x)Ar	0.558	1.729	0.944	1.144
xCH$_4$ + (1 − x)N$_2$	0.559	1.006	0.736	0.783
xC$_6$F$_6$ + (1 − x)C$_6$H$_6$	2.057	1.133	1.791	1.595

for a binary mixture and ρ_{OZ} of its pure components, which is usable at least for all kinds of the investigated binary mixtures given in Table 1. Using $p-v-T$ data for a mixture and its pure components and LIR, along with eqs 7a and 9, we may calculate $(\rho_{OZ})_{11}$, $(\rho_{OZ})_{22}$, and $(\rho_{OZ})_{mix}$. Knowing ρ_{OZ} for a mixture with a given composition, and those for its pure components, eq 14 can be used to calculate $(\rho_{OZ})_{12}$. Since ρ_{OZ} is related to the ratio of the intermolecular attraction to repulsion, i.e $\rho_{OZ} = (A'/B')^{1/2}$, we may compare $(\rho_{OZ})_{12}$ with $[(\rho_{OZ})_{11} + (\rho_{OZ})_{22}]/2$ to get information about the magnitude of unlike interactions, relative to the like ones. Note that for an ideal solution for which all interactions are equal, we may expect that $(\rho_{OZ})_{11} = (\rho_{OZ})_{22} = (\rho_{OZ})_{12}$; therefore $(\rho_{OZ})_{12} = [(\rho_{OZ})_{11} + (\rho_{OZ})_{22}]/2$. However, in a real solution the values of $(\rho_{OZ})_{12}$ and $[(\rho_{OZ})_{11} + (\rho_{OZ})_{22}]/2$ are different, and such a difference can be considered as a measure for the deviation of real solution from ideality. For instance, in the $C_6F_6 + C_6H_6$ mixture, $[(\rho_{OZ})_{11} + (\rho_{OZ})_{22}]/2 = 1.595$ g cm^{-3} and $(\rho_{OZ})_{12}$ is equal to 1.791 g cm^{-3}. Therefore, we may conclude that the attraction forces among unlike molecules are stronger than the average attraction forces among the pure components. Such a conclusion is in accordance with the experimental observation, for which the negative deviation (negative excess enthalpy, H^E) is reported for such a mixture.[14]

Similar argument may be used, along with the results of Table 3, to conclude that $CH_4 + Ar$, $CH_4 + N_2$, DCE +TMP, $CH_3CN + C_6H_6$, $C_{16}H_{34} + C_6H_{14}$, $C_2H_5OH + C_7H_{16}$, and $CH_3CH_2F + CHF_2CH_3$ mixtures have positive deviations from ideality ($H^E > 0$). Such conlusions are in agreement with experimental observations.[15−20]

For the $CH_3OH + H_2O$ system, the excess enthalpy strongly depends on the pressure and temperature,[21] in such a way that, for an isobar, $H^E < 0$ at low temperatures and $H^E > 0$ for high temperatures. However, from the results given in Table 3, we may conclude that the attraction between unlike molecules (H_2O and CH_3OH) is smaller than the average attraction between like molecules in the temperature range of 283−345 K and pressure range of 0.1−206.7 MPa. In other words, the deviation is positive in such temperature and pressure ranges.

In the case of the $CF_3CH_2OH + H_2O$ mixture, the results given in Table 3 show that the attractions among CF_3CH_2OH molecules are stronger than those for water molecules ($\rho_{OZ} = 1.704$ g cm^{-3} for the former component and $\rho_{OZ} = 1.291$ g cm^{-3} for the latter one). Such a conclusion may be expected, because of the fact that the high electronegativity of F causes strong hydrogen bonding. However, the attractions between unlike molecules are stronger than those of its pure components [note that $(\rho_{OZ})_{12} = 1.845$ g cm^{-3}]. Therefore such a mixture is expected to have a strong negative deviation (from ideality). Unfortunately, no experimental data for the excess enthalpy of this mixture is reported in the literature, to evaluate our expectation.

Due to the fact that eqs 12 and 14 can be used for $(\rho_{OB})_{mix}$, except for an additional factor of $(0.6)^{1/2}$ on the right-hand sides of these equations, we may conclude that our presented results for the common compression points are valid for the common bulk modulus point as well. In other words, the density of the common bulk modulus for a binary mixture may be related to those of its pure components and the mixture composition as,

$$(\rho_{OB})_{mix} = x_1^2(\rho_{OB})_{11} + 2x_1x_2(\rho_{OB})_{12} + x_2^2(\rho_{OB})_{22} \quad (15)$$

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