

Prediction of the Temperature and Density Dependences of the Parameters of the Average Effective Binary Mixture Pair Potential Using Only the LIR Equation of State

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Recently, using the linear isotherm regularity (LIR) equation of state, the average effective pair potential parameters for dense fluids have been calculated, and it was shown that they are only temperature dependent. Those parameters were used to propose a strong principle of corresponding states. In the present work, the approach is extended to binary mixtures, from which we have found that the average effective pair potential parameters of mixtures depend on composition and temperature. We have also calculated the average effective unlike pair potential parameters of mixtures at various temperatures via the LIR parameters. The calculated like and unlike pair potential parameters of some mixtures have then been used to calculate their excess enthalpy. When the calculated average effective pair potential parameters of mixtures are used to reduce the LIR parameters, a strong principle of corresponding states has been observed for various mixtures with different compositions, as for the pure components. The calculated like and unlike pair potential parameters have been tested with different mixing rules based on the one-fluid approximation. The maximum differences of the calculated values with the mixing rules are lower than 10%.

KEY WORDS: average effective pair potential; conformal solution theory; corresponding-states principle; like and unlike pair potential.

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1. INTRODUCTION

One of the interesting problems in statistical mechanics is the prediction of mixture properties from those of the components forming the mixture. There are a number of ways to achieve this goal. Modern theories of fluids and fluid mixtures have benefited a great deal from the concept of the radial distribution function (RDF) [1]. All thermodynamic properties of a fluid can be related to the RDF, if we assume that the N -body potential is pairwise additive. The RDF theories have been quite successful in describing the behavior of simple liquids and liquid mixtures, although RDF analytical expressions could be provided only for very simple model fluids such as hard spheres and hard rods. Moreover, the validity of the results of the RDF method is limited to spherically symmetric potentials, and therefore their application to polar nonspherical fluids is impossible. On the other hand, the Kirkwood–Buff theory [2] provides equations valid for any kind of molecular shape which allow the calculation of thermodynamic properties of mixtures such as compressibility, partial molar volumes, and chemical potentials only requiring the knowledge of the integrals over the distance of the radial distribution functions. Although Kirkwood solution theory is practical for any kind of molecular shape, its calculation is limited to the case of dilute solutions.

Perturbation theory [3] divides the potential function into a reference part and a perturbed part. The reference part represents a potential model for which the thermodynamic properties are known, such as the hard-sphere model. Variational theory [4] provides inequalities that may give the least upper bound and the highest lower bound to the Helmholtz free energy in terms of the effective hard-sphere diameter. The technique then finds the diameter that minimizes the numerical value of the upper bound. The last procedure is readily extended to mixtures, but its application to a binary mixture, for example, requires the determination of two effective diameters by minimizing a function of two variables. This approach presents a formidable computational task for multicomponent systems. In both the perturbation and the variational theories, a reference system for which the thermodynamic properties and radial distribution functions are known is needed. Mixture calculations based on these theories are simpler than the integral equations approach, but they are still lengthy and usually no closed form expressions can be obtained.

As far as practical applications are concerned, the most successful theories in predicting the thermodynamic properties of multicomponent mixtures have been the corresponding state or conformal solution theories of mixtures [5]. In the conformal solution theory (CST), it is assumed that a hypothetical pure fluid exists that has the same properties as the mixture

at the same density and temperature. This hypothetical fluid is described by the same equation of state as that of the pure fluids which form the mixture. The parameters of the hypothetical fluid are related to those of the pure fluids, composition, and possibly temperature and density by relations which are usually called the mixing rules. Many mixing rules have been suggested. Some of those are empirically determined, and others are derived by making some assumptions about the mixture RDF. (For a useful review, see Ref. 6.)

The van der Waals (vdW) one-fluid theory is a widely used two-parameter conformal solution theory. The van der Waals theory was extended to a three-parameter potential in which the stiffness of the potential function can be varied [7]. A number of other conformal solution theories have been derived, some of which are the mean density approximation (MDA) [8], the hard-sphere expansion (HSE) [7], and the density expansion theories [9].

In the development of the CST for mixtures, two principles are considered. One is the choice of an accurate equation of state for the reference pure system. The second is the choice of mixing rules for parameters of the pure reference equation of state, to generalize them for mixtures. The parameters of the pure reference equation of state are usually either intermolecular potential parameters or the critical properties. Based on this fact, the equation of state obtained from HSE theory has been extended to multicomponent mixtures using the CST [10], and the approach has been successful in predicting the vapor-liquid equilibrium behavior of a limited number of mixtures. However, application of the HSE technique to any other mixtures requires detailed knowledge about the intermolecular potential functions of the components of that mixture, which is lacking at the present time.

Recently, we have presented a method to predict the temperature and density dependencies of the pair potential parameters of dense fluids using the LIR equation of state [11]. The method is simple and practical to use for all types of dense fluids and even gives analytical expressions for temperature dependencies of the pair potential parameters. In our approach, only p - v - T experimental data are needed. Our aim in the present work is the extension of that method to binary mixtures using CST.

The LIR equation of state has been extended to mixtures using the CST and the random mixing approximation (RMA) [12]. Assuming that the effects of long-range interactions and the fluid medium on the charge distribution of a nearest-neighbor pair are added to the potential energy of the pair, the pairwise additive approximation for the configurational potential energy will be exact and may be used to define the concept of an average effective pair potential [11]. Using the Lennard-Jones (12,6)

potential energy function for the average effective pair potential of the components of a mixture to obtain the internal pressure of a binary mixture along with the mixture internal pressure predicted by the LIR equation of state, one can obtain the average effective pair potential parameters of mixtures in terms of the LIR parameters. The approach is exactly the same as that used for the pure fluids [11].

In the present work, we have used the CST and the one-fluid approximation via the LJ (12,6) potential function (for the average effective pair potential) to obtain the average effective pair potential parameters of mixtures, ϵ_x and σ_x , at various temperatures and compositions. We have also obtained the average effective unlike pair potential parameters, ϵ_{12} and σ_{12} , at various temperatures for some binary mixtures. The calculated average effective like and unlike pair potential parameters for a given mixture have been used to calculate the excess enthalpy of that mixture. The calculated average effective pair potential parameters of mixtures have then been used to introduce a strong principle of corresponding states similar to that obtained for pure fluids. The calculated average effective like and unlike pair potential parameters have also been used to calculate the average effective pair potential parameters of some mixtures using various one-fluid approximation mixing rules.

2. CALCULATION OF THE AVERAGE EFFECTIVE PAIR POTENTIAL PARAMETERS OF BINARY MIXTURES

In the LIR equation of state, it is assumed that only nearest-neighbor interactions exist. In other words, the entire potential energy of the fluid is attributed to nearest-neighbor interactions. This means that the longer-range interactions of a given neighboring pair with other molecules, which are mainly attractive, and the effect of the fluid medium on the charge distributions of the pair are both added to the potential energy of the isolated nearest-neighbor pair. Such a potential is called the average effective pair potential [11]. Regarding such a pair potential, the potential energy of a fluid can be written as the sum of all the average effective pair interaction potentials, exactly. Such an exact treatment of the fluid potential energy has been considered in the LIR derivation, and it was shown that the LJ(12,6) potential is appropriate for such a potential. Using this potential along with the exact thermodynamic expression

$$p = -(\partial E / \partial v)_T + T(\partial p / \partial T)_v \quad (1)$$

the LIR has been derived as [13]

$$(Z-1)v^2 = A + B\rho^2 \quad (2)$$

where Z is the compressibility factor and $\rho = 1/v$ is the molar density. The temperature dependencies of the A and B parameters are obtained as [11]

$$A = A_0 - \frac{A'}{RT} \quad (3)$$

$$B = B_0 + \frac{B'}{RT}$$

In Eq. (3), A' and B' are related to the intermolecular attraction and repulsion forces and are proportional to $\epsilon\sigma^6$ and $2\epsilon\sigma^{12}$, respectively, while the nonideal thermal pressure parameter A'' , $A'' = (1/\rho^2)[(\partial p/\partial T)_\rho/\rho R - 1]$, is related to the A_0 and B_0 constants via $A'' = A_0 + B_0\rho^2$, where R is the gas constant.

The proportionality of A' and B' to $\epsilon\sigma^6$ and $2\epsilon\sigma^{12}$, respectively, is used to calculate the potential parameters at any given temperature via the relations

$$\epsilon/k = 2A'^2/B' \quad (4)$$

$$\sigma = (B'/2A')^{1/6}$$

The A' and B' parameters can be obtained according to Eq. (3) from the slopes of lines of A and B versus $1/T$, respectively. Such calculations were carried out to obtain the average effective pair potential parameters for pure fluids [11]. It was found that the distance parameter of the potential, σ , increases with temperature, while its depth parameter, ϵ , decreases.

In the present work, we have extended this approach to mixtures for determining the average effective pair potential parameters, knowing that the LIR is based on the CST and one-fluid approximation.

Assuming that the average effective pair interaction potential for any pair in a mixture is the LJ(12,6), as for the pure fluid, and that different molecules are randomly distributed in the mixture, the total configurational potential energy of a binary mixture may be derived as

$$U = 2z_0N \sum_{i,j} x_i x_j \left[\epsilon_{ij} \sigma_{ij}^{12} \left(\frac{1}{\bar{r}} \right)^{12} - \epsilon_{ij} \sigma_{ij}^6 \left(\frac{1}{\bar{r}} \right)^6 \right] \quad (5)$$

where ϵ_{ij} and σ_{ij} are potential parameters for an ij pair, x_i is the mole fraction of component i , N is the number of molecules, \bar{r} is the average nearest-neighbor separation, and z_0 is the proportionality constant for the coordination number with density. On the basis of the one-fluid approximation, according to which the expression for the potential energy of a mixture is exactly the same as that for the pure fluid but its parameters are composition dependent, the potential energy of a mixture may be generally given as

$$U = 2z_0N \left[\epsilon_x \sigma_x^{12} \left(\frac{1}{\bar{r}} \right)^{12} - \epsilon_x \sigma_x^6 \left(\frac{1}{\bar{r}} \right)^6 \right] \quad (6)$$

where ϵ_x and σ_x are the average effective pair potential parameters of the mixture, which depend on the system composition, in addition to the temperature. The differentiation of the total potential energy, Eq. (6), with respect to volume gives the mixture internal pressure as $-2\epsilon_x \sigma_x^6 \rho^3 + 4\epsilon_x \sigma_x^{12} \rho^5$ (note that $v \propto \bar{r}^3$). The internal pressure can also be obtained from the LIR equation of state as $-A'\rho^3 + B'\rho^5$ (note that the thermal pressure is given as $p_{th} = T(\partial p/\partial T)_v$, and the internal pressure is obtained by subtracting the thermal pressure from the total pressure). According to the one-fluid approximation, the internal pressure for a mixture is given as $-A'_{mix}\rho^3 + B'_{mix}\rho^5$. Comparison of these expressions for the internal pressure gives $A'_{mix} \propto \epsilon_x \sigma_x^6$ and $B'_{mix} \propto \epsilon_x \sigma_x^{12}$, from which the average effective pair potential parameters of mixture are

$$\begin{aligned} \epsilon_x/k &= 2A'_{mix}{}^2/B'_{mix} \\ \sigma_x &= (B'_{mix}/A'_{mix})^{1/6} \end{aligned} \quad (7)$$

The LIR parameters are obtained for each isotherm by plotting $(Z-1)v^2$ versus ρ^2 . The resulting values of A_{mix} and B_{mix} then can be plotted versus $1/T$ to obtain A'_{mix} and B'_{mix} from the slopes. These quantities then serve to calculate the average effective mixture pair potential parameters via Eq. (7). Such a calculation for obtaining A_{mix} and B_{mix} at different temperatures was carried out for a (x)methyl 1,1-dimethylethyl ether (MTBE) + (1-x) C_7H_{16} mixture for different compositions. The experimental p - v - T data were taken from Ref. 14, and one sample result is plotted in Fig. 1 for $x=0.8555$. Such a plot has been used to calculate the average effective pair potential parameters for this mixture at 243.16 and 333.14 K through Eq. (7). (The approach is exactly the same as that presented for pure fluids in Ref. 11.) The results for this composition, along with those for some other compositions, are given in Table I.

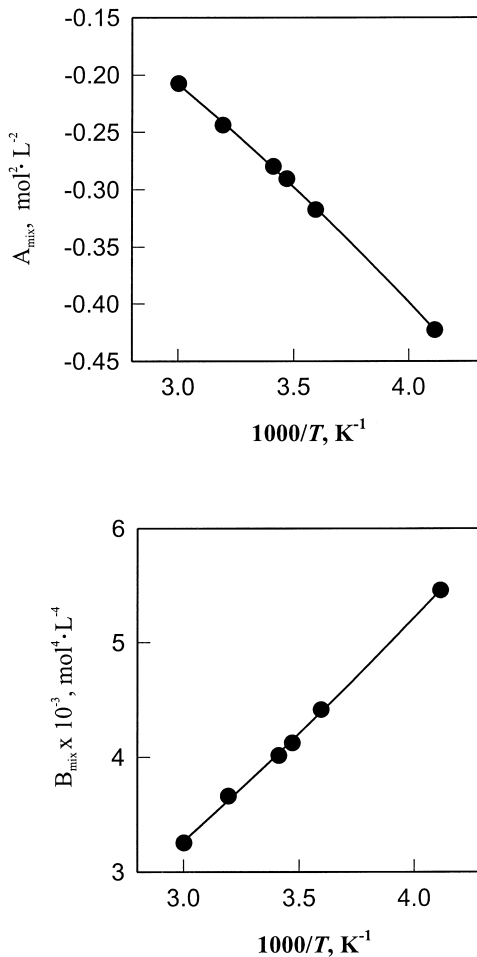


Fig. 1. The temperature dependences of the LIR parameters for an $x\text{MTBE} + (1-x)\text{C}_7\text{H}_{16}$ mixture at $x=0.8555$.

It has been shown that $(Z-1)v^2$ against ρ^2 is linear for many mixtures for densities greater than the Boyle density [12], and therefore we may conclude that the potential parameters are independent of density, exactly as found for the pure components.

If we differentiate Eq. (5) with respect to volume, and ignore the density dependence of the kinetic part of the internal energy [13], the mixture internal pressure would be obtained as $\sum x_i x_j [-2\epsilon_{ij}\sigma_{ij}^6 \rho^3 + 4\epsilon_{ij}\sigma_{ij}^{12} \rho^5]$. By

Table I. Calculated Average Pair Potential Parameters of x MTBE + $(1-x)$ C₇H₁₆ Mixtures, Using Eq. (7)

x	$T = 243.16$ K		$T = 333.14$ K	
	ϵ_x/k (K)	σ_x (Å)	ϵ_x/k (K)	σ_x (Å)
0.0000	6446.16	5.21	4567.27	5.39
0.0498	6673.07	5.22	4409.17	5.24
0.1013	6558.28	5.19	4487.56	5.25
0.1523	6729.35	5.19	4328.57	5.22
0.2988	6630.53	5.13	4169.69	5.16
0.5053	6630.53	5.08	3787.79	5.07
0.7013	5755.64	4.96	3842.23	5.03
0.8555	5347.38	4.88	3755.54	4.96
0.9479	5898.76	4.88	3513.59	4.91
1.0000	5358.96	4.82	3645.53	4.90

comparing this summation with that obtained from the LIR equation of state ($-A'_{\text{mix}}\rho^3 + B'_{\text{mix}}\rho^5$), we get A'_{mix} and B'_{mix} for a binary mixture as quadratic functions in terms of fluid composition. Each includes three terms, where two of them are related to the potential parameters of pure components and the third represents a hypothetical fluid only with the unlike interactions. Comparison of the two mentioned expressions for the internal pressure gives the unlike parameters of the LIR (A'_{12} and B'_{12}) in terms of the unlike potential parameters (ϵ_{12} and σ_{12}) as

$$\begin{aligned} A'_{12} &\propto \epsilon_{12}\sigma_{12}^6 \\ B'_{12} &\propto 2\epsilon_{12}\sigma_{12}^{12} \end{aligned} \quad (8)$$

from which the unlike potential parameters of a binary mixture can be derived as

$$\begin{aligned} \epsilon_{12}/k &= 2A'_{12}{}^2/B'_{12} \\ \sigma_{12} &= (B'_{12}/2A'_{12})^{1/6} \end{aligned} \quad (9)$$

Based on the random distribution assumption, the composition dependences of the LIR parameters have been derived as [12]

$$\begin{aligned} B_{\text{mix}} &= \sum_{i,j} x_i x_j B_{ij} \\ (A/B)_{\text{mix}} &= \sum_{i,j} x_i x_j (A/B)_{ij} \end{aligned} \quad (10)$$

Because the values of B_{11} , B_{22} , $(A/B)_{11}$, and $(A/B)_{22}$ can be obtained from the experimental p - v - T data of pure fluids and the values of B_{mix} and $(A/B)_{\text{mix}}$ can be calculated from the LIR for the mixture (using the experimental p - v - T data of the mixture), we may use such results to calculate B_{12} and $(A/B)_{12}$ for the unlike interaction at any given temperature. If the distribution of molecules in the mixture is random, it is expected that the LIR unlike parameters become composition independent. A strong deviation from such an expectation was first observed for the $\text{CHCl}_3 + \text{C}_2\text{H}_5\text{OH}$ mixture due to complex formation [12]. Also, such a deviation is expected to be observed when the interactions are associated, for which the random mixing is certainly false. The unlike parameters are calculated from Eq. (10) for $x\text{MTBE} + (1-x)\text{C}_7\text{H}_{16}$ and $x\text{CO}_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$ mixtures, using the experimental p - v - T data given in Refs. 14 and 15, respectively. The calculated unlike LIR parameters for these mixtures are given in Table II at given temperatures. As shown in this table, the unlike parameters for the former mixture are almost independent of composition, while those for the latter are certainly composition dependent. This dependency is expected since ethanol has a significant association interaction. For the cases in which the parameters $(A/B)_{12}$ and B_{12} are almost composition independent, we may use their average values for each temperature to plot them versus $1/T$ to obtain A'_{12} and B'_{12} , from the slopes of the lines. Having A'_{12} and B'_{12} , we may calculate the unlike potential parameters, using Eq. (9). The calculated average effective unlike pair potential parameters are given in Table III for three mixtures at some given temperatures, along with the average effective like pair potential parameters [14, 16–19].

To evaluate the calculated average effective like and unlike pair potential parameters, we have used them to calculate the excess enthalpy of a mixture. To do so, we may use the average effective like and unlike pair potential parameters to calculate the excess internal energy of a binary mixture, U^E , from

$$U^E = U_{\text{mix}} - x_1 U_{11} - x_2 U_{22}$$

where U_{mix} , U_{11} , and U_{22} are the molar configurational potential energies of the mixture and the pure components, respectively. (We have assumed that the kinetic energy of system does not change when mixing takes place.) The potential energies U_{mix} , U_{11} , and U_{22} are calculated from Eq. (5). The excess enthalpy, H^E , can be calculated using the calculated U^E and the experimental p - v - T data (of the mixture and pure components) from

$$H^E = U^E + pv^E$$

Table II. Calculated Like and Unlike LIR Parameters Using Experimental pvT Data and Eq. (9) for $x\text{MTBE} + (1-x)\text{C}_7\text{H}_{16}$ at 243.16 K and $x\text{CO}_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$ at 323.14 K

$x\text{MTBE} + (1-x)\text{C}_7\text{H}_{16}$				$x\text{CO}_2 + (1-x)\text{C}_2\text{H}_5\text{OH}$			
x	Number of points	$B_{12} \times 10^3$ ($\text{mol}^4 \cdot \text{L}^{-4}$)	$-(A/B)_{12}$ ($\text{mol}^{-2} \cdot \text{L}^2$)	x	Number of points	$B_{12} \times 10^5$ ($\text{mol}^4 \cdot \text{L}^{-4}$)	$-(A/B)_{12}$ ($\text{mol}^{-2} \cdot \text{L}^2$)
0.0498	18	9.3634	62.6423	0.5115	39	0.3266	355.8908
0.1013	18	9.4160	62.4878	0.7095	45	1.9981	329.3506
0.1523	18	9.4187	62.4928	0.8072	52	1.1374	345.2187
0.2988	18	8.6556	62.3400	0.9041	43	1.5447	332.5838
0.5053	18	9.1871	61.8665				
0.7013	18	8.6313	61.4888				
0.8555	18	8.2796	61.2233				
0.8970	18	9.5991	60.5731				
0.9479	18	10.1060	60.3342				

Table III. Calculated Like and Unlike Pair Potential Parameters for $x\text{Ar} + (1-x)\text{Kr}$, $x\text{MTBE} + (1-x)\text{C}_7\text{H}_{16}$, $x\text{CO}_2 + (1-x)\text{C}_2\text{H}_6$, $x\text{CO}_2 + (1-x)\text{C}_6\text{H}_5\text{CH}_3$, and $x\text{CO}_2 + (1-x)\text{CH}_3\text{COCH}_3$ Mixtures Using Eqs. (4) and (9)

Mixture	Ref.	T (K)	ϵ_{11}/k (K)	ϵ_{22}/k (K)	ϵ_{12}/k (K)	σ_{11} (Å)	σ_{22} (Å)	σ_{12} (Å)
Ar + Kr	16	135.00	519.84	817.08	649.16	2.96	3.19	2.86
		140.00	536.84	856.12	722.43	2.92	3.17	3.07
		145.00	561.28	894.61	882.81	2.87	3.15	3.14
MTBE + C_7H_{16}	14	278.15	4551.98	5512.17	5172.51	4.85	5.29	5.12
		288.17	4359.13	5302.35	4757.14	4.86	5.31	5.09
		293.10	4269.40	5206.41	4568.68	4.87	5.32	5.07
		313.14	3935.72	4858.61	3921.95	4.88	5.36	4.97
		333.14	3645.53	4567.27	3564.98	4.90	5.39	4.79
$\text{CO}_2 + \text{C}_2\text{H}_6$	17	250.00	1388.25	1138.30	1056.02	3.22	3.83	3.33
		270.00	1461.44	1211.96	1036.11	3.09	3.71	3.33
		290.00	1823.01	1408.15	1018.94	2.89	3.54	3.34
$\text{CO}_2 + \text{toluene}$	18	335.00	1668.14	4126.38	70.69	2.96	4.67	5.26
		360.00	1044.22	3827.57	112.68	3.19	4.25	4.79
		385.00	2672.47	5196.08	466.33	2.53	4.84	3.73
$\text{CO}_2 + \text{acetone}$	19	335.00	2429.45	2554.87	9.50	2.74	4.06	7.06
		360.00	1132.60	2477.44	90.70	3.13	3.98	5.66
		385.00	4621.49	2413.63	367.44	2.31	3.88	4.81

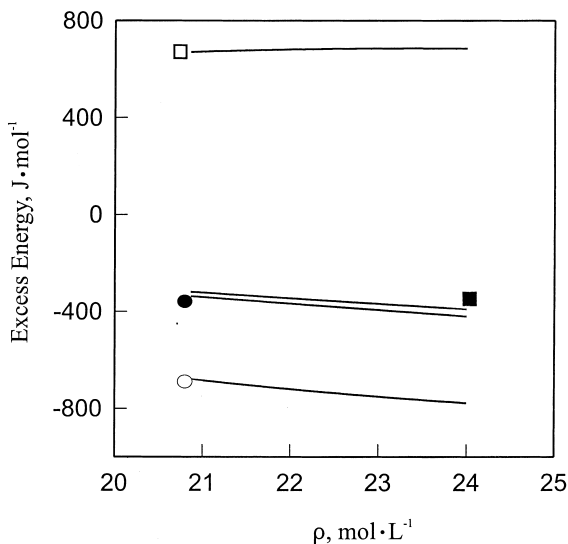


Fig. 2. The calculated excess molar enthalpy (□) and configurational potential energies of U_{11} (●), U_{22} (○), and U_{12} (■) for an $x\text{Ar}+(1-x)\text{Kr}$ mixture versus mixture density at $T=135$ K; experimental data taken from Ref. 16.

The calculated molar configurational potential energies of a pure and a hypothetical mixture (with unlike interactions only) along with the calculated excess enthalpy are plotted versus density in Fig. 2 for a $x\text{Ar}+(1-x)\text{Kr}$ mixture with $x=0.485$ at $T=135$ K for the density range where experimental data are available. (The experimental $p-v-T$ data are taken from Ref. 16.) Note that for such a density range, the interaction energies are all negative, and the magnitudes of U_{11} and U_{12} are almost the same, but the magnitudes of U_{22} is significantly larger. Such a behavior is the main reason that H^E is positive, from which we may conclude that the average pair interaction energy for the mixture is weaker than the average of that for the pure components [$U_{12} < (U_{11} + U_{22})/2$]. Our conclusion that $H^E > 0$ is in accordance with the experimental data [16].

3. A STRONG PRINCIPLE OF CORRESPONDING STATES

Comparing the right-hand sides of Eqs. (5) and (6), we can obtain the following expressions for the average effective pair potential parameters of a mixture in terms of those of the pure and hypothetical components:

$$\begin{aligned}\epsilon_x \sigma_x^{12} &= \sum_{i,j} x_i x_j \epsilon_{ij} \sigma_{ij}^{12} \\ \epsilon_x \sigma_x^6 &= \sum_{i,j} x_i x_j \epsilon_{ij} \sigma_{ij}^6\end{aligned}\quad (11)$$

As for the pure fluids [11], the combination of Eqs. (3) and (11) gives

$$\begin{aligned}\frac{(A-A_0)_{\text{mix}}}{\sigma_x^6} &= \frac{\alpha}{T^*} \\ \frac{(B-B_0)_{\text{mix}}}{\sigma_x^{12}} &= \frac{2\beta}{T^*}\end{aligned}\quad (12)$$

where α and β are constants and $T^* = kT/\epsilon_x$. We can use the calculated values of ϵ_x and σ_x to reduce $(A-A_0)_{\text{mix}}$, $(B-B_0)_{\text{mix}}$, and T . According to Eq. (12), the reduced quantities, $(A-A_0)_{\text{mix}}/\sigma_x^6$ and $(B-B_0)_{\text{mix}}/\sigma_x^{12}$ are expected to be linear versus $1/T^*$ and the lines superimposed on each other for a mixture with different compositions and even for different mixtures. To investigate such an expectation, we have used the mixture average effective pair potential parameters for $x\text{MTBE}+(1-x)\text{C}_7\text{H}_{16}$, given in Table I, to plot $(A-A_0)_{\text{mix}}/\sigma_x^6$ and $(B-B_0)_{\text{mix}}/\sigma_x^{12}$ versus $1/T^*$ for some given compositions in Fig. 3. Also, a similar attempt has been made for different binary mixtures, for which the results are given in Fig. 4. The experimental data are taken from Refs. 14–19. As expected, these two figures predict a strong principle of corresponding states, according to which the results for a mixture at different compositions (Fig. 3) and for different mixtures (Fig. 4) both give a single line with $\alpha = -8.30$ and $\beta = 8.30$. Note that these values are exactly the same as those for the pure compounds, from which we may conclude that the one-fluid approximation is accurate for such mixtures.

4. MIXING RULES

To see which mixing rules for the potential parameters are suitable, we have used the average effective pair potential parameters for both like and unlike pairs of different mixtures to calculate those for the mixtures, using various models for the one-fluid approximation theories. The average effective pair potential parameters of a mixture can be calculated using either the random mixing approximation (RMA), van der Waals (vdW), or hard-sphere expansion (HSE) theories through the following expressions [6].

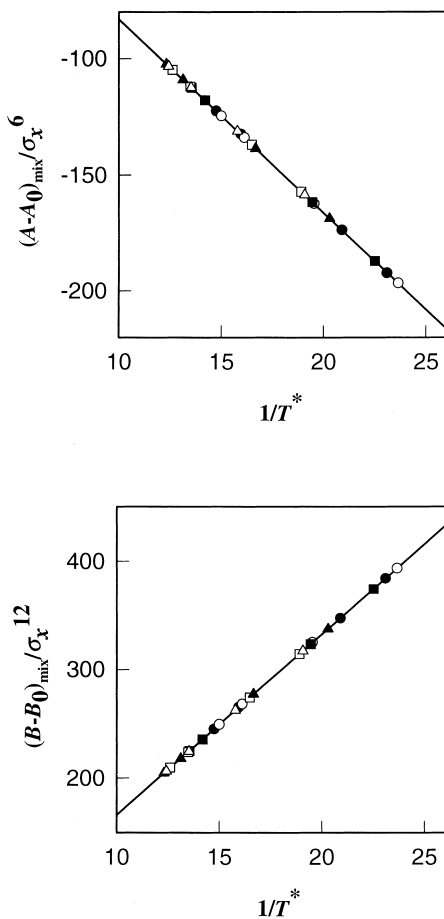


Fig. 3. The expected corresponding-states behavior for an $x\text{MTBE}+(1-x)\text{C}_7\text{H}_{16}$ mixture with $x=0.0498$ (\bullet), $x=0.1523$ (\circ), $x=0.5053$ (\blacksquare), $x=0.8555$ (\square), $x=0.9479$ (\blacktriangle), and $x=1.0000$ (\triangle) according to Eq. (12), using experimental data from Ref. 14.

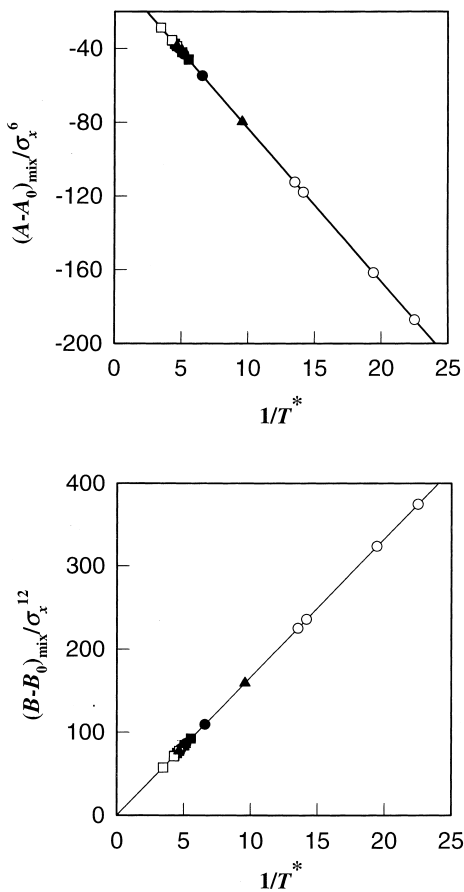


Fig. 4. Same as Fig. 3 for different mixtures at given compositions: $x\text{Ar} + (1-x)\text{Kr}$ at $x=0.4850$ (●) [16], $x\text{MTBE} + (1-x)\text{C}_7\text{H}_{16}$ at $x=0.5053$ (○) [14], $x\text{CO}_2 + (1-x)\text{C}_6\text{H}_5\text{CH}_3$ at $x=0.7430$ (■) [18], $x\text{CO}_2 + (1-x)\text{CH}_3\text{COCH}_3$ at $x=0.5689$ (□) [19]; and $x\text{CO}_2 + (1-x)\text{C}_2\text{H}_6$ at $x=0.4925$ (▲) [17].

$$\begin{aligned} \text{RMA:} \quad \epsilon_x \sigma_x^3 &= \left[\sum_{i,j} x_i x_j \epsilon_{ij} \sigma_{ij}^6 \right]^{3/2} / \left[\sum_{i,j} x_i x_j \epsilon_{ij} \sigma_{ij}^{12} \right]^{1/2} \\ \sigma_x^3 &= \left[\sum_{i,j} x_i x_j \epsilon_{ij} \sigma_{ij}^{12} / \sum_{i,j} x_i x_j \epsilon_{ij} \sigma_{ij}^6 \right]^{1/2} \end{aligned} \quad (13)$$

$$\begin{aligned} \text{vdW:} \quad \epsilon_x \sigma_x^3 &= \sum_{i,j} x_i x_j \epsilon_{ij} \sigma_{ij}^3 \\ \sigma_x^3 &= \sum_{i,j} x_i x_j \sigma_{ij}^3 \end{aligned} \quad (14)$$

$$\begin{aligned} \text{HSE:} \quad \epsilon_x \sigma_x^3 &= \sum_{i,j} x_i x_j \epsilon_{ij} \sigma_{ij}^3 \\ \sigma_x^3 &= \left[\sum_{i,j} x_i x_j \epsilon_{ij} \sigma_{ij}^3 \right]^2 / \sum_{i,j} x_i x_j \epsilon_{ij}^2 \sigma_{ij}^3 \end{aligned} \quad (15)$$

On one hand, we may use the average effective pair potential parameters for both like and unlike pairs along with any of the above mixing rules to calculate the parameters for the mixture at any given temperature and composition. On the other hand, the parameters can be calculated directly from the LIR. The results of such calculations are given in Table IV for

Table IV. Mixture Potential Parameters, ϵ_x and σ_x , Calculated from Various Mixing Rules and the LIR for $x\text{Ar} + (1-x)\text{Kr}$ at $x=0.485$, $x\text{MTBE} + (1-x)\text{C}_7\text{H}_{16}$ at $x=0.5053$, and $x\text{CO}_2 + (1-x)\text{C}_2\text{H}_6$ at $x=0.4925$

Mixture	Ref.	$T(\text{K})$	$\epsilon_x/k(\text{K})$				$\sigma_x(\text{\AA})$			
			LIR	RMA	vdW	HSE	LIR	RMA	vdW	HSE
Ar + Kr	16	135.00	673.70	606.23	673.96	692.43	3.01	3.05	2.98	2.95
		140.00	758.61	697.34	723.91	740.80	3.02	3.10	3.07	3.04
		145.00	838.25	788.52	825.07	844.88	3.03	3.12	3.08	3.06
MTBE + C ₇ H ₁₆	14	278.15	5306.35	4948.84	5128.77	5151.08	5.08	5.14	5.10	5.09
		288.17	4986.41	4629.79	4820.20	4843.82	5.08	5.14	5.09	5.08
		293.10	4837.04	4480.88	4680.58	4706.55	5.08	5.14	5.09	5.08
		313.14	4278.30	3924.32	4198.96	4241.78	5.07	5.13	5.05	5.03
		333.14	3787.79	3436.46	3896.58	3949.02	5.07	5.12	4.98	4.95
CO ₂ + C ₂ H ₆	17	250.00	1163.09	946.06	1150.48	1163.70	3.46	3.59	3.45	3.44
		270.00	1319.25	1002.39	1174.22	1195.38	3.34	3.50	3.39	3.37
		290.00	1609.02	1111.00	1274.04	1343.63	3.19	3.38	3.29	3.24

$x\text{Ar} + (1-x)\text{Kr}$ at $x=0.485$, $x\text{MTBE} + (1-x)\text{C}_7\text{H}_{16}$ at $x=0.5053$, and $x\text{CO}_2 + (1-x)\text{C}_2\text{H}_6$ at $x=0.4925$ at the given temperatures. The results obtained from the LIR differ from those calculated with the mixing rules by less than 10%.

5. CONCLUSION

In this work, a new approach is presented to obtain the average effective pair potential parameters of a mixture, ϵ_x and σ_x , at various temperatures and compositions, from which the unlike potential parameters, ϵ_{12} and σ_{12} , are obtained and shown to be only temperature dependent. Since the presented approach is based on the random mixing approximation, it is limited to mixtures without strongly associated interactions, as shown for a mixture with a $\text{C}_2\text{H}_5\text{OH}$ component. (See Table II.) Using the calculated average effective pair potential parameters of a mixture to reduce the LIR parameters, we have introduced a strong principle of corresponding states valid both for binary mixtures with different compositions (see Fig. 3) and mixtures with different components (see Fig. 4). Also, using the calculated unlike potential parameters along with the average effective pair potential parameters of pure components, the mixture potential parameters predicted by our approach are compared with those obtained from the mixing rules. (See Table IV.) Our calculated results are different from those obtained from the mixing rules only by a few percent. Finally, the calculated like and unlike potential parameters along with the experimental p - v - T data have been used to calculate the excess enthalpy of a mixture of $x\text{Ar} + (1-x)\text{Kr}$, which at least predicts the correct sign for it.

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