

CORRESPONDING STATES THEORY OF MIXTURES OF LENNARD-JONES 6 : 12 LIQUIDS

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New combination rules for the equivalence substance parameters in the one-liquid corresponding states theory were found, which reproduce the thermodynamic excess properties of equimolar mixtures of Lennard-Jones 6 : 12 liquids as determined recently by the Monte-Carlo method with a better accuracy than the hitherto used van der Waals combination rules proposed by Leland and coworkers. Attempts to find similar combination rules for the two-liquid version of the theory of the corresponding states were not successful.

It has been found¹ that in calculating the excess properties of mixtures of hard spheres at a constant pressure from the corresponding states theory we may replace the usually used van der Waals combination rules² by another rules with which a better agreement with the Percus-Yevick compressibility equation of state of hard sphere mixtures can be obtained. Now that rather accurate Monte-Carlo results for equimolar mixtures of Lennard-Jones 6 : 12 liquids at a zero pressure are available³ we may try to search for combination rules for the equivalence substance parameters in both one- and two-liquid versions of the corresponding states theory, which would reproduce the thermodynamic excess functions of "real" Lennard-Jones 6 : 12 liquids with a better accuracy than the van der Waals ones.

THEORETICAL

For a pure liquid with the intermolecular potential of the form

$$u(r) = f\varepsilon_{00}\varphi(r^3/h\sigma_{00}^3) \quad (1)$$

and whose total configurational energy u may be written as a sum of pair interactions only

$$u = \sum_{i < j} u(r_{ij}), \quad (2)$$

the following relation for the configurational Helmholtz free energy F holds⁴

$$F(V, T) = fF_0(V|h, T|f) - NkT \ln h. \quad (3)$$

In Eq. (1), φ is a common function for all liquids under consideration, r is the intermolecular distance, ε_{00} and σ_{00} are the potential energy parameters of a reference substance, and f and h are parameters scaling the departure of the depth of the potential well and the intermolecular distance of a particular liquid from the respective properties of the reference substance potential. In Eq. (3), V is the molar volume, T absolute temperature, and F_0 the configurational Helmholtz free energy of the reference substance. Analogically we may write for the configurational Helmholtz or Gibbs free energy of a mixture

$$F_x(V, T) = f_x F_0(V/h_x, T/f_x) - NkT \ln h_x, \quad \text{or} \quad (4)$$

$$G_x(p, T) = f_x G_0(ph_x/f_x, T/f_x) - NkT \ln h_x. \quad (5)$$

Here, f_x and h_x are corresponding scaling parameters of the mixture. They are analogues of f and h for pure liquids and are usually called the equivalent substance parameters. For the matter of convenience, Eq. (5) is usually used in calculations of thermodynamic properties at a zero pressure. Combination rules for f_x and h_x employed in the literature may be all expressed by the following equations

$$f_x^v h_x^\mu = \sum_{i,j=1}^n x_i x_j f_{ij}^v h_{ij}^\mu \quad \text{and} \quad f_x^\eta h_x^\kappa = \sum_{i,j=1}^n x_i x_j f_{ij}^\eta h_{ij}^\kappa, \quad (6)$$

where x_i is the mole fraction of the i -th component, n the total number of components, f_{ij} and h_{ij} the respective potential energy parameters of the i - j pair, and v , μ , η , and κ arbitrary numbers. These equations reduce to the van der Waals combination rules for $v = 0$ and $\mu = \eta = \kappa = 1$. Eqs (5) and (6) express the so called one-liquid version of the corresponding states theory. By differentiating Eq. (5) we may obtain for the enthalpy and volume of a mixture

$$H_x(p, T) = f_x H_0(ph_x/f_x, T/f_x) \quad \text{and} \quad (7)$$

$$V_x(p, T) = h_x V_0(ph_x/f_x, T/f_x). \quad (8)$$

The two-liquid version may be introduced by the equations^{1,2,5}

$$G_x(p, T) = \sum_{r=1}^n x_r [f_{xr} G_0(ph_{xr}/f_{xr}, T/f_{xr}) - NkT \ln h_{xr}] \quad (9)$$

$$\text{with } f_{xr}^v h_{xr}^\mu = \sum_{s=1}^n x_s f_{rs}^v h_{rs}^\mu \quad \text{and} \quad f_{xr}^\eta h_{xr}^\kappa = \sum_{s=1}^n x_s f_{rs}^\eta h_{rs}^\kappa. \quad (10)$$

TABLE I

Standard Deviations of the Excess Functions Calculated from the One-Liquid Corresponding States Theory as Given by Eqs (5) and (6)

ν	μ	η	\varkappa	$G^E/NkT \cdot 10^3$	$H^E/NkT \cdot 10^3$	$V^E, \text{cm}^3/\text{mol}$
0	1	1	1	16	51	0.329
0	$4/3$	1	1	42	49	0.093
0	1	$4/3$	1	21	63	0.346
0	$4/3$	$4/3$	1	22	33	0.112
0	$4/3$	1.3	1	23	32	0.110
0	$4/3$	1.4	1	20	35	0.117
0	$4/3$	$5/3$	1	28	54	0.138
0	$4/3$	2	1	47	83	0.165
$1/3$	1	$4/3$	1	35	84	0.437
0	$4/3$	$5/3$	$2/3$	43	75	0.121
0	$4/3$	2	$2/3$	54	96	0.153
0	$4/3$	1	$4/3$	59	93	0.182
0	1	$2/3$	1	29	55	0.315
0	$6/5$	$4/3$	$4/5$	25	44	0.173

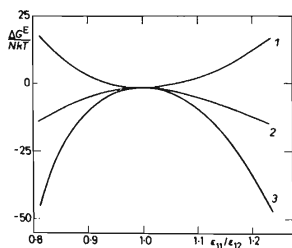


FIG. 1

Dependence of the Difference between the Excess Gibbs Free Energy Calculated from the One-Liquid Corresponding States Theory and that Determined by the Monte-Carlo Method on $\varepsilon_{11}/\varepsilon_{12}$ at Constant $\sigma_{11}/\sigma_{12} = 1.00$ and $\nu = 0$

The curves are indexed by triples (μ, η, \varkappa) of the meaning indicated in Eq. (6): 1 $(1, 1, 1) \equiv (4/3, 1, 1)$; 2 $(1, 4/3, 1) \equiv (4/3, 4/3, 1) \equiv (6/5, 4/3, 4/5)$; 3 $(4/3, 5/3, 1)$.

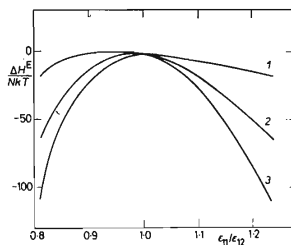


FIG. 2

Dependence of the Difference between the Excess Enthalpy Calculated from the One-Liquid Corresponding States Theory and that Determined by the Monte-Carlo Method on $\varepsilon_{11}/\varepsilon_{12}$ at Constant $\sigma_{11}/\sigma_{12} = 1.00$ and $\nu = 0$

The curves are indexed by triples (μ, η, \varkappa) of the meaning indicated in Eq. (6): 1 $(1, 1, 1) \equiv (4/3, 1, 1)$; 2 $(1, 4/3, 1) \equiv (4/3, 4/3, 1) \equiv (6/5, 4/3, 4/5)$; 3 $(4/3, 5/3, 1)$.

$$\text{Further } H_x(p, T) = \sum_{r=1}^n x_r f_{xr} H_0(p h_{xr} / f_{xr}, T / f_{xr}) \quad \text{and} \quad (11)$$

$$V_x(p, T) = \sum_{r=1}^n x_r h_{xr} V_0(p h_{xr} / f_{xr}, T / f_{xr}).$$

The excess properties at a constant temperature and zero pressure are defined by the equations

$$\begin{aligned} G^E(T) &= G_x(0, T) - \sum_{i=1}^n x_i G_i(0, T), \\ H^E(T) &= H_x(0, T) - \sum x_i H_i(0, T), \\ V^E(T) &= V_x(0, T) - \sum X_i V_i(0, T), \end{aligned} \quad (12)$$

where G_i , H_i and V_i denote the pure component properties.

Now it would be possible to minimize the differences between the excess properties calculated from the corresponding states theory and those determined by the Monte-Carlo method with respect to the indices ν , μ , η and κ in Eqs (6) or (10). This is a rather difficult task as it would involve the nonlinear minimization of a complicated

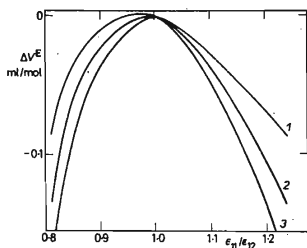


FIG. 3

Dependence of the Difference between the Excess Volume Calculated from the One-Liquid Corresponding States Theory and that Determined by the Monte-Carlo Method on $\varepsilon_{11}/\varepsilon_{12}$ at Constant $\sigma_{11}/\sigma_{12} = 1.00$ and $\nu = 0$

The curves are indexed by triples (μ, η, κ) of the meaning indicated in Eq. (6): 1 $(1, 1, 1) \equiv ({}^4/3, 1, 1)$; 2 $(1, {}^4/3, 1) \equiv ({}^4/3, {}^4/3, 1)$; 3 $({}^6/5, {}^4/3, {}^4/5)$; 3 $({}^4/3, {}^5/3, 1)$.

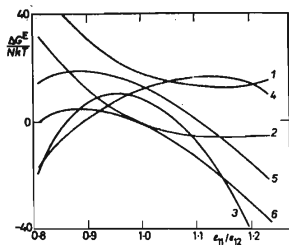


FIG. 4

Dependence of the Difference between the Excess Gibbs Free Energy Calculated from the One-Liquid Corresponding States Theory and that Determined by the Monte-Carlo Method on $\varepsilon_{11}/\varepsilon_{12}$ at Constant $\sigma_{11}/\sigma_{12} = 1.06$ and $\nu = 0$

The curves are indexed by triples (μ, η, κ) of the meaning indicated in Eq. (6): 1 $({}^4/3, 1, 1)$; 2 $(1, 1, 1)$; 3 $({}^4/3, {}^5/3, 1)$; 4 $(6/5, {}^4/3, {}^4/5)$; 5 $({}^4/3, {}^4/3, 1)$; 6 $(1, {}^4/3, 1)$.

function with respect to 4 parameters. Instead, we will make use of some previous calculations^{1,6} which suggest that

$$\nu = 0, \quad \mu \in (1, 2), \quad \eta \in (1, 2), \quad \text{and} \quad \kappa = 1 \quad (13)$$

might be a good approximation. We will search empirically in the vicinity of the range indicated for such values of the 4 parameters that would give the best fit with the Monte-Carlo results.

CALCULATIONS

The Singers³ reported the results of the Monte-Carlo calculations of the excess properties of equimolar binary mixtures of liquids obeying the Lennard-Jones 6 : 12 potential

$$u_{ij}(r) = 4\epsilon_{ij}[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6], \quad (14)$$

which is of the necessary form given in Eq. (1). They employed the usually used Lorentz-Berthelot rules

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2} \quad \text{and} \quad \sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2. \quad (15)$$

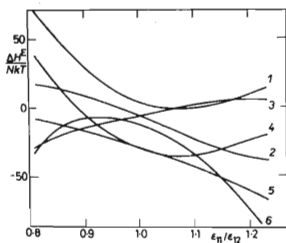


FIG. 5

Dependence of the Difference between the Excess Enthalpy Calculated from the One-Liquid Corresponding States Theory and that Determined by the Monte-Carlo Method on $\epsilon_{11}/\epsilon_{12}$ at Constant $\sigma_{11}/\sigma_{12} = 1.06$ and $\nu = 0$

The curves are indexed by triples (μ, η, κ) of the meaning indicated in Eq. (6): 1 ($4/3, 1, 1$); 2 ($4/3, 4/3, 1$); 3 ($6/5, 4/3, 4/5$), 4 (1, 1, 1); 5 (1, $4/3, 1$); 6 ($4/3, 5/3, 1$).

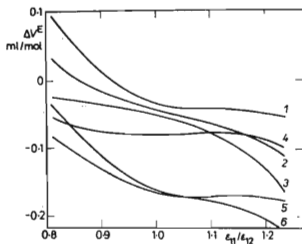


FIG. 6

Dependence of the Difference between the Excess Volume Calculated from the One-Liquid Corresponding States Theory and that Determined by the Monte-Carlo Method on $\epsilon_{11}/\epsilon_{12}$ at Constant $\sigma_{11}/\sigma_{12} = 1.06$ and $\nu = 0$

The curves are indexed by triples (μ, η, κ) of the meaning indicated in Eq. (6): 1 ($4/3, 1, 1$); 2 ($4/3, 4/3, 1$); 3 ($4/3, 5/3, 1$); 4 ($6/5, 4/3, 4/5$); 5 (1, 1, 1); 6 (1, $4/3, 1$).

Their calculations were performed for $p = 0$, $T = 97$ K, $\epsilon_{12}/k = 133.5$ K, and $\sigma_{12} = 3.596$ Å and the parameter range covered was $\sigma_{11}/\sigma_{12} = 1.00-1.12$ and $\epsilon_{11}/\epsilon_{12} = 0.810-1.235$. They also reported the necessary properties of the reference Lennard-Jones 6:12 liquid valid in the range $kT/\epsilon = 0.63-0.98$. We used these reference liquid properties for our calculations of the excess properties from both the one- or two-liquid corresponding states theory with the appropriate combination rules as given by Eqs (5), (6), (9) and (10). We calculated the excess properties

TABLE II

Standard Deviations of the Excess Functions Calculated from the Two-Liquid Corresponding States Theory as Given by Eqs (9) and (10) for $\nu = 0$

μ	η	\varkappa	$G^E/NkT \cdot 10^3$	$H^E/NkT \cdot 10^3$	$V^E, \text{cm}^3/\text{mol}$
1	1	1	58	105	0.289
$5/3$	1	1	72	105	0.158
1	$4/3$	1	59	107	0.291
$5/3$	$4/3$	1	64	98	0.143
$5/3$	1	0	129	204	0.162

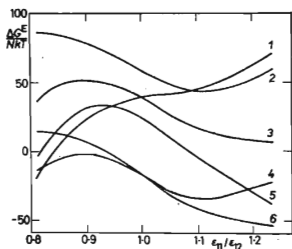


FIG. 7

Dependence of the Difference between the Excess Gibbs Free Energy Calculated from the One-Liquid Corresponding States Theory and that Determined by the Monte-Carlo Method on $\epsilon_{11}/\epsilon_{12}$ at Constant $\sigma_{11}/\sigma_{12} = 1.12$ and $\nu = 0$

The curves are indexed by triples (μ, η, \varkappa) of the meaning indicated in Eq. (6): 1 ($6/5, 4/3, 4/5$); 2 ($4/3, 1, 1$); 3 ($4/3, 4/3, 1$); 4 ($1, 1, 1$); 5 ($4/3, 5/3, 1$); 6 ($1, 4/3, 1$).

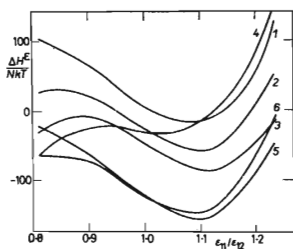


FIG. 8

Dependence of the Difference between the Excess Enthalpy Calculated from the One-Liquid Corresponding States Theory and that Determined by the Monte-Carlo Method on $\epsilon_{11}/\epsilon_{12}$ at Constant $\sigma_{11}/\sigma_{12} = 1.12$ and $\nu = 0$

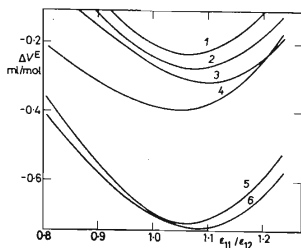
The curves are indexed by triples (μ, η, \varkappa) of the meaning indicated in Eq. (6): 1 ($4/3, 1, 1$); 2 ($4/3, 4/3, 1$); 3 ($4/3, 5/3, 1$); 4 ($6/5, 4/3, 4/5$); 5 ($1, 4/3, 1$); 6 ($1, 1, 1$).

in the parameter range covered by the Monte-Carlo calculations for different values of ν , μ , η and κ in Eqs (6) and (10). Some of our results are given in Tables I and II and in Figs 1–9. We report here only the respective deviations from the Monte-Carlo calculations, not the absolute values themselves. The values of the standard rms deviations in Tables I and II were calculated from all $5 \times 5 = 25$ calculated points from the formula $\text{rms} = \{[\sum(Q_{\text{calculated}}^E - Q_{\text{Monte-Carlo}}^E)^2]/25\}^{1/2}$.

FIG. 9

Dependence of the Difference between the Excess Volume Calculated from the One-Liquid Corresponding States Theory and that Determined by the Monte-Carlo Method of $\varepsilon_{11}/\varepsilon_{12}$ at Constant $\sigma_{11}/\sigma_{12} = 1.12$ and $\nu = 0$

The curves are indexed by triples (μ, η, κ) of the meaning indicated in Eq. (6): 1 ($4/3, 1, 1$); 2 ($4/3, 4/3, 1$); 3 ($6/5, 4/3, 4/5$); 4 ($4/3, 5/3, 1$); 5 ($1, 1, 1$); 6 ($1, 4/3, 1$).



DISCUSSION

From Table I and Figs 1–9 we can see that the van der Waals method, *i.e.* Eq. (6) for $\nu = 0$ and $\mu = \eta = \kappa = 1$, for calculating the equivalence substance parameters in the one-liquid corresponding states theory is very good at predicting the G^E values, while for the H^E and especially for the V^E values it yields considerably worse agreement. Large deviations in the V^E values are characteristic for all approximations with $\mu = 1$. When $\mu = 4/3$ is used, the agreement in the V^E values improves remarkably. This behaviour was observed also in a previous work¹. We can also see that the agreement is in all approximations better for mixtures of molecules of equal sizes, but as the ratio σ_{11}/σ_{12} increases, it becomes gradually worse. A local minimum in all deviations is observed near the point $\nu = 0$, $\mu = 4/3$, $\eta = 4/3$, and $\kappa = 1$. The agreement is unfortunately still far from perfect, as the standard deviations of the Monte-Carlo calculations reported by the Singers are 1.5 for G^E/NkT , 15 for H^E/NkT , and $0.045 \text{ cm}^3/\text{mol}$ for V^E . However, we believe that for practical calculations this may be quite sufficient if we take into account the wide range of the intermolecular parameters covered and therefore we recommend for practical purposes the following rules for f_x and h_x

$$h_x^{4/3} = \sum x_i x_j h_{ij}^{4/3} \quad \text{and} \quad f_x^{4/3} h_x = \sum x_i x_j f_{ij}^{4/3} h_{ij} \quad (16)$$

At present we can hardly infer what would result if we use for h_{ij} and f_{ij} other rules

than the Lorentz-Berthelot ones as given in Eq. (15). We are not aware of any Monte-Carlo or molecular dynamics calculations with other rules and so we may expect to test Eq. (16) only on experiments with nonpolar liquids mixtures, perhaps in the same way as Leland and coworkers⁷ did it. In this respect it would be tempting to try recently proposed combination rules for h_{ij} and f_{ij} by Kramer⁸, Good⁹, or Sikora¹⁰. Eq. (16) could be used also in deriving new rules for pseudocritical constants or equation of state constants for mixtures employed in predicting the properties of liquid mixtures from the pure component ones. Our attempts to find some combination rules which could be used in the two-liquid corresponding states theory as given in Eqs (9) and (10) failed almost completely (Table II). A good agreement comparable with the one-liquid theory was observed only for mixtures of molecules of equal sizes. As the ratio σ_{11}/σ_{12} increased, the deviations rose very rapidly. We conclude by stating that the described method of determining the combination rules for the equivalence substance parameters in the corresponding states theory should be preferred before that using a direct comparison with real experiments as a real fluid may behave quite differently from the Lennard-Jones 6 : 12 one. At the same time we believe that some other functional form for determining f_x and h_x will be developed in the future, which would give a still better fit with the Monte-Carlo results than Eq. (16).

REFERENCES

1. Hlavatý K.: This Journal 37, 210 (1972).
2. Leland T. W., Rowlinson J. S., Sather G. A.: Trans. Faraday Soc. 64, 1447 (1968).
3. Singer J. V. L., Singer K.: Mol. Phys. 19, 279 (1970).
4. Pitzer K. S.: J. Chem. Phys. 7, 583 (1939).
5. Bellemans A., Mathot V., Simon M.: Advan. Chem. Phys. 1967, 117.
6. Leland T. W., Chappellear P. S., Gamson B. W.: A.I.Ch.E. J. 8, 482 (1962).
7. Leland T. W., Rowlinson J. S., Sather G. A., Watson I. D.: Trans. Faraday Soc. 65, 2034 (1969).
8. Kramer H. L., Herschbach D. R.: J. Chem. Phys. 53, 2792 (1970).
9. Good R. J., Hope C. J.: J. Chem. Phys. 53, 540 (1970).
10. Sikora P. T.: J. Phys. B 3, 1475 (1970).

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