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Equation of State for Complex Liquid Mixtures from Surface Tension

M. H. Mousazadeh[1, 2] **and A. Boushehri**[1]

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The present work shows a successful extension of previous studies to molecular liquids for which the second virial coefficients are not known. Recent advances in the statistical mechanical theory of equilibrium fluids can be used to obtain an equation of state (EOS) for compressed normal liquids and molten alkali metals. Three temperature-dependent quantities are needed to use the EOS: the second virial coefficient, $B(T)$, an effective van der Waals covolume, $b(T)$, and a scaling factor, $\alpha(T)$. The second virial coefficients are calculated from a correlation that uses the surface tension, γ_{tr}, and the liquid density at the triple point. Calculation of $\alpha(T)$ and $b(T)$ follows by scaling. Thus, thermodynamic consistency is achieved by use of two scaling parameters (γ_{tr}, ρ_{tr}). The correlations embrace the temperature range $T_{tr} < T < T_c$ and can be used in a predictive mode. The remaining constant parameter is best found empirically from ρ_{tr} data for pure dense liquids. The equation of state is tested on 42 liquid mixtures The results indicate that the liquid density at any pressure and temperature can be predicted within about 5%, over the range from T_{tr} to T_c.

KEY WORDS: complex liquid mixtures; corresponding states; equation of state; surface tension.

1. INTRODUCTION

The mechanical behavior of compressed liquids, i.e., the equation of state, is needed for the design and analysis of many processes at high pressures. Many equations of state, dating back to the work of Tait over 100 years ago, have been proposed for the correlation and prediction of the P–V–T properties of compressed liquids [1–6]. However, almost all require at least a few measurements at high pressures for any particular liquid of interest; many also require knowledge of the critical constants. For example,

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[1] Department of Chemistry, Shiraz University, Shiraz 71454, Iran.

[2] To whom correspondence should be addressed.

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many empirical equation of states are based on some variation of the fact that the isothermal bulk modulus (reciprocal compressibility) is very nearly linear in the pressure over the entire range from the vapor-pressure curve to the freezing line. Thus, each p–ρ isotherm involves at least four constants: the pressure P and the density ρ at some reference state and two constants needed to characterize such a linear relationship. Unfortunately, all four constants are temperature dependent.

Recent works on the statistical–mechanical theory of the equation of state for fluids has yielded accurate results for pure liquids and for mercury [7, 8]. The minimum information needed to reduce the P–V–T surface to a single curve is the surface tension and the liquid density at the triple-point temperature. From these two properties, three temperature-dependent parameters are obtained, an effective van der Waals covolume $b(T)$, a scaling factor $\alpha(T)$, which is equivalent to the contribution to the second virial coefficient $B(T)$ from just the repulsive branch of the intermolecular force, and $B(T)$ itself. In addition to B, b, and α, one temperature-independent constant that is characteristic of the particular substance is needed. It should be noted that the accuracy is not necessarily enhanced by greater complexity.

We tested the equation of state for 42 liquid mixtures. The results show that the density of the liquid mixtures can be predicted within about 5% at any temperature and pressure.

In short, the purpose of this work was to correlate and to predict the behavior of complex liquid mixtures based on the surface tension and the liquid density at the triple point. An empirical feature is incorporated in the corresponding-states principle, which enables us to describe the thermodynamic properties of mixtures at all liquid densities, temperatures, and compositions.

2. EQUATION OF STATE

We consider the statistical–mechanical equation of state derived by Song and Mason [9], which is based on the Week–Chandler–Anderson (WCA) perturbation theory for the condensed state. The derivation begins with the equation relating the pressure to the pair distribution function, $g(r)$,

$$\frac{P}{\rho kT} = 1 - (2\pi\rho/3kT) \int_0^\infty \left[\frac{\partial u}{\partial r}\right] g(r)\, r^3\, dr \tag{1}$$

where P is the pressure, ρ is the density, kT is the thermal energy per molecule, and $\partial u/\partial r$ 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 state reads [10]

$$\frac{P}{\rho kT}=1-\left[\frac{(\alpha-\beta_2)\,\rho}{(1+0.22\Gamma b\rho)}\right]+\alpha\rho G(b\rho) \tag{2}$$

where the new corresponding-states principle has the form

$$G(b\rho)^{-1}=\left\{\left(\frac{1}{\alpha\rho}\right)\left[z-1+\frac{(\alpha-\beta_2)\,\rho}{(1+0.22\Gamma b\rho)}\right]\right\}^{-1}\approx(1-\Gamma b\rho) \tag{3}$$

and where $Z=P/\rho kT$ is the compressibility factor. Here $G(b\rho)$ is the average pair distribution function at contact for equivalent hard convex bodies that still have the pairwise additivity of the intermolecular forces as in $g(r)$. The many-body nature of the system may be contained in $G(b\rho)$ [10]. The value of B_2 can be calculated by integration if the form of the potential function is known. α is the contribution of the repulsive part of the potential function to the second virial coefficient, and it takes care of the softness of the potential function. b is the analogue of the van der Waals covolume. Both $\alpha(T)$ and $b(T)$ can be calculated by integration if the potential function is known. $G(b\rho)^{-1}$ is a function of $b\rho$ only and satisfies corresponding states, varying linearly with slope Γ over the entire range of temperature from the freezing line up to the critical point. The functional form of $G(b\rho)^{-1}$ implies that, according to corresponding states, all P–V–T data collapse onto a single line. The value of Γ, determined from P–V–T data by iteration, along with $B_2(T)$, $\alpha(T)$, and $b(T)$, characterize the thermodynamic properties of particular systems.

According to Eq. (2), from knowing the form of the potential function, the thermophysical properties of both spherical and nonspherical fluids can be characterized over the entire range of temperatures including the compressed liquid state. The Lennard–Jones (12–6) potential function reproduces the thermophysical properties within experimental uncertainty [10]. More accurate potential functions based on a Hartree–Fock dispersion interaction potential are also available [10]. However, it is not the purpose of this paper to use any of these functions. Rather, it is shown that the idea of minimal as well as practical input data for analytical equations of state can be extended nicely to include other thermodynamic functions, e.g., the surface energy.

The method we follow here is to use an energy function involving the surface tension as a scaling parameter for the calculation of the temperature-dependent constants, $B_2(T)$, $\alpha(T)$, and $b(T)$, in Eq. (2). This is based on the fact that the surface tension is a measure of the cohesive energy density and that the range of the effective forces are not larger than the molecular dimension [11, 12]. A suitable form of the energy function is $\gamma\rho^{-2/3}N^{1/3}$, where γ is the surface tension, ρ is the molar liquid density, and N is Avogadro's number. Compared with the thermal energy, the reduced form of the function, with the triple point as a reference temperature, takes the form $\gamma_{\mathrm{tr}}\rho_{\mathrm{tr}}{}^{-2/3}N^{1/3}/RT$, where RT has its usual meaning, and ρ_{tr} is the molar liquid density at the triple point. The term $\gamma_{\mathrm{tr}}\rho_{\mathrm{tr}}{}^{-2/3}N^{1/3}/R$ is referred to as T_{ref}. It should be emphasized that the reference temperature is not an essential choice, but merely a convenient one. Our final correlation scheme is self-correcting. The normal freezing temperature would probably work as well. Apparently the shape effects described by ω, the acentric factor, affect the γ_{tr} and ρ_{tr} in such a way as to tend to compensate for their influence on $B_2(T)$.

The central idea is to use second virial-coefficient data to determine the parameters for the corresponding states that are related to the scaling parameters, γ_{tr} and ρ_{tr}. The resulting correlation can then be used to calculate $B_2(T)$, which is quite universal. It is remarkable that one functional (B_2^*) does suffice for all nonpolar liquids, where $B_2^* = \rho_{\mathrm{tr}} B(T)$. The values of $B(T)$ are correlated as

$$B_2^* = 0.0804 - 2.1288T^{*-1} - 8.5597T^{*-2} + 7.4294T^{*-3} - 3.3494T^{*-4} \quad (4)$$

with

$$T^* = [TT^{1/2}/T_{\mathrm{ref}}T_{\mathrm{f}}^{1/2}]^{3/4} \quad (5)$$

where T_{f} is the freezing temperature. This correlation gives good second virial coefficients for different classes of substances up to the critical temperature T_{c} [7, 13]. It should be mentioned that T^* is original and is responsible for a promising correlation, allowing the second virial coefficient to be calculated accurately.

For Lennard–Jones fluids, Song and Mason [14] have obtained relationships that allow the calculation of $\alpha(T)$ and $b(T)$, taking into account that they depend only slightly on the details of the shape of the potential function. The procedure is based on the fact that the reduced quantities of α/v_{B} and b/v_{B} are almost universal functions of the reduced function of T/T_{B}. In practice, this requires Eq. (4) to be solved for the reduced Boyle temperature and the reduced Boyle volume, so that

$$\rho_{\mathrm{tr}}\alpha = a_1[\exp(-c_1T^*)] + a_2[1 - \exp(c_2/T^{*1/4}] \quad (6)$$

and

$$\rho_{\mathrm{tr}} b = a_1(1 - C_1 T^*)[\exp(-C_1 T^*)] + a_2 \left\{ 1 - \left[1 + \left(\frac{0.25 C_2}{T^{*1/4}} \right) \right] \left[\exp\left(\frac{-C_2}{T^{*1/4}} \right) \right] \right\} \tag{7}$$

with

$$a_1 = -0.01054, \qquad C_1 = 0.7613$$

$$a_2 = 2.9387, \qquad C_2 = 1.3227$$

The characteristic free parameter of the fluids in the equation of state, Γ, can be calculated from the two scaling constants at the freezing temperature (γ_{f} and ρ_{f}) in a single iteration because it is just a correction factor.

The present correlation procedure can be generalized to mixtures of any number of components; a formal extension of Eq. (2) to mixtures can be written as [15]

$$P/\rho RT = 1 + \rho \sum_{i,j} x_i x_j (B_{ij} - \alpha_{ij}) F_{ij} + \rho \sum_{ij} x_i x_j \alpha_{ij} G_{ij} \tag{8a}$$

where x_i and x_j are mole fractions, $F_{ii}^{-1} = 1 + 0.22 b^* \Gamma \rho^*$ and $G_{ii}^{-1} = 1 - b^* \Gamma \rho^*$. $\alpha^*(T)$ and $b^*(T)$ are predicted over a similar wide temperature range, where $\alpha^*(T) = \alpha(T)\, \rho_{\mathrm{tr}}$ and $b^*(T) = b(T)\, \rho_{\mathrm{tr}}$. The simplest combining rules for predicting unlike-molecule interactions from the like-molecule interactions are a geometric mean for γ and an arithmetic mean for ρ_{tr}. Thus, our combining rules would be

$$(\gamma_{\mathrm{tr}})_{ij} = [(\gamma_{\mathrm{tr}})_i (\gamma_{\mathrm{tr}})_j]^{1/2} \tag{8b}$$

and

$$(\gamma_{\mathrm{tr}})_{ij}^{-1/3} = 1/2[(\rho_{\mathrm{tr}})_i^{-1/3} + (\rho_{\mathrm{tr}})_j^{-1/3}] \tag{8c}$$

Once $(\gamma_{\mathrm{tr}})_{ij}$ and $(\rho_{\mathrm{tr}})_{ij}$ are known, the values of α_{ij}, b_{ij}, and B_{ij} follow from Eqs. (4)–(7) as for pure substances. The quantities G_{ij} and F_{ij} for mixtures have been given elsewhere [15]. We had to test the combining rules, given by Eqs. (8b) and (8c), on compressed liquid mixtures. The results show that the density of liquid mixtures can be predicted within 5%. These results are shown in Tables I and II. The density and surface tension data were taken from Refs. 11, 17, and 18.

Table I. Volumetric Behavior of 0.5 Benzene + 0.5 Hexane Liquid Mixture; Molar Volume, $cm^3 \cdot mol^{-1}$

T (K)	*P* (bar)	COSTALD[a]	Calc.	% Dev.
343.15	15.0	118.39	115.84	2.20
	20.0	118.25	115.79	2.13
	25.0	118.10	115.73	2.05
	30.0	117.96	115.68	1.97
	35.0	117.82	115.62	1.90
	40.0	117.68	115.56	1.84
	45.0	117.54	115.51	1.76
	50.0	117.40	115.45	1.69
	100.0	116.13	114.92	1.06
	150.0	114.98	114.42	−0.07
	200.0	113.94	113.95	−0.01
	250.0	112.99	113.51	−0.46
	300.0	112.11	113.09	−0.87
	400.0	110.53	112.31	−1.58
353.15	15.0	120.30	117.14	2.70
	20.0	120.14	117.07	2.63
	25.0	119.98	117.01	2.54
	30.0	119.82	116.94	2.47
	35.0	119.66	116.87	2.38
	40.0	119.51	116.81	2.32
	45.0	119.36	116.75	2.24
	50.0	119.21	116.68	2.17
	100.0	117.80	116.07	1.49
	150.0	116.55	115.50	0.91
	200.0	115.42	114.97	0.39
	250.0	114.40	114.46	−0.05
	300.0	113.45	133.99	−0.47
	400.0	111.77	113.12	−1.19
373.15	15.0	124.49	119.82	3.90
	20.0	124.29	119.73	3.81
	25.0	124.08	119.64	3.71
	30.0	123.88	119.56	3.62
	35.0	123.69	119.47	3.54
	40.0	123.49	119.39	3.45
	45.0	123.30	119.30	3.36
	50.0	123.12	119.22	3.28
	100.0	121.39	118.43	2.50
	150.0	119.89	117.70	1.86
	200.0	118.55	117.03	1.30
	250.0	117.35	116.39	0.83
	300.0	116.26	115.80	0.40
	400.0	114.34	114.74	−0.35

Table I. *(Continued)*

T (K)	P (bar)	COSTALD[a]	Calc.	% Dev.
393.15	15.0	129.30	122.62	5.45
	20.0	129.03	122.51	5.31
	25.0	128.77	122.40	5.21
	30.0	128.51	122.29	5.09
	35.0	128.26	122.18	4.98
	40.0	128.01	122.07	4.87
	45.0	127.77	121.97	4.56
	50.0	127.53	121.86	4.66
	100.0	125.37	120.86	3.73
	150.0	123.53	119.95	2.99
	200.0	121.93	119.11	2.37
	250.0	120.51	118.34	1.84
	300.0	119.24	117.63	1.37
	400.0	117.04	116.34	0.60

[a] Corresponding-states liquid density [16].

Table II. Volumetric Behavior of Benzene + Octane Liquid Mixtures at 373.15 K and Six Compositions; Molar Volume, $cm^3 \cdot mol^{-1}$

$x(C_6H_6)$	P (bar)	COSTALD[a]	Calc.	% Dev.
0.0	15.0	179.15	180.24	−0.60
	20.0	178.93	180.14	−0.67
	25.0	178.71	180.04	−0.74
	30.0	178.50	179.94	−0.80
	35.0	178.28	179.83	−0.86
	40.0	178.07	179.73	−0.92
	45.0	177.86	179.63	−0.96
	50.0	177.66	179.53	−1.04
	100.0	175.72	178.57	−1.60
0.20	15.0	162.57	163.08	−0.31
	20.0	162.37	162.99	−0.38
	25.0	162.17	162.90	−0.45
	30.0	161.98	162.80	−0.50
	35.0	161.78	162.71	−0.57
	40.0	161.59	162.62	−0.63
	45.0	161.40	162.54	−0.70
	50.0	161.22	162.45	−0.76
	100.0	159.46	161.61	−1.33

Table II. *(Continued)*

$x(C_6H_6)$	P (bar)	COSTALD[a]	Calc.	% Dev.
0.40	15.0	146.20	145.97	0.16
	20.0	146.03	145.89	0.10
	25.0	145.85	145.81	0.03
	30.0	145.68	145.73	−0.03
	35.0	145.51	145.65	−0.10
	40.0	145.34	145.57	−0.16
	45.0	145.17	145.50	−0.23
	50.0	145.01	145.42	−0.28
	100.0	143.45	144.69	−0.86
0.60	15.0	130.06	128.93	0.88
	20.0	129.91	128.86	0.82
	25.0	129.76	128.80	0.75
	30.0	129.61	128.73	0.68
	35.0	129.46	128.66	0.62
	40.0	129.32	128.60	0.56
	45.0	129.17	128.53	0.50
	50.0	127.69	127.83	0.45
	100.0	127.69	127.83	−0.11
0.80	15.0	114.16	112.01	1.92
	20.0	114.03	111.95	1.86
	25.0	113.90	111.89	1.80
	30.0	113.78	111.84	1.74
	35.0	113.66	111.78	1.62
	40.0	113.54	111.72	1.63
	45.0	113.42	111.67	1.57
	50.0	113.30	111.61	1.51
	100.0	112.18	111.08	0.99
1.0	15.0	98.49	95.25	3.40
	20.0	98.39	95.20	3.35
	25.0	98.29	95.15	3.30
	30.0	98.19	95.11	3.24
	35.0	98.10	95.06	3.20
	40.0	98.00	95.01	3.15
	45.0	97.90	94.97	3.09
	50.0	97.81	94.92	3.01
	100.0	96.91	94.48	2.57

[a] Corresponding-states liquid density [16].

3. RESULTS AND DISCUSSION

The previous statistical–mechanical theory would take ε and r_m (ε is the depth of the potential well and r_m is its minimum position) based on the experimental values of $B_2(T)$, the second virial coefficient of the vapor [9]. However, since $B_2(T)$ would not be known experimentally for many compressed liquids of interest, another method for finding a suitable scaling factor is needed. The present work shows how the equation of state of a compressed liquid can be given a statistical–mechanical basis: this method is needed for applications to real molecular liquid mixtures. Binary compressed liquid mixtures have been tested in the temperature range 100 to 500 K, the pressure range 15 to 400 bar, and different compositions, for a total of 5292 data points, where 110 points are shown in Tables I and II. Knowledge of just the γ_{tr} and ρ_{tr} is sufficient to construct the entire equation of state and, hence, other thermodynamic parameters of liquids. No "mixing rules" are needed. The P–V–T values were calculated from Eq. (8a) by the use of Eqs. (4)–(7), (8b), and (8c). The agreement is fairly good. We repeat that Eq. (4) would be needed when the values of $B_2(T)$ are not experimentally known for most of the compressed liquids of interest.

The most important aspect of the present work is that the linear $b^*\Gamma\rho^*(\rho^* = \rho/\rho_{tr})$ dependence of the G^{-1} of any liquid can be given a strong basis in statistical mechanics. Moreover, G can be calculated if γ_{tr} and ρ_{tr} are known. The present work also shows to what extent the results for compressed liquids can be extended, namely, from freezing up to the critical temperature. This work shows useful applications to real molecular liquid mixtures. The procedure has been tested on liquid mixtures ranging in complexity from benzene + *n*-hexane to benzene + *n*-octane.

In summary, although theory indicates that G is a function of a single variable $b^*\rho^*$ for pure substances, the fact that G^{-1} is nearly linear in $b^*\rho^*$ is empirical, and the numerical value of Γ must be found from ρ_{tr}. Furthermore, our equation of state appears to give accurate P–V–T results at all pressures and temperatures. It is also simple in form and easy to use in practice.

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