A Generalized Isothermal Equation of State for Dense Liquids

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We presented earlier (Brelvi and O'Connell, 1972) a corresponding states correlation for the isothermal compressibility of pure liquids. Further, we suggested that the integrated form of this correlation could be useful in determining the volumes of isothermally compressed liquids. Such calculations are reported here for several representative liquids and compared with the predictions of the Yen and Woods correlation (1966), which is now widely used in computerized process design.

The generalized correlation for the isothermal compressibility is based on a statistical mechanical solution theory. It contains only one adjustable parameter, a characteristic volume, for each liquid. For many substances, this parameter can be approximated by the critical volume. This feature makes the method potentially very attractive for handling substances for which no compression data are available.

The correlation is

$$1 + \frac{1}{\rho\kappa RT} = \exp\left[- .42704(\tilde{\rho} - 1) + 2.089(\tilde{\rho} - 1)^2 - .42367(\tilde{\rho} - 1)^2\right] \equiv F(\tilde{\rho}) \quad (1)$$

where

$$\tilde{\rho} \doteq \rho v^* \quad (2)$$

is the reduced density and v^* is the characteristic volume parameter tabulated previously for many substances (Brelvi and O'Connell, 1972). Equation (1) describes experimental compressibility data for most liquids in the range $1.6 \leqq \tilde{\rho} \leqq 3.7$. For nonpolar fluids v^*, as fitted from experimental data, is close to the critical volume. For polar fluids, however, v^* is less than the critical volume.

From the definition of the isothermal compressibility κ, we have

$$\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \quad (3)$$

where ρ is the density. Then

$$dP = \frac{d\rho}{d\kappa} \quad (4)$$

Substituting Equation (1) in (4)

$$\Delta P = \frac{RT}{v^*}\int_{\tilde{\rho}_1}^{\tilde{\rho}_2} [F(\tilde{\rho}) - 1]\, d\tilde{\rho} \quad (5)$$

or

$$\widetilde{\Delta P} \equiv \frac{(P_2 - P_1)}{RT} v^* = \int_{\tilde{\rho}_1}^{\tilde{\rho}_2} [F(\tilde{\rho}) - 1]\, d\tilde{\rho} \quad (6)$$

Equation (6) relates the isothermal change in density corresponding to a pressure change and holds over the same reduced density range as Equation (1). Table 1 shows numerically integrated values of the right-hand side of Equation (6) where $\tilde{\rho}_1$ is 1.4 and $\tilde{\rho}_2$ has the various values shown. A value for the left-hand side between two arbitrary values of $\tilde{\rho}_a$ and $\tilde{\rho}_b$ is obtained by subtracting the tabular value given for $\tilde{\rho}_a$ from that given for $\tilde{\rho}_b$. Interpolation is more easily done on the function $\ln(\Delta\tilde{p})$. Either the volume of, or pressure on, a compressed liquid can be determined if the other property is known. Thus, knowing v^*, for a given P_1, v_1, and v_2, a value of P_2 can be found directly. Given P_1, P_2, and v_1 the solution for v_2 is iterative since Equation (6) is implicit in v_2.

Compression calculations for several liquids, polar and nonpolar, with Equation (6) and with the Yen and Woods method are shown in Table 2. In most cases the initial state is the saturated liquid so P_1 is the saturation pressure at T_1 and v_1 is the saturated liquid volume. Equation (6) is seen to predict the compressed liquid values quite accurately even at the highest pressures covered here, for example, *n*-decane at 358.2°K compressed to a reduced pressure greater than 300. The calculated volumes agree significantly better with experimental data than do those from the Yen and Woods correlation. This is so even at the lower reduced pressure ranges in which the generalized charts of Lyderson et al. (1955), on which the Yen and Woods method is based, were derived from experimental data. Volumes calculated with v_c, the critical volume, in Equation (2), instead of the fitted v^*, are in generally good agreement with experiment for nonpolar compounds, for example, benzene and *n*-octane, but using v_c for polar compounds is not very successful.

Work is presently underway to apply the correlation to compressibilities and isothermal equation of state of mixtures. There is no simple mixing rule to obtain a mixture v^* for use in Equations (2)and (6) from pure component values. However, several possibilities do exist which will be described in a forthcoming publication.

In conclusion, Equation (6) is shown to represent the volumetric behavior of isothermally compressed liquids accurately in the dense liquid region. For nonpolar liquids the critical volume may be used as the characteristic parameter without much loss of accuracy although for polar liquids a single characteristic parameter fitted to experimental data is required.

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TABLE 1. REDUCED INTEGRALS FOR ISOTHERMAL EQUATION OF STATE

$\tilde{\rho}$	$\Delta\tilde{P}$	$\ln\Delta\tilde{P}$	$\tilde{\rho}$	$\Delta\tilde{P}$	$\ln\Delta\tilde{P}$
1.4	0	—	2.6	5.2596	1.6601
1.5	0.0214	−3.844	2.7	7.3427	1.9937
1.6	0.0603	−2.808	2.8	10.1895	2.3214
1.7	0.1237	−2.090	2.9	14.056	2.6431
1.8	0.2209	−1.510	3.0	19.268	2.9584
1.9	0.3641	−1.010	3.1	26.225	3.2667
2.0	0.5705	−0.561	3.2	35.403	3.5668
2.1	0.8631	−0.1472	3.3	47.345	3.8575
2.2	1.2739	0.2420	3.4	62.636	4.1374
2.3	1.8469	0.6135	3.5	81.856	4.4050
2.4	2.6423	0.9716	3.6	105.516	4.6589
2.5	3.7427	1.3198			

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TABLE 2. VOLUMES OF COMPRESSED LIQUIDS

Liquid	v^* cc/g-mole	T °K	$P_2 - P_1$ bar	$(v_2 - v_1)$ cc/g-mole Calculated (a)	(b)	(c)	Expt.	References for compression data
Methane	99.5	114.5	304	−1.980	*	−1.429	−2.039	Itterbeek (1963)
		134.3	303	−3.188		−2.536	−3.189	
		158.2	282	−5.835		−4.983	−5.578	
		172.7	287	−10.791		−8.805	−10.366	
		179.5	257	−12.921		−11.223	−12.142	
n-Decane	602	288.2	2,340	−23.68	*	†	−23.35	Snyder and Winnick (1970)
		318.2	3,749	−32.91			−32.53	
		338.2	4,900	−40.03			−39.68	
		358.2	6,558	−48.68			−47.78	
Water	45.2	273.2	911	−0.655	−0.172	−0.150	−0.724	Dorsey (1940)
		293.2	1,012	−0.683	−0.167	−0.217	−0.726	
		323.2	1,012	−0.689	−0.167	−0.305	−0.706	
		373.2	1,012	−0.791	−0.200	−0.500	−0.783	
		471.2	963	−1.395	−0.419	−1.188	−1.294	
Ammonia	65.18	253.2	1,417	−1.912	−0.987	−1.370	−2.037	Kumagai and Toriumi (1971)
		273.2	1,415	−2.425	−1.308	−1.809	−2.502	
		293.2	1,408	−3.322	−1.939	−2.442	−3.392	
		313.2	1,402	−4.061	−2.485	−3.165	−3.988	
Benzene	255	292.2	101	−0.840	−0.766	−0.872	−0.840	Holder and Whalley (1962)
		323.2	101	−1.085	−0.929	−1.183	−1.042	
		348.2	100	−1.360	−1.182	−1.570	−1.325	
		403.2	178	−4.172	−3.626	−4.799	−4.015	Connolly and Kandalic (1962)
		443.2	174	−6.624	−5.870	−7.348	−5.936	
		483.2	165	−11.432	−10.425	−11.833	−10.022	
		523.2	153	−22.645	−21.109	−21.648	−19.863	
n-Octane	489	443.2	179	−14.126	−14.588	−18.738	−14.175	Connolly and Kandalic (1962)
		483.2	175	−23.617	−24.192	−29.165	−21.965	
		523.2	169	−44.564	−45.483	−49.993	−40.904	
Cyclohexane	311	298.2	101	−1.276	−1.347	−1.400	−1.175	Holder and Whalley (1962)
		323.2	101	−1.604	−1.646	−1.900	−1.496	
		348.2	100	−1.964	−2.146	−2.510	−1.903	
Carbon tetrachloride	276	298.2	101	−1.043	*	−1.086	−1.136	Holder and Whalley (1962)
		323.2	101	−1.318		−1.468	−1.252	
		343.2	100	−1.622		−1.950	−1.595	

(a) Equation (6) with v^*; (from Brelvi and O'Connell, 1972).
(b) Equation (6) with v_c; (from Reid and Sherwood, 1966).
(c) Yen and Woods method.
* v^* is equal to v_c.
† Outside reduced pressure range. $\Delta P_r > 30$.

NOTATION

$\underset{\sim}{P}$ = pressure bar
ΔP = reduced pressure change, Equation (6)
R = universal gas constant = 83.143 bar-cm^3/g-mole-°K
T = absolute temperature, °K
v^* = characteristic molar volume, cm^3/g-mole
v = volume, cm^3/g-mole

Greek Letters

κ = compressibility, bar^{-1}
ρ = density, g-mole/cm^3 = $1/v$

Superscripts

$\sim$ = reduced quantity

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Unlike Pair Potential Interaction Force Constants for Hydrogen-Light Hydrocarbon Systems

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A similar earlier study by Hu, Chappelear, and Kobayashi (1970) following the suggestion by Reid (1968) determined unlike pair potential interaction force constants for the argon-helium and nitrogen-helium systems from diffusivity, viscosity, and second virial data. That study showed that the Buckingham Exp-6 potential gives a better fit than the two parameter Lennard-Jones (L-J) 12-6 potential for this combination of thermodynamic and transport properties. The present study for the four hydrogen-light hydrocarbon systems uses the data sources listed in Table 1.

Evaluations are presented here for two potential functions, the Lennard-Jones (12-6) and the Modified Buckingham Exp-6. The tables of Klein and Smith (1968) for the L-J (12-6) potential were used to evaluate the collision integrals $\Omega^{(1,1)*}$ and $\Omega^{(2,2)*}$ and the function B^*_{12}. For the Modified Buckingham Exp-6 potential, the tables in Hirschfelder, Curtiss, and Bird (1964) were used. The correlation functions f_D and f_μ were nearly unity for the systems studied in this work. In the calculations of transport properties, the lowest temperature was well above 200°K so that the quantum corrections were always negligible in comparison with the experimental error.

METHOD OF CALCULATION

At each experimental condition, values for B_{12} were calculated from

$$B_M = x_1^2 B_{11} + 2x_1x_2 B_{12} + x_2^2 B_{22} \qquad (1)$$

and values for μ_{12} were calculated from the Chapman-Enskog theory (Hirschfelder, Curtiss, and Bird, 1964). Evaluations of the results of the computations were based on two considerations: (1) evaluation of the intermolecular parameters ϵ_{12}/k vs. σ_{12} should give the same curve independent of the particular experimental temperature, and (2) the values of μ_{12} should be independent of the concentration as required by the theoretical model.

The calculations for three systems were straightforward; however, calculations for the H_2-C_3H_8 system seemed to indicate a concentration dependence in μ_{12}. This contradicts the model so the average μ_{12} was selected as a first trial. However, this gave different ϵ_{12}/k vs. σ_{12} for the four experimental temperatures. The diffusivity experiments were conducted with the hydrocarbon at infinite dilution in hydrogen; hence, a value for μ_{12} in the hydrogen rich region was selected. This gave a single curve for the ϵ_{12}/k vs. σ_{12} and formed an internally consistent set with the homologous series.

Finally, the least-squares method was used on all experimental temperature conditions (except as noted above) to evaluate the best ϵ_{12}/k vs. σ_{12} for each property. The standard deviation was 5% for B_{12}, 1% for D_{12}, and 0.5% for μ_{12} for the four systems.

COMPARISON OF POTENTIAL FUNCTIONS

The results of the calculations outlined above are presented in Figures 1 and 2. The values of σ_{12} and ϵ_{12}/k selected as nearest to the intersection of the three loci are given in Table 2 for the L-J (12-6) and Exp-6 potentials.

If the potential function correctly and uniformly represents the three properties, the three lines will have a single mutual intersection of values for σ_{12} and ϵ_{12}/k. However, the loci for μ_{12} and D_{12} for the L-J (12-6) potential are spread apart over a wide range, as shown in Figure 1. A region of intersection is defined by the intersection of the line for B_{12} with these loci. On the other hand, Figure 2 shows a much smaller region of intersection for the three loci. This, and specific computations given in the following section, show that the three parameter Exp-6 model, perhaps owing to the extra parameter to adjust the repulsive portion of the potential, is better than the two parameter L-J model for the properties and systems studied here.

The figures show that ϵ_{12}/k is determined by B_{12}. Preliminary calculations showed that the third parameter α shifted the line for B_{12} but did not change its orientation. A larger α gives a larger value for ϵ_{12}/k. The comparisons here are presented at $\alpha = 12$.

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