Calculation of the Bubble-Point Volumes of Hydrocarbon Mixtures

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The equation for the saturated volume of pure liquids, log $(V/V_c) = (1 - T/T_c)^{2/7} \log Z_c$, is extended to the bubble-point volume of hydrocarbon mixtures. Mole-average V_c and Z_c values are used in this equation, but the higher T_c values of the components are weighted more heavily in the determination of T_c used for a mixture. The equation then gives bubble-point volumes that agree with experimental volumes with an average error of about 2%.

An equation for the saturated volume of pure liquids (*17, 18*) can be written in the form

$$V = V_c Z_c^{[(1 - T/T_c)^{2/7}]} \tag{1}$$

An extension of this equation to the bubble-point volume of mixtures of aliphatic hydrocarbons (*18*) is here described.

In this extension mole-average V_c and Z_c are used—i.e., $V_{cm} = \Sigma x_i V_{ci}$ and $Z_{cm} = \Sigma x_i Z_{ci}$. The critical pressure does not appear in Equation 1, nor was it introduced into the extension to mixtures. The averaging method for T_c was devised in the following way to best fit the equation to measured densities. With V_{cm} and Z_{cm} inserted into Equation 1, this equation can be rearranged into a form explicit in T_c.

$$T_c = T/\{1 - [\log (V/V_{cm})/\log Z_{cm}]^{7/2}\} \tag{2}$$

Values of V reported in the literature were used to determine the best values of T_c for those mixtures.

Bubble-point liquid-volume data of 10 aliphatic hydrocarbon binary systems (*8-10, 14, 22, 28, 29, 31-33*) were examined (*18*). For most of these mixtures, T_c given by Equation 2 varied only slightly with temperature. The value of T_c to be used with a mixture is taken to vary only with composition, not with temperature.

For each of the binary systems examined, the following equation gives suitable values of T_c, now labeled T_{cb}, as a function of composition.

$$T_{cb} = \frac{x_1(b_1/b_2)T_{c1} + x_2 T_{c2}}{x_1(b_1/b_2) + x_2} \tag{3}$$

The quantities b_1 and b_2 are termed weighting factors. They are written here as a ratio; only their relative values can be determined or have any meaning. Rearranging Equation 3 gives

$$b_1/b_2 = \frac{x_2(T_{cb} - T_{c2})}{x_1(T_{c1} - T_{cb})} \tag{4}$$

The value of T_{cb} used in this equation is T_c given by Equation 2.

For each of the 10 binary systems, a single value of (b_1/b_2) was extracted. The following equation satisfactorily reproduces these (b_1/b_2) values as a function of $(T_{c1} - T_{c2})$, the difference between the critical temperatures of the two components.

$$b_1/b_2 = \exp [0.000633(T_{c1} - T_{c2})^{9/7}] \tag{5}$$

T_{c1} and T_{c2} have units of °K in Equation 5. This equation was formulated solely on the basis of data for binary mixtures of aliphatic hydrocarbons. It should not be used unwarily for other mixtures.

This method of calculating the critical temperature to be used with binary mixtures was extrapolated to multicomponent mixtures by taking each b_i, the weighting factor for component i, to be the geometric mole average of b_i/b_j—i.e.,

$$b_i = \prod_{j=1}^{n} (b_i/b_j)^{x_j} \tag{6}$$

The selection of a geometric mole average rather than some other average is arbitrary. Substituting Equation 5 into Equation 6 gives

$$b_i = \exp \left[0.000633 \sum_{j=1}^{n} x_j (T_{ci} - T_{cj})^{9/7} \right] \tag{7}$$

For a binary mixture, b_1 and b_2 given by this equation vary with composition, but their ratio, b_1/b_2, is constant. Equation 3 now becomes

$$T_{cb} = \sum_{i=1}^{n} x_i b_i T_{ci} / \sum_{i=1}^{n} x_i b_i \tag{8}$$

Equation 1 for use with mixtures thus becomes

$$V = V_{cm} Z_{cm}^{[(1 - T/T_{cb})^{2/7}]} \tag{9}$$

and the densities of the mixtures are given by

$$\rho = \sum_{i=1}^{n} x_i M_i / V \tag{10}$$

The weighted mole-average critical temperature, T_{cb}, is always higher than the mole-average critical temperature, T_{cm}. In Table I are listed the experimental densities and the densities calculated by the method here described and by several other methods (*2, 6, 7, 13, 35*) of bubble-point mixtures of methane and *n*-pentane (*33*) along the 100° F isotherm. For two of these mixtures $T/T_{cm} > 1$, and only methods that use weighted average critical temperatures can estimate these densities.

Table I. Experimental and Calculated Densities of Bubble-Point Mixtures of Methane and *n*-Pentane at 100° F

Mole fraction methane	Density, g/cm^3 Experimental (*33*)	Equations 8-10, 12	Harmens method (*6, 7*)	NGPSA method (*13*)	Yen-Woods method (*35*)	API method (*2*)[a]	T/T_{cb}	T/T_{cm}	Pressure, psia
0.3077	0.5436	0.5425	0.536	0.544	0.520	0.556	0.729	0.810	1000
0.3749	0.5247	0.5236	0.516	0.520	0.498	0.546	0.750	0.851	1250
0.4391	0.5031	0.5029	0.494	0.492	0.474	0.537	0.774	0.895	1500
0.5042	0.4770	0.4786	0.468	0.455	0.446	0.529	0.803	0.944	1750
0.5788	0.4401	0.4445	0.432	0.397	$T/T_{cm} > 1$		0.843	1.008	2000
0.6770	0.3794	0.3813	0.364	Off chart			0.914	1.106	2250

[a] In the API method, the chart of Lu (*11*) has been adapted to mixtures.

Table II. Weighting-Factor Adjustment Coefficients and their Logarithms

Substance	Ln *c*	*c*
Cyclopentane	−0.3	0.74
Cyclohexane	−0.25	0.78
Benzene	−0.4	0.67
Toluene	−0.35	0.70
Xylenes	−0.3	0.74
Nitrogen	−0.2	0.82[a]
Carbon monoxide	−0.2	0.82
Carbon dioxide	+0.15	1.16[a]
Hydrogen sulfide	−0.3	0.74[a]

[a] These values taken from ref. *4*.

For binary systems in which one of the components is either an aromatic hydrocarbon or a nonhydrocarbon, a more suitable weighting-factor ratio can be obtained by multiplying the ratio given by Equation 5 by a multiplier, *c*, that is specific and constant for that aromatic or nonhydrocarbon in all of its mixtures. For a multicomponent mixture containing one or more aromatics or nonhydrocarbons, Equation 7 then becomes

$$b_i = c_i \exp\left[0.000633 \sum_{j=1}^{n} x_j(T_{ci} - T_{cj})^{9/7}\right] \tag{11}$$

or

$$b_i = \exp\left[0.000633 \sum_{j=1}^{n} x_j(T_{ci} - T_{cj})^{9/7} + \ln c_i\right] \tag{12}$$

The values of ln *c* assigned to several aromatic hydrocarbons, nonhydrocarbons, and cycloalkanes are listed in Table II. For other aliphatic hydrocarbons, $c = 1$—i.e., $\ln c = 0$.

Although T_{cb} is always larger than T_{cm}, for all of the systems examined T_{cb} is never larger than the actual critical temperature of the mixture. Equation 9 gives $dV/dT = \infty$ at $T = T_{cb}$. For any mixture, this derivative actually becomes infinite neither at T_{cb} nor at the higher actual critical temperature, but at the even higher maximum temperature—i.e., cricondentherm—point. Equation 9 can therefore not be expected to hold as well at high as at low reduced temperatures. A criterion for confidence in the calculated volumes or densities is either $T/T_{cb} < 0.95$ or $T/T_{cm} < 1.00$. Only if both $T/T_{cb} > 0.95$ and $T/T_{cm} > 1.00$ must the calculated volume or density be used with more than normal caution. In Table III are listed the mean and maximum errors given by Equation 9 (and Equations 8 and 12) for 22 systems. Carbon dioxide mixtures and nitrogen mixtures containing more than 0.5 mole-fraction carbon dioxide or nitrogen were excluded from

Table III. Deviations of Calculated Bubble-Point Volumes from Literature Values

Components of mixture	% Deviation Mean	Bias	Max.	No. of data points	No. of compositions	Temp range, ° F	Source of data	Table(s) no. in cited source
Methane, propane	0.83	−0.59	−1.61	8	5	40–160	(*24*)	I
Methane, propane, *n*-decane	1.77	+0.85	−8.83	55		40–460	(*34*)	IV
Methane, *n*-butane, *n*-decane	1.58	+1.50	+4.90	32	8	100–280	(*23*)	II
Methane, *iso*butane	0.92	+0.09	+1.46	5	3	100–160	(*16*)	I
Methane, *n*-pentane	0.52	+0.50	+1.36	9	3	100–280	(*33*)	I
Methane, *n*-heptane	1.10	+1.10	+4.13	40	8	40–400	(*28*)	II
Methane, *n*-decane	2.79	+2.79	+4.28	30	6	70–250	(*32*)	I
Methane, cyclohexane	0.73	+0.47	+4.17	38	8	70–340	(*3*)	I, II
Methane, hydrogen sulfide	4.67	−3.84	−7.58	9	5	40–160	(*25*)	I
Ethane, *n*-pentane	1.22	+0.16	−7.73	34	9	40–340	(*29*)	I
Ethane, propylene	0.51	−0.06	+1.03	10	3	10–160	(*12*)	I
Propane, *n*-butane	1.64	−1.33	−5.49	28	6	100–280	(*14*)	I
Propane, *n*-pentane	1.69	−0.29	−4.09	22	4	130–310	(*31*)	II
Propane, *n*-decane	0.76	+0.43	−2.09	61	9	40–460	(*21*)	I
Propane, benzene	0.93	−0.93	−2.69	21	4	100–460	(*5*)	I
Propane, carbon dioxide	4.10	−4.10	−6.18	5	2	40–160	(*26*)	II
n-Butane, *n*-decane	0.72	+0.45	−2.09	54		100–460	(*19*)	II
n-Butane, carbon dioxide	2.04	−2.04	−4.31	8	3	100–220	(*15*)	I
n-Pentane, hydrogen sulfide	1.48	−0.88	+4.97	19	4	40–340	(*27*)	I
n-Heptane, nitrogen	3.50	+3.29	+11.1	19		90–375	(*1*)	I
n-Decane, carbon dioxide	1.65	+1.65	+6.41	39	5	40–460	(*20*)	II, III
n-Decane, hydrogen sulfide	1.87	+1.66	+2.85	24	4	40–340	(*30*)	I

A mean deviation is the mean of the absolute values of the deviations; a bias is the mean of the deviations taken with their sign. Where the two are numerically equal, all of the deviations are of the same sign.

this test. All other data points that satisfy the $T/T_{cb} < 0.95$ or $T/T_{cm} < 1.00$ criterion were included.

This method for estimating the volumes or densities of liquid mixtures of aliphatic hydrocarbons is strictly applicable only to bubble-point mixtures. At temperatures not close to T_{cb}—e.g., $T/T_{cb} < 0.8$—the method can also be used at higher pressures, because at low temperatures the compressibility of liquids is quite small. This method should not be used, however, at extremely high pressures at any temperature.

NOMENCLATURE

b = weighting factor in T_{cb} determination
c = adjustment coefficient in weighting-factor determination
M = molecular weight
n = number of components in the mixture
T = temperature, °K
V = molar bubble-point volume
x = mole fraction of a component of the mixture
Z_c = critical compressibility factor
ρ = density

Subscripts

b = weighted mole average
c = critical
i, j = components of a multicomponent mixture
m = mole average
1, 2 = components of a binary mixture

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A Ternary Positive-Negative Azeotrope: Acetone–Chloroform–Ethanol

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The ternary positive-negative system composed of acetone, chloroform, and ethanol was investigated at 710 mm Hg by a combined ebulliometric-distillation method. In this system a positive-negative (saddle) azeotrope is formed. The azeotrope contains acetone 33.4, chloroform 48.3, and ethanol 18.3% by mole and boils at 61.17° C. The azeotropic parameters of the ternary saddle system were also computed from binary azeotropic data assuming that the components form a regular solution.

Saddle azeotropic systems, called also positive-negative systems, exhibit a hyperbolic point which is neither a minimum nor maximum in either boiling temperature or vapor pressure and are characterized by the presence of the "top-ridge line." They also exhibit some peculiar properties called distillation anomalies. The first ternary positive-negative (saddle) azeotrope, in spite of the fact that its existence was predicted by W. Ostwald at the end of last century, was found in 1945 by Ewell and Welch (*2*) in the system acetone–chloroform–methanol.

Since then Bushmakin and Kiss (*1*) and Molodenko and Bushmakin (*5*) have described two other saddle azeotropes obtained by replacing one of the constituents by another substance. In other similar systems, only ternary positive azeotropes were found. Historical outline of azeotropy with special emphasis on saddle azeotropes is given in Swietoslawski's book (*8*). The purpose of this work was to confirm a suggestion that replacement of methanol by ethanol in the system examined by Ewell and Welch would result in the formation of the saddle azeotrope and to