Figure 4. Variation in B/V_0 (g-mol/cm^3 cP) with mole fraction of acetone or acetic acid x for systems toluene–acetone ▲ and 4-methyl-2-pentanone–acetic acid ■

Binary systems. Unsmoothed density and viscosity data for the two systems at the four temperatures are listed in Tables III and IV. Cullilan and Kosanovich (5) have suggested that Equation 1 can be used for any mixture so that V in Equation 1 be the molecular volume of the solution and ϕ be the fluidity of the mixture, respectively. Plots of ϕ against V for the two systems are shown in Figures 1 and 2. Unlike the data reported by Cullilan and Kosanovich (5) for the system acetone–carbon tetrachloride, the present data show a regular increase in the value of B/V_0 and an almost linear decrease in the value of V_0 as the mole fraction of acetone in the first system and acetic acid in the second system increase, as shown in Figures 3 and 4.

Nomenclature

B = constant in Equation 1, cP^{-1}
M = molecular weight
V = molecular volume, cm^3/g-mol
V_0 = ultimate molecular volume, cm^3/g-mol
x = mole fraction

Greek Letters

ρ = density, g/ml
η = viscosity, cP
ϕ = fluidity, cP^{-1}

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Binary Vapor-Liquid Equilibria of Some Amyl Alcohols

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Vapor-liquid equilibrium data were determined at 760 mm Hg for the binary systems *tert*-amyl–isoamyl alcohol, isoamyl–*n*-amyl alcohol, and *tert*-amyl–*n*-amyl alcohol with a Dvorak-Boublik recirculation still. The three binaries presented small negative deviations from ideal solution behavior. Liquid activity coefficients were correlated with the Redlich-Kister and Wilson equations. Boiling points were predicted by a two-constant empirical correlation.

The amyl isomer systems reported here represent an example of vapor-liquid equilibria where the chemical species differ only in the geometrical position of the alcohol function. Amyl alcohols are a by-product of the fermentation of grain (fusel oil), and their main use is in the manufacture of solvents.

Ocon et al. (*6, 7*) measured the vapor-liquid equilibrium at 760 mm Hg of mixtures of active amyl alcohol (1-rotatory 2-methyl-1-butanol) and isoamyl alcohol (3-methyl-1-butanol)

without determining the activity coefficients, and claimed that their data were more reliable than those of Hafslund and Lovell (*3*). Ivanov et al. (*5*) determined the vapor-liquid equilibrium of the same system at various constant compositions of isoamyl alcohol and calculated the relative volatility and the coefficients of the Van Laar equations at 100, 300, 500, and 760 mm Hg. Their results showed that the binary was symmetric and presented small negative deviations from ideal solutions. Brusset et al. (*2*) determined the degree of association of the different pentanols at 25 °C and found that the tertiary form presented the highest degree of association and that the association decreased substantially when adding spherical solvents like carbon tetrachloride.

Experimental

Purity of materials. Analytical grade reagents purchased from Merck and Fluka were used without further purification after gas chromatography analysis failed to show any significant impurities, particularly water. Physical properties of the pure components appear in Table I.

Apparatus and procedure. An all-glass modified Dvorak and Boublik recirculation still (1) was used in the equilibrium determinations. The experimental features have been described previously (11). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and an Autolab Model 6300 electronic integrator. The column was 200 cm long and 0.2 cm diameter and was packed with a 10% Hall-comid M-18-01 on 80–100 Supelcoport and operated isothermally at 70 °C. Injector temperature was 170 °C, and the detector operated at 150 mA and 180 °C. Calibration analyses were carried on to convert the peak area ratio to the weight composition of the mixture. Concentration measurements were generally accurate to ±0.3%.

Results

Constant pressure equilibria determinations were made at 760 mm, and the experimental results appear in Tables III–V. Activity coefficients were calculated from the equation

$$\gamma_i = \frac{P y_i}{P_i^\circ x_i} \tag{1}$$

since no information was available regarding the virial coefficients of the components and their mixtures. According to Hudson and Van Winkle (4), Equation 1 is a reasonable approximation for most real systems at atmospheric pressure.

Vapor pressures P_i° were calculated according to Antoine's equation

$$\log P_i^\circ = \alpha_i - \beta_i/(t + \delta_i) \tag{2}$$

The constants α_i, β_i, and δ_i appear in Table II (9).

The activity coefficients reported in Tables III–V show that the three binaries present small negative deviations from ideal solution behavior. These coefficients were well correlated by a Redlich-Kister expansion of the type (8)

$$\ln \gamma_i = a(i)x_j^2 + b(i)x_j^3 + c(i)x_j^4 \tag{3}$$

$$\ln \gamma_j = a(j)x_i^2 + b(j)x_i^3 + c(j)x_i^4 \tag{4}$$

with a relative error smaller than 1%, and a Wilson correlation (10)

$$\ln \gamma_i = -\ln (x_i + \Lambda_{ij}x_j) + x_j \left[\frac{\Lambda_{ij}}{x_i + \Lambda_{ij}x_j} - \frac{\Lambda_{ji}}{\Lambda_{ji}x_i + x_j} \right] \tag{5}$$

$$\ln \gamma_j = -\ln (x_j + \Lambda_{ji}x_i) - x_i \left[\frac{\Lambda_{ij}}{x_i + \Lambda_{ij}x_j} - \frac{\Lambda_{ji}}{\Lambda_{ji}x_i + x_j} \right] \tag{6}$$

with a relative error smaller than 2%. The corresponding coefficients appear in Table VI.

Analysis of the results for the three systems show that the addition of *tert*-amyl alcohol causes increased deviation from ideal behavior.

Boiling points of the binary systems were correlated with the equation suggested by Wisniak and Tamir (12).

$$T = x_1 T_1^\circ + x_2 T_2^\circ + w + x_1 x_2 \sum_{k=0}^{l} C_k(x_1 - x_2)^k \tag{7}$$

$$w = x_1 \ln (y_1/x_1) + x_2 \ln (y_2/x_2) \tag{8}$$

The corresponding constants appear in Table VII together with the root-mean-square deviation. Equation 7 with two constants is able to predict the binary boiling point to within 0.2–0.3 °C.

Table I. Physical Properties of Pure Compounds

Index	Compound	Refractive index at 25 °C	Bp, °C
1	*tert*-Amyl alcohol	1.4025	102.2
		1.4024 (9)	102.0 (9)
2	Isoamyl alcohol	1.4053	130.6
		1.4052 (9)	130.5 (9)
3	*n*-Amyl alcohol	1.4079	137.6
		1.4079 (9)	137.8 (9)

Table II. Antoine Constants

Compound	α_i	β_i	δ_i
Tert-amyl alcohol	6.51930	863.4	135.3
Isoamyl alcohol	6.95361	1128.19	146.47
n-Amyl alcohol	7.17758	1314.56	168.11

Table III. Experimental Vapor-Liquid Equilibrium Data for System *tert*-Amyl Alcohol(1)–Isoamyl Alcohol(2)

T_{exp}, °C	T_{calc}	x_1	x_2	γ_1	γ_2
129.10	128.86	0.051	0.110	0.9188	0.9848
127.20	127.22	0.099	0.206	0.9309	0.9880
126.80	126.77	0.112	0.235	0.9496	0.9793
126.40	126.26	0.127	0.264	0.9517	0.9719
124.30	124.01	0.193	0.380	0.9586	0.9535
123.30	123.17	0.218	0.420	0.9662	0.9538
122.00	122.06	0.251	0.475	0.9866	0.9444
119.50	119.61	0.325	0.570	0.9864	0.9401
117.40	117.62	0.387	0.635	0.9846	0.9497
115.60	115.76	0.446	0.697	0.9923	0.9334
113.60	113.75	0.512	0.752	0.9939	0.9360
111.30	111.45	0.591	0.812	1.002	0.9255
110.10	109.90	0.647	0.850	0.9962	0.8969
109.50	109.47	0.663	0.860	1.0034	0.8979
107.80	107.70	0.732	0.896	1.0022	0.8976
106.80	106.74	0.772	0.915	1.004	0.8978
106.70	106.50	0.782	0.921	1.000	0.8763
104.20	104.31	0.883	0.962	1.009	0.8700

Table IV. Experimental Vapor-Liquid Equilibrium Data for System *tert*-Amyl Alcohol(1)-*n*-Amyl Alcohol(3)

T_{exp}, °C	T_{calc}	x_1	y_2	γ_1	γ_2
104.35	104.54	0.895	0.974	1.002	0.8352
107.39	107.31	0.781	0.938	0.997	0.8447
110.50	110.32	0.670	0.892	0.9964	0.8638
112.30	112.35	0.601	0.858	1.007	0.8761
117.60	117.33	0.450	0.750	0.9939	0.9159
119.90	120.14	0.374	0.683	1.014	0.9376
122.35	122.84	0.306	0.608	1.025	0.9571
124.60	124.72	0.262	0.531	0.9780	0.9939
127.40	127.15	0.207	0.449	0.9648	0.9853
129.30	129.15	0.164	0.374	0.9607	0.9946
130.50	130.70	0.132	0.306	0.9440	1.019
131.36	131.35	0.119	0.278	0.9286	1.015
132.19	132.00	0.106	0.249	0.9124	1.012
132.45	132.06	0.105	0.235	0.8631	1.020

Table V. Experimental Vapor-Liquid Equilibrium Data for System Isoamyl Alcohol(2)-*n*-Amyl Alcohol(3)

T_{exp}, °C	T_{calc}	x_2	y_2	γ_1	γ_2
131.30	131.18	0.924	0.940	0.9914	0.9797
131.90	131.86	0.827	0.862	0.9955	0.9700
132.10	132.17	0.782	0.822	0.9972	0.9863
132.30	132.33	0.757	0.796	0.9909	1.0073
133.20	133.15	0.628	0.677	0.9859	1.011
133.75	133.80	0.522	0.580	0.9978	1.004
134.20	134.18	0.462	0.516	0.9882	1.013
134.21	134.22	0.455	0.516	1.003	0.9998
134.80	134.82	0.362	0.420	1.006	1.004
135.30	135.31	0.289	0.345	1.019	1.000
136.30	136.19	0.168	0.206	1.013	1.003
136.80	136.86	0.085	0.103	0.9848	1.014

Table VI. Redlich-Kister and Wilson Constants

System	Redlich-Kister						Wilson	
	$a(i)$	$b(i)$	$c(i)$	$a(j)$	$b(j)$	$c(j)$	Λ_{ij}	Λ_{ji}
tert-Amyl–iso-amyl alcohol	−0.35028	1.12452	−1.12069	−0.90486	1.86398	−1.12069	0.88175	1.13388
Isoamyl–*n*-amyl alcohol	0.31829	−2.42531	2.22929	1.13888	−3.51944	2.22929	0.66549	1.50289
tert-Amyl–*n*-amyl alcohol	−0.24781	0.36152	−0.03783	0.21812	−0.26031	−0.03783	0.57013	/54—96

Table VII. Correlation of Boiling Points

System	C_0	C_1	rmsd
tert-Amyl–isoamyl alcohol	−8.63380	−3.37356	0.151
Isoamyl–*n*-amyl alcohol	−1.63890	3.10665	0.236
tert-Amyl–*n*-amyl alcohol	−0.60536	1.53588	0.060

Acknowledgment

Nomenclature

α, β, δ = constants, Equation 2
$a(i), b(i), c(i)$ = constants, Equations 3 and 4
C_k = constant, Equation 7
l = number of terms in the series expansion of $(x_1 - x_2)$
P = overall pressure, mm Hg
P_i° = vapor pressure of component i pure, mm Hg
rmsd = root-mean-square deviation, $\sqrt{\Sigma(T_{exp} - T_{calc})^2 / n}$
n = number of experimental points
t, T = temperature, °C, K
T_i° = boiling temperature of component i pure at pressure P, K
x_i, y_i = mole fraction composition of component i in the liquid and vapor phases
γ_i = activity coefficient of component i
$\Lambda_{ij}, \Lambda_{ji}$ = Wilson constants, Equations 5 and 6

Subscripts

exp = experimental
calc = calculated
i = component i

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Vapor-Liquid Equilibria of Methyl Ethyl Ketone–Diethyl Ketone, Methyl Ethyl Ketone–Methyl Isobutyl Ketone, and Diethyl Ketone–Methyl Isobutyl Ketone Systems

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Vapor-liquid equilibrium data were determined at 760 mm Hg for the binary systems methyl ethyl ketone–diethyl ketone, methyl ethyl ketone–methyl isobutyl ketone, and diethyl ketone–methyl isobutyl ketone. The three systems presented small deviations from ideal solution behavior. The activity coefficients were correlated by the Redlich-Kister correlation. Boiling points were predicted by an empirical expression to within a maximum error of ±0.25 °C and a mean error of ±0.05 °C.

The present work was undertaken as part of a project devoted to the prediction of thermodynamic properties for chemically similar compounds. The ketone compounds investigated here differ in chain length and in spatial symmetry.

Experimental

Purity of materials. Analytical grade reagents purchased from Fluka were used without further purification after gas chromatography analysis failed to show any significant impurities. Physical properties of the pure components appear in Table I.

Apparatus and procedure. An all-glass modified Dvorak and Boublik recirculation still (*1*) was used in the equilibrium determinations. The experimental features have been described previously (*6*). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and an Autolab Model 6300 electronic integrator. The column was 200 cm long and 0.2 cm internal diameter and packed with Chromosorb 101 and operated isothermally at 155 °C. Injector temperature was 210 °C, and the detector operated at 150 mA and 210 °C. Calibration analyses were carried out to convert the peak area ratio to the actual weight composition of the mixture. Concentration measurements were generally accurate to ±0.2%.

Table I. Physical Properties of Pure Compounds

Index	Compound	Refractive index at 25 °C	Bp, °C
1	Methyl ethyl ketone	1.3764	79.56
		1.3764 (*5*)	79.64 (*5*)
2	Diethyl ketone	1.39003	101.7
		1.39002 (*5*)	101.77 (*5*)
3	Methyl isobutyl ketone	1.3935	116.30
		1.3933 (*5*)	116.50 (*5*)

Table II. Vapor-Pressure Constants

Compound	α_i	β_i	δ_i
Methyl ethyl ketone	7.20867	1368.21	236.50
Diethyl ketone	6.97840	1281.2	210.9
Methyl isobutyl ketone	6.67272	1168.41	191.94