Table II. Soave Correlation of Carbon Dioxide-Benzene Data

temp, K	optimum parameters C_{12}	D_{12}	rms errors in x	y	P, MPa (psi)
		Present Work (P-T-x-y)			
313.2	0.083		0.024	0.001	
313.2	0.065	0.041	0.006	0.002	
		Ohgaki and Katayama (P-T-x-y)			
313.2	0.069		0.024	0.004	
313.2	0.055	0.035	0.014	0.003	
		Present Work (Bubble Points)			
313.2	0.088				0.19 (27)
353.2	0.079				0.40 (58)
393.2	0.088				0.24 (35)
all T	0.084				0.31 (46)
313.2	0.065	0.039			0.03 (5)
353.2	0.065	0.049			0.03 (4)
393.2	0.071	0.036			0.03 (5)
all T	0.066	0.043			0.06 (9)

only ($D_{ij} = 0$) does not lead to satisfactory fit of the data by the Soave equation. However, use of both C_{ij} and D_{ij} (as in ref 1) produces an excellent representation of the data. Individual isotherms can be fitted to root-mean-square errors of 0.03 MPa (5 psi) while all isotherms can be fitted simultaneously with errors of 0.06 MPa (9 psi).

Glossary

a, b	parameters in Soave equation of state
C_{ij}, D_{ij}	interaction parameters between components i and j in mixing rules for Soave equation
M	number of data points
N	number of components in mixture
P	system pressure
T	system temperature
x	liquid mole fraction of CO_2
y	vapor mole fraction of CO_2
Δ	difference between calculated and experimental values

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Excess Volumes of Ternary Mixtures Containing Methyl Ethyl Ketone, 1-Alkanols, and *n*-Octane

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The excess volumes, V^E_{123}, for ternary mixtures of methyl ethyl ketone + 1-alkanols + *n*-octane have been measured at 303.15 K, by using a new dilatometer. The alkanols include 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol. Experimental results for the ternary mixtures are positive over the whole range of composition in all of the systems. excess volumes for binary system of methyl ethyl ketone + *n*-octane have also been measured at 303.15 K by using a two-limbed dilatometer.

In continuation of earlier work on excess volumes of ternary mixtures containing methyl ethyl ketone and *n*-heptane as common components and a homologous series of *n*-alkanols as noncommon components (*1*), we report here new excess-volume data for four ternary systems. The mixtures include methyl ethyl ketone and *n*-octane as common components. The alkanols, used as noncommon components, include 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol. The measurements were made to understand the effect of chain length of 1-alkane on excess volumes.

Purification of Materials. The alcohols (BDH) were purified by the method described by Rao and Naidu (*2*). Methyl ethyl ketone (BDH) was purified by the method described by Reddy and Naidu (*3*). The sample was dried over anhydrous potassium carbonate and fractionally distilled. *n*-Octane (Riedel) was purified by drying it over sodium for 1 day. It was then refluxed for 4 h and finally fractionally distilled. The purities of the liquids were checked by comparing the measured densities with those reported in the literature (*4*). The data are given in Table I. Densities were measured by using a bicapillary pycnometer described by Rao (*5*). Excess volumes for ternary systems were measured with the dilatometer described earlier (*1*).

Table I. Densities of Pure Substances at 303.15 K

	ρ, g cm^{-3} present work	lit.
methyl ethyl ketone	0.794 49	0.794 52
1-propanol	0.795 62	0.795 67
1-butanol	0.802 02	0.802 06
1-pentanol	0.807 62	0.807 64
1-hexanol	0.811 98	0.812 01
n-octane	0.694 45	0.694 50

The mixing cell contains three limbs of different capacities. Mercury was taken at the bottom of the dilatometer to separate the three components. One of the bulbs was fitted with a capillary (i.d. 1.0 mm), and the other two bulbs were fixed with ground-glass stoppers. Four dilatometers with different capacities were used to cover the mole-fraction range 0.1-0.8. The V^E values were accurate to ± 0.003 cm^3 mol^{-1}.

The experimental results for the binary systems *n*-octane with 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol, reported in the literature (*6*), have been used to obtain excess volume-

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Table II. Equations Fitting the Experimental Data of the Excess Volumes for the Various Binary Systems and the Standard Deviation $\sigma(V^E)$ at 303.15 K

system	equation fitting the data[a]	$\sigma(V^E)$, cm³ mol⁻¹
methyl ethyl ketone + *n*-octane[b]	$X_1X_3[3.46203 - 0.43891(X_1 - X_3) - 0.21713(X_1 - X_3)^2]$	0.007
methyl ethyl ketone + 1-propanol[c]	$X_1X_2[-0.1709 + 0.0122(X_1 - X_2) + 0.0118(X_1 - X_2)^2]$	0.001
methyl ethyl ketone + 1-butanol[c]	$X_1X_2[0.0598 + 0.0283(X_1 - X_2) + 0.0156(X_1 - X_2)^2]$	0.002
methyl ethyl ketone + 1-pentanol[c]	$X_1X_2[0.1615 + 0.0662(X_1 - X_2) - 0.0960(X_1 - X_2)^2]$	0.004
methyl ethyl ketone + 1-hexanol[c]	$X_1X_2[0.3133 + 0.0051(X_1 - X_2) + 0.1721(X_1 - X_2)^2]$	0.002
1-propanol + *n*-octane[d]	$X_2X_3[1.74374 + 0.47997(X_2 - X_3) - 0.08646(X_2 - X_3)^2]$	0.001
1-butanol + *n*-octane[d]	$X_2X_3[1.4946 + 0.48424(X_2 - X_3) + 0.47887(X_2 - X_3)^2]$	0.006
1-pentanol + *n*-octane[d]	$X_2X_3[0.98656 + 0.67995(X_2 - X_3) + 0.33009(X_2 - X_3)^2]$	0.005
1-hexanol + *n*-octane[d]	$X_2X_3[0.52886 + 0.95803(X_2 - X_3) - 0.01797(X_2 - X_3)^2]$	0.001

[a] X_1, X_2, and X_3 refer to the mole fractions of methyl ethyl ketone, an alkanol, and *n*-octane, respectively, in the various binary systems. [b] Equation based on the values of V^E obtained during the work. [c] Reference 3. [d] Reference 6.

Table III. Excess Volumes of Ternary Systems Methyl Ethyl Ketone (1) + 1-Alkanol (2) + *n*-Octane (3) at 303.15 K

X_1	X_2	V^E_{123}, cm³ mol⁻¹	V^E_{123}(a), cm³ mol⁻¹	ΔV^E_{123}, cm³ mol⁻¹	V^E_{123}(b), cm³ mol⁻¹	ΔV^E_{123}*, m³ mol⁻¹	δ^E,[a] cm³ mol⁻¹
			Methyl Ethyl Ketone (1) + 1-Propanol (2) + *n*-Octane (3)				
0.7470	0.1461	0.321	0.034	0.287	0.258	0.063	0.000
0.6122	0.2765	0.276	0.042	0.234	0.245	0.031	−0.004
0.6143	0.2909	0.233	0.032	0.201	0.206	0.027	0.004
0.4992	0.3737	0.291	0.047	0.244	0.263	0.028	−0.003
0.4555	0.4148	0.293	0.048	0.245	0.264	0.029	0.000
0.3293	0.5736	0.205	0.034	0.171	0.183	0.022	0.004
0.3060	0.5745	0.251	0.047	0.204	0.226	0.025	0.002
0.1998	0.7101	0.175	0.031	0.144	0.164	0.011	−0.005
0.0996	0.8063	0.197	0.033	0.164	0.173	0.024	0.001
			Methyl Ethyl Ketone (1) + 1-Butanol (2) + *n*-Octane (3)				
0.7603	0.1318	0.245	0.034	0.211	0.282	−0.037	−0.003
0.6455	0.2551	0.206	0.035	0.171	0.255	−0.049	0.005
0.5309	0.3658	0.222	0.036	0.186	0.253	−0.031	0.001
0.4250	0.4592	0.236	0.044	0.192	0.265	−0.029	−0.002
0.3694	0.5284	0.220	0.036	0.184	0.234	−0.014	−0.005
0.3402	0.5351	0.235	0.046	0.189	0.270	−0.035	0.001
0.2512	0.6485	0.189	0.035	0.154	0.217	−0.028	0.000
0.1465	0.7457	0.181	0.036	0.145	0.220	−0.039	0.002
			Methyl Ethyl Ketone (1) + 1-Pentanol (2) + *n*-Octane (3)				
0.7864	0.1028	0.258	0.030	0.228	0.291	−0.033	0.000
0.6746	0.2218	0.206	0.032	0.174	0.270	−0.064	−0.001
0.5578	0.3010	0.238	0.046	0.192	0.331	−0.093	−0.003
0.5409	0.3400	0.232	0.033	0.199	0.287	−0.055	0.001
0.4101	0.4692	0.246	0.034	0.212	0.266	−0.020	0.008
0.3746	0.4817	0.227	0.045	0.182	0.295	−0.068	−0.011
0.2792	0.6032	0.200	0.042	0.158	0.232	−0.032	0.001
0.1329	0.7431	0.157	0.030	0.127	0.206	−0.049	0.000
0.1236	0.7729	0.141	0.029	0.112	0.178	−0.037	0.002
			Methyl Ethyl Ketone (1) + 1-Hexanol (2) + *n*-Octane (3)				
0.7957	0.0906	0.287	0.030	0.257	0.311	−0.024	0.008
0.6966	0.1982	0.236	0.031	0.205	0.292	−0.056	−0.004
0.6283	0.2450	0.254	0.039	0.215	0.326	−0.072	−0.001
0.5759	0.3026	0.226	0.033	0.193	0.308	−0.082	0.002
0.5217	0.3431	0.224	0.041	0.183	0.321	−0.097	0.000
0.4295	0.4424	0.189	0.033	0.156	0.289	−0.100	−0.009
0.2973	0.5860	0.147	0.031	0.116	0.240	−0.093	0.000
0.1430	0.7154	0.157	0.028	0.129	0.217	−0.060	−0.006
0.1527	0.7437	0.130	0.027	0.103	0.183	−0.053	−0.007

[a] δ^E is the deviation in the experimental value of V^E_{123} from that calculated according to eq 2.

composition plots. The plots are included in Figure 1 along with the measured excess volumes for methyl ethyl ketone + *n*-octane. These were fitted to the equations given in Table II by the method of least squares. The experimental data for the ternary systems methyl ethyl ketone + an alkanol + *n*-octane are given in the third column of Table III. The V^E_{123} values of these systems are more positive than those than contained *n*-heptane as one of the components. This shows that an increase in chain length between *n*-heptane and *n*-octane leads to an increase in positive values of V^E. This may be ascribed to (a) size difference and (b) greater ability of *n*-octane as a structure-breaking component.

Excess volume, V^E_{123}, for a ternary mixture containing n_1, n_2 and n_3 moles of components 1–3, respectively, is expressed as

$$V^E_{123} = \tfrac{1}{2}[(n_1 + n_2)V^E_{12} + (n_2 + n_3)V^E_{23} + (n_3 + n_1)V^E_{31}] \quad (1)$$

where V^E_{12} is the excess volume per mole of a binary mixture in which the mole fraction of component 1 is $n_1/(n_1 + n_2)$ and that of component 2 is $n_2/(n_1 + n_2)$, V^E_{23} is the excess volume per mole of a binary mixture in which the mole fraction of component 2 is $n_2/(n_2 + n_3)$ and that of component 3 is $n_3/(n_2 + n_3)$, and V^E_{31} is the excess volume per mole of a binary

Table IV. Values of the Constants A, B, and C and σ at 303.15 K

system	A, cm^3 mol^{-1}	B, cm^3 mol^{-1}	C, cm^3 mol^{-1}	σ, cm^3 mol^{-1}
methyl ethyl ketone (1) + 1-propanol (2) + n-octane (3)	7.6330	−84.2989	267.1542	0.004
methyl ethyl ketone (1) + 1-butanol (2) + n-octane (3)	−2.4852	−45.5432	372.0609	0.004
methyl ethyl ketone (1) + 1-pentanol (2) + n-octane (3)	−3.8684	−28.4518	329.3148	0.006
methyl ethyl ketone (1) + 1-hexanol (2) + n-octane (3)	−3.7609	10.7499	−121.1847	0.006

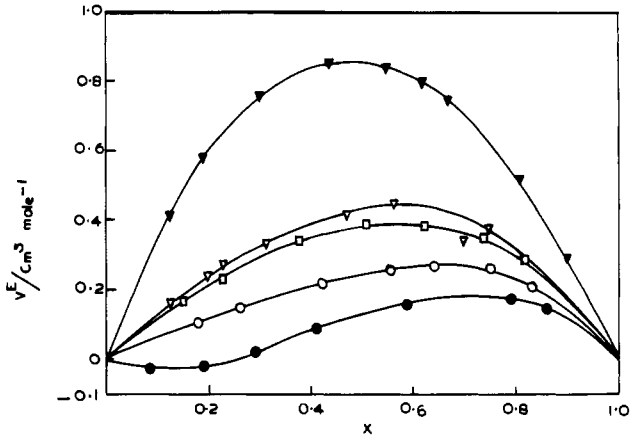

Figure 1. Variation of excess volume with mole fraction for (▼) methyl ethyl ketone + n-octane, (▽) 1-propanol + n-octane, (□) 1-butanol + n-octane, (○) 1-pentanol + n-octane, and (●) 1-hexanol + n-octane at 303.15 K.

mixture in which the mole fraction of component 3 is $n_3/(n_3 + n_1)$ and that of component 1 is $n_1/(n_3 + n_1)$. The values of V^E_{123} obtained from eq 1 are denoted by V^E_{123}(a) and presented in the fourth column of Table III. The deviation $\Delta V^E_{123} = V^E_{123} - V^E_{123}$(a) represents the ternary contribution. The values of ΔV^E_{123} are given in the fifth column of Table III.

The experimental results of V^E_{123} for the ternary systems were fitted by the method of least squares to the equation

$$V^E_{123} = V^E_{12}{}^* + V^E_{23}{}^* + V^E_{31}{}^* + X_1X_2X_3[A + BX_1(X_2 - X_3) + CX_1{}^2(X_2 - X_3)^2] \quad (2)$$

where X_1, X_2, and X_3 are the mole fractions of methyl ethyl ketone, an alkanol, and n-octane, respectively, and A, B, and C are constants. The starred quantities were evaluated by using the procedure described by Rastogi et al. (7) and the equations in Table II. The sum of $V^E_{12}{}^* + V^E_{23}{}^* + V^E_{31}{}^*$ for a ternary mixture is represented as V^E_{123}(b), and its values are included in the sixth column of Table III. The deviation $\Delta V^E_{123}{}^*$ was obtained by subtracting V^E_{123}(b) from those of the experimental values given in the third column of Table III. The values of $\Delta V^E_{123}{}^*$ are presented in the seventh column of Table III. These were used to evaluate the constants A, B, and C in eq 2 by the least-squares method. The values of the constants and the standard deviation, σ, are given in Table IV.

Glossary

ρ	density, g cm^{-3}
X	mole fraction
V	volume, cm^3
n	mole
A, B, C	ternary constants in eq 2
σ	standard deviation, cm^3 mol^{-1}
V^E_{123}	measured excess volume of ternary systems, cm^3 mol^{-1}
V^E_{123}(a)	binary effects in a ternary system calculated on the basis of number of moles
ΔV^E_{123}	ternary effect ($V^E_{123} - V^E_{123}$(a))
V^E_{123}(b)	sum of binary contributions in ternary mixtures calculated in terms of mole fractions
$\Delta V^E_{123}{}^*$	the difference between the measured excess volume and the sum of binary contributions calculated in terms of mole fractions
V^E_{12}, V^E_{23}, V^E_{31}	excess volume per mole of a binary mixture
$V^E_{12}{}^*$, $V^E_{23}{}^*$, $V^E_{31}{}^*$	excess volume of any two components in the ternay mixture
δ^E	difference between experimental value and the value calculated according to eq 2

Subscripts

1, 2, 3	components

Superscript

E	excess property

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