Table III. Values of Coefficients in Empirical Polynomia[a] for Densities of the Molten KCl-$CuCl_2$ System in Different Composition Ranges

	$0.4500 \leqslant X_{KCl} \leqslant 0.7000$ ($n = 3$, $m = 2$)	$0.4500 \leqslant X_{KCl} \leqslant 1.000$ ($n = 3$, $m = 2$)
A_0	3.9004	3.0309
A_1	−7.2316	−2.5295
A_2	10.5471	2.1903
A_3	−5.8879	−1.0065
B_0	-2.6197×10^{-3}	-2.0011×10^{-3}
B_1	5.0360×10^{-3}	2.7013×10^{-3}
B_2	-3.3919×10^{-3}	-1.2832×10^{-3}
SE, g/cm^3	0.0013	0.0023

[a] $\rho = \Sigma_0{}^n A_n X^n + (\Sigma_0{}^m B_m X^m)(t - 500)$.

In Figure 1 $A(X)$ and $B(X)$ are shown as functions of the composition. The curved lines show the best polynomials of third degree fitted (by the least-squares method) to the data. The parameters used are given in the figure caption. It is especially useful in connection with computer programs to have all of the data represented by one empirical equation of the form $\rho = \sum_0{}^n A_n X^n + (\sum_0{}^m B_m X^m)(t - 500)$. This equation has been examined for the two different mole-fraction ranges of X_{KCl}: one including only our own measurements (i.e., $0.4500 \leq X_{KCl} \leq 0.7000$) and one including also the literature values for pure KCl (i.e., $0.4500 \leq X_{KCl} \leq 1.0000$). The constants are given in Table III. As indicated by the dashed curves in Figure 1, it is recommended only to apply these equations for calculation of densities in the range $0.40 \leq X_{KCl} \leq 0.75$. However, as a linear relationship exists between density and temperature at all measured compositions, the relationships for the density given in Table III can probably be extrapolated to temperatures considerably beyond the temperature ranges employed in this investigation.

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Excess Volumes of Ternary Mixtures Containing Methyl Ethyl Ketone, 1-Alkanols, and an Alkane

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A dilatometer which could be used for the determination of excess volumes of ternary mixtures has been described. Excess volumes of four ternary mixtures which contained methyl ethyl ketone and *n*-heptane as common components and a homologous series of 1-alkanols as noncommon components have been measured at 303.15 K by employing the dilatometer. Experimental data for the ternary mixtures are positive over the whole range of composition in all of the systems. Excess volumes for binary mixtures of *n*-heptane with 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, and methyl ethyl ketone have been measured at 303.15 K by using a two-limbed dilatometer.

The dilatometer, which resembles the two-limbed dilatometer described by Rao and Naidu (*1*), has been designed and fabricated. The special feature of the dilatometer is that it permits the estimation of expansion or contraction in volume through the measurement of change in height of a liquid column. In this respect it differs from that described by Rastogi et al. (*2*) wherein the expansion or contraction in volume is determined by the change in height of a mercury column which introduces an error due to pressure difference. The accuracy of the dilatometer has been checked by measuring the excess-volume data for the test binary system benzene (1) + cyclohexane (2) at 298.15 K. New experimental results have been obtained for four ternary systems at 303.15 K. These systems contained methyl ethyl ketone and *n*-heptane as common components. 1-Propanol, 1-butanol, 1-pentanol, and 1-hexanol, which form a homologous series, formed the noncommon components.

Table I. Densities of Pure Substances at 303.15 K

	ρ, cm^{-3}	
	present work	lit.
benzene	0.868 47	0.868 50
cyclohexane	0.769 24	0.769 28
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
methyl ethyl ketone	0.794 49	0.794 52
n-heptane	0.675 04	0.675 10

Also, new V^E data for five binary mixtures, methyl ethyl ketone with *n*-heptane and *n*-heptane with 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol, have been measured at 303.15 K. These systems were choosen as no V^E data are available for the ternary mixtures made up of methyl ethyl ketone, 1-alkanols, and an aliphatic hydrocarbon.

Experimental Section

Purification of Materials. Benzene (AR) and cyclohexane (BDH) were purified by the methods described by Naidu and Krishnan (*3*). The alcohols (BDH) were purified by the method described by Rao and Naidu (*1*). 1-Propanol, 1-butanol, 1-pentanol, and 1-hexanol were refluxed over lime for 5 h and then distilled through a fractionating column having 30 theoretical plates. Methyl ethyl ketone (BDH) was purified by the method described by Reddy and Naidu (*4*). The sample was

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

system	equation fitting the data[a]	$\sigma(V^E)$, cm^3 mol^{-1}
methyl ethyl ketone + *n*-heptane[b]	$X_1X_3[2.1829 - 0.22109\,(X_1 - X_3) + 0.20465\,(X_1 - X_3)^2]$	0.004
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*-heptane[b]	$X_2X_3[1.3472 - 0.43715\,(X_2 - X_3) - 0.15407\,(X_2 - X_3)^2]$	0.006
1-butanol + *n*-heptane[b]	$X_2X_3[0.87729 - 0.43338\,(X_2 - X_3) + 0.14511\,(X_2 - X_3)^2]$	0.004
1-pentanol + *n*-heptane[b]	$X_2X_3[0.40782 - 1.1036\,(X_2 - X_3) + 0.07149\,(X_2 - X_3)^2]$	0.008
1-hexanol + *n*-heptane[b]	$X_2X_3[-0.14034 - 0.64463\,(X_2 - X_3) + 0.14482\,(X_2 - X_3)^2]$	0.005

[a] X_1, X_2, and X_3 refer to the mole fractions of methyl ethyl ketone, an alkanol, and *n*-heptane, respectively, in the various binary systems. [b] Equations based on the values of V^E obtained during this work. [c] Reference *4*.

dried over anhydrous potassium carbonate and finally fractionated. *n*-Heptane (England BDH) was dried over sodium hydroxide pellets for several days and then distilled with a 2-m column. The purities of the liquids were checked by measuring densities at 303.15 K. The results agreed to within 0.000 05 g cm^{-3} with those reported in the literature (*5*). The data are given in Table I. Densities were measured by using a bicapillary pycnometer described by Rao (*6*). Mercury was purified by using the method described by Vogel (*7*).

Procedure. The dilatometer is shown in Figure 1. The three limbs, A, B and C, have the capacities 7, 4, and 7 cm^3, respectively. Mercury was taken at the bottom of the dilatometer to separate the three components. Limbs A and C of the dialtometer were made up of B-14 standard joints (sockets), and limb B was constructed by using a B-10 standard joint (socket). Two of the three limbs (A anc C) of the dilatometer were closed with B-14 ground glass stoppers, and limb B was fixed with a standard B-10 (cone B-14) fused onto a suitable capillary tube (i.d. 1.0 mm) having a Teflon cap with a small orifice to ensure that the pressure inside the capillary tube was equal to the atmospheric pressure. Silicone grease was used on the ground-glass joints. The amount of grease varied between 15 and 20 mg. Even when the entire amount of grease dissolves in the components, it introduces an impurity of 0.01%. This small amount of impurity does not affect directly the measured excess volume as reported by McLure and Swinton (*8*). Stoppers on A and C are interchangeable. This provides for the measurement of excess volume at different concentrations of the components. One of the components was injected into the middle limb of the dilatometer with the help of a hypodermic syringe and fitted with a cone. The liquid in the joint portion enters the capillary. The other two components were introduced successively into the remaining limbs. The weight of each component was determined by weighing the dilatometer before and after introducing the components into the respective limbs. The filled dilatometer, mounted on an iron stand, was immersed in a water thermostat maintained at ±0.01 °C. The dilatometer was allowed to stand in the thermostat until it attained the temperature of the bath. This was indicated by the constancy of the liquid level in the capillary as seen through a traveling microscope which could read to 0.01 mm. The position of the constant liquid level relative to a reference mark on the capillary tube was then read. The liquid in the capillary was drained into limb B by placing the dilatometer in powdered ice, and mixing was effected by rocking the apparatus. This was done to ensure that the liquid in the capillary mixes with the mixture in the dilatometer. The apparatus was then placed in the thermostat, and the position of the liquid level relative to the reference mark was again read. Excess volume V^E_{123} was calculated by using eq 1, where r is the radius of the capillary,

$$V^E_{123} = \pi r^2 \Delta h / (n_1 + n_2 + n_3) \qquad (1)$$

Δh is the change in the liquid level on mixing, and n_1, n_2, and n_3 are the moles of liquids 1, 2, and 3, respectively. Excess volumes were accurate to ±0.003 cm^3 mol^{-1}. Four dilatometers with different capacities were used to cover the mole-fraction range from 0.1 to 0.8.

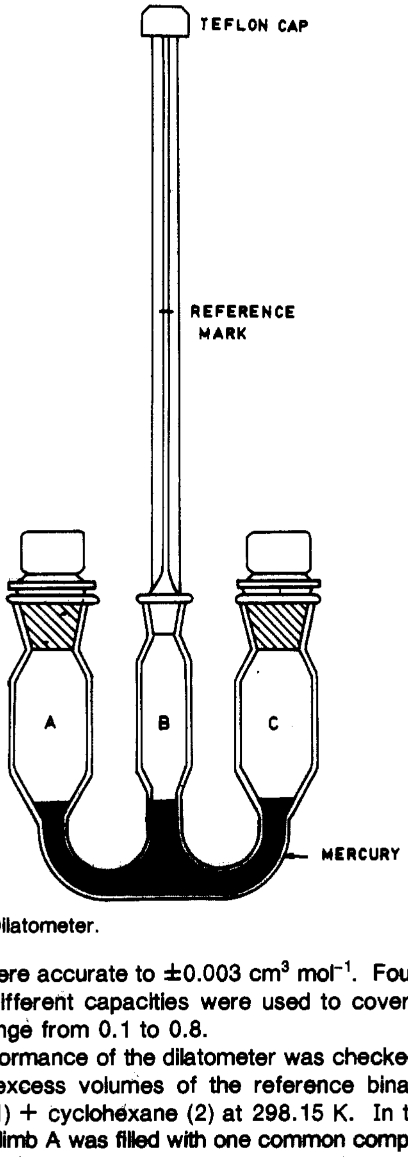

Figure 1. Dilatometer.

The performance of the dilatometer was checked by measuring the excess volumes of the reference binary system: benzene (1) + cyclohexane (2) at 298.15 K. In these measurements limb A was filled with one common component while limbs B and C held the other component. The results of the present investigation and those reported by Stookey et al. (*9*) at 298.15 K are graphically presented in Figure 2. The excess-volume composition curve in the figure shows that the results of the present investigation agree with those of Stookey et al. within the experimental error.

The experimental results for the binary systems of *n*-heptane with 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, and methyl ethyl ketone are included in Figure 3. These were fitted by the method of least squares to the equations given in Table II. The experimental data for the ternary systems methyl ethyl ketone (1) + an alkanol (2) + *n*-heptane (3) are recorded in the third column of Table III.

Table III. Experimental Values for the Excess Volume of Ternary Systems: Methyl Ethyl Ketone (1) + 1-Alkanol (2) + *n*-Heptane (3) at 303.15 K

X_1	X_2	V^E_{123}, cm^3 mol^{-1}	V^E_{123} (a), cm^3 mol^{-1}	ΔV^E_{123}, cm^3 mol^{-1}	V^E_{123} (b), cm^3 mol^{-1}	ΔE^E_{123}*, cm^3 mol^{-1}	$\sigma(V^E)$, cm^3 mol^{-1}
		Methyl Ethyl Ketone (1) + 1-Propanol (2) + *n*-Heptane (3)					
0.7538	0.1287	0.294	0.025	0.269	0.193	0.101	−0.004
0.7211	0.1556	0.328	0.026	0.302	0.196	0.132	0.008
0.6078	0.2912	0.238	0.021	0.217	0.138	0.100	−0.002
0.4794	0.4105	0.228	0.021	0.207	0.133	0.095	−0.003
0.4579	0.4126	0.282	0.031	0.251	0.159	0.123	0.000
0.3235	0.5486	0.246	0.029	0.217	0.138	0.108	0.002
0.2183	0.6865	0.158	0.018	0.140	0.086	0.072	0.000
0.1108	0.7873	0.151	0.018	0.133	0.088	0.063	−0.002
		Methyl Ethyl Ketone (1) + 1-Butanol (2) + *n*-Heptane (3)					
0.7899	0.1245	0.209	0.021	0.188	0.161	0.048	−0.001
0.7771	0.1087	0.286	0.024	0.262	0.206	0.080	0.002
0.6460	0.2395	0.222	0.024	0.198	0.191	0.031	−0.001
0.5350	0.3202	0.224	0.031	0.193	0.212	0.012	−0.004
0.3186	0.5400	0.098	0.028	0.070	0.161	−0.063	0.002
0.2466	0.6364	0.072	0.021	0.051	0.121	−0.049	0.002
0.1261	0.7586	0.111	0.018	0.093	0.094	0.017	−0.003
0.1208	0.7960	0.082	0.015	0.067	0.069	0.013	0.002
		Methyl Ethyl Ketone (1) + 1-Pentanol (2) + *n*-Heptane (3)					
0.7749	0.1062	0.293	0.023	0.270	0.214	0.079	0.001
0.6508	0.2270	0.253	0.021	0.232	0.202	0.051	−0.004
0.5516	0.2939	0.277	0.019	0.258	0.220	0.057	−0.005
0.4399	0.4232	0.143	0.022	0.121	0.163	−0.020	0.001
0.3579	0.4829	0.147	0.022	0.125	0.152	−0.005	−0.001
0.2703	0.6142	0.053	0.013	0.040	0.079	−0.026	0.002
0.1483	0.7194	0.057	0.010	0.047	0.033	0.024	−0.001
0.1228	0.7711	0.036	0.008	0.028	0.011	0.025	0.003
		Methyl Ethyl Ketone (1) + 1-Hexanol (2) + *n*-Heptane (3)					
0.8119	0.0985	0.209	0.019	0.190	0.186	0.023	0.000
0.6933	0.1926	0.229	0.019	0.210	0.212	0.017	0.001
0.5783	0.2621	0.260	0.026	0.234	0.238	0.022	0.001
0.5160	0.3401	0.187	0.026	0.160	0.201	−0.014	0.007
0.4373	0.3975	0.166	0.023	0.143	0.190	−0.024	0.001
0.3797	0.4548	0.131	0.021	0.110	0.165	−0.034	0.000
0.2863	0.5883	0.058	0.014	0.044	0.102	−0.044	−0.002
0.1491	0.7337	0.027	0.010	0.017	0.037	−0.010	−0.004

Table IV. Values of the Constants *A*, *B*, and *C* and $\sigma(V^E)$ at 303.15 K

system	*A*, cm^3 mol^{-1}	*B*, cm^3 mol^{-1}	*C*, cm^3 mol^{-1}	$\sigma(V^E)$, cm^3 mol^{-1}
methyl ethyl ketone (1) + 1-propanol (2) + *n*-Heptane (3)	9.3846	−16.2678	−133.8945	0.004
methyl ethyl ketone (1) + 1-butanol (2) + *n*-heptane (3)	7.8522	−60.1236	−178.3820	0.003
methyl ethyl ketone (1) + 1-pentanol (2) + *n*-heptane (3)	7.3829	−61.3709	−31.1279	0.003
methyl ethyl ketone (1) + 1-hexanol (2) + *n*-heptane (3)	3.5955	−48.8942	49.0982	0.004

Results and Discussion

Excess volume, V^E_{123}, for a ternary mixture containing n_1, n_2, and n_3 mol of components 1, 2, and 3, respectively, is expressed by eq 2, where V^E_{12} is the excess volume per mole

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

of a binary mixture in which the mole fraction of component 1 is $n_1/(n_1 + n_2)$ and 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 of component 3 is $n_3/(n_2 + n_3)$, and V^E_{31} is the excess volume per mole of a binary mixture in which the mole fraction of component 3 is $n_3/(n_3 + n_1)$ and of component 1 is $n_1/(n_3 + n_1)$. The values of V^E_{123} obtained from eq 2 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.

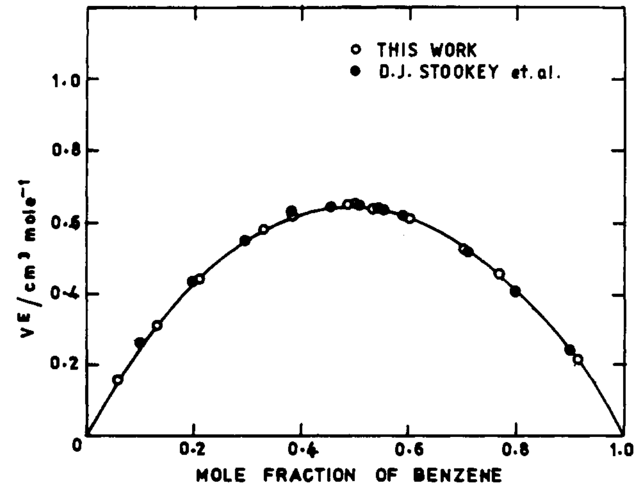

Figure 2. Comparison of our results for V^E of benzene (1) + cyclohexane (2) at 298.15 K with values reported by Stookey et al. (*9*): (○) this work; (●) Stookey et al.

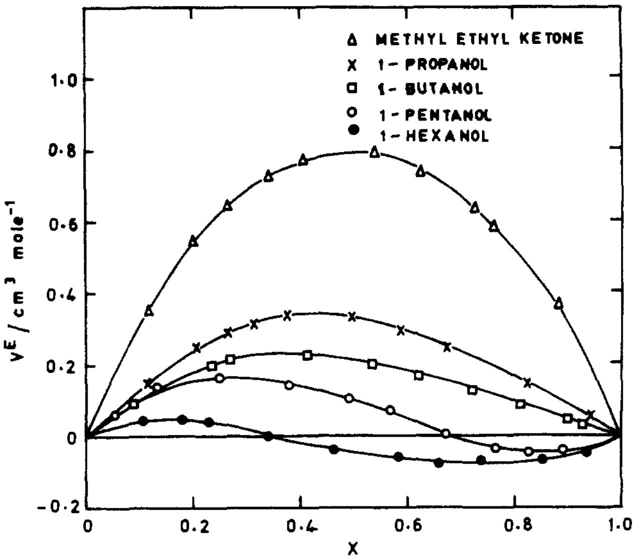

Figure 3. Plot of V^E as a function of composition for methyl ethyl ketone (1) + *n*-heptane (2) and 1-alkanol (1) + *n*-heptane (2) at 303.15 K: (△) methyl ethyl ketone; (X) 1-propanol; (□) 1-butanol; (○) 1-pentanol; (●) 1-hexanol.

The values of this ternary contribution 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 the least squares to eq 3, where

$$V^E_{123} = V^E_{12}{}^* + V^E_{23}{}^* + V^E_{31}{}^* + X_1X_2X_3\,[A + BX_1(X_2 - X_3) + CX_1{}^2(X_2 - X_3)^2] \quad (3)$$

X_1, X_2, and X_3 are the mole fractions of methyl ethyl ketone, an alkanol, and *n*-heptane, respectively, and A, B, and C are constants. The starred quantities were evaluated by using the procedure described elsewhere (*2*) 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 calculated by subtracting the sum $\sum V^E_{ij}{}^*$ from those of the experimental values given in the third column of Table III. 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 3 by the least-squares method. The values of the constants and the standard deviations are presented in Table IV. The analysis shows that eq 3 satisfactorily represents the ternary data for the four systems.

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Vapor–Liquid Phase Equilibrium in the Methane–Ethane–Propane–Toluene–1-Methylnaphthalene System at 220–400 °F and 200–2000 psia

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A static experimental cell was used for vapor–liquid phase equilibrium measurements on a methane–ethane–propane–toluene–1-methylnaphthalene system. Measurements were made at 220, 280, 340, and 400 °F and at pressures from 200 to 2000 psia. The data of this study were well represented by the Soave equation of state. Average errors in the predicted *K* values were ca. 5% for methane, ethane, propane, and toluene and 7% for 1-methylnaphthalene.

Introduction

The well-publicized energy situation in the United States has provided strong impetus toward the conversion of coal to liquid and gaseous products. However, coal-conversion processes often operate in regions of combined temperatures, pressures, and compositions not experienced in typical petroleum processing. Presently, much of the thermodynamic property information used in process calculations is based upon fragmentary data or, more often, upon considerable extrapolation (with respect to temperature and composition) of correlations designed for petroleum processing operations.

This study was designed to obtain experimental data on phase equilibrium in systems which simulate those found in various stages of coal-fluid processing. Based upon a literature survey (*1–4*), a system was chosen for study composed of 7% methane, 3.5% ethane, 3.5% propane, 43% toluene, and 43% 1-methylnaphthalene (weight basis). The results should be useful for testing models for prediction of phase behavior in some stages of coal-conversion processes.

Experimental Section

A static type of apparatus was adopted for vapor-liquid equilibrium measurements. It is similar to the apparatus described by Jacoby (*5*) and has been described in detail elsewhere (*6*).

Temperatures in the cell were measured by a calibrated platinum resistance thermometer to ±0.1 °F. The pressure in the system was monitored by a high temperature pressure

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