that, in the temperature range 350–420 K covered during the first step of the orthorhombic canal complexes investigation, the contribution of the vapor of DCA to the total pressure is negligible and below the instrument sensitivity.

From the pressure–temperature equation determined in this step, the enthalpy change associated with reaction 1 was derived, where X represents the guest.

$$(\mathrm{DCA})_2\mathrm{X(s)} \rightarrow 2\mathrm{DCA(s)} + \mathrm{X(g)} \tag{1}$$

The values $\Delta H^\circ_{383} = 57 \pm 5$ and $\Delta H^\circ_{390} = 72 \pm 5$ kJ mol^{-1} for DCASTY and DCANAF, respectively, were determined, where the errors were estimated by taking into account only the uncertainties in the temperature measurements. In addition, it is interesting to derive the heat of formation of the canal complexes at 298 K according to the condensed phase reaction (eq 2). Since the mean experimental temperatures are very close to 298 K, the ΔH°_T of reaction 1 equal to ΔH°_{298} was assumed. Combining these values with the guest vaporization enthalpies $\Delta H^\circ_{298,\mathrm{vap}} = 42$ (*8*) and 48 kJ mol^{-1} (*9*) for styrene and naphthalene, respectively, we derived the heats associated with reaction 2: $\Delta H^\circ_{298} = 15 \pm 5$ and 24 ± 5 kJ mol^{-1} for DCASTY and DCANAF, respectively.

$$\mathrm{X} + 2\mathrm{DCA} \rightarrow (\mathrm{DCA})_2\mathrm{X} \tag{2}$$

The crystal packing of the bilayers formed by DCA molecules is nearly equal in DCASTY and DCANAF, which present only a very small change for the *b* and *c* parameters, connected with the bilayer structure, and for the *a* parameter, influenced by the separation between two adjacent bilayers (*2*). Moreover, the cell constants of DCASTY and DCANAF are nearly identical with those of the *p*-diiodobenzene–choleic acid, which has the same crystal structure as that found for the phenanthrene-choleic acid (*3*). Thus, a bilayer packing similar to that of Figure 2 occurs in DCASTY and DCANAF. This statement, supported by van der Waals energy calculations (*2*), allows us to suppose that the most important host–guest interactions are due to the methyl groups of DCA which point approximately toward the centers of aromatic rings, giving rise to "polarization bonding" involving the π charge cloud, as observed in the phenanthrene-choleic acid (*3*). Therefore, it is reasonable to hypothesize that the more polarizable the guest molecule, the more strongly the host–guest interaction occurs. In the case of the aromatic hydrocarbons, for example, it can be expected that the attractive energy between DCA and guest molecules improves by increasing the number of the condensed rings. In this connection the enthalpic values found for DCASTY and DCANAF are in agreement with the above-mentioned trend, styrene being anchored to the methyl groups of DCA more weakly than naphthalene.

Such a study, extended to other guest molecules, can provide useful information for the replacement technique employed in the inclusion polymerization (*10*). This technique concerns the replacement by new molecules of the guest molecules released from the canals of their corresponding choleic acids by heating. Obviously, the ease of releasing and replacement depends on the size and the shape of the canals as well as on the interaction energy between DCA and guest molecules. Hence, the releasing temperature, which also affects the replacement procedure, may be expressed as an empirical function of the interaction energy. An estimate of this term can be achieved from vapor-pressure measurements and, more roughly, by means of potential-energy calculations.

Literature Cited

(1) Wieland, H.; Sorge, H. *Z. Physiol. Chem.* **1916**, *97*, 1.
(2) Candeloro De Sanctis, S.; Giglio, E. *Acta Crystallogr., Sect. B* **1979**, *35*, 2650.
(3) Candeloro De Sanctis, S.; Giglio, E.; Pavel, V.; Quagliata, C. *Acta Crystallogr., Sect. B* **1972**, *28*, 3656.
(4) Freeman, R. D. In "The Characterization of High Temperature Vapours"; Margrave, J. L., Ed.; Wiley: New York, 1967.
(5) Piacente, V.; De Maria, G. *Ric. Sci.* **1960**, *39*, 545.
(6) Freeman, R. D.; Searcy, A. W. *J. Chem. Phys.* **1954**, *22*, 762.
(7) Hultgren, R.; Orr, R. L.; Kelley, K. K. "Select Values of Thermodynamic Properties of Metals and Alloys"; Wiley: New York, 1963.
(8) Chaiyavech, P.; Van Winkle, M. *J. Chem. Eng. Data* **1959**, *4*, 53.
(9) Fowler, L.; Trump, N. W.; Vogler, C. E. *J. Chem. Eng. Data* **1968**, *13*, 209.
(10) Miyata, M.; Takemoto, K. *Makromol. Chem.* **1978**, *179*, 1167.

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Densities of Molten KCl–$CuCl_2$ Obtained by the Automated Float Method

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Densities of liquid KCl–$CuCl_2$ mixtures were measured by using the automated float method. The compositions measured in mole fractions of potassium chloride (X_{KCl}) were as follows: 0.4500, 0.5000, 0.6000, 0.6667, and 0.7000. The obtained densities were at each composition fitted to an equation of the form $\rho = A(X) + B(X)(t - 500)$. $A(X)$ and $B(X)$ were again fitted by polynomia of X_{KCl} in the mole fraction range 0.4500–1.0000. Finally all of the measured data were fitted to one equation of the form $\rho = \sum_0^n A_n X^n + (\sum_0^m B_m X^m)(t - 500)$.

The molten KCl–$CuCl_2$ system can be used as a catalyst for production of various chlorinated hydrocarbons (*1*, *2*). In connection with a potentiometric investigation of the KCl–$CuCl_2$ system, density measurements were necessary (*3*). Because of the dark color of the KCl–$CuCl_2$ system and the rather high chlorine pressure (0.5 atm at room temperature) necessary to keep the disproportination of Cu(II) to Cu(I) low, the "automated float method" (*4*–*6*) is one of the few methods suited for such a density examination.

Experimental Section

The automated float method (*4*) is based on the use of a differential transformer to detect the passage of quartz floats

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Table I. Experimental Densities and Temperatures of the Molten KCl-$CuCl_2$ System

densities of floats, g/cm³		measd temp at the given X_{KCl} mole fractions, °C				
at 20 °C	at measd temp	0.4500	0.5000	0.60000	0.6667	0.7000
1.8975	1.8956					619.0(6)[a]
1.8975	1.8955				660.3(8)	
1.9246	1.9226				627.0(8)	
1.9246	1.9228					584.3(6)
1.9653	1.9635				573.6(10)	
1.9653	1.9637					529.9(9)
2.0019	2.0003				525.8(8)	
2.0984	2.0968			484.6(15)		
2.1334	2.1319			443.2(12)		
2.1404	2.1389			435.4(11)		
2.1674	2.1660		519.9(10)			
2.1674	2.1656			403.4(10)		
2.1762	2.1749			394.3(9)		
2.1851	2.1834		501.7(10)			
2.2271	2.2255		460.1(8)			
2.2401	2.2384	507.6(10)				
2.2536	2.2518	493.3(9)				
2.2722	2.2705	475.6(9)				
2.2822	2.2805	466.2(8)				
2.3205	2.3189	428.7(7)				

[a] I.e., 619.0 ± 0.6.

Table II. Linear Density Equations and Molar Volumes of the Molten KCl-$CuCl_2$ System[a]

mole fraction KCl	$A(X)$,[b] g/cm³	$10^3B(X)$, g/(cm³ deg)	SD, g/cm³	molar vol at 500 °C, cm³/mol
0.4500	2.2456(3)	−1.027(9)	0.0005	47.87
0.5000	2.1854(2)	−1.004(9)	0.0004	47.82
0.6000	2.0834(5)	−0.860(6)	0.0005	47.28
0.6667	2.0205(7)	−0.776(7)	0.0007	46.79
0.7000	1.9866(7)	−0.762(8)	0.0005	46.57
1.0000[c]	1.6858(6)	−0.585(3)	0.0005	44.22[d]

[a] For the measured temperature ranges, see Table I. [b] $\rho = A(X) + B(X)(t - 500)$. [c] Values calculated from ref 7. [d] Extrapolated value.

with iron cores as they rise or fall, due to a density change of the melt. Passage temperatures were detected either by chromel-alumel thermocouples (from Pyrotenax) which were calibrated at the freezing points of pure (99.99%) zinc and lead to within ±0.5 °C or better by platinum resistance thermometers (from Degussa).

The KCl used (analytical-grade reagent from Riedel-de Haën) was purified by treatment with HCl gas as described earlier (*5*). The $CuCl_2$ used was obtained by dehydrating reagent-grade material ($CuCl_2 \cdot 2H_2O$). The salt was first dried in an oven at 120 °C. It was then further treated by dry HCl gas at 80 °C. An analysis of material prepared in this way gave a copper content of 47.22 ± 0.04. The theoretical value for $CuCl_2$ is 47.26%.

All handling of the solid salts was performed in a nitrogen-filled glovebox with a measured water content of ~5 ppm and continuous gas purification by forced recirculation through external molecular sieves.

Results

The experimental densities and temperatures of the KCl-$CuCl_2$ system are given in Table I. The densities of the floats used were obtained from 8–10 determinations at room temperature and corrected for the thermal expansion of quartz at the measured temperature. The standard deviation on the measured temperatures is calculated in accordance with the procedure described previously (*4*).

The measured densities are for each measured composition expressed by $A(X)$ and $B(X)$ in Table II. $A(X)$ is the density in g/cm³ at 500 °C and $B(X)$ is the density change per degree. The expression $\rho = A(X) + B(X)(t - 500)$ (where ρ is the density) gives a more satisfactory representation of the measured data than the usually employed equation $\rho = A(X) + B(X)t$. The $A(X)$ and $B(X)$ values for molten KCl are taken from the work by Van Artsdalen and Yaffe (*7*). Since KCl melts at 772 °C, extrapolated values for KCl are used below this temperature. The molar volumes at 500 °C are not far from being a linear function of the composition. The maximum deviation from linearity for the given compositions is −0.6%.

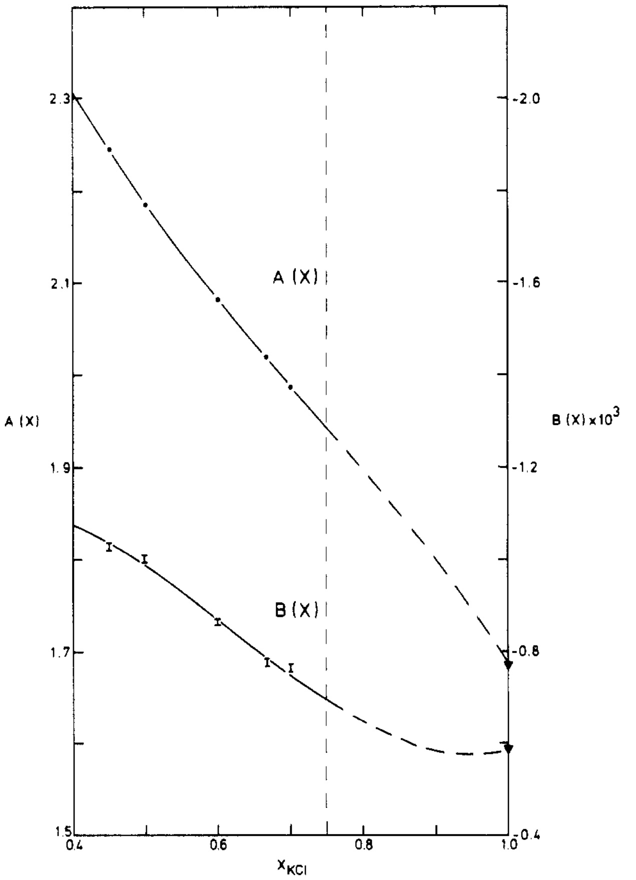

Figure 1. Variations of the parameters $A(X)$ and $B(X)$ vs. mole fraction: curved lines, $A(X) = 3.1138 - 2.9081X + 2.7365X^2 - 1.2565X^3$, $B(X) = 0.7015 \times 10^{-3} + (3.1583 \times 10^{-3})X - (7.0784 \times 10^{-3})X^2 + (3.8034 \times 10^{-3})X^3$; (●, I) this work; (▼) values calculated from ref 7.

J. Chem. Eng. Data 1981, 26, 197-200

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

	$0.4500 \leq X_{KCl} \leq 0.7000$ ($n = 3$, $m = 2$)	$0.4500 \leq X_{KCl} \leq 1.000$ ($n = 3$, $m = 2$)
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.

Literature Cited

(1) Riegel, H.; Schindler, H.; Sze, M. C. *Chem. Eng. Prog.* **1973**, *69*, 89.
(2) Riegel, H.; Schindler, H.; Sze, M. C. *AIChe Symp. Ser.* **1973**, *No. 69*, 96.
(3) Andreasen, H. A.; Brekke, P. B.; Bjerrum, N. J., to be submitted for publication.
(4) Andreasen, H. A.; Bjerrum, N. J.; Foverskov, C. E. *Rev. Sci. Instrum.* **1977**, *48*, 1340.
(5) Andreasen, H. A.; Bjerrum, N. J.; Hansen, N. H. *J. Chem. Eng. Data* **1980**, *25*, 236.
(6) Hansen, N. H.; Bjerrum, N. J. *J. Chem. Eng. Data*, in press.
(7) Van Artsdalen, E. R.; Yaffe, I. S. *J. Phys. Chem.* **1955**, *59*, 118.

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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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