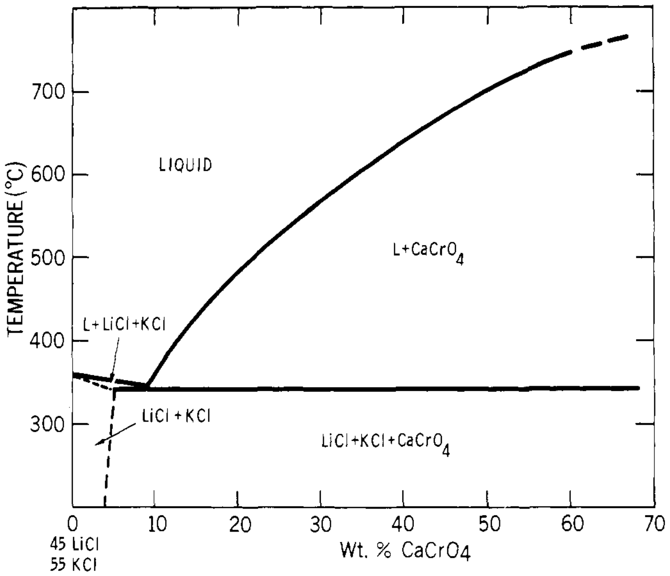

Figure 10. Section E (Figure 5) through the LiCl–KCl–CaCrO$_4$ phase diagram

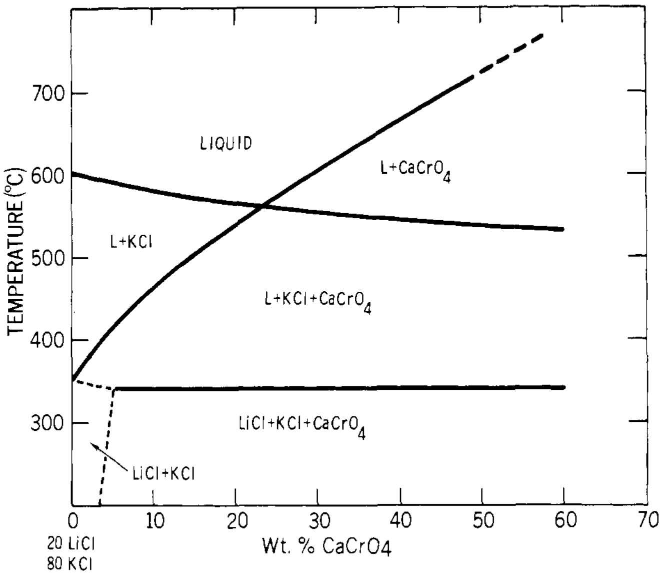

Figure 11. Section F (Figure 5) through the LiCl–KCl–CaCrO$_4$ phase diagram

Table I. Samples Prepared to Verify LiCl–KCl–CaCrO$_4$ Stability

Sample No.	Wt. % CaCrO$_4$	LiCl	KCl	K$_2$CrO$_4$	Li$_2$CrO$_4$	CaCl$_2$
1	9.00	41.00	50.00	...	...	...
2	...	41.00	41.40	11.20	...	6.40
3	...	36.11	50.00	...	7.49	6.40

ACKNOWLEDGMENT

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Density and Viscosity of Mixtures of 1,1,2,2-Tetrabromoethane and 1-Bromododecane

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Measurements of the density and viscosity of mixtures of 1,1,2,2-tetrabromoethane and 1-bromododecane have been carried out at atmospheric pressure over the entire composition range and in the temperature range between 25° and 40° C. The molal volume of a mixture calculated as the mole fraction weighted average of the pure component molal volumes is within 0.14% of the correct value. Several predictive techniques for the visocosity of a liquid binary mixture were unsatisfactory.

IN STUDYING the rheology of suspensions of solid particles, it is often desirable to use a liquid phase which has the same density as the solid particles, a relatively low viscosity, a very low vapor pressure, especially if a multicomponent fluid, a very low mutual solubility with water, and which does not react with the particles. For many solid particles, mixtures of 1,1,2,2-tetrabromoethane and 1-bromododecane meet these criteria. The density and viscosity of such mixtures were determined at atmospheric pressure and in a temperature range near room temperature.

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Table I. Manufacturer's Specifications for Chemicals

1-Bromododecane
Melting point: −11° to −9° C.
Refractive index: $n_D^{20} = 1.4584 \pm 0.0005$

1,1,2,2-Tetrabromoethane
Melting point: 0° to 2° C.
Refractive index: $n_D^{20} = 1.6377 \pm 0.0005$
Specific gravity: $\rho_4^{20} = 2.96$ to 2.97
pH: neutral to universal indicator paper

MATERIALS

Both materials were "White Label" chemicals (Distillation Products) and were used as purchased. The exact purity of the chemicals is not known. The specifications for the chemicals as given by the producer (3) are listed in Table I.

METHODS

The pure chemicals were each weighed in a weighing burette. Each chemical was dispensed into a third weighing burette, and the dispensing burettes were again weighed. Weights were determined on an Ainsworth double-beam balance with a precision of 0.2 mg.

After thorough mixing in the weighing burette, approximately 10 ml. of the mixture was drained into a Cannon-Fenske type capillary tube viscometer. The viscometer and contents were allowed to equilibrate in a constant-temperature bath. Efflux times were determined five times for each mixture; the standard deviation for the mixture efflux times was at most 0.10% of the average efflux time, and generally was about a third of that value.

The viscometer was calibrated in the temperature range in which it was used to obtain the viscosity of mixtures. Both water and ASTM standard viscosity oils were used in the calibration procedure. The Bell-Cannon equation

$$\nu = k_1\theta - k_2\theta^{\ 2}$$

was used to calibrate the instrument. Using this equation to calculate the kinematic viscosity of a mixture, the kinetic energy correction term was never more than 0.2% of the kinematic viscosity. Nevertheless, the correction term was retained in the calculations. The precision of the experimental kinematic viscosity is at least 0.20%. The accuracy is better than the precision.

The density of a mixture was determined by the usual pycnometer technique. Two pycnometers were employed, and they were calibrated with deaerated distilled water in the temperature range of use. The precision of the experimental density values is at least 0.02%.

The temperature of the constant-temperature bath was determined with a mercury-in-glass thermometer which had been calibrated by comparison with a certified ASTM thermometer in the same constant-temperature bath. The accuracy of the temperature values is believed to be 0.03° C. The variation with time of the temperature of the bath was within 0.02° C. of the mean temperature recorded. The same calibrated thermometer and constant-temperature bath were used in making density and viscosity measurements.

RESULTS

Molal Volumes. The experimental results are tabulated in Table II, together with the calculated mixture molal volumes.

When the molal volume of a mixture is plotted against the mole fraction of one of the components, each isotherm appears to be a straight line. A linear least squares technique, using the molal volume as the dependent variable, was used to get an analytical expression between the mixture molal volume and the 1-bromododecane mole fraction. These relationships are given in Table III, together with values of the variance of estimate.

Inspection of the linear relationships for mixture molal volume as a function of composition shows the constants to be linear functions of temperature. Consequently, a linear least squares technique was used to express each constant as a function of temperature. The resulting equation for the mixture molal volume is

$$V = \left(114.86\ \frac{\text{ml.}}{\text{mole}} + 0.0876t\ \frac{\text{ml.}}{\text{mole}\ ^\circ\text{C.}}\right) + \left(120.6\ \frac{\text{ml.}}{\text{mole}} + 0.117t\ \frac{\text{ml.}}{\text{mole}\ ^\circ\text{C.}}\right) X \quad (1)$$

The variance of estimate for the first temperature-dependent constant on the right side of the equation is 0.0001, while that for the second constant is 0.0005.

The difference between mixture molal volume calculated from Equation 1 and the corresponding experimental volume is shown as a function of composition in Figure 1 for all the experimental mixtures. For these mixtures, there is a very small volume change of mixing. Also, the maximum error encountered using Equation 1 is less than 0.15% of the experimental molal volume. A single data point, at 29.95° C. and 1-bromododecane mole fraction of 0.65413, seems to be in error, probably due to an incorrect reading of the pycnometer.

Viscosities. The absolute viscosities of the experimental mixtures are listed in Table II and shown in Figure 2 as a function of temperature and composition. Several methods of predicting the viscosity of a mixture from the data of the pure components were investigated, and the

Table II. Molal Volume and Viscosity of Mixtures

Temp., ° C.	Bromododecane Mole Fraction	Density, Gm./Ml.	Molal Volume, Ml./Mole	Viscosity, Cp.
24.93	0.00000	2.9578	116.88	9.687
	0.15858	2.4183	136.63	7.196
	0.30035	2.0540	154.20	5.936
	0.44932	1.7519	172.59	5.091
	0.61657	1.4809	193.28	4.392
	0.77725	1.2706	213.07	3.877
	1.00000	1.0366	240.44	3.373
29.95	0.00000	2.9462	117.34	8.414
	0.13762	2.4703	134.57	6.506
	0.28551	2.0798	152.98	5.399
	0.42554	1.7887	170.32	4.580
	0.65413	1.4238	198.48	3.787
	0.77735	1.2655	213.92	3.437
	1.00000	1.0322	241.46	3.024
34.96	0.00000	2.9351	117.78	7.313
	0.13631	2.4647	134.93	5.669
	0.28903	2.0633	154.03	4.673
	0.44148	1.7513	173.08	4.027
	0.62149	1.4618	195.48	3.498
	0.75955	1.2809	212.69	3.147
	1.00000	1.0277	242.52	2.689
39.96	0.00000	2.9239	118.23	6.406
	0.14555	2.4278	136.61	5.011
	0.29244	2.0472	155.09	4.238
	0.42859	1.7681	172.14	3.667
	0.63396	1.4382	197.85	3.093
	0.78200	1.2492	216.35	2.781
	1.00000	1.0234	243.54	2.437

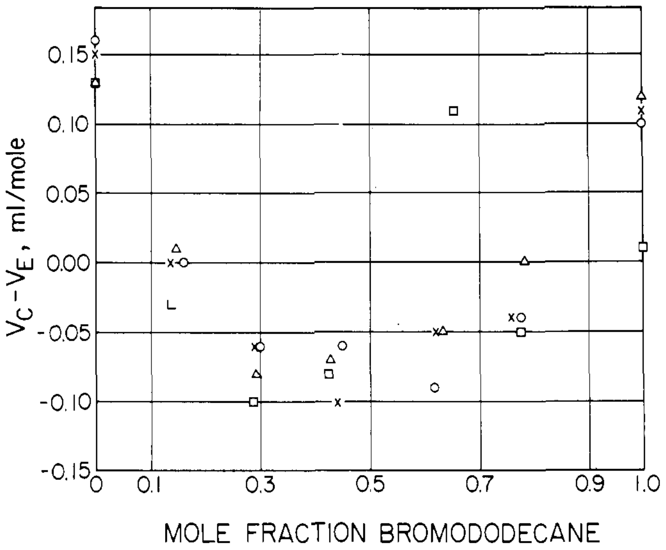

Figure 1. Difference between a mixture specific volume calculated from Equation 1 and experimental specific volume as function of composition and temperature

○ 24.93° C.
□ 29.95° C.
X 34.96° C.
△ 39.96° C.

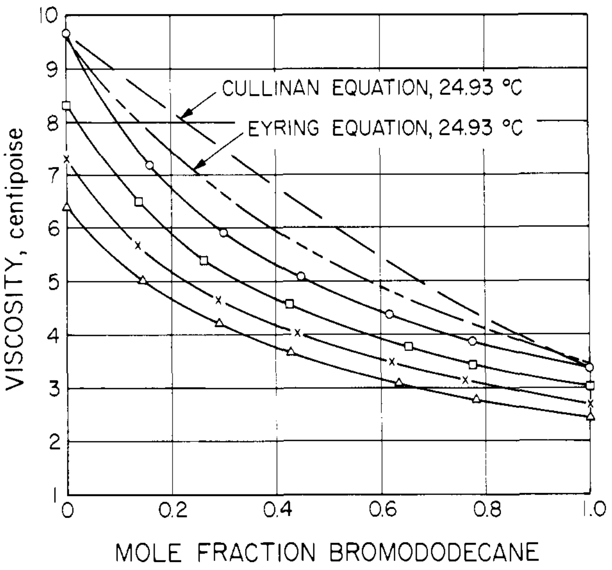

Figure 2. Viscosity of a mixture as a function of composition and temperature; curves predicted by two theories are shown for 24.93° C.

○ 24.93° C.
□ 29.95° C.
X 34.96° C.
△ 39.96° C.

predictions of some of these methods at 24.93° C. are also shown in Figure 2.

Cullinan (*1*) has recently suggested, for mixtures which show no volume change on mixing and radial distribution functions which are independent of composition, the predictive equation

$$\eta = (\eta_1)^{X_1} (\eta_2)^{X_2} \left(\frac{V}{V_G}\right) \tag{2}$$

where

$$V_G = (V_1)^{X_1} (V_2)^{X_2}$$

In view of some of Cullinan's examples, it might be expected that Equation 2 would be a useful correlative tool in this instance.

The predictive equation proposed by Eyring and coworkers (*2*)

$$\eta = \frac{hN}{V} \exp\left[\frac{\Delta G}{RT}\right] \tag{3}$$

was also considered. The value of ΔG for a particular mixture at a given temperature was calculated from

$$\Delta G = X_1 \Delta G_1 + X_2 \Delta G_2 \tag{4}$$

Equations 3 and 4 represent ideal behavior. Eyring found empirically that nonideal mixtures require an additional term in Equation 4, which is proportional to the excess Gibbs free energy of mixing. Lacking data with which to calculate the excess Gibbs free energy of mixing, Equation 4 was used.

The values of ΔG for the pure components were obtained by plotting $\ln(\eta V)$ *vs.* reciprocal absolute temperature for each component; such plots were linear over the experimental range of temperature. A linear least-square technique was used to obtain analytical expressions for the linear plots; the value of ΔG for the 1-bromododecane was 3.883 kcal. per gram mole, and for 1,1,2,2-tetrabromoethane was 4.965 kcal. per gram mole.

The predictions of these two methods are shown in Figure 2; while the predictions of Eyring's equation are better than those from Cullinan's equation, the error in prediction is still appreciable—as much as 9% of the experimental value for some mixtures.

The viscosity-composition isotherms could be represented by the equation

$$\eta = \eta_0 - \frac{x}{ax - b} \tag{5}$$

where η_0, a, and b are functions of temperature. By a linear least squares technique, the values of the constants, a and b, were determined. These values are listed in Table III, along with values of the variance of estimate.

Table III. Equations for Molal Volume and Viscosity Isotherms

Temp., ° C.	Equation, Ml./Mole or Cp.	Variance of Estimate
24.93	$V = 117.04 + 123.5\,X$	0.0105
	$\eta = 9.6865 - \dfrac{X}{0.1124\,X + 0.04647}$	0.000673
29.95	$V = 117.47 + 124.0\,X$	0.0098
	$\eta = 8.4138 - \dfrac{X}{0.1274X + 0.05718}$	0.00148
34.96	$V = 117.93 + 124.7\,X$	0.0105
	$\eta = 7.3128 - \dfrac{X}{0.1542X + 0.06459}$	0.00222
39.96	$V = 118.36 + 125.3\,X$	0.0090
	$\eta = 6.4060 - \dfrac{X}{0.1706X + 0.08246}$	0.000781

Variance of Estimate, $S_e^2 = \sum_{i=1}^{n} (V_{c_i} - V_{e_i})^2/(n-2)$

NOMENCLATURE

a = constant, Equation 5, $cp.^{-1}$
b = constant, Equation 5, $cp.^{-1}$
ΔG = activation energy for viscous flow, cal. per mole
h = Planck's constant
k_1 = constant, cp. per (gram per ml.)(sec.)
k_2 = constant, (cp.)($sec.^2$) per (gram mole)
n = number of points
N = Avogadro's number
t = temperature, ° C.
v = molal volume, ml. per mole
V_G = geometric mean molal volume, ml. per mole
X = mole fraction bromododecane
η = absolute viscosity, cp.
θ = time, sec.
ν = kinematic viscosity, cp. per (gram per ml.)
Σ = summation operator

Superscripts

0 = pure component

Subscripts

1,2 = species 1, species 2
C = calculated value
E = experimental value

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Solubility of C_6-C_8 Aromatic Hydrocarbons in Liquid CO_2

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Solubility data of benzene, toluene, ethylbenzene, o-, p-, and m-xylene in liquid CO_2 are given for temperatures from −15° to −55° C.

THE SOLUBILITY of hydrocarbons in liquid CO_2 was studied by Gore (*14*) as early as 1861, and the first comprehensive review on the subject dates back to 1906 (*7*). Although several decades have since gone by, there are only a few investigators who have published additional data on this subject (*2*-*16*). Of these, the work of Francis (*8*-*13*) stands out as being the most comprehensive, covering the solubility behavior of several hundred binary and ternary systems of liquid CO_2.

Interest in the subject has been reawakened recently because of the possible use of liquid CO_2 as a gentle refining and extracting agent—e.g., in the manufacture of extractable oils and natural products (*1*) and in the isolation of *p*-xylene from a mixture of C_8 aromatic hydrocarbons. The following study has been carried out to obtain more accurate data on the solubility behavior of these aromatic hydrocarbons in this particular solvent.

MATERIALS

CO_2 was obtained from siphon tube cylinders (Air Reduction Co., Richmond, Calif.) and passed through a $CaSO_4$ drying tube prior to use. This CO_2 is at least 99.99% pure.

The aromatic hydrocarbons were obtained from different commercial suppliers and further purified by silica gel treatment and distillation, where necessary. Purity analyses were carried out by determining the freezing point with a platinum resistance thermometer calibrated by the National Bureau of Standards and/or analysis with a Perkin-Elmer 900 gas chromatograph equipped with a flame-ionization detector on a 100-foot by 0.02-inch i.d. support-coated capillary column coated with an MBM-Apiezon-Igepal liquid substrate. Additional analyses with an Aerograph 1520 gas chromatograph equipped with a thermal conductivity detector using a 5-foot by ¼-inch Porapak R column showed that there cannot be more than 0.01% water in the investigated compounds. The purity of the hydrocarbons and the identified impurities are shown in Table I.

EXPERIMENTAL

A sketch of the apparatus is given in Figure 1. A 7.5-inch long, 1-inch i.d. Lab-Crest glass pressure reaction vessel (Fischer and Porter Co., Warminster, Pa.) is connected to a manifold and immersed in an acetone bath. Stirring in the tube is provided by a ½-inch diameter Teflon-covered finned magnetic stirring bar, which is driven by a 2-inch by 1.75-inch U-shaped magnet. A thermocouple, which is inserted through the cross into the glass tube, is used to determine the temperature of the solution. CO_2 is introduced into the system from the cylinder by opening valves *A* and *C*. Excess CO_2 from the vessel is vented into the atmosphere through the side arm via valves *A* and *B*. The dry nitrogen at the end of valve *B* prevents moisture from entering the unit when the system is at atmospheric or subatmospheric pressure. The volume of the solution in the tube is determined with a cathetometer. Liquid levels are measured relative to reference lines which are inscribed on the tube.

The volume of the tube is calibrated with distilled water by weighing in incremental amounts of water and determining the resultant level with a cathetometer. Since measurements are carried out at levels well above the bottom curvature of the tube, the volume of the tube between this point and the top can be computed from

$$V = aH + b$$