Table III. Vapor-Liquid Isotherm at 61° C. in the Ethane–n-Octacosane System

Pressure, Atm.	Composition of Liquid Phase, Mole Fraction Ethane	Molar Volume of Liquid Phase, Ml./G. Mole	Fugacity of Ethane, Atm.
[a]	...	504.9	...
1	0.028	492.1	0.9946
5	0.133	446.8	4.880
10	0.240	400.7	9.489
15	0.338	357.8	13.85
20	0.421	321.8	17.95
25	0.492	290.6	21.81
30	0.552	278.0	25.41
35	0.600	243.2	28.77
40	0.645	224.5	31.88

[a] Normal vapor pressure of n-octacosane.

coefficients for ethane. The standard state for ethane was taken as the hypothetical incompressible liquid of unit mole fraction which obeys Henry's Law. These calculated activity coefficients agreed within 0.2% with those calculated from data taken along the solid-liquid-vapor line at compositions up to 50 mole % ethane.

NOMENCLATURE

ΔH_f = heat of fusion of n-octacosane
L = liquid phase
L_1 = liquid phase rich in heavy hydrocarbon
L_2 = liquid phase rich in ethane
L.C.S.T. = point at which L_1 is identical with L_2
S = solid phase
Type K = point at which two phases are in critical identity in the presence of a third noncritical phase
V = vapor phase
γ = activity coefficient

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Thermodynamics of Solutions-Volume Change on Mixing for Four Systems

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Pure component densities and volume change on mixing were determined for four hydrocarbon systems: 2,2,4-trimethylpentane–toluene, 2,4-dimethylpentane–cyclohexane, cyclohexane–1,4-dioxane, and 2,4-dimethylpentane–1,4-dioxane over the temperature range 28° to 90° C. Maximum values for ΔV^M were 2,4,4-trimethylpentane–toluene, 0.087; 2,4-dimethylpentane–1,4-dioxane, 0.44; cyclohexane-1,4 dioxane, 1.0 ml. per gram mole. Measurements for 2,4-dimethylpentane–cyclohexane indicated that ΔV^M was less than 0.015 ml. per gram mole and within the margin of experimental error. The densities as a function of temperature, and ΔV^M as a function of composition were correlated by empirical functions.

AS PART of a program on thermodynamics of nonelectrolyte solutions, liquid density data were determined for 2,2,4-trimethylpentane, toluene, 2,4-dimethylpentane, cyclohexane, and 1,4-dioxane, and for mixtures of four binary systems of the components. The latter were measured to determine the isothermal volume change on mixing ΔV^M, in order that better energy change on mixing ΔE^M values could be calculated. This work was concurrent with enthalpy of mixing ΔH^M measurements, reported elsewhere (*4*).

EXPERIMENTAL APPARATUS

Pycnometers. Calibrated 25-ml. dual stem borosilicate glass pycnometers were used to determine the densities at 28.00° C.; each stem had a 2-mm. bore × 20-mm. long section, topped by a 0.5-mm. bore × 70-mm. long section with an etched scale to obviate the tedious adjustment of volume by bringing the miniscus exactly to some particular mark. The latter was determined by using a cathetometer.

In order to obtain 5×10^{-6} accuracy, Bureau of Standards Class S weights were used, and weighings on an analytical balance were made to the nearest 0.01 mg. Corrections were made for buoyancy, changes in the lengths of the balance arms, and adsorbed surface moisture. By these precautions densities were determined with a reproducibility of 1×10^{-4}

Expansion Pipet. At elevated temperatures, the density was determined by enclosing the material in a calibrated expansion pipet sealed off with a mercury filled U-tube which was raised and lowered to maintain equilibrium pressure. The pipet was surrounded by circulating water and insulated by a silvered vacuum jacket. The circulating

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[1] Deceased.

water was controlled by a microset differential thermoregulator to ±0.005° C., and the temperature around the pipet was determined to 0.005° C. by means of four long stem calibrated total immersion thermometers read with a cathetometer. The top of the pipet was closed by a Teflon, instead of glass, stopcock to eliminate the use of stopcock lubricant. A bolt with washers, spring, and nut ran lengthwise through the stopcock and permitted a tight seal to be maintained at all times.

MATERIALS

2,2,4-Trimethylpentane, Phillip's spectro grade was of sufficient purity that no purification was needed.

Toluene, Baker's analyzed grade had a density of 0.85951 gram per ml. at 28.00° C. as compared to an interpolated API (*1*) density of 0.85955 gram per ml. and was used without further purification.

2,4-Dimethylpentane, Phillip's pure grade had a density of 0.66573 gram per ml. at 28.00° C. as compared to an interpolated API (*1*) density of 0.66561, and was used without purification.

1,4-Dioxane, Eastman's histological grade had a density of 1.01306 gram per ml. at 28.00° C. Literature values for the density of dioxane are considerably in variance. Frey and Gilbert (*3*) report a density of 1.02687 at 25.00° C. Few and Smith (*2*) report a density of 1.0280 gram per ml. at 25.00° C. Weissberger (*6*) gives a density of 1.03375 at 20.00° C. and uses Frey and Gilbert's density at 25.00° C. Scatchard and Benedict (*5*) report a density of 1.0377 at 20° C. and recommend refluxing 8 hours with $\frac{1}{10}$ of its weight with concentrated HCl to destroy any peroxides which may be present. This was accomplished and after decanting the acid layer and neutralizing with NaOH pellets, the material was dried using successively $CaCl_2$ and sodium; following this the material was fractionated through a Davis Column and the middle two-thirds fraction retained.

Since the main impurity was probably water, the material was dried with sodium metal, refluxed for 4 hours, and finally fractionated through a 6-foot glass helix packed column with a 20 to 1 reflux ratio. From 1.5 kg. charged to the distillation flask, 215 ml. of forerun boiling from 92° to 100.5° C. was collected, and 800 ml. of product (density 28°/4° 1.02434) was collected boiling from 100.5° to 100.8° C.

Cyclohexane, Phillip's pure grade had a density of 0.77031 gram per ml. compared to an interpolated API (*1*) density of 0.77109 gram per ml. To bring the purity up to standard, the cyclohexane was distilled through a 6-foot glass helix packed column, with sodium metal as a drying agent. The initial boiling point with a reflux ratio of 35, was 79° C.; 500 ml. was taken off as forerun, 1500 ml. boiling at 80° C. was taken off as product, and 500 ml. remained as residue. The density of the product was 0.77076 grams per ml.

The product was nitrated in a separatory funnel using 31.5 grams of HNO_3 and 36 grams of H_2SO_4. The acid layer was drawn off, and the product neutralized with NaOH, then washed with four portions of distilled water. The product then was dried with $CaCl_2$ and distilled over sodium. One-hundred milliliters of forerun boiling at 79.5–80.0° C. and 250 ml. of product boiling at 80° C. were taken off, which had a density of 0.77070. The nitration was repeated as above, except the nitrating mixture was stirred and heated in a three-necked flask for 30 minutes before drawing off the acid layer and neutralizing. Density of the distilled product was 0.77056.

RESULTS

Density data were determined as a function of temperature for the pure components and certain selected mixtures corresponding to the approximate maximum ΔV^M (Table I).

Densities of the pure components and various mixtures were determined at 28° C., and volume change on mixing values were calculated for the four systems involved (Table II). ΔV^M for the system 2,4-dimethylpentane–cyclohexane is negligible, within the experimental accuracy of the measurements.

CORRELATION OF RESULTS

The liquid density data for the pure components can be represented by the following temperature function,

$$\frac{\rho}{\rho_0} = 1 + \sum_{i=1}^{n} a_i t^i \qquad (1)$$

where ρ_0 is obviously the density at 0° C.

Table I. Densities at Various Temperatures

T, ° C.	This Work, G./Ml.	*API* 44[a]	This Work, G./Ml.	*API* 44	This Work, G./Ml.	ΔV^M
	2,2,4-Trimethylpentane		Toluene		$x_1 = 0.45754$[b]	
28.00	0.68536	...	0.85951	...	0.76018	0.093
40.00	0.67528	0.6754	0.84803	0.8485	0.74944	0.096
50.00	0.66680	0.6670	0.83851	0.8392	0.74045	0.098
60.00	0.65845	0.6585	0.82913	0.8300	0.73164	0.092
70.00	0.64991	0.6498	0.81948	0.8208	0.72252	0.103
80.00	0.64062	0.6408	0.80971	0.8115	0.71321	0.085
90.00	0.64141	0.6314	0.79985	0.8023	0.79379	0.045
	2,4-Dimethylpentane		1,4-Dioxane		$x_1 = 0.68200$	
28.00	0.66573	...	1.02434	...	0.73868	0.440
40.00	0.65478	0.6550	1.01041	...	0.72690	0.458
50.00	0.64560	0.6461	0.99883	...	0.71709	0.468
60.00	0.63650	...	0.98759	...	0.70736	0.482
70.00	0.62692	...	0.97600	...	0.69718	0.488
	Cyclohexane		1,4-Dioxane		$x_1 = 0.58884$	
28.00	0.77112	0.7711	1.02434	...	0.85255	0.988
40.00	0.75946	...	1.01041	...	0.83985	1.035
50.00	0.74972	...	0.99883	...	0.82930	1.070
60.00	0.74025	...	0.98759	...	0.81901	1.102
70.00	0.73020	...	0.97600	...	0.80816	1.152

[a] For cyclohexane, API is interpolated. [b] x_1 refers to the first component of the system listed.

Table II. Densities and ΔV^M at 28° C.

2,2,4-Trimethylpentane–Toluene

x_1	ρ, G./Ml.	ΔV^M, Ml./G. Mole
0.00000	...	0
0.264296	0.79671	0.0576
0.390673	0.77209	0.0830
0.426480	0.76564	0.0856
0.457542	0.76016	0.0978
0.462568	0.75938	0.0917
0.462761	0.75924	0.0958
0.502218	0.75272	0.0810
0.744929	0.71645	0.0527
1.000000		0

2,4-Dimethylpentane–1,4-Dioxane

x_1	ρ, G./Ml.	ΔV^M Ml./G. Mole
0.00000	1.02434	0
0.144289	0.94136	0.129
0.280521	0.87674	0.256
0.487653	0.79761	0.391
0.625838	0.75446	0.434
0.739673	0.72346	0.429
0.873353	0.69184	0.274
1.000000	0.66573	0

Cyclohexane–1,4-Dioxane

x_1	ρ, G./Ml.	ΔV^M, Ml./G. Mole
0.000	1.02434	0
0.249537	0.94247	0.656
0.500607	0.87382	0.978
0.588843	0.85255	0.988
0.750576	0.81716	0.824
1.00000	0.77112	0

2,4-Dimethylpentane–Cyclohexane

x_1	ρ, G./Ml.	ΔV^M Ml./G. Mole
0.00000	0.77112	0
0.296694	0.73212	0.0144
0.404594	0.71999	0.004
0.512433	0.70874	−0.014
1.00000	0.66573	0

$\Delta V^M = V_x - (X_1 V_1 + X_2 V_2)$

1 Ml. = 1.000028 cc.

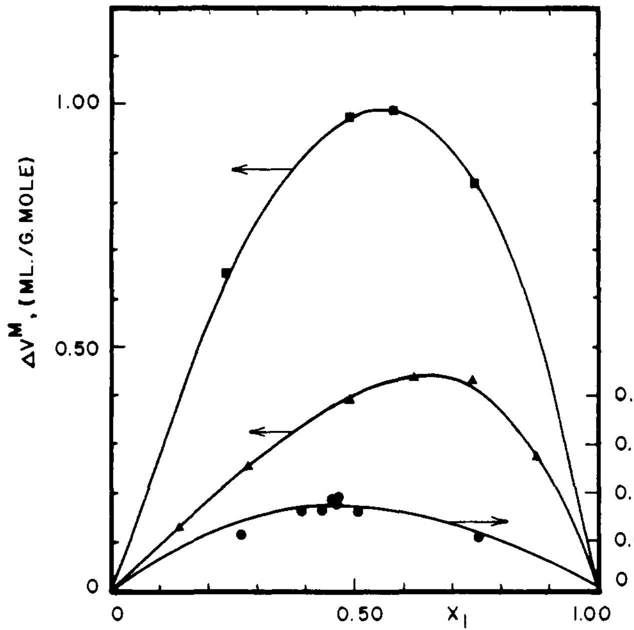

Figure 1. ΔV^M for the binary systems at 28° C.

Curves are calculated; points are experimental

● 2,2,4-Trimethylpentane–toluene

▲ 2,4-Dimethylpentane–1,4-dioxane

■ Cyclohexane–1,4-dioxane

Table III. Values of Pure Component Constants

	2,2,4-Trimethylpentane C_8H_{18}	Toluene C_7H_8	2,4-Dimethylpentane C_7H_{16}	1,4-Dioxane $C_4H_8O_2$	Cyclohexane C_6H_{12}
M	114.224	92.134	100.198	88.104	84.156
ρ_0	0.71023	0.88719	0.69357	1.05968	0.80192[a]
$a_1 \times 10^2$	−0.13279	−0.11550	−0.15626	−0.12820	−0.15348
$a_2 \times 10^4$	+0.035224	+0.017933	+0.058947	+0.039607	+0.072894
$a_3 \times 10^6$	−0.027532	−0.012407	−0.045422	−0.025141	−0.051597
Av. Dev.	7.0×10^{-5} 0.011%	3.0×10^{-5} 0.0036%	3.3×10^{-3} 0.0052%	4.7×10^{-5} 0.0047%	5.4×10^{-5} 0.0072%

[a] This is a hypothetical density since cyclohexane freezes at +6.554° C. (*1*).

Table IV. Values of Mixture Constants at 28° C.

	2,2,4-Trimethylpentane–Toluene	2,4-Dimethylpentane–1,4-Dioxane	Cyclohexane–1,4-Dioxane
B_0	0.3396	1.6212	3.914
B_1	−0.03934	0.9863	0.8976
B_2	0	0.2651	0.1545
Max. ΔV^M, approx.	0.090	0.440	0.988
Av. Dev.	0.007	0.003	0.0004

The temperature derivative of density and the coefficients of expansion can be obtained from Equation 1 and are,

$$\left(\frac{\partial \rho}{\partial t}\right) = \rho_0 \sum_{i=1}^{n} (i a_i t^{i-1}) \tag{2}$$

$$\alpha_0 \equiv \frac{1}{V_0}\left(\frac{\partial V}{\partial t}\right) = \frac{-1}{\rho_0}\left(\frac{\partial \rho}{\partial t}\right) = -\sum_{i=1}^{n} (i a_i t^{i-1}) \tag{3}$$

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial \rho}{\partial t}\right) = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial t}\right) = -\sum_{i=1}^{n} (A_i t^{i-1}) \tag{4}$$

where,

$$A_1 = a_1;\ A_2 = (2a_2 - a_1^2);\ A_3 = (3a_3 - 3a_1a_2 + a_1^3);\ A_4 = (4a_4 - 4a_1a_3 - 2a_2^2 + 4a_1^2a_2 - a_1^4) \tag{5}$$

Values of the α-constants, determined by least squares, for the pure components are given in Table III.

The volume change on mixing data can be correlated by a typical composition function (*4*),

$$\Delta V^M \text{(ml./gram mole)} = X_1X_2 \sum_{i=1}^{n} B_i (X_1 - X_2)^i \tag{6}$$

least squares values of the B-constants are given in Table IV for the three systems at 28.00° C.

Figure 1 presents the experimental ΔV^M values and the least squares curves. Also, Table I shows that the approximate maximum ΔV^M values are fairly independent of temperature; in the two systems with dioxane the values appear to increase slightly.

NOMENCLATURE

A_1, A_2, A_3, A_4 = Constants in empirical coefficient of expansion function, Equation 4
a_1, a_2, a_3, a_4 = Constants in empirical density function, Equation 1
B_0, B_1, B_2 = Constants in empirical ΔV^M function, Equation 6
ΔE^M = Energy change on mixing
ΔH^M = Enthalpy change on mixing
M = Molecular weight
t = Temperature, ° C.
V, V_0, V_x = Volume, volume at 0° C., and volume of the mixture, respectively
ΔV^M = Volume change on mixing
X_1, X_2 = Mole fractions of components 1 and 2, respectively

Greek Letters

α, α_0 = Coefficient of expansion, coefficient of expansion at 0° C., respectively
ρ, ρ_0 = Density, density at 0° C., respectively

Standard mathematical operators have not been included.

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Vapor Pressure of Fluoroalcohols

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The vapor pressures of the following fluoroalcohols were measured in the range of temperatures between 0° C. and room temperature: 2,2,2-trifluoroethanol (T.F.E.); 2,2,3,3,3-pentafluoropropanol (P.F.P.); 2,2,3,3,4,4,4-heptafluorobutanol (H.F.B.).

IN CONNECTION with a study of solvents for polymers, the vapor pressures of three fluoroalcohols were measured: 2,2,2-trifluoroethanol (T.F.E.); 2,2,3,3,3-pentafluoropropanol (P.F.P.); 2,2,3,3,4,4,4-heptafluorobutanol (H.F.B.). The purity of each sample was determined from the presence of only a single significant peak in the vapor phase chromatogram. Alcohol P.F.P. was purified to this standard by preparative scale vapor phase chromatography.

A small sample of the alcohol (1 to 2 cc.) was placed in a tube connected to a mercury manometer (*1*) and to a vacuum system. After degassing the specimen by several successive freezing and thawing cycles under vacuum, the vapor pressures were measured over the range of temperatures between 0° C. and room temperature. Pressures were measured by means of a cathetometer capable of being read to ±0.005 cm. Temperatures were measured by a calibrated platinum resistance thermometer and were accurate to ±0.05°.

Table I. Vapor Pressures of Fluoroalcohols

2,2,2-Trifluoroethanol		2,2,3,3,3-Pentafluoropropanol		2,2,3,3,4,4,4-Heptafluorobutanol	
Temperature, ° C.	Vapor pressure, mm.	Temperature, ° C.	Vapor pressure, mm.	Temperature, ° C.	Vapor pressure, mm.
−0.40	13.55	0.15	8.31	0.00	6.73
0.30	13.80	3.00	10.45	5.10	9.75
2.25	16.05	3.70	10.80	7.15	11.40
4.10	18.55	5.40	12.40	9.35	12.90
5.85	21.00	5.80	12.70	9.80	13.10
7.55	23.55	7.60	14.55	11.00	14.75
8.75	25.60	8.70	15.75	13.20	17.30
9.30	26.50	9.70	17.00	15.20	18.80
11.10	29.90	11.40	19.10	15.35	19.55
12.40	32.85	12.70	20.90	16.90	21.25
15.00	38.65	14.90	24.30	18.40	23.25
16.80	43.15	15.20	24.60	19.90	24.15
19.80	52.05	17.50	28.85	21.40	27.40
20.60	54.40	18.25	30.45	23.90	31.90
23.10	63.35	20.10	34.15	24.80	34.15
25.40	72.50	20.65	35.55		
		22.40	39.30		
		23.05	41.00		

Table II. Values of *A* and *B* and the Probable Error of Estimate of log *P*

Fluoroalcohol	*A*	*B*	Probable Error of Estimate of log *P*
2,2,2-Trifluoroethanol	9.651	2325	2.92×10^{-3}
2,2,3,3,3-Pentafluoropropanol	9.921	2459	2.10×10^{-3}
2,2,3,3,4,4,4-Heptafluorobutanol	9.173	2277	5.74×10^{-3}

RESULTS

Table I shows the vapor pressures of each alcohol as a function of temperature determined from two samples freshly distilled into the system. The best straight line through the points of a plot of log (pressure) *vs.* reciprocal temperature was computed by the method of least squares, the data being fitted to an equation of the form:

$$\log P = A - B/T$$

where P = vapor pressure in millimeters, and A and B are constants. T is absolute temperature. Table II shows the calculated values of A and B together with the probable error of estimate of a calculated log P.

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