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Thermodynamics of Solutions

Low-Temperature Densities and Excess Volumes of *cis*-Pentene-2 and Mixtures

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Temperature-dependent densities were determined for *n*-pentane and *cis*-pentene-2 from 25°C down to approaching the triple points. Excess volumes at 25°C were determined for binary mixtures of *cis*-pentene-2 with *n*-pentane, acetonitrile, toluene, and diethyl ether; all showed negative deviations except the mixture with diethyl ether which was slightly positive. The densities as a function of temperature and excess volumes as a function of composition were correlated by empirical functions.

As part of a continuing program on thermodynamics of solutions, liquid density data were determined for *cis*-pentene-2, *n*-pentane, toluene, acetonitrile, and diethyl ether, and mixtures of the latter four components with *cis*-pentene-2. The work was concurrent with infrared shift measurements as a function of density to determine intermolecular field effects.

EXPERIMENTAL

Pycnometers. The type of pycnometer used for the room-temperature densities of the pure components and mixtures, and the method of use have been described previously (*9*). By calibration, the pycnometer used was determined to have a stem cross-sectional area of 0.002351 ml/cm and a volume of 30.65259 ml.

Two modified Lipkin bicapillary pycnometers (*2*) were used for the low-temperature measurements, and consisted of a bulb blown into a piece of capillary tubing with two vertical graduated sections, one rising from the top and the other making a bend from the bottom, and then rising vertically. The top of each capillary was fitted with a $^{7}/_{15}$ ground glass cap, to reduce vaporization loss and sample contamination. The graduated sections were 20 cm × 1 mm i.d. borosilicate glass capillary. The bulb volume and stem cross sections were; pycnometer #1, 4.12563 ml, 0.0096900 ml/cm; pycnometer #2, 3.72290 ml, 0.0096285 ml/cm.

Room-Temperature Bath. The volume measurements were made in a well-stirred water bath, controlled by a Melabs CTC-1A, proportional controller (*8*), using a 500-Ω platinum resistance sensing element and a 200-W electric heater. The temperature was measured with a short-range Kessler, precision mercury-in-glass thermometer, with 0.05°C smallest scale division. The liquid level in the pycnometer, and the mercury level in the thermometer were read by a cathetometer with a vernier scale.

Low-Temperature Bath. A constant-temperature refrigerated bath was used for the low-temperature densities. The system consists of an outer bath, a large strip-silvered glass dewar, and an inner bath made of a closed-off section of glass pipe. The pycnometer rests in the inner bath. The bath liquid (both baths) is a mixture of low-freezing point liquid hydrocarbons, a 60–40 mol % isopentane and 2-methylpentane.

The outer bath is cooled by flowing liquid nitrogen through coils in the bath. A copper-constantan thermocouple in the bath senses the temperature and provides a signal to an on-off temperature controller, which actuates a solenoid valve regulating the flow of liquid nitrogen. The temperature controller is a West Instrument Corp. Model JS-14 on-off controller (*14*), and the solenoid valve is an ITT model K27 35 psi, liquid nitrogen solenoid valve. The outer bath vessel is a pyrex vacuum dewar, 25 cm i.d. × 40 cm deep, with a $^{3}/_{4}$ in. wide unsilvered stripe.

The inner bath is cooled by the outer bath and heated by heat leakage into it. The temperature is controlled by a 250-W heater, actuated by a Melabs CTC-1A Proportional Temperature Controller (*8*) with a platinum resistance sensing element. The inner bath temperature can be maintained at some temperature above the mean outer bath temperature. The heater is a 50-Ω coil of #26 B&S Nichrome wire, 650 cm long, coiled into a multiple helix. The inner bath is a 10 cm i.d. × 36 cm deep section of glass pipe, closed off at the bottom. Each bath is stirred through a pulley and belt system by a Precision Scientific Co. 1525 rpm, 20-W motor, with a variable speed control.

The entire bath system is enclosed in an insulated box, with a port in the front for viewing the pycnometer. A small neon

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Table I. Measured Densities of Pure Materials at 25°C

Substance		ρ, g/ml	Lit., ρ, g/ml
Distilled water (for calibration check)		0.99707	0.99707 (*3*)
		0.99707	
		0.99707	
		0.99708	
	Av	0.99707	
cis-Pentene-2		0.65147	0.6504 (*1*)
		0.65158	
	Av	0.65152	
n-Pentane		0.62140	0.62139 (*1*)
		0.62139	
Toluene		0.86228	0.86230 (*1*)
Acetonitrile		0.77674	0.7766 (*7*)
		0.77671	
Diethyl ether		0.70812	0.7077 (*12*)
		0.70941	
		0.70941	

Table II. *cis*-Pentene-2 Properties

	Lit.
Critical temp, 201.8°C	(*6*)
Critical pressure, (36.3) atm	(*6*)
Critical density, (0.237), g/ml	(*5*)
Normal boiling point, 36.942°C	(*1*)
Triple point temp, −151.39°C	(*13*)
ΔH fusion at t_p, 1699.7 ± 1.3 cal/g-mol	(*13*)
ΔS fusion at t_p, 13.955 cal/mol K	(*13*)
Cryoscopic constant A, 0.05768 mol/°C	(*1*)
Cryoscopic constant B, 0.0048 mol/°C	(*1*)

bulb is mounted inside the box directly behind the bath system to aid in viewing inside the bath. The temperature of the inner bath (sample temperature) was measured with a calibrated iron-constantan thermocouple using a L&N Model 8690-1 Potentiometer and a L&N Model 9834-1 Electronic DC Null Detector. The thermocouple was calibrated at the ice point and the boiling point of liquid nitrogen.

Errors. Three experimental quantities were measured: temperature, density, and composition. An error analysis was made and led to the following estimates of error: temperature, ±0.005°C; density, $\pm 2 \times 10^{-6}$ to 7×10^{-5} g/ml; mole fraction, $\pm 8 \times 10^{-5}$; excess volume determined from densities was estimated at $\pm 3 \times 10^{-4}$ ml/g-mol.

MATERIALS

The *cis*-pentene-2 used was Phillips' Technical grade, specified as being 95 mol %, with 5% impurities, primarily the *trans*-isomer. The *n*-pentane used was Fisher spectroquality; the toluene, acetonitrile, and diethyl ether were Matheson spectroquality materials, all having <1 mol % impurities. All materials, except acetonitrile, were refluxed over P_2O_5 to remove water. Since the acetonitrile dissolved some of the P_2O_5, it was refluxed at boiling to remove dissolved gases.

The densities of all pure components were measured at 25.00°C and are presented in Table I; the values are in good agreement with accepted literature values.

RESULTS

Lenoir et al. (*6*) reported the critical properties of *cis*-pentene-2 to be 201.8°C and 36.3 atm, for a sample obtained from the same source. Doss (*4*) reports the critical properties of 2-pentene as 40.4 atm and 202.4°C, and the freezing point of *cis*-pentene-2 as −179°C. These values appear to be estimates and not measurements. The freezing point value appears to be completely out of range; Todd et al. (*13*) report a measured value of −151.39°C. Fox (*5*), Seyer (*11*), and API Project 44 (*1*) present liquid density data; the Seyer data were determined in 1931, before the two structural isomers were isolated.

For purposes of this work, the values presented in Table II

Table III. Measured Densities of *n*-Pentane and *cis*-Pentene-2

t, °C	ρ, g/ml	ρ, g/ml (*1*)
	n-Pentane	
25.00	0.62139[a]	0.62139
17.2	0.6290	0.6287
1.14	0.6447	0.6442
−14.06	0.6592	0.6586
−31.20	0.6750	0.6740
−33.70	0.6773	0.6763
−47.50	0.6900	0.6886
−59.50	0.7017	0.6992
−61.80	0.7027	0.7012
−76.70	0.7170	0.7141
−77.60	0.7167	0.7148
−93.40	0.7320	0.7287
−95.70	0.7326	0.7309
−112.60	0.7495	0.7463
−124.50	0.7594	0.7569
−129.72 t_p	(0.7643)	
	cis-Pentene-2	
25.00	0.65152[a]	0.6504
16.50	0.6614	
1.10	0.6772	
−14.20	0.6926	
−30.20	0.7087	
−44.80	0.7227	
−61.25	0.7387	
−75.75	0.7526	
−90.75	0.7675	
−108.60	0.7869	
−129.10	0.8014	
−138.00	0.8193	
−151.39 t_p	(0.8307)	

[a] Measured with 30-ml pycnometer.

Table IV. Excess Volumes of *cis*-Pentene-2 Mixtures at 25°C

Solvent	Mole fraction, *cis*-pentene-2	Vol, ml/g-mol	V^E, ml/g-mol
n-Pentane	1.0000	107.649	0
	0.7049	110.037	−0.111
	0.4923	111.664	−0.282
	0.2618	113.782	−0.114
	0.000	116.112	0
Acetonitrile	1.0000	107.649	0
	0.7433	93.342	−0.241
	0.5983	85.264	−0.374
	0.2480	66.179	−0.264
	0.000	52.854	0
Toluene	1.0000	107.649	0
	0.7579	107.601	−0.129
	0.4986	107.404	−0.435
	0.2552	107.691	−0.240
	0.000	108.028	0
Diethyl ether	1.000	107.649	0
	0.5025	106.234	0.158
	0.5032	106.317	0.239
	0.000	104.487	0

$V^E = V - (X_1V_1 + X_2V_2)$

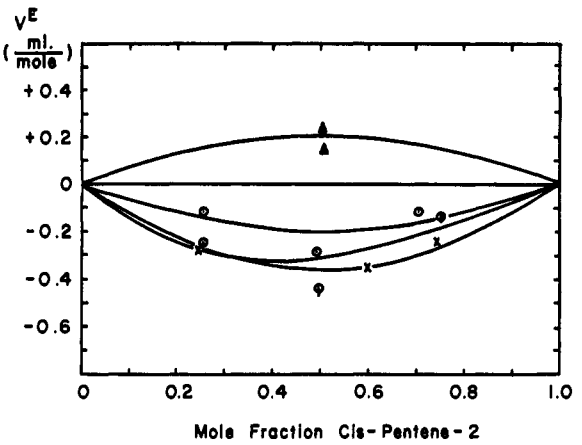

Figure 1. V^E for mixtures at 25°C

× acetonitrile ⊙ n-pentane
φ toluene △ diethylether

Table V. Values of Pure Component Constants

	n-Pentane	*cis*-Pentene-2
M	72.146	70.130
ρ_0	0.64580	0.67850
$a_1 \times 10^3$	−1.4811	−1.4820
$a_2 \times 10^6$	−1.1044	−1.0715
$a_3 \times 10^9$	−6.0969	−7.0662
$a_4 \times 10^{11}$	−1.1788	...
Av dev	4.37×10^{-4} (0.040%)	1.86×10^{-3} (0.178%)

were used; the critical volume was estimated by currently accepted methods (*10*).

Our measure densities for *n*-pentane and *cis*-pentene-2 from 25°C down to approaching the triple point are presented in Table III, and the excess volumes for the four mixtures are given in Table IV. The V^E values for the diethyl ether mixture were quite small; consequently, only two points at about 50 mol % were determined.

CORRELATION OF RESULTS

The empirical correlation functions for the density as a function of temperature and excess volume as a function of mole fraction are

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

and

$$V^E = X_1 X_2 \sum_{i=0}^{n} B_i (X_1 - X_2)^i \qquad (2)$$

The constants obtained by a least-squares fit of the density function for *n*-pentane and *cis*-pentene-2 are presented in Table V. The constants for the excess volume function for the four mixtures studied are presented in Table VI. Figure 1 is a plot of the experimental V^E values along with the least-squares curves.

Table VI. Values of Mixture Constants at 25°C

	cis-Pentene-2 with			
	n-Pentane	Acetonitrile	Toluene	Diethyl ether
B_0	−0.75052	−1.4087	−1.2397	0.79403
B_1	...	..	0.57231	...
Max V^E (approx.)	−0.188	−0.352	−0.325	+0.199
Av dev	0.057	0.021	0.073	0.040

NOMENCLATURE

$a_1, a_2, a_3 \ldots$ = constants in empirical density function
$B_0, B_1, B_2 \ldots$ = constants in empirical V^E function
M = molecular weight
t = temperature, °C
V, V_1, V_2, V^E = mole volumes: total, component 1, component 2, and excess, respectively
x_1, x_2 = mole fractions
ρ, ρ_0 = density (g/ml), density at 0°C, respectively
$\Delta H, \Delta S$ = enthalpy change, entropy change, respectively

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