y_i vapor mole fraction of component i

Registry No. CO_2, 124-38-9; 2,2-dimethylpropane, 463-82-1.

Literature Cited

(1) Cheng, H.; Pozo de Fernández, M. E.; Zollweg, J. A.; Streett, W. B. *J. Chem. Eng. Data* **1989**, *34*, 319.
(2) Pozo de Fernández, M. E.; Zollweg, J. A.; Streett, W. B. *J. Chem. Eng. Data* **1989**, *34*, 324.
(3) Shah, N. N.; Zollweg, J. A.; Streett, W. B. *J. Chem. Eng. Data*, to be submitted for publication.
(4) Schwartz, A. S.; Donnelly, H. G. *Chem. Eng. Prog. Symp. Ser.* **1968**, *64*, 44.
(5) Stead, K.; Williams, J. M. *J. Chem. Thermodyn.* **1980**, *12*, 265.
(6) Leu, A.-D.; Robinson, D. B. *J. Chem. Eng. Data* **1988**, *33*, 313.
(7) Pozo, M. E.; Streett, W. B. *J. Chem. Eng. Data* **1983**, *29*, 324.
(8) Chang, E.; Calado, J. C. G.; Streett, W. B. *J. Chem. Eng. Data* **1982**, *27*, 293.
(9) Tsang, C. Y.; Streett, W. B. *J. Chem. Eng. Data* **1981**, *26*, 155.
(10) Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197.
(11) Peng, D.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
(12) Panagiotopoulos, A. Z.; Reid, R. C. In *Equations of State*; Chao, K. C., Robinson, R. L., Eds.; ACS Symposium Series 300; American Chemical Society: Washington, DC, 1986; p 570.

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Liquid-Phase Excess Enthalpies for the Binary Systems of 1,3-Dioxolane with *n*-Pentane, 3-Methylpentane, or Methylcyclopentane

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Enthalpies of mixing H^E for the binary systems of 1,3-dioxolane with *n*-pentane, 3-methylpentane, or methylcyclopentane were measured by means of an isothermal flow microcalorimeter as a function of composition, under atmospheric pressure and at 298.15 K. All these systems show endothermic mixing with maxima at a mole fraction of about 0.5. Qualitative considerations are added to explain the effects of branching and cyclization on H^E.

Introduction

As a continuation of a long-term study on the thermodynamic properties of mixtures containing 1,3-dioxolane as a common solvent, we report in the present paper the liquid-phase enthalpies of mixing (excess enthalpies) for the binary systems of 1,3-dioxolane with *n*-pentane, 3-methylpentane, or methylcyclopentane.

Other authors have studied the excess enthalpies for mixtures of several cyclic diethers with *n*-alkanes of different chain length (*1*, *2*).

Taking as a basis the pentane structure, the purpose of this paper is also to study the effects of ring closure, the increasing number of ring atoms and side groups in the cyclic structure on the energy interactions responsible for the measured excess enthalpies when mixtures with 1,3-dioxolane are considered.

Chemicals

1,3-Dioxolane, Fluka product, purum, analytical grade 99%, was allowed to stand over a saturated solution of sodium bisulfite so as to remove any aldehydes. It was further purified by refluxing for about 10 h over Na wire in N flow, then distilled over Na, and finally fractionated on a Vigreux column. The fraction boiling in the range 347–348 K was collected.

Methylpentane and methylcyclopentane were Carlo Erba products, analytical grade respectively 99% and 98.5%, while *n*-pentane was a Merck product, analytical grade 99%.

Table I. Densities ρ of Pure Components as a Function of Temperature T; Coefficients A and B, Equation 1; Standard Deviations $\sigma(\rho)$,; and Correlation Coefficients R

	n-pentane		3-methylpentane		methylcyclopentane	
	T/K	ρ/(kg m^{-3})	T/K	ρ/(kg m^{-3})	T/K	ρ/(kg m^{-3})
	295.75	623.96	293.35	664.25	293.55	748.30[c]
	296.25	623.53	294.15	663.50	295.55	746.51
	297.05	622.77	294.85	662.81	296.75	745.37
	298.65	621.14[a]	296.15	661.75	299.35	742.89
	299.35	620.41	297.25	660.66	299.85	742.40
	300.75	619.10	298.25	659.94[b]	303.15	739.28
	301.65	618.12	298.75	659.33	303.75	738.69
			299.45	658.67	304.75	737.94
			302.25	656.14	305.95	736.68
			303.45	654.95	306.45	736.14
A	646.372		682.753		767.571	
B	−0.98996		−0.91606		−0.94301	
$\sigma(\rho)$	0.03		0.06		0.02	

$R = 0.999$

[a] At $T = 298.15$; $\rho = 621.39$ (*9*). [b] At $T = 298.15$; $\rho = 659.76$ (8). [c] At $T = 293.15$; $\rho = 748.64$ (8).

The commercial products were purified by passing through a column filled with silver nitrate on alumina, to remove traces of olefins and aromatics, and then fractionated.

The pure liquids were finally stored over molecular sieves type 4A (C. Erba). After these treatments, a gas chromatographic analysis gave no evidence of significant impurities.

Calorimetric Measurements

Calorimetric measurements at 298.15 K were made by means of an LKB Model 2107 flow microcalorimeter (LKB, Produkter AB, Bromma, Sweden) described elsewhere (*3*). Details on calibration, analytical measurements, and the accuracy of the results are given in ref 4. The performance of the

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Table II. Experimental Molar Excess Enthalpies H^E for 1,3-Dioxolane (1) + Solvent (2) Systems as a Function of the Mole Fraction x_1 of 1,3-Dioxolane at 298.15 K; Coefficients c_k, Equation 2; and Standard Deviations $\sigma(H^E)$

	n-pentane		3-methylpentane		methylcyclopentane	
	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})
	0.0340	256.2	0.0722	418.4	0.0631	370.2
	0.1214	720.1	0.1346	748.6	0.1187	658.0
	0.1718	947.2	0.1921	976.1	0.1681	879.9
	0.2166	1118.2	0.2373	1166.9	0.2122	1058.7
	0.3561	1472.8	0.3182	1423.3	0.2879	1324.9
	0.4534	1646.0	0.3836	1564.4	0.3502	1495.9
	0.5251	1698.8	0.4828	1700.1	0.4471	1641.1
	0.6240	1689.2	0.5545	1710.4	0.5188	1677.3
	0.7134	1565.3	0.6512	1615.9	0.6179	1593.4
	0.7684	1403.6	0.7369	1422.2	0.7081	1419.9
	0.8127	1179.8	0.7888	1244.4	0.7638	1243.2
	0.9087	758.6	0.8486	984.5	0.8291	1043.5
	0.9299	616.1	0.8819	817.3	0.8661	840.1
	0.9522	459.4	0.9373	480.9	0.9066	638.6
	0.9755	239.1	0.9782	168.6	0.9510	369.7
c_0	6710.4		6816.5		6636.4	
c_1	1452.9		957.3		343.8	
c_2	1941.1		407.5		355.6	
c_3					704.7	
$\sigma(H^E)$	13.5 J mol^{-1}		8.1 J mol^{-1}		13.7 J mol^{-1}	

calorimeter was checked by measuring the molar excess enthalpy H^E of the test mixture cyclohexane–*n*-hexane, and the agreement with literature data was better than 0.5% (*4*).

Density Measurements

Densities ρ were determined as a function of temperature with a two-capillary glass pycnometer calibrated with distilled mercury at atmospheric pressure (Table I). The density of 1,3-dioxolane has been reported earlier (*5*). The densities of the pure components, necessary to evaluate fluxes in the calorimetric measurements (*5*), were calculated by the formula

$$\rho/(\mathrm{kg\ m^{-3}}) = A - B((T/\mathrm{K}) - 273.15) \qquad (1)$$

with coefficients A and B, correlation coefficients R, and sample standard deviations $\sigma(\rho)$ obtained from least-squares analysis (Table I).

Results and Data Treatments

The results of our calorimetric measurements are presented in Table II.

The experimental data were fitted by using the Redlich–Kister expression

$$H^E/(\mathrm{J\ mol^{-1}}) = x_1 x_2 \sum_{k\geq 0} c_k (x_1 - x_2)^k \qquad (2)$$

The adjustable parameters c_k were evaluated by means of the least-squares method described previously (*6*) (Table II).

Discussion of the Results and Conclusions

The binary systems show endothermic mixing of the components, with H^E vs x_1 curves nearly symmetric and a maximum of H^E close to 1700 J mol^{-1}. As can be seen from Table II, substitution of a H atom of *n*-pentane with a CH_3 group or cyclization of the molecule does not affect the molecular interactions in the mixture and only slight variations of H^E are observed. These conclusions agree with the interaction picture of the binary systems of the present paper, where strong interactions, such as hydrogen bonding, can be excluded and the second components have nonpolar molecule and comparable molecular size (if the molecular distances r_k in the liquid state are calculated through the Kohler equation (*7*), a ratio r_1/r_2 is obtained ranging from 0.81 to 0.85).

Glossary

A, B	coefficients, eq 1
c_k	parameters in the empirical Redlich–Kister expression correlating the H^E's, eq 2, J mol^{-1}
H^E	liquid-phase molar enthalpy of mixing, J mol^{-1}
R	correlation coefficient
x_1,x_2	mole fractions of 1,3-dioxolane and component 2 in liquid phase

Greek Symbols

ρ	density of component, eq 1, kg m^{-3}
$\sigma(\rho)$	sample standard deviation, Table I
$\sigma(H^E)$	sample standard deviation, Table II

Registry No. 1,3-Dioxolane, 646-06-0; pentane, 109-66-0; 3-methylpentane, 96-14-0; methylcyclopentane, 96-37-7.

Literature Cited

(1) Inglese, A.; Wilhelm, E.; Grolier, J.-P. E.; Kehiaian, H. V. *J. Chem. Thermodyn.* **1980**, *12*, 1047.

(2) Inglese, A.; Wilhelm, E.; Grolier, J.-P. E.; Kehiaian, H. V. *J. Chem. Thermodyn.* **1980**, *12*, 217.

(3) Monk, P.; Wadsö, I. *Acta Chem. Scand.* **1968**, *22*, 1842.

(4) Benson, G. C. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1974**, 19.

(5) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1986**, *31*, 250.

(6) Francesconi, R.; Comelli, F.; Giacomini, D. *J. Chem. Eng. Data*, in press.

(7) Prausnitz, J. M. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1969.

(8) Weissberger, A. *Organic Solvents*, 2nd ed.; Interscience: New York, 1955; Vol. VII.

(9) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986; Vol. II.

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