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Excess enthalpies of 1,1,2,2-tetrachloroethane + methyl n-alkanoates Ortega, J.

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Enthalpy-of-mixing measurements are reported at 298.15 K for methyl n-alkanoates (ethanoate through pentadecanoate) + 1,1,2,2-tetrachloroethane. All the mixtures are strongly exothermic suggesting the existence of strong specific interactions due to hydrogen bonding between the H atoms of the 1,1,2,2-tetrachloroethane and the O atoms of the n-alkanoates.

1. INTRODUCTION

In continuation of our systematic experimental studies on the excess molar enthalpies H^E of 1,1,2,2-tetrachloroethane + ethyl n-alkanoates or + propyl n-alkanoates (ORTJ0915), we have determined H^E of 1,1,2,2-tetrachloroethane + methyl n-alkanoates. These data, along with data on vapor-liquid equilibria (FARJ0950) and excess volumes (LINJ0950), will be used to test the applicability of various group-contribution models to mixtures involving complex formation. As far as we know, no H^E measurements have been published previously on this class of mixtures.

2. EXPERIMENTAL SECTION

2.1. Apparatus and Procedure

The experimental data were taken at atmospheric pressure by means of a Calvet type microcalorimeter, model MS-80D (SETARAM, Lyon, France) with a stainless steel batch mixing cell (volume ca. 8 cm³) and with negligible vapor phase. The temperature T was maintained constant to within 0.02 K at (298.15 \pm 0.02) All temperatures are on ITS-90. The microcalorimeter was calibrated electrically after each measurement (see ORTJ0881). Check measurements on cyclohexane + hexane and benzene + heptadecane are in agreement to within 1 % (over central range of concentration) with the data reported in (MCGM0690) and (DIAM0742). The estimated uncertainties in the mole fraction composition x_i and H^E are, respectively, $\sigma(x_i) = 0.0005$ and $\sigma(H^E) = 0.02 |H^E|$ (over central range of concentration).

2.2. Materials

C₂H₂Cl₄, 1,1,2,2-Tetrachloroethane Aldrich Chem. Co., Inc. (Milwaukee, WI, USA) material of stated

purity > 99 mole %, was degassed ultrasonically, dried over molecular sieves Type 3A (reference 69828, from Fluka), and used without further purification. n(D,298.15 K) = 1.4918; $\rho_i(298.15 \text{ K})/\text{kg m}^{-3} = 1588.37$.

 $C_3H_6O_2$, Methyl ethanoate (Methyl acetate). Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 99.0 mole %, purified as above; n(D, 293.15 K) = 1.3589; $\rho_i(298.15 \text{ K})/\text{kg m}^{-3} = 927.03$.

 $C_4H_8O_2$, Methyl propanoate (Methyl propionate). Fluka AG (Buchs, Switzerland) 'purum' grade material of stated GLC purity > 99.0 mole %, purified as above; n(D, 293.15 K) = 1.3745; $\rho_i(298.15 \text{ K})/\text{kg m}^{-3} = 909.30$.

 $C_5H_{10}O_2$, Methyl butanoate (Methyl butyrate). Fluka AG (Buchs, Switzerland) 'purum' grade material of stated GLC purity > 99.0 mole %, purified as above; n(D, 293.15 K) = 1.3849; $\rho_i(298.15 \text{ K})/\text{kg m}^{-3} = 892.31$.

 $C_6H_{12}O_2$, Methyl pentanoate (Methyl valerate). Fluka AG (Buchs, Switzerland) 'purum' grade material of stated GLC purity > 99.0 mole %, purified as above; n(D, 293.15 K) = 1.3947; $\rho_i(298.15 \text{ K})/\text{kg m}^{-3} = 884.52$.

 $C_7H_{14}O_2$, Methyl hexanoate (Methyl caproate). Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 99.0 mole %, purified as above; n(D, 293.15 K) = 1.4035; $\rho_i(298.15 \text{ K})/\text{kg m}^{-3} = 879.52$.

 $C_8H_{16}O_2$, Methyl heptanoate (Methyl enanthate). Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 99.0 mole %, purified as above; n(D, 293.15 K) = 1.4095; $\rho_i(298.15 \text{ K})/\text{kg m}^{-3} = 875.40$.

 $C_9H_{18}O_2$, Methyl octanoate (Methyl caprylate). Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 99.0 mole %, purified as above; n(D, 293.15 K) = 1.4148; $\rho_i(298.15 \text{ K})/\text{kg m}^{-3} = 872.38$.

 $C_{10}H_{20}O_2$, Methyl nonanoate (Methyl pelargonate). Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 99.0 mole %, purified as above; n(D, 293.15 K) = 1.4208; $\rho_i(298.15 \text{ K})/\text{kg m}^{-3} = 870.11$.

 $C_{11}H_{22}O_2$, Methyl decanoate (Methyl caprinate). Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 99.0 mole %, purified as above; n(D, 293.15 K) = 1.4235; $\rho_i(298.15 \text{ K})/\text{kg m}^{-3} = 868.09$.

 $C_{12}H_{24}O_2$, Methyl undecanoate. Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 98.0 mole %, purified as above; n(D, 293.15 K) = 1.4270; $\rho_i(298.15 \text{ K})/\text{kg m}^{-3} = 866.75$.

 $C_{13}H_{26}O_2$, Methyl dodecanoate (Methyl laurate). Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 99.5 mole %, purified as above; n(D, 293.15 K) = 1.4298; $\rho_i(298.15 \text{ K})/\text{kg m}^{-3} = 865.12$.

 $C_{14}H_{28}O_2$, Methyl tridecanoate. Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 98.0 mole %, purified as above; n(D, 293.15 K) = 1.4329; $\rho_i(298.15 \text{ K})/\text{kg m}^{-3} = 863.94$.

 $C_{15}H_{30}O_2$, Methyl tetradecanoate (Methyl myristate). Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 99.5 mole %, purified as above; n(D, 293.15 K) = 1.4345; $\rho_i(298.15 \text{ K})/\text{kg m}^{-3} = 863.27$.

 $C_{16}H_{32}O_2$, Methyl pentadecanoate. Fluka AG (Buchs, Switzerland) 'puriss' grade material of stated GLC purity > 99.0 mole %, purified as above; n(D, 293.15 K) = 1.4370; $\rho_i(298.15 \text{ K})/\text{kg m}^{-3} = 862.35$.

3. RESULTS

The direct experimental H^E values are tabulated and graphed in the Appendix and saved on disk as Standard ELDATA Files **ORTJ0951.001** through **ORTJ0951.014**. The data were fitted to Eq. (1):

$$H^{E}_{calo}J \text{ mol}^{-1} = x_1x_2\Sigma A_i[x_1/(x_1 + kx_2)]^{i-1}$$
 (1)

all points weighted equally. With an adjusted coefficient k and n=4 coefficients A_i the standard deviations $\sigma(H^E)$, defined by Eq.(2):

$$\sigma(H^E) = [\Sigma (H^E_{\text{calc}} - H^E)^2 / (N - n)]^{1/2}$$
 (2)

where N is the number of experimental values, are le_{SS} than 10 J mol⁻¹ (ca. 0.4 % at $x_1 = 0.5$).

4. DISCUSSION AND CONCLUSIONS

The excess enthalpies of all the systems studied are strongly negative, of the order of -2500 J mol-1 at the minimum, close to the equimolar composition. This suggests that in 1,1,2,2-tetrachloroethane + methyl n-alkanoates there exist specific interactions between the unlike molecules mainly due to hydrogen bonding.

5. REFERENCES

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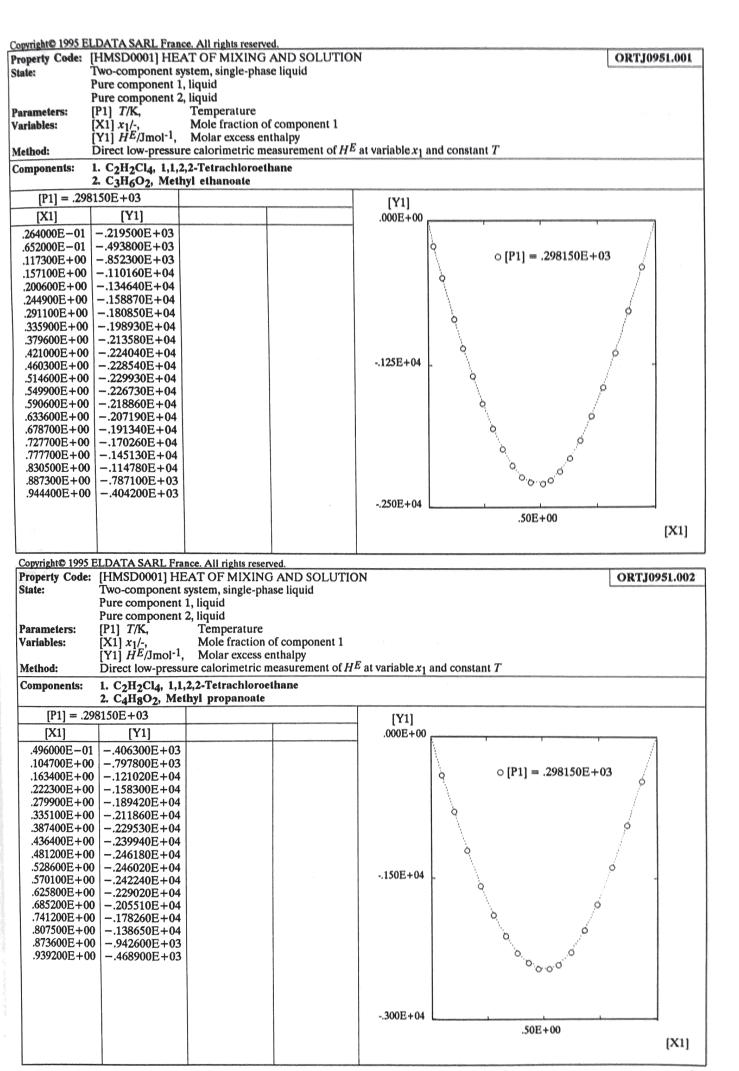
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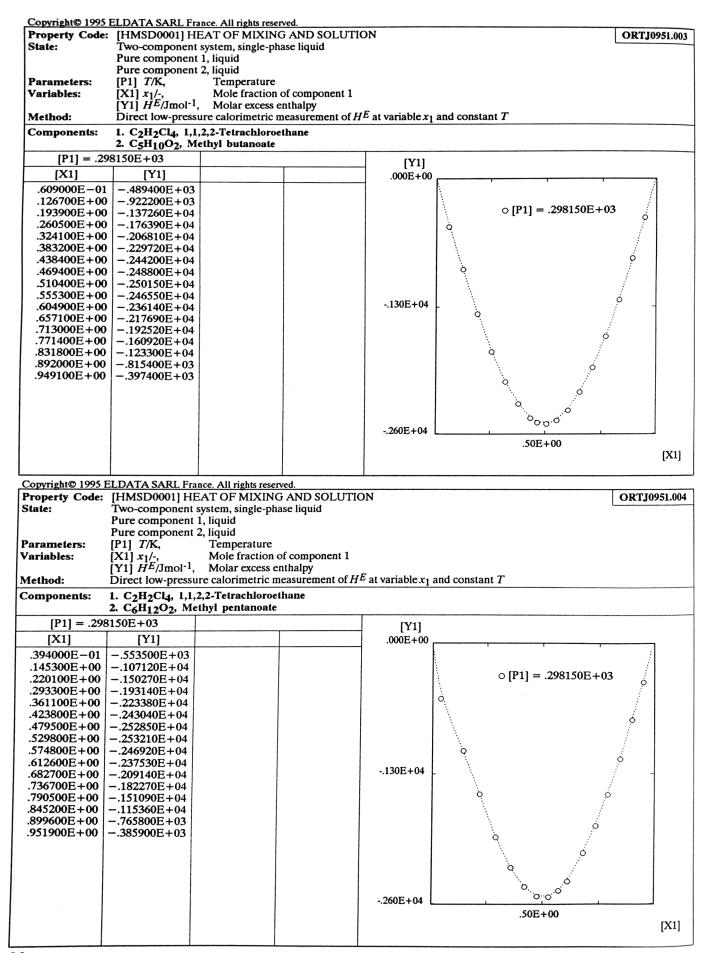
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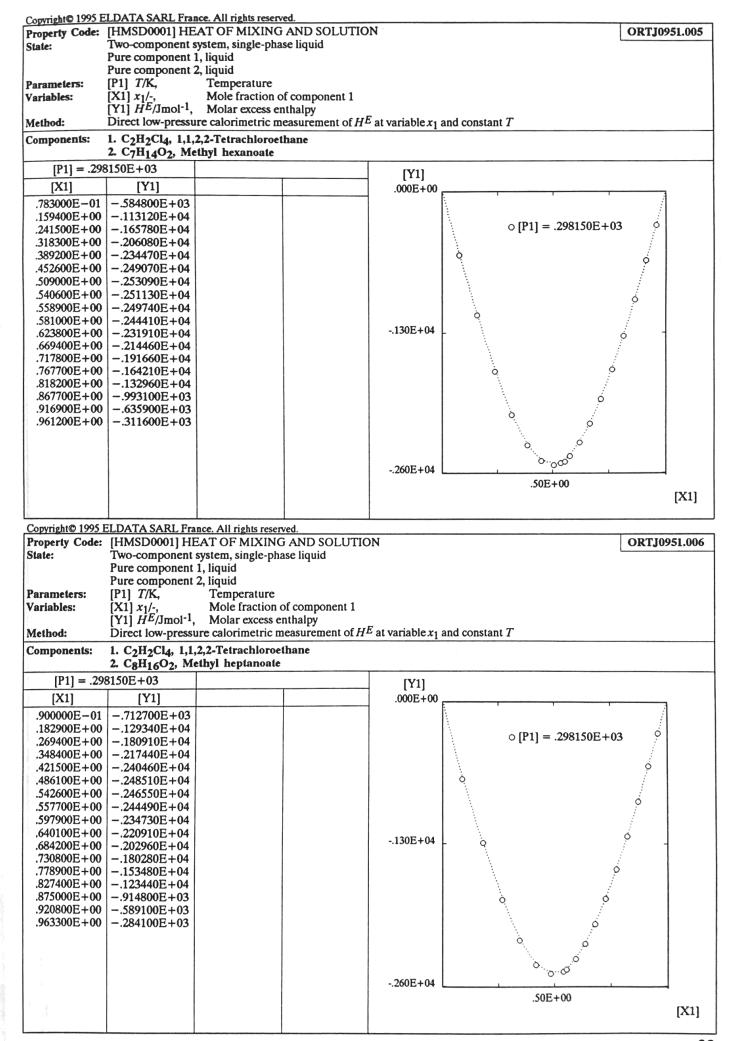
Ortega, Juan*

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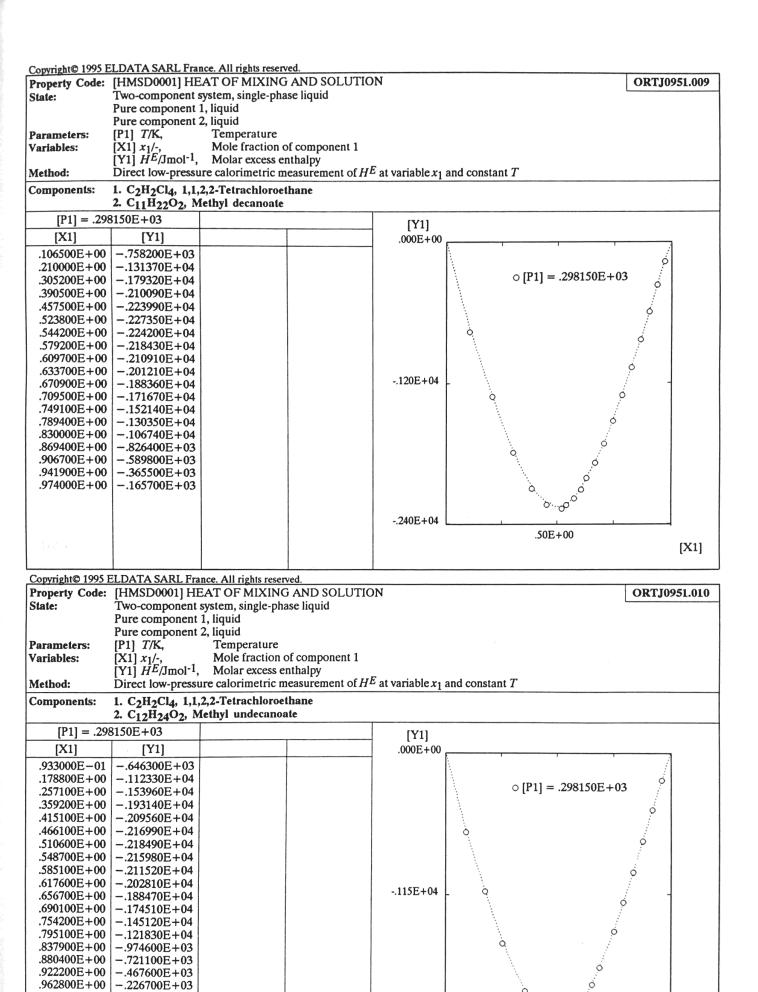
*Author to whom correspondence should be addressed: FAX +34-28-451022







Copyright© 1995 ELDATA SARL France. All rights reserved. ORTJ0951.007 Property Code: [HMSD0001] HEAT OF MIXING AND SOLUTION State: Two-component system, single-phase liquid Pure component 1, liquid Pure component 2, liquid Parameters: [P1] T/K, Temperature Variables: Mole fraction of component 1 [Y1] H^E /Jmol⁻¹, Molar excess enthalpy Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant TMethod: Components: 1. C2H2Cl4, 1,1,2,2-Tetrachloroethane 2. C9H18O2, Methyl octanoate [P1] = .298150E + 03[Y1] [X1] [Y1] .000E+00 .742000E-01 -.568200E+03 .146200E+00 -.103260E+04 \circ [P1] = .298150E+03 .212800E+00 -.145690E+04 .274300E+00 -.179140E+04.331700E+00 -.204220E+04 .385200E+00 -.222320E+04 .433000E+00 -.233570E+04 -.239120E+04 .476300E+00 .516100E+00 -.239570E+04.551800E+00 -.237640E+04 -.125E+04 .588200E+00 -.229790E+04.631500E+00 -.218290E + 04.676400E+00 -.199860E+04 .718800E+00 -.180510E+04 .762300E+00 -.157620E+04 .806100E+00 -.132260E+04.849700E+00 -.105120E+04 .891100E+00 -.774200E+03 .932500E+00 -.486700E+03 .968900E+00 -.234700E+030.000 -.250E+04 .50E+00 [X1] Copyright© 1995 ELDATA SARL France. All rights reserved. [HMSD0001] HEAT OF MIXING AND SOLUTION Property Code: ORTJ0951.008 State: Two-component system, single-phase liquid Pure component 1, liquid Pure component 2, liquid Parameters: [P1] T/K, Temperature Variables: [X1] $x_1/-$ Mole fraction of component 1 [Y1] H^E/Jmol^{-1} , Molar excess enthalpy Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant TMethod: $1. \ C_2H_2Cl_4, \ 1,1,2,2\text{-Tetrachloroethane}$ Components: 2. $C_{10}H_{20}O_2$, Methyl nonanoate [P1] = .298150E + 03[Y1] [X1] [Y1] .000E+00 -.669000E + 03.921000E-01 .188500E+00 -.125010E+04 \circ [P1] = .298150E+03 .284100E+00 -.176380E + 04.369000E+00 -.210990E+04.446300E+00 -.230680E+04 .514200E+00 -.234720E + 04.572800E+00 -.227290E+04 .623600E+00 -.214730E+04 .666500E + 00-.198810E+04.723400E+00 -.171750E+04-.125E+04 .766600E+00 -.149210E+04.807700E + 00-.125470E+04 .850200E+00 -.992900E+03 .892900E+00 -.724300E+03.931900E+00 -.461900E+03.969400E+00 -.214700E + 03-.250E+04 .50E+00 [X1]



-.230E+04

.50E+00

[X1]

Copyright© 1995 ELDATA SARL France. All rights reserved. Property Code: [HMSD0001] HEAT OF MIXING AND SOLUTION ORTJ0951.011 Two-component system, single-phase liquid State: Pure component 1, liquid Pure component 2, liquid Parameters: [P1] T/K, Temperature [X1] $x_1/-$, Mole fraction of component 1 [Y1] H^E/Jmol^{-1} , Molar excess enthalpy Direct low-pressure calorimetric measurement of H^E at variable x_1 and constant TVariables: Method: 1. C2H2Cl4, 1,1,2,2-Tetrachloroethane Components: 2. C₁₃H₂₆O₂, Methyl dodecanoate [P1] = .298150E + 03[Y1] [X1] [Y1] .000E+00 .849000E-01 -.569300E+03 .168200E+00 -.101990E+04 \circ [P1] = .298150E+03 .246200E+00 -.142040E+04 .316700E+00 -.171180E+04 .380500E+00 -.191730E+04 .437500E+00 -.204000E+04 .487700E+00 -.207880E+04 .532900E+00 -.207300E+04 .573100E+00 -.201160E + 04.609000E+00 -.194630E+04 -.110E+04 .653900E+00 -.179780E+04 .691500E+00 -.165720E+04 .729600E+00 -.148510E+04 .768800E+00 -.129080E+04 .809100E+00 -.107660E+04 .849300E+00 -.853400E+03 -.623900E+03 .889600E+00 .928600E+00 -.399800E+03 -.196100E+03 .965900E+00 -.220E+04 .50E+00 [X1]

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Property Code:	[HMSD0001] H	EAT OF MIXING	AND SOLUTIO	ON	ORT	J0951.012				
State:	Two-component system, single-phase liquid									
	Pure component 1, liquid									
	Pure component	2, liquid								
Parameters:	[P1] <i>T/</i> K,	Temperature								
Variables:	[X1] $x_{1}/_{-}$,	Mole fraction of	of component 1							
	[Y1] H^E/Jmol^{-1} ,	Molar excess e	nthalpy	_						
Method:	Direct low-press	ure calorimetric m	easurement of H	E at variable x_1	and constant T					
Components:	1. C ₂ H ₂ Cl ₄ , 1,1	2,2-Tetrachloroe	hane							
	2. C ₁₄ H ₂₈ O ₂ , N									
[P1] = .298	8150E+03			[Y1]						
[X1]	[Y1]			.000E+00						
.110100E+00	676500E+03					/				
.212100E+00	114860E+04					9				
.301600E+00	153670E+04	1.			\circ [P1] = .298150E+03	<i>i</i>				
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	[HMSD0001] H			ON		ORTJ0951.01
State:		system, single-pha	se liquid			
	Pure component					
	Pure component					
Parameters: Variables:	[P1] <i>T/</i> K,	Temperature	f commonant 1			
variables:	[X1] $x_1/-$,	Mole fraction of Molar excess en	of component 1			
Method:	Direct low press	ire calorimetric m	illialpy easurement of Hi	E at variable ra	and constant T	
				at variable x1	and constant 1	
Components:	1. C ₂ H ₂ Cl ₄ , 1,1,	2,2-Tetrachloroet lethyl pentadecar	nane			
[D4] 00/		letnyi pentadecai	loate	Γ		
	8150E+03			[Y1]		
[X1]	[Y1]			.000E+00	E	
.116800E+00	683000E+03				<u></u>	
.222000E+00	111200E+04				o (D1) = 200150E + 02	<i>/</i>
	148170E+04				\circ [P1] = .298150E+03	0
	170790E+04					/
	180410E+04					9
	181200E+04				\	
	177520E+04				ف	0
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	105310E+04					
	859900E+03				/	
	661500E+03				<u> </u>	
	463900E+03					
.931900E+00	283000E+03					
.968000E+00	127700E+03					
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