Excess Enthalpies of Nitrous Oxide + Pentane at 308.15 and 313.15 K from 7.64 to 12.27 MPa

Juan A. R. Renuncio,* Concepcion Pando, Carlos Menduiña, and R. Cesar Castells[†]

Departamento de Química Física I, Universidad Complutense, E-28040 Madrid, Spain

The excess molar enthalpies H_m^E of nitrous oxide + pentane were measured in the vicinity of the critical locus and in the supercritical region by means of an isothermal flow calorimeter. Smooth representations of the results are presented. Values for H_m^E are similar to those previously found for carbon dioxide + pentane mixtures.

Introduction

Nitrous oxide is often used in supercritical fluid extraction, and several authors such as Sakaki (1992) or Alexandrou *et al.* (1992) have reported that N_2O is a better solvent than carbon dioxide for certain compounds. The measurement of thermodynamic properties such as the excess molar enthalpies (H_m^E) of binary mixtures of nitrous oxide with a hydrocarbon in the vicinity of the critical locus and in the supercritical region would be necessary for understanding the practical uses of N_2O. Pando *et al.* (1983) reported previously measurements of H_m^E for carbon dioxide + pentane at 308.15 and 323.15 K and pressures up to 12.45 MPa. Castells *et al.* (1994a,b) reported previously measurements of H_m^E for nitrous oxide + toluene at 308.15, 313.15 and 323.15 K and pressures up to 15.00 MPa. This paper reports values of H_m^E for nitrous oxide + pentane at 308.15 K and 9.49 and 12.27 MPa and at 313.15 K and 7.64, 9.44, and 12.26 MPa. The pressure and temperature conditions of the measurements were chosen to compare results for nitrous oxide + pentane with those previously obtained for carbon dioxide + pentane.

Experimental Section

The high-pressure flow calorimeter from Hart Scientific (Model 7501) used for the experiments and the experimental procedure have been described by Christensen and Izatt (1984) and by Gmehling (1993). The calorimeter consists of two thermostated pumps (ISCO, Model LC2600), a thermostated flow cell, and a back pressure regulator. The flow cell with a pulsed heater, a calibration heater, a Peltier cooler, and a mixing tube wound around a copper cylinder is located in a stainless steel cylinder which is immersed in a thermostat. The combination Peltier cooler/pulsed heater allows the determination of both endothermic and exothermic effects. The flow cell is thermostated in a silicon oil bath (±0.0005 K) and a manually controlled piston acts as a fine adjustment of the nitrogen pressure over the back pressure regulator. Oscillations in pressure are smaller than ±0.01 MPa.

The materials employed were nitrous oxide (SEO, 99.99 mol % pure) and pentane (Aldrich, 99+ mol % pure, HPLC grade) previously dehydrated with sodium.

All runs were made in the steady-state fixed composition mode. Flow rates were selected to cover the whole mole fraction range. In most cases, the measurements were carried out at a total flow rate of 0.010 $cm^3 \cdot s^{-1}$. A few measurements were carried out at a total flow rate of 0.005 $cm^3 \cdot s^{-1}$. Reproducibility of results was estimated to be $\pm(1 + 0.01 H_m^E)$ $J \cdot mol^{-1}$. The flow rates measured in cubic centimeters per second were converted to moles per second and to mole fractions using the densities of the two materials estimated as follows. The densities of N_2O at the temperature of the pump and at pressures of 7.64, 9.44, 9.49, 12.26, and 12.27 MPa were calculated by interpolation of the pressure–volume isotherms of the liquid nitrous oxide measured by Couch *et al.* (1962). The densities of pentane at the temperature of the pump and at pressures of 7.64, 9.44, 9.49, 12.26, and 12.27 MPa were calculated from the densities at atmospheric pressure given in the *TRC Thermodynamic Tables* (1994) and the isothermal compressibilities obtained from the data of Sage and Lacey (1942).

Results and Discussion

Excess molar enthalpies were determined for nitrous oxide + pentane over the entire composition range at 308.15 K and 9.49 and 12.27 MPa and at 313.15 K and 7.64, 9.44, and 12.26 MPa. The results are given in Table 1. For pentane T_c is 469.7 K and p_c is 3.37 MPa, while for nitrous oxide T_c is 309.6 K and p_c is 7.24 MPa (Reid *et al.*, 1988). Owing to the proximity to the nitrous oxide critical point, excess molar enthalpies could not be determined at 308.15 K and 7.64 MPa. Values for H_m^E at each pressure and temperature studied were fitted to the equation

$$H_m^E/(J \cdot mol^{-1}) = [x(1-x)/[1 + k(2x-1)]] \sum_{n=0}^{N} C_n (2x-1)^n \quad (1)$$

where x is the N_2O mole fraction. The coefficients C_n and k are given in Table 2 together with the standard deviations, s, between experimental and calculated H_m^E values and the ratio s/H_{max}^E of the standard deviation and the maximum absolute value of H_m^E. Values for s/H_{max}^E are higher than the estimated reproducibility for the flow calorimeter due to the fluctuations in density always present when the critical point is approached.

Figures 1 and 2 are plots of H_m^E against x for the isobars studied at 308.15 and 313.15 K, respectively. Mixtures at 308.15 K and 9.49 and 12.27 MPa and at 313.15 K and 12.26 MPa show moderately endothermic mixing. Mixtures at 313.15 K and 9.44 MPa show moderately endothermic and exothermic mixing in the pentane-rich region and nitrous oxide-rich region, respectively. Mixtures at 313.15 K and 7.64 MPa show very exothermic mixing.

---

* Author to whom correspondence should be addressed (fax 341-3944135; e-mail mendu@quim.ucm.es).

[†] On leave from Universidad de La Plata–CIDEPINT, Argentina.

0021-9568/95/1740-0642$09.00/0

Table 1. Experimental Excess Enthalpies H_m^E for [$xN_2O + (1 - x)C_5H_{12}$]

x	H_m^E/(J·mol^{-1})	x	H_m^E/(J·mol^{-1})	x	H_m^E/(J·mol^{-1})
		308.15 K, 9.49 MPa			
0.049	24	0.388	230	0.744	99
0.098	85	0.440	231	0.788	61
0.145	126	0.492	221	0.847	23
0.191	161	0.543	209	0.894	−24
0.243	196	0.594	174	0.978	−26
0.285	205	0.644	158		
0.343	226	0.670	136		
		308.15 K, 12.27 MPa			
0.050	61	0.373	344	0.701	282
0.100	119	0.437	361	0.750	263
0.130	149	0.498	364	0.796	231
0.198	220	0.550	362	0.841	192
0.248	272	0.602	347	0.881	134
0.311	307	0.652	308	0.950	59
		313.15 K, 7.64 MPa			
0.044	−81	0.518	−907	0.878	−1642
0.089	−141	0.569	−973	0.922	−1572
0.135	−234	0.623	−1081	0.946	−1511
0.226	−374	0.672	−1195	0.969	−1339
0.324	−547	0.728	−1314	0.989	−929
0.427	−764	0.779	−1478		
0.471	−812	0.835	−1551		
		313.15 K, 9.44 MPa			
0.045	22	0.331	105	0.676	−56
0.089	50	0.373	102	0.718	−88
0.090	51	0.376	106	0.721	−93
0.135	72	0.424	91	0.727	−100
0.138	69	0.467	64	0.832	−204
0.140	72	0.474	70	0.836	−205
0.179	82	0.515	38	0.859	−226
0.233	100	0.525	42	0.888	−241
0.280	98	0.571	16	0.948	−177
0.281	111	0.575	27	0.992	−23
0.323	101	0.621	−24		
		313.15 K, 12.26 MPa			
0.047	43	0.442	284	0.698	205
0.097	79	0.491	284	0.742	180
0.147	143	0.541	274	0.800	125
0.195	180	0.542	275	0.844	85
0.247	220	0.544	280	0.896	44
0.296	240	0.587	270	0.951	1
0.345	266	0.638	246		
0.439	287	0.695	218		

Figure 3 is a plot of p against T for the nitrous oxide + pentane system showing the vapor pressure equilibrium curve of nitrous oxide measured by Couch *et al.* (1962), the critical locus in the vicinity of the N_2O critical point, and the points at which experimental measurements of H_m^E have been made. Vapor–liquid equilibrium data or critical locus data are not available for nitrous oxide + pentane. The critical locus shown in Figure 3 has been estimated using the procedure developed by Heidemann and Khalil (1980) and the equation of state proposed by Peng and Robinson (1976).

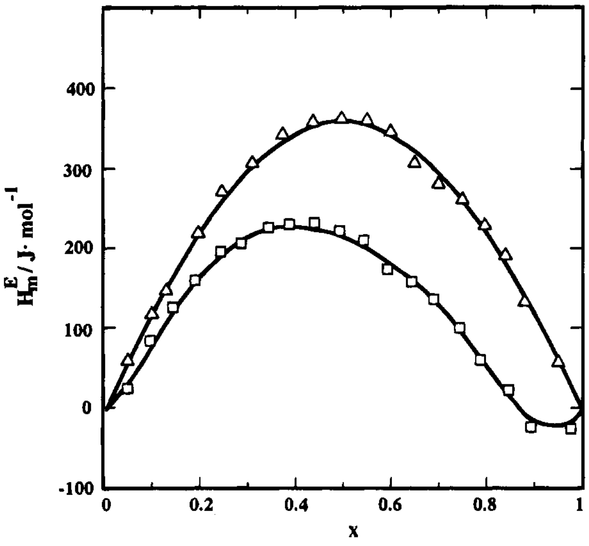

Figure 1. Excess molar enthalpies H_m^E against N_2O mole fraction for nitrous oxide + pentane at 308.15 K as a function of pressure: □, 9.49 MPa; △, 12.27 MPa; —, calculated from eq 1.

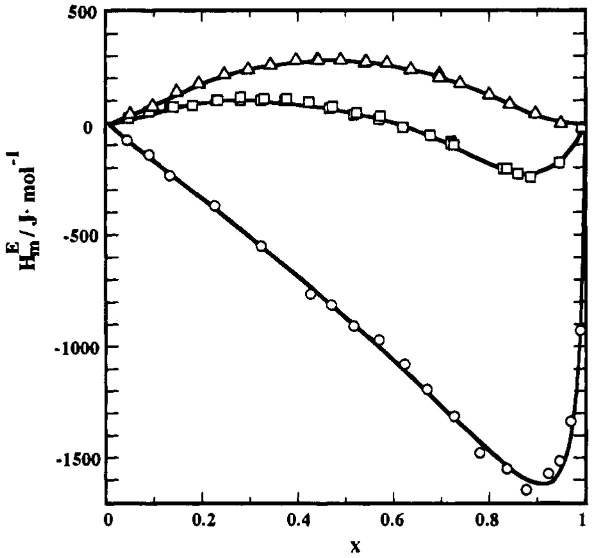

Figure 2. Excess molar enthalpies H_m^E against N_2O mole fraction for nitrous oxide + pentane at 313.15 K as a function of pressure: ○, 7.64 MPa; □, 9.44 MPa; △, 12.26 MPa; —, calculated from eq 1.

The changes observed in the excess enthalpy with temperature and pressure may be discussed in terms of liquid–vapor equilibrium and critical constants for the nitrous oxide + pentane mixtures and the densities of N_2O and pentane at the conditions of temperature and pressure of the experiments. A detailed discussion of these changes has been given for carbon dioxide + pentane by Pando *et al.* (1983) and for nitrous oxide + toluene by Castells *et al.* (1994a,b). When the states and densities of the pure components and the mixture are similar, the values of H_m^E are negative or slightly positive. This is so for the nitrous oxide

Table 2. Coefficients, Standard Deviation, s, and Ratio s/H_{max}^E for Least-Squares Representation of H_m^E/(J·mol^{-1}) for Nitrous Oxide + Pentane by eq 1

	308.15 K		313.15 K		
	9.49 MPa	12.27 MPa	7.64 MPa	9.44 MPa	12.26 MPa
C_0	861.31	1463.3	−3465.4	222.50	1138.0
C_1	474.68	−43.799	417.99	806.91	188.63
C_2	−21.875	−236.09	−354.30	−655.80	−165.44
C_3	366.34			1759.5	292.52
C_4	−1268.9			−1893.7	−810.71
k			0.96972		
s/J·mol^{-1}	6.5	7.7	33	7.5	4.7
$100s/H_{max}^E$	2.8	2.1	2.0	3.1	1.6

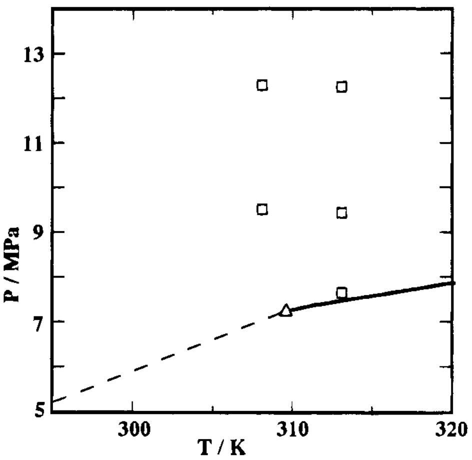

Figure 3. Plot of p against T for nitrous oxide + pentane showing the nitrous oxide vapor–liquid equilibrium curve (- - -) measured by Couch *et al.* (1962), the nitrous oxide critical point (△) taken from Reid *et al.* (1988), the critical locus (—) estimated using the Peng–Robinson equation of state (Peng and Robinson, 1976), and (T,p) coordinates (□) where experimental measurements were made.

+ pentane mixtures at 308.15 K for isobars at 9.49 and 12.27 MPa and at 313.15 K for isobars at 9.44 and 12.26 MPa when the values of density are similar for N_2O and pentane. When the states and densities of the pure components differ and the resulting mixture is a liquid, large negative values of H_m^E are observed. This is so for the isobar at 313.15 K and 7.64 MPa when a value of 326 $kg{\cdot}m^{-3}$ is obtained for the N_2O density from the data of Couch *et al.* (1962), while a value of 615 $kg{\cdot}m^{-3}$ is obtained for the pentane density from the *TRC Thermodynamic Tables* (1994) and the data of Sage and Lacey (1942). The large negative values of H_m^E seem to be a consequence of the nitrous oxide change of state from that of a low-density fluid to that of a liquid mixture component.

The shape of the isobars in Figures 1 and 2 denotes a behavior similar to that previously reported for carbon dioxide + pentane by Pando *et al.* (1983). The critical temperature ($T_c = 304.21$ K) and pressure ($p_c = 7.38$ MPa) of carbon dioxide are taken from the *Carbon Dioxide, IUPAC Thermodynamic Tables of the Fluid State* (1976) and are very close to those of nitrous oxide, and the carbon dioxide + pentane and nitrous oxide + pentane critical loci are very similar. The temperature and pressures at which experimental measurements have been made for carbon dioxide + pentane and nitrous oxide + pentane have a similar position with respect to the critical locus in the p against T plot. This may be seen by comparing the plot of Figure 3 with a similar one shown for carbon dioxide + pentane by Pando *et al.* (1983) in Figure 2 of their paper.

Acknowledgment

We appreciate the aid given to us in estimating the critical locus by Dr. R. A. Heidemann.

Literature Cited

Alexandrou, N.; Lawrence, M. J.; Pawliszyn, J. Cleanup of Complex Organic Mixtures Using Supercritical Fluids and Selective Adsorbents. *Anal. Chem.* **1992,** *64*, 301–311.

Carbon Dioxide, IUPAC Thermodynamic Tables of the Fluid State, Pergamon: Oxford, U.K., 1976.

Castells, R. C.; Menduiña, C.; Pando, C.; Renuncio, J. A. R. The Excess Enthalpies of (Dinitrogen Oxide + Toluene) at the Temperature 313.15 K and at Pressures from 7.60 MPa to 15.00 MPa. *J. Chem. Thermodyn.* **1994a,** *26*, 641–646.

Castells, R. C.; Menduiña, C.; Pando, C.; Renuncio, J. A. R. Excess Molar Enthalpies of Nitrous Oxide-Toluene in the Liquid and Supercritical Regions. *J. Chem. Soc., Faraday Trans.* **1994b,** *90*, 2677–2681.

Christensen, J. J.; Izatt, R. M. An isothermal flow calorimeter designed for high temperature, high pressure operation. *Thermochim. Acta* **1984,** *73*, 117–129.

Couch, E. J.; Hirth, L. J.; Kobe, K. A. Volumetric Behavior of Nitrous Oxide. Pressure-Volume Isotherms at High Pressures. Gas Compressibilty Factors at Low Pressures. *J. Chem. Eng. Data* **1962,** *6*, 229–237.

Gmehling, J. Excess Enthalpies for 1,1,1-Trichloroethane with Alkanes, Ketones, and Esters. *J. Chem. Eng. Data* **1993,** *38*, 143–146.

Heidemann, R. A.; Khalil, A. M. The Calculation of Critical Points. *AIChE J.* **1980,** *26*, 769–779.

Pando, C.; Renuncio, J. A. R.; Izatt, R. M.; Christensen, J. J. The Excess Enthalpies of (Carbon Dioxide + Toluene) at 308.15 and 323.15 K and from 7.58 to 12.45 MPa. *J. Chem. Thermodyn.* **1983,** *15*, 259–266.

Peng, D.-Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976,** *15*, 59–64.

Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*; McGraw-Hill: Singapore, 1988.

Sage, B. H.; Lacey, W. N. Phase Equilibria in Hydrocarbon Systems. Thermodynamic Properties of *n*-Pentane. *Ind. Eng. Chem.* **1942,** *34*, 730–736.

Sakaki, K. Solubility of β-Carotene in Dense Carbon Dioxide and Nitrous Oxide from 308 to 323 K and from 9.6 to 30 MPa. *J. Chem. Eng. Data* **1992,** *37*, 249–251.

TRC Thermodynamics Tables; TRC data bases for Chemistry and Engineering; Thermodynamics Research Center of the Texas Engineering Experiment Station, Texas A&M University System: College Station, TX, 1994.

Received for review October 18, 1994. Accepted January 10, 1995.[⊗] This work was funded by the Spanish Ministry of Education (DGICYT) Research Project PB-91-0392. R.C.C. acknowledges the Universidad Complutense of Madrid for a visiting research professorship at the Department of Physical Chemistry.

JE9402177

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1995.