International Journal of Thermophysics, Vol. 27, No. 1, January 2006 (© 2006)
DOI: 10.1007/s10765-006-0033-6

Burnett Measurements and Virial Coefficients for the R32 + N_2O System[1]

G. Di Nicola,[2,3] G. Giuliani,[2] F. Polonara,[2] and R. Stryjek[4]

Experimental results for the difluoromethane (R32) + nitrous oxide (N_2O) system are presented in this paper. The Burnett apparatus was calibrated using helium, and its performance was confirmed by measurements for pure N_2O. The values of the virial coefficients for R32 were adopted from previous measurements as the same sample was used in the present study. *PVTx* measurements were performed for the binary R32 + N_2O system for four isotherms (303, 323, 343, and 364 K). Twenty Burnett expansions were performed in a pressure range from 5000 to 150 kPa. The second and third virial coefficients along with the cross second and third virial coefficients were derived from experimental results.

KEY WORDS: Burnett apparatus; N_2O; *PVTx*; R32; virial coefficients.

1. INTRODUCTION

The system under study here has been chosen as a working fluid for low temperature applications because of its promising features. In particular, this system could be a valid alternative for the low temperature stage of a cascade cycle. The thermodynamic properties of both mixture constituents are well known from the literature, but no experimental results have been published so far on the *PVTx* properties of this specific binary system.

In our recent papers, the virial coefficients for the two pure compounds were derived from experimental measurements [1, 2]. Fourteen

---

[1] Paper presented at the Seventh Asian Thermophysical Properties Conference, August 23–28, 2004, Hefei and Huangshan, Anhui, P. R. China.

[2] Dipartimento di Energetica, Università Politecnica delle Marche, Via Brecce Bianche, 60100 Ancona, Italy.

[3] To whom correspondence should be addressed. E-mail: g.dinicola@univpm.it

[4] Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland.

Burnett runs along 7 isotherms from 283 to 363 K and in a pressure range from 4500 to 150 kPa were reported for nitrous oxide in Ref. 1, while nine series along 5 isotherms were collected in the temperature range from 303 to 343 K and for pressures from 125 to 4370 kPa for difluoromethane in Ref. 2. The second and third virial coefficients were derived, and good consistency was found after comparison with data in the literature for both pure compounds. Here, the *PVTx* properties of the binary system have been measured along four different isotherms (20 runs in total), and the virial coefficients of the mixture, together with the cross virial coefficients, are derived.

The experimental uncertainty in the second and third virial coefficients is estimated to be within $\pm 1.5\,\mathrm{cm^3 \cdot mol^{-1}}$ and $\pm 500\,\mathrm{cm^6 \cdot mol^{-2}}$, respectively.

2. EXPERIMENTAL

N_2O and R32 were supplied by Sol SpA and Ausimont SpA, respectively; their purity was checked by gas chromatographic analysis using a thermal conductivity detector. The purities were found to be 99.99% for N_2O and 99.98% for R32 on an area-response basis.

A schematic diagram of the present experimental apparatus is shown in Fig. 1. It is almost the same as the one described elsewhere [3] and used with only minimal modifications already described [4]. It consists of two pressure vessels, the measurement chamber, V_A, and the expansion chamber, V_B, both spherical in shape, with volumes of approximately 70 and 35 cm^3, respectively, plus some auxiliary systems for filling and mixing the compounds in the Burnett vessels and for controlling and measuring the pressure and temperature. The vessels are made of Invar, given its excellent corrosion resistance and low thermal expansion coefficient. The measurement vessel is connected to a diaphragm-type differential pressure transducer (Ruska Model 2413), coupled to an electronic null indicator (Ruska Model 2416). The pressure on either side of the diaphragm is balanced with nitrogen by means of a precision pressure controller (Ruska Model 3981), and the pressure is read by a digital pressure gauge (Ruska Model 7000).

The vessels with the magnetic pump and the pressure transducer are immersed in a thermostatic bath filled with about 45 L of silicon oil. The temperature of the bath is kept constant by means of a PID device, piloted by a computer to which the temperature measurement system is also connected. The temperature control and acquisition system relies on two platinum resistance thermometers calibrated according to ITS 90 at

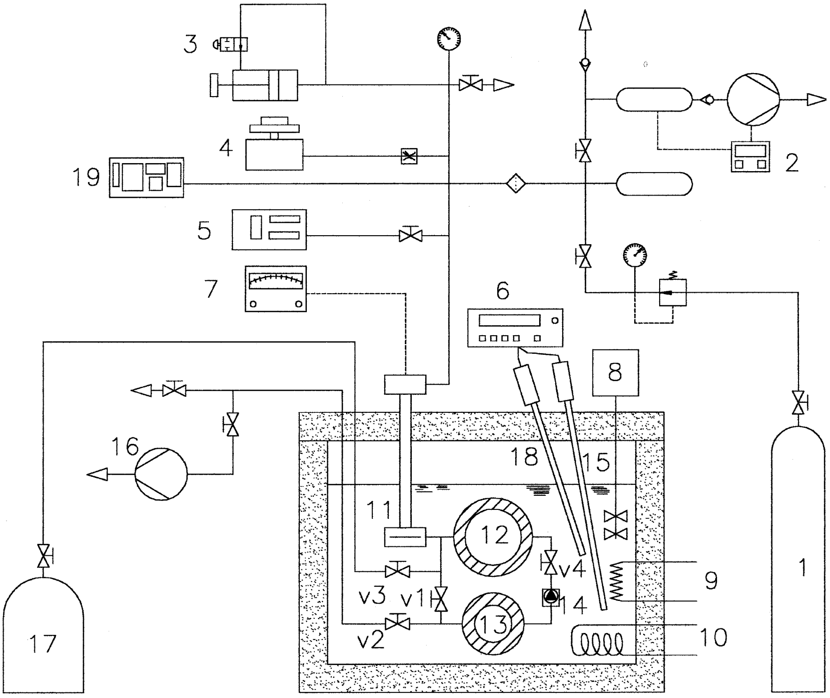

Fig. 1. Schematic diagram of the experimental apparatus. 1, Nitrogen reservoir; 2, Vacuum pump (Vacuubrand Mod. RZ2); 3, Precision pressure controller (Ruska Mod. 3981); 4, Gas lubricated dead weight gage (Ruska Mod. 2465); 5, Vibr. cylinder pressure gage (Ruska Mod. 6220); 6, Digital temperature indicator (Corradi, RP 7000); 7, Electronic null indicator (Ruska Mod. 2416); 8, Stirrer; 9, Heater; 10, Cooling coil connected to an auxiliary bath; 11, Differential press. transducer (Ruska Mod. 2413); 12, Measurement chamber (V_A); 13, Expansion chamber (V_B); 14, Magnetic recirculating pump; 15, Pt resistance thermometer (Tersid, Pt 100); 16, Vacuum pump for V_B (Vacuubrand Mod. RZ2); 17, Charging fluid reservoir; 18, Pt resistance thermometer (Hart Scientific, Pt 25); 19, Digital pressure indicator (Ruska Mod. 7000) V_1,V_2,V_3,V_4 Constant volume valves.

the Istituto di Metrologia “G. Colonnetti” (IMGC) of Turin. A Hart Scientific Pt 25 Ω resistance thermometer (Hart Model 5680) and a Tersid Pt 100 Ω resistance thermometer are used, respectively, for temperature measurement and control. Both thermometers are connected to a digital temperature indicator (Corradi, RP 7000).

The Burnett constant, *N*, defined as the ratio of the volumes of cell A and the sum of the volumes of cells A and B at zero pressure, was determined using gaseous helium measurements. After taking measurements at several isotherms, the constant was found to be $N = 1.4961 \pm 0.0001$. This

Burnett constant reproduces the pressures of helium with absolute average deviations, AAD = 0.483 kPa or AAD = 0.171%.

The uncertainty in the temperature measurements is due to the thermometer and any instability of the bath. The stability of the bath was found to be less than ±0.015 K and the uncertainty of the thermometer was found to be less than ±0.010 K in our temperature range. The total uncertainty in the temperature measurements was thus less than ±0.04 K.

The uncertainty in the pressure measurements is due to the transducer and null indicator system, and to the pressure gauge. The digital pressure indicator (Ruska Model 7000) has an uncertainty of ±0.003% of the full scale. The total uncertainty in the pressure measurement, also influenced by temperature fluctuations due to bath instability, was found to be less than ±1 kPa.

The composition of the mixture is measured by a gas chromatograph following its calibration using samples prepared by the gravimetric method. The samples for the composition measurements are collected during the first Burnett expansion. The uncertainty of the mixture's composition was found to be consistently less than 0.5% in mole fraction.

3. RESULTS AND DISCUSSION

The experimental *PVT* measurements were used to derive the second, *B*, and third, *C*, virial coefficients of the truncated virial equation:

$$P = \frac{RT}{V}\left(1 + \frac{B}{V} + \frac{C}{V^2}\right) \tag{1}$$

In the regression, each run was treated separately and $(dP)^2$ was used as an objective function, applying the Burnett constant from the helium calibration. The pressure distortion of the Burnett cells was taken into account, as explained elsewhere [3].

A summary of the second and third virial coefficients obtained for the pure compounds [1, 2] are reported in Table I. These results were adopted in the present work because the same samples were used for the mixture measurements.

The second and third virial coefficients for nitrous oxide, together with the coefficients available in the literature [5–10], are reported elsewhere [1]. For second virial coefficients the comparisons at the same reduced temperatures showed fair agreement, considering also the mutual uncertainties, with the sources. For the third virial coefficients only one source of data was available [7]. The agreement with this source was rather

Table I. Second and Third Virial Coefficients for N_2O and R32

	N_2O			R32		
Series	T (K)	B ($cm^3 \cdot mol^{-1}$)	C ($cm^6 \cdot mol^{-2}$)	T (K)	B ($cm^3 \cdot mol^{-1}$)	C ($cm^6 \cdot mol^{-2}$)
1	283.51	−150.3	6410.51	303.15	−284.3	24420
2	283.50	−151.1	6911.01	303.16	−283.5	23940
3	304.09	−127.3	5376.18	313.15	−257.5	20650
4	304.10	−128.4	5670.57	313.16	−257.4	19890
5	314.42	−119.1	5471.23	323.16	−238.7	19570
6	314.41	−119.2	5466.06	323.16	−238.3	18980
7	324.78	−109.9	4776.90	333.16	−220.8	17380
8	324.79	−111.2	5427.21	343.16	−203.2	16070
9	335.18	−101.5	4387.63	343.16	−202.3	15760
10	335.16	−100.1	3774.42			
11	345.58	−95.0	4223.44			
12	345.52	−95.5	4428.41			
13	364.36	−82.7	3540.37			
14	364.36	−81.3	2943.91			

good. The same level of agreement with literature sources was obtained for R32, as reported elsewhere [2].

For the binary system, 180 experimental points along 20 sets and 4 isotherms were measured within a temperature range from 303.23 to 364.36 K and a pressure range from 114 to 5229 kPa. These values along with regressed compressibility factors of mixtures are reported in Table II.

The virial coefficients for the mixtures were found by applying the same procedure as for the pure compounds. The values of the second and third virial coefficients (Table III), along with the virial coefficients for the pure compounds (smoothed as a function of reduced temperature), were used to derive cross virial coefficients shown in Table IV.

The cross second virial coefficients were calculated from the expression

$$B_{\mathrm{m}} = \sum_{i=1}^{n} \sum_{j=1}^{n} B_{ij} x_i x_j \tag{2}$$

for each experimental datum point. Next, the B_{12} values found for each temperature were averaged; the averaged B_{12} values, given in Table IV, were used to calculate the deviations of B_{m} from the experimental values shown in Table III. The cross third virial coefficients were calculated from the defining equation:

Table II. Experimental Pressures Measured during Burnett Expansions and Regressed Compressibility Factors of the N_2O (1) + R32 (2) System

Series 1		Series 2		Series 3		Series 4	
$T = 303.23$ K		$T = 303.23$ K		$T = 303.23$ K		$T = 303.23$ K	
$x_1 = 0.2958$		$x_1 = 0.3826$		$x_1 = 0.4480$		$x_1 = 0.6589$	
P (kPa)	z	P (kPa)	z	P (kPa)	z	P (kPa)	z
2454.7	0.7378	2551.4	0.7516	2954.5	0.7169	4005.3	0.6684
1822.0	0.8193	1881.5	0.8292	2214.2	0.8037	3079.5	0.7688
1303.4	0.8768	1340.2	0.8837	1593.4	0.8653	2252.0	0.8412
910.7	0.9166	933.9	0.9213	1117.6	0.9081	1596.2	0.8920
626.7	0.9437	641.7	0.9470	771.2	0.9375	1108.8	0.9270
427.1	0.9622	436.8	0.9645	526.5	0.9574	760.2	0.9509
289.2	0.9746	295.5	0.9761	356.8	0.9708	516.7	0.9669
194.9	0.9827	199.1	0.9838	244.5	0.9951	349.2	0.9776
131.0	0.9882	133.7	0.9887	164.5	0.9983	235.1	0.9847

Series 5		Series 6		Series 7		Series 8	
$T = 303.23$ K		$T = 323.45$ K		$T = 323.45$ K		$T = 323.45$ K	
$x_1 = 0.7326$		$x_1 = 0.2465$		$x_1 = 0.3236$		$x_c = 0.4108$	
P (kPa)	z	P (kPa)	z	P (kPa)	z	P (kPa)	z
3848.9	0.7119	2021.2	0.8388	2610.3	0.8003	2499.7	0.8269
2892.7	0.8004	1433.4	0.8899	1881.4	0.8629	1781.4	0.8816
2086.1	0.8636	996.3	0.9254	1321.6	0.9069	1242.3	0.9198
1465.6	0.9077	683.5	0.9499	912.9	0.9372	854.1	0.9460
1012.1	0.9378	464.8	0.9664	623.6	0.9578	581.5	0.9636
691.2	0.9582	314.1	0.9771	422.8	0.9714	393.4	0.9754
468.8	0.9723	211.5	0.9840	285.1	0.9802	265.0	0.9831
316.4	0.9819	141.9	0.9883	191.7	0.9860	178.0	0.9879
213.1	0.9893			128.6	0.9894	119.4	0.9909

Series 9		Series 10		Series 11		Series 12	
$T = 323.44$ K		$T = 323.44$ K		$T = 343.77$ K		$T = 343.78$ K	
$x_1 = 0.5714$		$x_1 = 0.7450$		$x_1 = 0.2266$		$x_1 = 0.3594$	
P (kPa)	z	P (kPa)	z	P (kPa)	z	P (kPa)	z
3228.5	0.8011	4726.6	0.7299	2865.7	0.8122	2917.9	0.8330
2325.6	0.8633	3513.7	0.8117	2053.8	0.8708	2073.7	0.8857
1633.3	0.9071	2519.5	0.8708	1438.1	0.9123	1443.8	0.9225
1128.0	0.9372	1764.2	0.9123	991.2	0.9407	991.4	0.9477
770.4	0.9577	1215.8	0.9406	676.2	0.9601	674.7	0.9649
522.4	0.9714	829.3	0.9598	458.0	0.9730	456.2	0.9762
352.4	0.9806	561.8	0.9727	308.8	0.9814	307.3	0.9836
237.0	0.9864	378.8	0.9812	207.5	0.9867	206.4	0.9884
159.0	0.9902	254.6	0.9868	139.1	0.9898	138.3	0.9911

Table II. (*Continued*)

Series 13 $T = 343.77\,K$		Series 14 $T = 343.78\,K$		Series 15 $T = 343.77\,K$		Series 16 $T = 364.36\,K$	
$x_1 = 0.4666$		$x_1 = 0.5908$		$x_1 = 0.7567$		$x_1 = 0.2563$	
P (kPa)	z	P (kPa)	z	P (kPa)	z	P (kPa)	z
3911.6	0.7901	3879.6	0.8149	4620.1	0.8033	2528.1	0.8762
2828.1	0.8546	2776.8	0.8726	3321.8	0.8641	1766.2	0.9157
1992.6	0.9008	1942.8	0.9134	2331.4	0.9073	1216.0	0.9432
1379.1	0.9328	1338.5	0.9415	1609.7	0.9372	828.8	0.9619
943.3	0.9546	912.7	0.9605	1099.4	0.9577	561.2	0.9743
640.2	0.9692	618.2	0.9733	745.4	0.9714	378.2	0.9825
432.2	0.9788	416.8	0.9817	502.9	0.9804	254.2	0.9878
290.7	0.9850	280.1	0.9872	338.1	0.9863	170.5	0.9913
195.1	0.9890	187.9	0.9906	226.8	0.9899	114.2	0.9933
Series 17 $T = 364.36\,K$		Series 18 $T = 364.36\,K$		Series 19 $T = 364.35\,K$		Series 20 $T = 364.36\,K$	
$x_1 = 0.3300$		$x_1 = 0.4559$		$x_1 = 0.5606$		$x_1 = 0.7632$	
P (kPa)	z	P (kPa)	z	P (kPa)	z	P (kPa)	z
2942.6	0.8636	4122.8	0.8262	4225.6	0.8370	5229.0	0.8240
2064.5	0.9064	2935.9	0.8802	2996.2	0.8879	3725.1	0.8782
1425.9	0.9367	2047.8	0.9185	2083.5	0.9237	2598.5	0.9166
974.3	0.9575	1408.0	0.9448	1430.0	0.9485	1788.6	0.9438
660.6	0.9712	959.0	0.9628	972.8	0.9653	1218.7	0.9621
445.6	0.9802	649.0	0.9748	657.8	0.9766	824.6	0.9740
299.7	0.9864	437.3	0.9828	443.0	0.9839	556.1	0.9827
200.9	0.9892	294.0	0.9885	297.5	0.9887	373.5	0.9875
134.6	0.9913	197.0	0.9909	199.4	0.9913	250.5	0.9908

$$C_m = \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} C_{ijk} x_i x_j x_k \tag{3}$$

The averaged values of the cross third virial coefficients are included in Table IV. Using these average values, the third virial coefficients for the mixtures were recalculated for each point. The results, together with the deviations, are also given in Table III. The overall AAD for B_m was evaluated at $0.9\,cm^3 \cdot mol^{-1}$, while the AAD for C_m was $363\,cm^6 \cdot mol^{-2}$.

For the system being plotted against the mole fraction in Figs. 2 and 3, the second and third virial coefficients show very small positive and negative deviations, respectively, from ideality, defined here as

$$B_{12} = \frac{(B_{11} + B_{22})}{2} \tag{4}$$

Table III. Experimental and Calculated Second and Third Virial Coefficients for the N_2O (1) + R32 (2) System

		B_m exp	B_m calc	dB_m	C_m exp	C_m calc	dC_m
T(K)	x_1	($cm^3 \cdot mol^{-1}$)			($cm^6 \cdot mol^{-2}$)		
303.23	0.2958	−217.3	−216.7	−0.6	14110	14480	−370
303.23	0.3826	−200.4	−200.6	0.1	11870	12420	−550
303.23	0.4480	−193.2	−189.4	−3.7	12220	11060	1160
303.23	0.6589	−157.6	−159.3	1.7	7610	7760	−150
303.23	0.7326	−148.8	−150.8	2.0	6750	6990	−240
323.45	0.2465	−191.4	−190.4	−1.0	12860	12490	370
323.45	0.3236	−177.7	−177.8	0.1	10720	10970	−250
323.45	0.4108	−164.5	−164.8	0.3	9330	9490	−160
323.44	0.5714	−143.8	−144.2	0.4	7380	7360	20
323.44	0.7450	−126.5	−126.9	0.4	5960	5860	100
343.77	0.2266	−165.1	−164.9	−0.2	10490	10470	20
343.78	0.3594	−146.0	−146.5	0.5	7930	8290	−360
343.77	0.4666	−134.1	−133.6	−0.5	7470	6990	480
343.78	0.5908	−120.9	−120.9	0.1	5850	5920	−70
343.77	0.7567	−107.6	−107.7	0.1	4880	5000	−120
364.36	0.2563	−136.6	−139.1	2.5	6930	8160	−1230
364.36	0.3300	−130.4	−129.8	−0.6	8060	6980	1080
364.36	0.4559	−115.3	−115.7	0.4	5910	5700	210
364.35	0.5606	−106.3	−105.7	−0.5	5080	5120	−40
364.36	0.7632	−93.0	−91.2	−1.8	4280	4560	−280

Table IV. Averaged Second and Third Virial Coefficents for the N_2O (1) + R32 (2) System

	B_{11}	B_{12}	B_{22}	C_{111}	C_{112}	C_{122}	C_{222}
T (K)	($cm^3 \cdot mol^{-1}$)			($cm^6 \cdot mol^{-2}$)			
303.23	−129.3	−156.3	−282.9	5740	5840	11220	23830
323.45	−110.9	−131.4	−237.5	4930	5300	8700	18780
343.77	−96.0	−110.7	−202.6	4220	5140	5880	16040
364.36	−82.0	−92.6	−178.0	3340	6410	1680	15670

$$C_{112} = \frac{(2C_{111} + C_{222})}{3} \tag{5}$$

$$C_{122} = \frac{(C_{111} + 2C_{222})}{3} \tag{6}$$

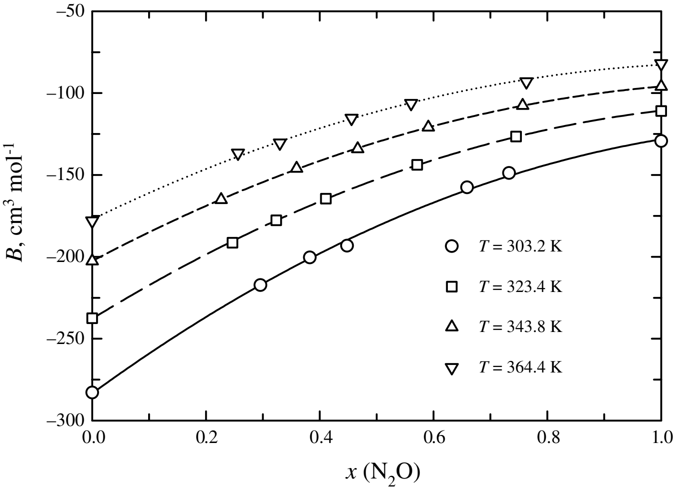

Fig. 2. Present second virial coefficients for the N$_2$O(1) + R32 (2) system vs. mole fraction at temperatures, T : (○)303.23 K; (□)323.45 K; (△)343.77 K; (▽)364.36 K, which include the smoothed values with respect to temperature for the pure compounds. Lines represent the trend of the values.

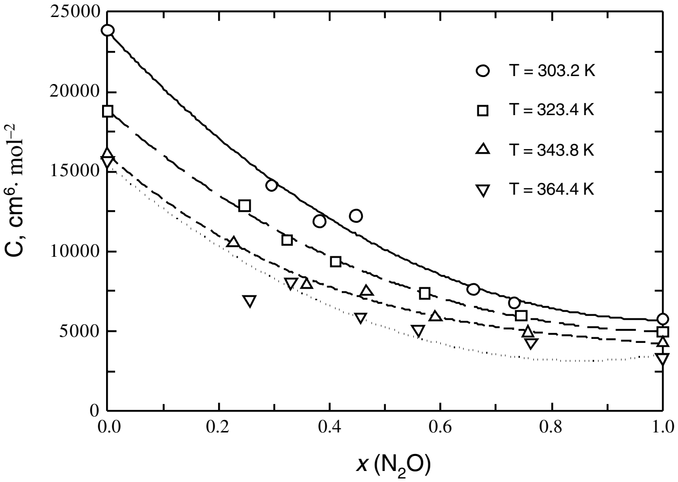

Fig. 3. Present third virial coefficients for the N$_2$O(1) + R32 (2) system vs. mole fraction at temperatures, T : (○)303.23 K; (□)323.45 K; (△)343.77 K; (▽)364.36 K, which include the smoothed values with respect to temperature for the pure compounds. Lines represent the trend of the values.

As shown in Fig. 3, it is also evident that two experimental runs show large scatter deviations at $T = 303.23$ K and $x_1 = 0.4480$ and $T = 363.36$ K and $x_1 = 0.2563$.

4. CONCLUSIONS

This work reports experimental results for the $N_2O + R32$ system obtained with the Burnett method. The performance of the apparatus was checked by means of measurements for N_2O, and good consistency was observed between the virial coefficients obtained and those reported in the literature. The $N_2O + R32$ system was studied over four isotherms, deriving cross second and third virial coefficients. Over the entire temperature range, the second virial coefficients showed positive deviations from ideality, while the third virial coefficients revealed negative deviations. No other $PVTx$ data are available in the literature on this specific binary system.

ACKNOWLEDGMENTS

This work was supported by MIUR, Ministry of Instruction, University and Research and by the government of Marche region.

REFERENCES

1. G. Di Nicola, G. Giuliani, R. Ricci, and R. Stryjek, *J. Chem. Eng. Data* **49**:1465 (2004).
2. G. Di Nicola, F. Polonara, and R. Stryjek, *J. Chem. Eng. Data* **47**:876 (2002).
3. S. Glowka, *Fluid Phase Equilib.* **78**:285 (1992).
4. G. Di Nicola, G. Giuliani, F. Polonara, and R. Stryjek, *Fluid Phase Equilib.* **199**:161 (2002).
5. E. J. Couch, K. A. Kobe, and L. J. Hirth, *J. Chem. Eng. Data* **6**:229 (1961).
6. B. L. Turlington and J. J. McKetta, *AIChE J.* **7**:336 (1961).
7. H. W. Schamp Jr., E. A. Mason, and K. Su, *J Phys. Fluids* **5**:769 (1962).
8. H. L. Johnston and H. R. Weimer, *J. Am. Chem. Soc.* **56**:625 (1934).
9. E. C. Ihmels and J. Gmehling, *Int. J. Thermophys.* **23**:709 (2002).
10. E. Elias, N. Hoang, J. Sommer, and B. Schramm, *Ber. Bunsenges. Phys. Chem.* **90**:342 (1986).