

Vapor Pressure, Liquid Density, and the Latent Heat of Vaporization as Functions of Temperature for Four Dipolar Aprotic Solvents

Phillip Kneisl and John W. Zondlo*

Department of Chemical Engineering, West Virginia University, Morgantown, West Virginia 26506

The vapor pressures and liquid densities of purified samples of 1,1,3,3-tetramethylurea (TMU), *N*-methyl-2-pyrrolidone (NMP), 1,3-dimethyl-2-imidazolidinone (DMEU), and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) were measured as a function of temperature. Liquid densities were determined from 298 to 373 K and vapor pressures from 5.0 to 1000 mbar. Extrapolation of the liquid density data allowed the calculation of pure component *a* and *b* parameters for the Peng-Robinson equation of state over a wide temperature range. Use of this equation of state and the measured vapor pressures allowed accurate determination of the latent heat of vaporization over most of the normal liquid range of these four compounds.

Introduction

Reliable values for the vapor pressure and liquid density of hygroscopic, high-boiling-point liquids are few. The absorption of even small quantities of water can have dramatic effects on these properties (1). Accurate measurement of these properties is especially important for the compounds in this study. The highly polar nature and lack of a measurable critical point render current predictive equations for various physical properties highly unreliable. This is particularly true when predicting fugacity coefficients in vapor-liquid equilibrium calculations.

With this objective in mind, the liquid densities of TMU, NMP, DMEU, and DMPU were determined at six temperatures from 298 to 373 K. In addition the vapor pressures of these compounds were measured over most of their normal liquid range. The use of a quadratic liquid density correlation fitted to the data allowed accurate prediction of the *a* and *b* parameters for the Peng-Robinson (P-R) equation of state. This particular equation of state was chosen because of its simple form and its ability to model both the liquid and the vapor phases of these types of compounds. The Clapeyron equation, with derivatives from the measured vapor pressure curve and volume changes of vaporization calculated from the equation of state, allowed accurate computation of the latent heat of vaporization.

Experimental Section

Materials. TMU was obtained from Sigma Chemical Co., and DMEU and DMPU were purchased from Aldrich Chemical Co. All had a reported purity of 98+ mol %. NMP was supplied gratis by BASF Wyandotte. Its stated purity was 99.9+ mol % with less than 0.01 mol % water and 0.05 mol % methylamine. After gas chromatographic analysis on a Poropak Q column, further purification of the TMU, DMEU, and DMPU by vacuum distillation was required as their purities were in fact below the reported values. The distillation was performed at 5 mmHg through a 40-cm packed column of barium oxide to remove contaminating water. A dry nitrogen blanket was used to prevent oxidation. The supplied NMP was of sufficient purity so as not to warrant this treatment. Final purity of all four solvents was better than 99.95 mol %.

Apparatus and Procedure. Liquid densities were measured with pycnometers with a nominal volume of 25 cm³, calibrated with triple distilled water at 298 K. Standard temperature and

Table I. Comparison of Observed Density Values of Triple Distilled Water vs. Literature Values^a

T, K	ρ_{obsd} , g/cm ³	$\rho_{\text{lit.}}$, g/cm ³	abs % error
293.24	0.9983	0.9982	0.01
293.24	0.9982	0.9982	0.00
298.14	0.9971	0.9971	0.00
314.34	0.9919	0.9918	0.01
332.94	0.9835	0.9833	0.02
353.34	0.9719	0.9717	0.02
363.50	0.9630	0.9631	0.01
			0.01 ^b

^a Values listed are the average of two measurements. ^b Mean percent error.

Table II. Experimental Density Data^g

T, K	ρ , g/cm ³			
	this work	lit.	this work	lit.
	TMU		NMP	
298.14	0.9620	0.9619 ^{c,f} 0.9622 ^e	1.0278	1.027-1.028 ^b 1.0259 ^a
305.14	0.9557		1.0215	
313.14	0.9485		1.0144	1.0120 ^a
318.14		0.9458 ^e		
333.14	0.9303		0.9968	0.9934 ^a
353.14	0.9115	0.9131 ^e	0.9790	
373.14	0.8922		0.9606	
	DMEU		DMPU	
298.14	1.0516	1.044 ^d	1.0593	1.060 ^d
305.14	1.0455		1.0535	
313.14	1.0383		1.0467	
333.14	1.0209		1.0301	
353.14	1.0037		1.0135	
373.14	0.9860		0.9969	

^a Reference 7. ^b Reference 8. ^c Reference 6. ^d Reference 11. ^e Reference 5. ^f Reference 17. ^g Values listed are the average of two measurements.

air density corrections were applied (2, 3). Temperature control of the oil bath was better than ± 0.01 K as measured by a Hy-Cal Engineering reference grade platinum resistance thermometer and a matched BA-500 bridge amplifier. Both were factory calibrated with a certified accuracy of ± 0.05 K, traceable to NBS. Weighing was performed on a Mettler analytical balance with an accuracy of ± 0.1 mg, traceable to NBS. Both the thermometer and balance were checked daily.

Vapor pressures were measured in a Union Carbide twin-arm ebullimeter described in ref 4. Dry nitrogen bled through a fine metering valve was used to control pressure. A control of ± 0.2 mbar, as measured by a Sensotec Model TJE pressure transducer, was obtained by this method. The manufacturer's stated accuracy of the transducer was ± 1.0 mbar. The transducer was checked daily at hard vacuum and at barometric pressure against a mercury barometer. Temperature measurement was accomplished with the previously mentioned equipment.

Results

Density Measurement. In order to test the accuracy of our density measurement, the density of triple-distilled water was determined at six temperatures from 293.24 to 366.50 K. The results, shown in Table I, were compared with those from ref

Table V. Antoine Coefficients (T in K, P in bar)

	A	B	C	std error × 10 ⁴
water	12.015 17	-4010.697	-39.020	0.963
n-tetradecane	9.525 80	-3992.162	-106.956	1.298
TMU	9.435 40	-3448.554	-84.133	1.208
NMP	9.624 82	-3811.448	-80.355	0.759
DMEU	9.310 24	-3805.766	-88.828	1.600
DMPU	9.262 24	-3867.206	-102.346	1.912

Table VI. Comparison of Measured Normal Boiling Points and Enthalpy of Vaporization with Literature Values

compd	bp, K		ΔH_{vap} , kJ/mol		ref
	measd	lit.	calcd	lit.	
water	373.19	373.14	40.87	40.62	3
n-tetradecane	526.63	526.7	48.75	47.61	12
		526.66		48.47	13
TMU	450.13	449.64	41.72		6
NMP	476.89	476.14	44.45	44.70	8
		475.93		46.45	9
		477.94			16
		475.14			10
DMEU	379.40	379-381 ^a			11
DMPU	421.99	419 ^b			11

^a 17 mmHg. ^b 44 mmHg.

Table VII. Latent Heat of Vaporization and Peng-Robinson Parameters as a Function of Temperature

T, K	ΔH_{vap} , kJ/mol	$10^{-7}a$, bar cm ⁶ /mol ²	b , cm ³ /mol
TMU			
450.13 ^a	41.72	5.0072	112.30
425.00	43.60	5.1982	112.31
400.00	45.46	5.3880	112.05
375.00	47.41	5.5829	111.58
350.00	49.59	5.7890	110.96
325.00	52.17	6.0141	110.23
320.00	52.75	6.0623	110.07
NMP			
476.89 ^a	44.45	4.5217	92.011
450.00	46.16	4.6642	91.775
425.00	47.74	4.7965	91.396
400.00	49.40	4.9319	90.902
375.00	51.23	5.0742	90.324
350.00	53.36	5.2279	89.687
340.00	54.32	5.2938	89.421
DMEU			
498.17 ^a	45.34	5.2712	103.90
475.00	46.88	5.4125	103.86
450.00	48.54	5.5648	103.65
425.00	50.26	5.7198	103.27
400.00	52.13	5.8812	102.78
375.00	54.27	6.0534	102.18
355.00	56.26	6.2026	101.64
DMPU			
520.46 ^{a,b}	48.10	6.1025	116.37
510.00	48.89	6.1837	116.45
500.00	49.64	6.2608	116.50
475.00	51.51	6.4542	116.46
450.00	53.47	6.6510	116.23
425.00	55.58	6.8559	115.84
400.00	57.98	7.0736	115.32
375.00	60.79	7.3104	114.69
370.00	61.42	7.3607	114.55

^a Normal boiling point. ^b Will polymerize slowly at this temperature.

The estimate of ΔV_{vap} was provided by the Peng-Robinson equation of state, eq 5.

$$P = \frac{RT}{(V-b)} - \frac{a}{(V^2 + 2Vb - b^2)} \quad (5)$$

To obtain the required coefficients a and b , the quadratic liquid density correlation was extrapolated up to the normal

boiling point. The accuracy of this extrapolation was tested on several data, from the International Critical Tables (14), on polar organic compounds. Typical errors for a 150 K extrapolation were 0.5% or less. An error of this magnitude has only minor effects upon the P-R parameters.

The liquid densities obtained in this manner were then combined with the vapor pressure data and a recently published correlation due to Panagiotopoulos (15) was applied to calculate a and b as a function of temperature for each compound. The resulting values for a , b , and the heat of vaporization are presented for each solvent in Table VII. The same method was used for the values presented previously for water and *n*-tetradecane, with good results as mentioned above. A similar accuracy is expected for each of the solvents.

Acknowledgment

We thank the Union Carbide Corporation for technical assistance with vapor pressure measurements and BASF Wyandotte for donation of the NMP.

Glossary

a, b	parameters for the Peng-Robinson equation of state
A, B, C	parameters for Antoine's equation
ΔH_{vap}	enthalpy of vaporization, kJ/mol
P	pressure, bar
P^{sat}	saturated vapor pressure
R	ideal gas constant
T	temperature, K
ΔV_{vap}	volume change of vaporization
α, β, γ	constants for eq 1
ρ	liquid density, g/cm ³

Registry No. TMU, 632-22-4; NMP, 872-50-4; DMEU, 80-73-9; DMPU, 7226-23-5.

Literature Cited

- Niesen, V. G.; Yesavage, V. F. "Vapor Liquid Equilibrium of Polar, Associating Binary Mixtures at Elevated Temperatures and Pressures"; presented at the AIChE 1986 Spring National Meeting, New Orleans, LA.
- Alkens, D. A. *Integrated Experimental Chemistry*; Allyn and Bacon: New York, 1978; Vol. 1.
- Weast, R. C. *CRC Handbook of Chemistry and Physics*, 57th ed.; CRC Press: Cleveland, OH, 1977-78.
- Olson, J. D. *J. Chem. Eng. Data* **1981**, *26*, 58-64.
- Lindfors, K. R.; Opperman, S. H.; Glover, M. E.; Seese, J. D. *J. Phys. Chem.* **1971**, *75*, 21.
- Barker, B. J.; Caruso, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 1341.
- Murrieta-Guevara, F.; Rodriguez, A. J. *J. Chem. Eng. Data* **1984**, *29*, 204-206.
- N-Methylpyrrolidone (NMP)*, BASF Wyandotte, West Germany, 1985.
- Glerycz, P.; Rogalski, M.; Malanowski, S. *Fluid Phase Equilib.* **1985**, *22*, 107-122.
- Riddick, J. A., Bunger, W. B., Eds. *Techniques of Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1970; Vol. II.
- Aldrich Catalog Handbook of Fine Chemicals, Milwaukee, WI, 1986-87.
- Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.
- API Technical Data Book-Petroleum Refining, 4th Ed., 1983.
- Washburn, E. W., Ed. *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, 1st ed.; McGraw-Hill: New York, 1928; Vol. 3.
- Panagiotopoulos, A. Z.; Kumar, S. K. *Fluid Phase Equilib.* **1985**, *22*, 77-88.
- Yarym-Agaev, N. L. et al. *Ukr. Khim. Zh.* **1980**, *46*, 12, 1331-33.
- Okpala, C.; Guiseppe-Elie A.; Maharajh, D. M. *J. Chem. Eng. Data* **1980**, *25*, 384-386.

Received for review May 27, 1986. Accepted August 11, 1986. Funding for this research was provided by the U.S. Department of Energy under Grant DE-FG05-82ER75056 and The Energy Research Center of the State of West Virginia under Grant ST86-CP7-2. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support.