Experimental Vapor Pressure Data and a Vapor Pressure Equation for *N*,*N*-Dimethylformamide

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New results of vapor pressure data for *N*,*N*-dimethylformamide (DMF) have been measured in the range of temperatures from (308.15 to 368.15) K. The measurement uncertainties in the present work were estimated to be within \pm 10 mK for temperature and \pm 0.103 kPa for pressure. Based on experimental data, a new Wagner-type vapor pressure equation for DMF was presented. The equation of DMF was also compared with available literature data. The purity of DMF sample used in the present measurements was 99.99 mass %.

Introduction

There is a growing interest in the absorption refrigeration system for upgrading waste heat to useful higher temperature levels. Besides the ammonia + water and lithium bromide + water refrigerant + absorbent pairs commercially utilized, numerous other refrigerant + absorbent pairs are currently being considered.^{1–5} Among these refrigerants, 1,1,1,2-tetrafluoro-ethane (R134a) and difluoromethane (R32) with suitable nonvolatile organic solvents such as dimethyl ether of tetra-ethylene glycol (DMETEG), dibutyl phthalate (DBPh) and *N*,*N*-dimethylformamide (DMF) appear to be promising. Compared with DMETEG and DBPh, DMF has several advantages, such as considerable lower price, significantly lower viscosity, and higher absorption capacity for R134a.⁶

Information about the vapor pressures of DMF is essential for its application as an absorbent in an absorption refrigeration system. It is also very useful in calculating the thermodynamic properties necessary for the design of such machinery. The thermodynamic properties of DMF and its experimental data are scarce in the literature.⁷

In this paper, the measurement of vapor pressure data for DMF in the range of temperatures from (308.15 to 368.15) K were presented. A new vapor pressure equation for DMF was developed.

Experimental Section

Materials. The sample of the DMF, provided by SamSung Fine Chemical Co. Ltd., Korea, had a purity of 99.99 mass %. It was used without further purification.

Apparatus. The apparatus used in this work is shown schematically in Figure 1. It includes a high-accuracy thermostatic bath, a sample cell, a pressure measurement system, a temperature measurement system, and a vacuum system. The temperature in the double-walled thermostat bath was controlled by a Shimadzu SR253 proportional controller, which can be varied from (243.15 to 368.15) K. The temperature fluctuation in the bath is less than ± 4 mK in 1 h. The temperature measurement are made with a four-lead 25- Ω platinum resist-

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Figure 1. Experimental apparatus: 1, thermostat bath; 2, stainless steel sample cell; 3, platinum resistance thermometer; 4, circulating pump; 5, Keithlely 2010 data acquisition/switch unit; 6, absolute pressure transmitter; 7, refrigeration system; 8, temperature sensor; 9, stirrer; 10, heater; 11, temperature controller; 12, vacuum pump; 13, DMF.

ance thermometer (Yunnan Instrument WZPB-2) with an uncertainty of \pm 5mK (ITS) and a Keithley 2010 data acquisition/switch unit with an uncertainty of less than \pm 1 mK. The overall error in the temperature measurement system was less than \pm 10 mK. The error of the absolute pressure transmitter (Druck PTX 610) is less than 0.08 % in the range of pressures from (0 to 120) kPa. The sample cell was vacuum pumped to about 0.06 Pa before the experiment.

After the sample cell was filled, the cell was evacuated for several minutes by means of a vacuum pump, and then the thermostat bath temperature was controlled at the experimental temperature. After thermal equilibrium was established between the sample and the heat transfer fluid in the bath and the pressure remained constant, the temperature and the pressure of the sample were recorded.

Vapor Pressure Data and Analysis

Thirty-two vapor pressure data points for DMF measured at temperatures from (308.15 to 368.15) K were measured, as listed in Table 1. The accuracy of the measured vapor pressure data

Table 1. Experimental Vapor Pressure Data of DMF

T/K	p/kPa	<i>T</i> /K	p/kPa	<i>T</i> /K	p/kPa
307.15	0.922	329.15	3.319	351.15	9.101
309.15	1.056	331.15	3.667	353.15	9.898
311.15	1.204	333.15	4.044	355.15	10.755
313.15	1.356	335.15	4.451	357.15	11.674
315.15	1.533	337.15	4.892	359.15	12.660
317.15	1.736	339.15	5.367	361.15	13.718
319.15	1.948	341.15	5.880	363.15	14.853
321.15	2.178	343.15	6.433	365.15	16.068
323.15	2.429	345.15	7.029	367.15	17.371
325.15	2.702	347.15	7.670	369.15	18.806
327.15	2.998	349.15	8.360		

is affected not only by pressure measurement system but also by temperature instability. The pressure uncertainty caused by the pressure measurement system ($\Delta p_{\rm m}$) and temperature instability($\Delta p_{\rm s}$)($\Delta p_{\rm s} = (dp/dT)_{\rm s}\Delta T$) were estimated as

$$\Delta p = \Delta p_{\rm m} + \left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{\rm s} \Delta T \tag{1}$$

where $(dp/dT)_s$ is the first deviation of the vapor pressure with temperature, which was determined from the experimental data or a vapor pressure equation, and ΔT is the temperature uncertainty. From apparatus conditions described above, the maximum overall pressure uncertainty was estimated to be not more than ± 0.103 kPa for DMF.

Vapor Pressure Equation

Based on the experimental data listed in Table 1, a Wagnertype⁸ vapor pressure equation of DMF was developed:

$$\ln\left(\frac{p}{p_{c}}\right) = \frac{T_{c}}{T}(a_{1}\tau + a_{2}\tau^{1.25} + a_{3}\tau^{3} + a_{4}\tau^{7})$$
(2)

where $\tau = 1 - T/T_c$, $a_1 = 36.48688$, $a_2 = -68.67427$, $a_3 = 62.2708$, $a_4 = -229.0057$. $T_c = 596.6$ K is the critical temperature, and $p_c = 5.220$ MPa⁹ is the critical pressure.

The relative deviation between the experimental data and the values calculated from eq 2 is shown in Figure 2. The present experimental data are well represented by eq 2, the maximum relative deviation is 0.391 %, and the root mean square (RMS) deviation is 0.025 %. Figure 2 also shows the deviations of the available literature data from eq 2. The maximum and RMS deviations of eq 2 from the literature⁷ are 3.428 % and 0.347 %, respectively.

Conclusion

Thirty-two vapor pressures data points for DMF have been measured in the range of temperatures from (308.15 to 368.15) K. The measurement uncertainties in the present work were estimated to be within \pm 10 mK for temperature and \pm 0.103 kPa for pressure. The results were fitted with a Wager-type vapor equation and compared with the available literature data.



Figure 2. Relative deviation of the vapor pressure data from eq 2: \blacktriangle , present work; \blacksquare , ref 7.

The applicable range of this equation was at temperatures from (308.15 to 368.15) K.

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