26 *J. Chem. Eng. Data* **2005,** *50,* 26−28

Vapor Pressures of Propylene Carbonate and *N*,*N*-Dimethylacetamide

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We have used a static method to measure vapor pressures of propylene carbonate ($C_4H_6O_3$) and *N*,*N*-dimethylacetamide (C_4H_9NO). Measurements for propylene carbonate were made over the temperature range from (298.15 to 473.15) K; pressures ranged from (0.003 to 37.76) kPa. Measurements for *N*,*N*-dimethylacetamide were made over the temperature range (298.15 to 423.15) K; pressures ranged from (0.29 to 64.8) kPa. The vapor pressure data are correlated with the Antoine and Wagner equations. From the measured vapor pressures, the enthalpies of vaporization are calculated. The results are compared with literature values.

Introduction

Reliable physical property data are required for efficient design in chemical engineering, as well as for progress in fundamental science. Propylene carbonate (PC, 4-methyl-2-dioxolone, $C_4H_6O_3$) goes into many different applications due to its high boiling point and favorable toxic and solvent properties. PC is an excellent solvent for many organic and inorganic materials in such applications as surface cleaners, degreasers, dyes, fibers, plastics, batteries, aromatic hydrocarbons, and natural gas. PC is a widely used solvent for lithium battery electrolytes because of its high relative permittivity (64.40 at 298.15 K), wide liquid range, and good solubilizing power for lithium salts.

N,*N*-Dimethylacetamide (DMA, C_4H_9NO) is a solvent with application in homogeneous synthesis and analysis of cellulose. A mixture with lithium chloride is used in industry to dissolve cellulose.[1] The thermodynamic properties of *N*,*N*-dimethylacetamide are poorly studied, and their experimental data are scarce in the literature. There is a large discrepancy between the vapor pressure of pure DMA reported in various sources.[2] Therefore, it seemed important to us to measure the vapor pressure of pure DMA as a function of temperature and to calculate the enthalpy of vaporization.

In this work, the vapor pressures of PC over the temperature range from (298.15 to 473.15) K and of DMA over the temperature range from (298.15 to 423.15) K were measured with 5 K intervals and correlated with the Antoine and Wagner[3] equations.

The purity of the samples employed in a measurement of a thermodynamic property can significantly affect the accuracy of the measurement. The degree of inaccuracy introduced by the presence of impurities depends on a number of factors. Measurements of a sample whose purity is better than 0.9995 mass fraction is one goal of this work.

Vaporization enthalpies are measurements based on mass transport and are used in evaluating environmental transport properties.[4] For the chemical engineer, the magnitude of this property needs to be taken into consideration in designing equipment for chemical processing and synthesis. From the measured vapor pressure values at different temperatures, the enthalpy of vaporization can be calculated.

Experimental Section

Materials. PC (Fluka, purum) was dried over a molecular sieve (5 Å) for several days, boiled for 2 h in the presence of dried CaO, and then distilled at reduced pressure ($\approx$2 mbar).[5] Nitrogen was bubbled through the solvent at 333 K to remove the volatile impurities. The final distillation was carried out in a specially degassed column[6] at reduced pressure ($\approx$2 mbar) to yield a product with organic impurities of <20 ppm (detected by gas chromatography) and undetectable water content (Karl Fischer titration).

DMA, obtained from Sigma-Aldrich chemical company as HPLC grade, was dried over 4 Å molecular sieves and was used without further purification. The water content in dry DMA as determined by Karl Fischer titration was <20 ppm. The organic impurities were lower than 30 ppm.

Vapor Pressure Measurements. The vapor pressure measurements were performed with a highly precise vapor pressure apparatus that yields the total vapor pressure of solutions. The apparatus was designed especially for vapor pressure measurements of pure fluids and of electrolyte solutions over a wide temperature range from T = (278.15 to 473.15) K with an overall uncertainty in temperature and pressure of 0.003 K and 0.01%, respectively. The temperature is based on the international temperature scale ITS-90. The apparatus and the measuring method as well as the degassing procedure of solution and pure solvent are described in detail in ref 7.

Results

The temperature-dependent vapor pressures of pure PC and DMA were measured in two series from T = (298.15 to 473.15) K for PC and from T = (298.15 to 423.15) K for DMA with 5 K intervals first by increasing temperature and second by decreasing temperature. The differences in repeatability of experimental values are lower than 0.02%. The results are reported in Tables 1 and 2.

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10.1021/je049950g CCC: $30.25

Table 1. Experimental Vapor Pressure Data for Propylene Carbonate

T	p	T	p	T	p
K	kPa	K	kPa	K	kPa
298.15	0.003066	358.15	0.4377	418.15	6.226
303.15	0.006533	363.15	0.5553	423.15	7.454
308.15	0.01293	368.15	0.7206	428.15	8.9594
313.15	0.02106	373.15	0.9231	433.15	10.782
318.15	0.03586	378.15	1.167	438.15	12.694
323.15	0.05240	383.15	1.478	443.15	14.806
328.15	0.07213	388.15	1.856	448.15	17.807
333.15	0.1028	393.15	2.284	453.15	20.501
338.15	0.1321	398.15	2.826	458.15	24.077
343.15	0.1872	403.15	3.482	463.15	27.956
348.15	0.2509	408.15	4.265	468.15	33.012
353.15	0.3277	413.15	5.153	473.15	37.768

Table 2. Experimental Vapor Pressure Data for *N,N*-Dimethylacetamide

T	p	T	p	T	p
K	kPa	K	kPa	K	kPa
298.15	0.2936	343.15	3.270	388.15	21.006
303.15	0.3925	348.15	4.135	393.15	25.028
308.15	0.5179	353.15	5.192	398.15	29.688
313.15	0.6782	358.15	6.467	403.15	35.017
318.15	0.8946	363.15	7.995	408.15	41.114
323.15	1.163	368.15	9.806	413.15	48.057
328.15	1.526	373.15	11.976	418.15	55.912
333.15	1.983	378.15	14.517	423.15	64.782
338.15	2.556	383.15	17.502		

Table 3. Constants of the Antoine Equation ln(*P*/kPa) = *A* − *B*/(*T*/K + *C*)

	temperature range				$\delta_{\mathrm{rms}}{}^{a}$
compound	K	A	B	C	kPa
propylene carbonate	298−473	17.034	6202.612	−10.289	0.079
N,N-dimethyl-acetamide	298−423	14.621	3759.913	−63.3707	0.023

[a] $\delta_{\mathrm{rms}} = [\sum(p - p_{\mathrm{calc}})^2/n]^{0.5}$, where n is the number of experimental points.

The temperature-dependent vapor pressure data are fitted with the Antoine equation

$$\ln(p/\mathrm{kPa}) = A - B/(T/K + C) \qquad (1)$$

where p is pressure, T is temperature, and A, B, and C are the Antoine constants. These constants are presented in Table 3.

For the Wagner equation,[3] the fitting parameters were derived by a nonlinear least-squares fit of the vapor pressures listed in Tables 1 and 2 using the formulation given by Ambrose and Ghiassee[3]

$$\ln(p_{\mathrm{r}}) = (1/T_{\mathrm{r}})(a\tau + b\tau^{1.5} + c\tau^{2.5} + d\tau^{5}) \qquad (2)$$

where p_{r} is the reduced vapor pressure, $p_{\mathrm{r}} = p/p_{\mathrm{c}}$, T_{r} is the reduced temperature, $T_{\mathrm{r}} = T/T_{\mathrm{c}}$, and τ is $1 - T_{\mathrm{r}}$. For PC the critical temperature, $T_{\mathrm{c}} = 762.7$ K, and critical pressure, $p_{\mathrm{c}} = 4.14$ MPa, are taken from Wilson et al.[8] For DMA, the values $T_{\mathrm{c}} = 658.0$ K and $p_{\mathrm{c}} = 4.03$ MPa (taken from DIPPR)[9] are used. The obtained Wagner parameters are given in Table 4.

In the literature, there are numerous vapor pressure data for PC and DMA. However, in the case of propylene carbonate, published data that span the complete temperature range of our study are rare. Hong et al.[10] reported vapor pressure values in the temperature range (368.15 to 455.15) K. They measured them by a dynamic method, using two ebulliometers connected in parallel to a pressure-controlling system with an accuracy of ±0.01 kPa in pressure and ±0.01 K in temperature. All values reported by Hong et al.[10] are lower than our data. Choi et al.[11] obtained four vapor pressure data points in the temperature range (328.2 to 369.6) K; the first two points are higher and the last two points are lower than our values. Stephenson and Malanowski[12] report Antoine constants in the temperature ranges from (323 to 370) K and (412 to 466) K without literature references. The values calculated from these parameters in the temperature range (323 to 370) K have unexpected high deviation from our measurements, whereas the values in the temperature range (412 to 466) K are similar to the values of Hong et al.[10] It seems that Stephenson and Malanowski[13] used the data of Hong et al.[10] for obtaining their Antoine constants in the temperature range (412 to 466) K. Chernyak et al.[13] obtained vapor pressure data points in the temperature range (459.85 to 506.65) K. Figure 1 shows a comparison of literature vapor pressure values for propylene carbonate with those obtained using the Wagner equation and the parameters listed in Table 4.

Table 4. Constants of the Wagner Equation (ln(*p*$_{\mathrm{r}}$) = (1/*T*$_{\mathrm{r}}$)(*aτ* + *bτ*$^{1.5}$ + *cτ*$^{2.5}$ + *dτ*^{5})

	temperature range					$\delta_{\mathrm{rms}}{}^{a}$
compound	K	a	b	c	d	kPa
PC	318−473[b]	82.100	−238.866	231.564	−434.645	0.019
DMA	298−423	18.978	−76.943	65.219	−302.707	0.010

[a] $\delta_{\mathrm{rms}} = [\sum(p - p_{\mathrm{calc}})^2/n]^{0.5}$, where n is the number of experimental points. [b] Temperatures ≤313.15 K not included in final fitting.

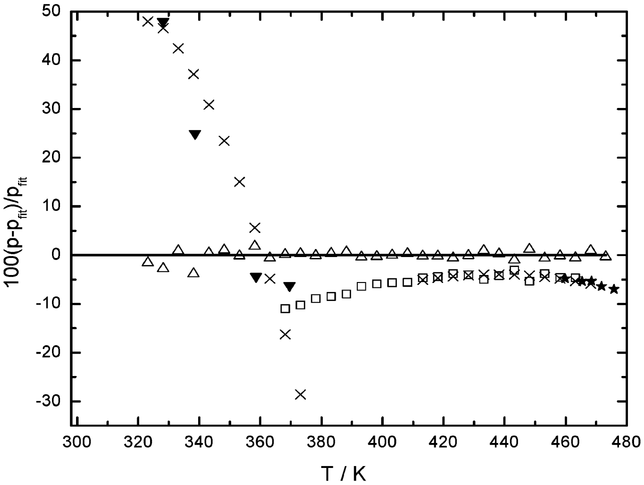

Figure 1. Comparison of literature vapor pressures for propylene carbonate with those obtained using the Wagner equation and the parameters listed in Table 4. The solid line represents the data smoothed with the Wagner equation. △, experimental; ×, Stephenson and Malanowski;[12] □, Hong et al.;[10] ▼, Choi et al.;[11] ★, Chernyak et al.[13]

For DMA, several vapor pressure measurements are reported in the literature. Stephenson and Malanowski[12] report Antoine constants for DMA in the temperature ranges (303 to 363) K and (371 to 423) K. Vapor pressures, calculated from these Antoine constants in the temperature range (371 to 423) K, correspond to our measurements with a deviation of <0.4%, but in the temperature range (303 to 363) K, a relative deviation of 80% is found. Boublík et al.[14] report the Antoine constants and experimental vapor

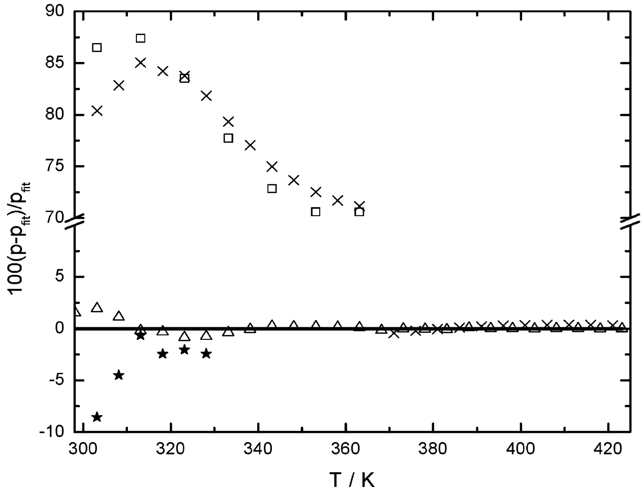

Figure 2. Comparison of literature vapor pressures for *N*,*N*-dimethylacetamide with those obtained using the Wagner equation and the parameters listed in Table 4. The solid line represents the data smoothed with the Wagner equation. △, experimental; ×, Stephenson and Malanowski;[12] □, Gopal et al.;[15] ★, Zielkiewicz.[2]

Table 5. Comparison of the Enthalpy of Vaporization Values for Propylene Carbonate and *N*,*N*-Dimethylacetamide with Literature Values

compound	T K	$\Delta_{vap}H$ kJ·mol^{-1}	$\Delta_{vap}H_{lit}$^{a} kJ·mol^{-1}	$\delta\Delta_{vap}H$^{b}
propylene carbonate	298.2	71.317	*c*	*c*
	323	58.875	55.2^{d}	6.65%
	338	58.489	33.8^{e,f}	73.04%
	383	56.045	57.8^{d}	−3.03%
	423	54.573	55.2^{d}	−1.14%
	427	54.523	54.4^{e}	0.226%
	443	53.451	53.0^{d}	0.851%
N,*N*-dimethylacetamide	298.2	45.818	50.2^{g}	−8.73%
	312	45.611	67.9^{g,h}	−32.83%
	386	44.081	45.1^{g}	−2.26%
	420	43.624	*c*	*c*

[a] Chickos and Acree.[4] [b] $\delta\Delta_{vap}H = (\Delta_{vap}H - \Delta_{vap}H_{lit})100/\Delta_{vap}H_{lit}$. [c] There is not a sufficient number of literature data in the measured range. [d] Hong et al.[10] [e] Stephenson and Malanowski.[12] [f] Choi and Joncich.[11] [g] Majer and Svoboda.[16] [h] Boublík et al.[14]

pressure values of Gopal et al.[15] in the temperature ranges (303.15 to 363.15) K. The relative deviation from our values is up to 80%. The vapor pressure data reported by Zielkiewicz[2] in the temperature range (303 to 328) K are close to the data from our measurements. All these literature data are compared with the vapor pressure values calculated by the Wagner equation with the coefficients of Table 4 obtained from our experimental measurements; see Figure 2. It should be noted here, as can be seen in Figure 2, that a large discrepancy between the vapor pressure of pure *N*,*N*-dimethylacetamide reported from various sources is observed at lower temperatures. The data reported by Stephenson and Malanowski[12] do not contain literature references. In this case, close examination of the values of Gopal et al.[15] indicates that the Antoine constants reported by Stephenson and Malanowski[12] in the temperature range (303 to 363) K are obtained from these values and that there are unexpected high deviations between these data and our measurements.

The Clausius−Clapeyron equation is a general equation originally relating the vapor pressure, temperature, volume change, and enthalpy of vaporization of a pure liquid in equilibrium with the gas phase. If the molar volume of the liquid is much smaller than that of the gas and if the gas phase can be considered as ideal, then the Clausius−Clapeyron equation

$$\frac{d\ln(p)}{d(1/T)} = \frac{-\Delta_{vap}H}{R} \tag{3}$$

can be applied. In this equation, p is the vapor pressure, $\Delta_{vap}H$ is the enthalpy of vaporization, T is the absolute temperature, and R is the gas constant. Our data show a linear relationship between $\ln(p)$ and $1/T$ over a temperature range of 30 K for both solvents. The inferred values of the enthalpy of vaporization are compiled in Table 5. Because of the significant discrepancies between our experimental vapor pressure and the corresponding literature data, it is not surprising that the enthalpy values also scatter a lot.

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Received for review January 30, 2004. Accepted October 4, 2004. We thank the Arbeitsgemeinschaft industrieller Forschung AiF "Otto von Guericke e. V." (AiF) for financial support. K.N. is grateful to the Iran Ministry of Science, Research and Technology for a grant.

JE049950G