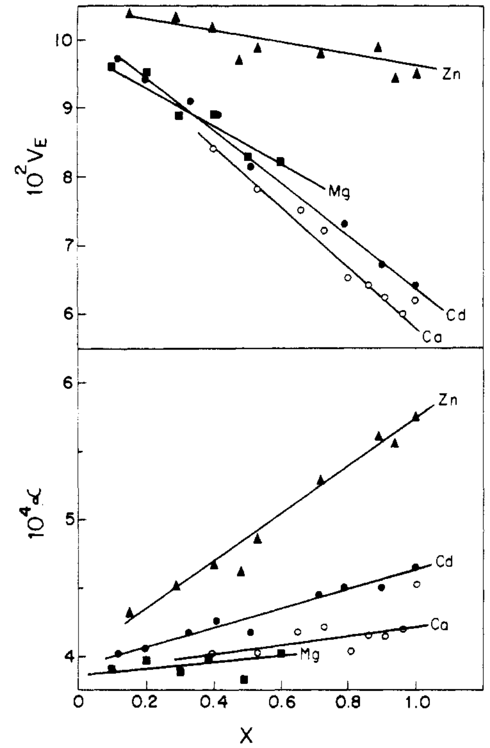

Figure 2. Composition variation of thermal expansion coefficient (α) and molar expansivity (V_E) of $Al(NO_3)_3 \cdot 10.03H_2O$ + $M(NO_3)_2 \cdot RH_2O$ systems at 300 K.

moles of water associated with the cations decrease from 10 to 4/6 per mole of mixture. Both the factors would markedly decrease V_0. It may be noticed that there is a parallelism between the composition variation of V_E and α of Ca^{2+}- and Cd^{2+}-containing mixtures while Zn^{2+}- and Mg^{2+}-containing mixtures exhibited a different trend. This may be attributed to an increased NO_3^--ZN^{2+} interaction (*16-18*). Zinc may undergo ion-pair formation resulting in an increase in V_0 and thereby a flattened curve for V_E and large changes in α.

Registry No. $Al(NO_3)_3$, 13473-90-0; $Ca(NO_3)_2$, 10124-37-5; $Cd(NO_3)_2$, 10325-94-7; $Zn(NO_3)_2$, 7779-88-6; $Mg(NO_3)_2$, 10377-60-3.

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Densities and Apparent Molar Volumes in the Binary System Dimethyl Sulfoxide–Water at 25, 40, 60, and 65 °C

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The densities of binary mixtures of dimethyl sulfoxide and water have been determined at 25, 40, and 60 °C. These data are presented, along with literature values at 45 and 65 °C, and used to calculate the apparent molar volume of each component at all five temperatures at compositions of 0–100 wt % water. The densities show a strong, positive deviation from ideality. Correlations are presented that allow the calculation of densities and apparent molar volumes at each temperature and all compositions.

Introduction

As part of an ongoing research effort designed to investigate the physicochemical properties of a variety of solvent systems, the densities of mixtures of dimethyl sulfoxide (Me_2SO) in water have been measured at 25, 40, and 60 °C across the entire range of composition. The apparent molar volume of each component was calculated by using these data and literature data at 45 and 65 °C (*1*). Both the densities and the apparent molar volumes were fit to equations of the form:

$$P_1 = P_2^0 + AC_1 + BC_1^2 + \ldots + EC_1^6 \qquad (1)$$

The agreement between values calculated by using these equations and the experimental values was approximately equal to the maximum experimental error of ±0.000 10 g/mL in the density measurements.

Experimental Method

Distilled water from the house supply was further purified by using a Millipore "Milli-Q" reagent water system. Ultrapure Me_2SO (Burdick and Jackson) was used without further purification. Water was determined by Karl Fischer titrations that are considered accurate to ±0.01 wt %. Densities were determined with a Mettler/Parr DMA 55 digital density meter calibrated with deaerated water and dry air. Temperatures were held to ±0.05 °C with a water bath.

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† Operated by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy.

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Table I. Densities of Me_2SO-H_2O Mixtures at 25, 40, and 60 °C

wt % Me_2SO	wt % H_2O	d^{25}, g/mL	d^{40}, g/mL	d^{60}, g/mL
100.00	0.00	1.09560	1.08046	1.06062
99.90	0.10	1.09579	1.08060	1.06079
99.75	0.25	1.09586	1.08066	1.06086
99.50	0.50	1.09596	1.08078	1.06099
99.25	0.75	1.09606	1.08089	1.06113
99.00	1.00	1.09615	1.08102	1.06126
98.00	2.00	1.09655	1.08149	1.06178
97.00	3.00	1.09695	1.08192	1.06229
96.00	4.00	1.09731	1.08236	1.06280
95.00	5.00	1.09750	1.08176	1.06326
94.00	6.00	1.09797	1.08316	1.06372
93.00	7.00	1.09827	1.08352	1.06414
92.00	8.00	1.09852	1.08385	1.06453
91.00	9.00	1.09876	1.08415	1.06490
90.00	10.00	1.09880	1.08443	1.06528
85.00	15.00	1.09919	1.08514	1.06630
80.00	20.00	1.09842	1.08475	1.06619
75.00	25.00	1.09640	1.08302	1.06484
70.00	30.00	1.09319	1.07999	1.06227
65.00	35.00	1.08865	1.07590	1.05871
60.00	40.00	1.08296	1.07076	1.05421
55.00	45.00	1.07647	1.06498	1.04915
50.00	50.00	1.06881	0.05862	1.04357
40.00	60.00	1.05389	1.04468	1.03130
30.00	70.00	1.03847	1.03073	1.01879
25.00	75.00	1.03096	1.02378	1.01271
20.00	80.00	1.02368	1.01714	1.00646
15.00	85.00	1.01650	1.01047	1.00037
10.00	90.00	1.01006	1.00431	0.99459
9.00	91.00	1.00837	1.00290	0.99331
8.00	92.00	1.00705	1.00165	0.99213
7.00	93.00	1.00576	1.00045	0.99097
6.00	94.00	1.00446	0.99923	0.98982
5.00	95.00	1.00319	0.99803	0.98869
4.00	96.00	1.00193	0.99684	0.98757
3.00	97.00	1.00068	0.99567	0.98647
2.00	98.00	0.99946	0.99451	0.98536
1.00	99.00	0.99823	0.99336	0.98428
0.00	100.00	0.99702	0.99223	0.98320

Statistical analysis of the data was carried out using the Statistical Analysis Pac for a Hewlett-Packard HP-87XM microcomputer.

Results and Discussion

The density-composition diagram for the Me_2SO-H_2O system (Figure 1), constructed from the data given in Table I, shows marked, positive deviations from ideality. This indicates that the interactions between Me_2SO and water are stronger than Me_2SO-Me_2SO or water-water interactions. These results are in good agreement with those of previous authors (*1-4*) who made similar measurements at 25 °C. There are no previously reported data on the density of Me_2SO-H_2O mixtures at 40 or 60 °C. Cowie (*1*) has reported measurements at 45 and 65 °C as shown in Table II.

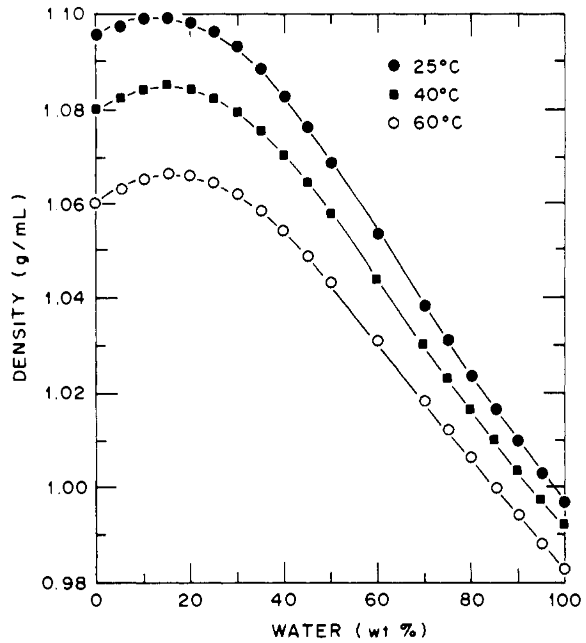

Figure 1. Density of Me_2SO-water mixtures at 25, 40, and 60 °C as a function of weight percent water.

Table II. Density of Me_2SO-H_2O Mixtures at 65 °C[a]

d^{45}, g/mL	d^{65}, g/mL	wt %[b] H_2O	wt %[b] Me_2SO
1.0756	1.0556	0.00	100.00
1.0762	1.0564	1.12	98.9
1.0768	1.0570	2.20	97.8
1.0781	1.0582	5.01	95.0
1.0799	1.0604	10.4	89.6
1.0802	1.0612	20.1	79.9
1.0787	1.0603	24.9	75.1
1.0756	1.0574	30.1	69.9
1.0715	1.0538	35.2	69.8
1.0667	1.0495	40.0	60.0
1.0548	1.0391	49.9	50.1
1.0411	1.0268	60.0	40.0
1.0280	1.0150	70.0	30.0
1.0146	1.0032	79.8	20.2
1.0026	0.9920	90.0	10.0
0.9902	0.9806	100	0.00

[a] Source: ref 1. [b] Cowie reported his data in terms of the mole fraction of water. These units were converted to wt % to facilitate comparisons with the values in Table I.

If Me_2SO and water formed an ideal solution, the density of a solution of any composition at a temperature of t °C could be calculated as

$$d_{DW}{}^{t} = X_D d_D{}^{t} + X_W d_W{}^{t} \qquad (2)$$

where d is the density, X is the mole fraction, D is Me_2SO, and W is water. Unfortunately, as is clear from the data in Figure 1, these solutions are far from ideal even when one component is quite dilute. Since there is no adequate theoretical treatment available to describe this behavior, we have adopted the purely empirical approach of fitting the density data to a polynomial in the concentration of Me_2SO or water (eq 3). In this equation,

$$d_{DW}{}^{t} = d_W{}^{t} + AC_D + BC_D{}^2 + \ldots + FC_D{}^6 \qquad (3)$$

$d_W{}^t$ is the density of pure water at t °C, C_D is the concentration of Me_2SO, and A, B, ..., F are empirical coefficients whose values depend on the temperature and on the units used for C_D as shown in Table III. If the weight percent or mole fraction of water is known, then the same equations are used by substituting the density of pure Me_2SO as the first term, and (100 - wt % H_2O) or (1 - mole fraction H_2O) for the concentration of Me_2SO. If the molarity of the water in the two-component system is known, then the first term of the equation will be the density of pure Me_2SO, and the coefficients for the remaining terms are those found in Table IV. In all cases, the equations yield density values that agree with the experimental results to within ±0.0001 g/mL. Note that the coefficients which correspond to $d_W{}^t$ and $d_D{}^t$ shown in Tables III and IV vary slightly from the actual measured values of these densities. These small variations arise from the statistical treatment of the data and are within the stated accuracy of the equations. Cowie's data were used to develop similar correlations at 45 and 65 °C; these results are also included in Tables III and IV.

In addition to their utility in calculating the density of a Me_2SO-H_2O solution (or in estimating the composition of a solution from the measured density), these correlations can be used to make an analytical determination of the composition at which the measured density of the solution deviates most strongly from the theoretical density of an ideal solution. Table

Table III. Coefficients Used with Eq 2 to Calculate the Density of 0-100 wt % Me_2SO in H_2O

[Me_2SO] units	d	A	B	C	D	E	F	temp, °C
X	0.99694	0.53415	-0.77701	-0.48068	2.40468	-2.33717	0.75485	25
X	0.99212	0.50517	-0.85941	0.07058	1.35155	-1.46786	0.48844	40
X^a	0.99033	0.49238	-0.86486	0.21406	1.03006	-1.17274	0.38999	45
X	0.98312	0.47952	-0.98135	0.74533	0.11786	-0.46791	0.18416	60
X^a	0.98079	0.45694	-0.91545	0.71020	-0.02604	-0.12513	-0.08430	65
wt %	0.99696	1.2284E-3^b	5.7577E-6	-7.6533E-8	3.7510E-9	-7.3704E-11	3.5687E-13	25
wt %	0.99221	1.1313E-3	8.0754E-6	-2.1169E-7	5.9897E-9	-8.7632E-11	3.8350E-13	40
wt %^{a}	0.99022	1.2079E-3	-8.7374E-7	6.2916E-8	1.8192E-9	-5.5789E-11	2.8643E-13	45
wt %	0.98320	1.0599E-3	9.5271E-6	-3.4652E-7	8.4507E-9	1.0437E-10	4.2134E-13	60
wt %^{a}	0.98062	1.1441E-3	-1.8551E-6	1.3147E-8	3.2696E-9	-6.8700E-11	3.2612E-13	65
M	0.99697	9.5764E-3	2.9301E-4	-3.8609E-5	7.6820E-6	-1.00179E-6	3.4128E-8	25
M	0.99226	8.7673E-3	4.7985E-4	-1.0464E-4	1.6383E-5	-1.5045E-6	4.4857E-8	40
M^a	0.99023	9.4083E-3	-5.0171E-5	1.8373E-5	2.5411E-6	-7.3962E-7	2.8188E-8	45
M	0.98327	8.2748E-3	5.6544E-4	-1.6093E-4	2.5108E-5	-2.0661E-6	5.8050E-8	60
M^a	0.98062	8.9292E-3	-1.3878E-4	1.0044E-5	5.5210E-6	-9.5810E-7	3.3446E-8	65

[a] Calculated by using data from ref 1. [b] 1.2284E-3 ≡ 1.2284 × 10^{-3} and so on.

Table IV. Coefficients Used with Eq 3 to Calculate the Density of 0-100 wt % Me_2SO in H_2O

[H_2O] units	d	A	B	C	D	E	F	temp, °C
M	1.09577	6.0711E-4	6.4016E-6	-4.0987E-6	9.2350E-8	-6.6569E-10	7.5398E-13	25
M	1.08054	7.6190E-4	3.2609E-6	-4.3607E-6	1.1619E-7	-1.1839E-9	4.2666E-12	40
M^a	1.07563	8.6708E-4	-9.1562E-6	3.5332E-6	8.6926E-8	-6.5241E-10	5.5142E-13	45
M	1.06072	8.9136E-4	2.7153E-6	-4.7860E-6	1.4639E-7	-1.8202E-9	8.5607E-12	60
M^a	1.05571	8.9777E-4	-2.0217E-6	-3.9512E-6	1.0512E-7	-9.7875E-10	2.5156E-12	65

[a] Calculated by using data from ref 1.

Table V. Composition of Me_2SO-H_2O Solutions Where the Density Deviates Most Strongly from Ideality

X_{H_2O}	X_{Me_2SO}	H_2O:Me_2SO	t, °C
0.68	0.32	2:1	25
0.72	0.28	3:1	40
0.77	0.23	3:1	45^a
0.83	0.17	5:1	60
0.83	0.17	5:1	65^a

[a] Calculated by using the data in ref 1.

V lists the composition of the solution at each temperature where the first derivative of eq 3 - eq 2 is zero. Cowie (*1*) and LeBel (*2*) have reported the maximum deviation at 25 °C occurs at a 2:1 water:Me_2SO ratio (Me_2SO mole fraction = 0.33), and noted that this maximum moves toward higher water:Me_2SO ratios as the temperature is increased. The results and data analysis reported here confirm and quantify these results.

***Apparent Molar Volumes*.** DeVisser et al. (*4*) summarized the previously reported values for the apparent molar volumes

Table VI. Coefficients Used with Eq 5 to Calculate the Apparent Molar Volume of Me_2SO in Me_2SO-H_2O Mixtures

[Me_2SO] units	$\phi_{V,Me_2SO}{}^0$	coefficient						temp, °C
		A	B	C	D	E	F	
X	68.88	-16.59562	77.60361	-123.35162	91.83254	-28.64812	1.58539	25
X	69.76	-15.31646	80.64292	-155.96202	164.39220	-94.06013	22.85754	40
X	69.39	-0.00539	-25.30698	177.06111	-360.04153	308.73885	-97.21113	45
X	70.45	-11.70184	72.75889	-160.53174	197.74736	-131.74399	36.38855	60
X	71.00	-5.57235	25.13298	-9.02224	-37.00037	44.15041	-14.67686	65
wt %	68.90	-4.4284E-2	5.6285E-4	1.0547E-5	1.6599E-7	3.2955E-10	-8.1486E-12	25
wt %	69.83	-5.5964E-2	1.6128E-3	-3.8853E-5	5.4458E-7	-2.3505E-9	-1.5993E-13	40
wt %	68.05	2.2640E-1	-1.3031E-2	3.4282E-4	-4.7332E-6	3.4505E-8	-1.0231E-10	45
wt %	70.84	-5.0429E-2	1.6012E-3	-2.9410E-5	2.6468E-7	3.9595E-10	-9.1730E-12	60
wt %	72.73	-2.4364E-1	1.1776E-2	-2.9108E-4	3.7594E-6	-2.2980E-8	5.2821E-11	65
M	68.90	-0.33169	2.2805E-2	-6.4157E-5	-1.2145E-4	3.6740E-5	-1.6411E-6	25
M	69.82	-0.40823	7.6256E-2	-1.0877E-2	9.4728E-4	-1.6417E-5	-5.7599E-7	40
M	68.17	1.57313	-6.8679E-1	0.13583	-1.3948E-2	7.4536E-4	-1.60117E-5	45
M	70.83	-0.37690	8.4951E-2	-9.9827E-3	4.9434E-4	2.4087E-5	-1.6992E-6	60
M	72.02	-1.12083	3.8418E-1	-6.7966E-2	6.2394E-3	-2.5771E-4	3.7378E-6	65

Table VII. Coefficients Used with Eq 5 to Calculate the Apparent Molar Volume of Water in Me_2SO-H_2O Mixtures

[Me_2SO] units	$\phi_{V,H_2O}{}^0$	A	B	C	D	E	F	temp, °C
X	15.46	4.9244	-16.8387	82.8214	-133.5635	115.0494	-39.7868	25
X	15.87	1.8314	-9.15080	29.8696	-48.4473	46.2955	-18.0514	40
X	15.97	-1.7500	16.0339	-47.2449	69.65757	-42.38327	7.91108	45
X	15.84	3.69664	-18.8751	54.2391	-77.8897	62.0761	-20.7674	60
X	15.68	5.93950	-24.77553	54.6087	-60.38224	39.66737	-12.37093	65
wt %	15.63	4.6930E-2	-2.0365E-3	8.7857E-5	-1.6176E-6	1.3253E-8	-4.0521E-11	25
wt %	15.87	1.7551E-2	1.2281E-4	1.8768E-5	-5.4169E-7	5.1689E-9	-1.6991E-11	40
wt %	15.89	1.3923E-2	6.8104E-4	-3.6621E-6	-1.4335E-7	1.8563E-9	-6.4722E-12	45
wt %	15.98	3.1832E-2	-7.4385E-4	4.4947E-5	-9.6358E-7	8.5521E-9	-2.7519E-11	60
wt %	15.88	7.1462E-2	-3.7061E-3	1.4368E-4	-2.5883E-6	2.1450E-8	-6.6944E-11	65
M	15.62	8.4393E-2	-7.0893E-3	5.1535E-4	-1.6099E-5	2.2711E-7	-1.2095E-9	25
M	15.87	3.3296E-2	-5.6703E-4	1.5721E-4	-6.4968E-6	1.0204E-7	-5.7412E-10	40
M	15.89	2.4934E-2	1.5373E-3	7.9205E-6	-1.7140E-6	2.966E-8	-1.5448E-10	45
M	15.97	5.9905E-2	-3.4816E-3	3.2754E-4	-1.1796E-5	1.8261E-7	-1.0432E-9	60
M	15.87	1.3404E-1	-1.3438E-2	9.1664E-4	-2.9621E-5	4.3878E-7	-2.4630E-9	65

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of both components of the Me_2SO-H_2O system as calculated from the usual equation

$$\phi_{V,A} = \frac{M_A}{d} - \frac{1000(d_{AB}{}^t - d_B{}^t)}{m_A d_{AB} d_B{}^t} \qquad (4)$$

where $\phi_{V,A}$, M_A, and m_A are the apparent molar volume, molecular weight, and molality of component A, respectively, $d_B{}^t$ is the density of pure component B at t °C, and $d_{AB}{}^t$ is the density of the AB mixture at temperature t.

Following the example of Kiyohara, Perron, and Desnoyers (*3*) we have used our density data to calculate the apparent molar volumes of both Me_2SO and water, and then correlate the results using polynomial equations in the concentration of each component (eq 5). The coefficients derived for calculating the apparent molar volumes of Me_2SO and H_2O at all concentrations (using a number of different units) at 25, 40, and 60 °C are listed in Tables IV and V, respectively. We have used the results of Cowie to derive similar equations for the apparent molar volume of water at 45 and 65 °C. These results are also included in Tables VI and VII.

$$\phi_{V,A} = \phi_{V,A}{}^0 + AC_A + BC_A{}^2 + ... + FC_A{}^6 \qquad (5)$$

Registry No. Me_2SO, 67-68-5.

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Vapor–Liquid Equilibrium for Four Mixtures Containing *N*,*N*-Dimethylformamide

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Low-pressure isothermal vapor–liquid equilibria have been measured for *N*,*N*-dimethylformamide (DMF)/benzaldehyde, *n*-butyl acetate/DMF, acetic acid/DMF, and cyclohexylamine/DMF. Activity coefficients derived from our measurements have been correlated with five thermodynamic models by using the maximum likelihood method, and used to estimate UNIFAC group contribution parameters.

Introduction

Two previous papers in this series (*1*, *2*) have reported vapor–liquid equilibrium (VLE) measurements of hydrocarbons/oxyhydrocarbon mixtures. These results were used to test activity coefficient models and to calculate parameters for the UNIFAC group contribution model (*3*). In this study we report measurements on systems containing *N*,*N*-dimethylformamide (DMF) as one component. DMF is a commonly used aprotic solvent. It is capable of separating saturated and unsaturated hydrocarbons either as a selective solvent or as a third component in extractive distillation. Because of the high dielectric constant of DMF, it is a good reaction solvent and, in some cases, it even has catalytic properties. These phenomena can be described if a model for the activity of compounds in mixtures with DMF is available. UNIFAC is an especially useful thermodynamic model because it only requires data on the interactions among individual chemical groups, such as a methylene group or an aldehyde group, and these are a relatively small number of groups compared to the number of molecules. If information is available on DMF and a relatively small number of groups, one can use these data to predict the activity of any compound in DMF, provided this compound is composed of the same chemical groups that are in the data base. This paper presents isothermal VLE values of DMF with four functional groups and makes estimates for previously unavailable group interaction parameters for DMF with each group.

Table I. Antoine Constants for Representation of Vapor Pressure of Compounds Used[a]

	A	*B*	*C*
DMF[d]	6.0459	1401.382	193.864
(lit.[b])	6.2334	1537.78	210.39
benzaldehyde[d]	6.3711	1691.620	210.02
n-butyl acetate[d]	6.0380	1294.2	195.09
(lit.[c])	6.1534	1368.50	204.00
acetic acid (lit.[b])	6.5522	1558.03	224.79
cyclohexylamine[d]	5.6851	1152.538	178.904

[a] $\log (p/p^0) = A - B/(T + C)$, where $p^0 = 1.0$ kPa, T in °C. [b] From ref 4. [c] From ref 5. [d] This work.

Experimental Section

DMF is embryotoxic to laboratory animals and should not be inhaled or allowed to contact skin; all experimental work was performed in a fume hood. Since DMF is such a good solvent, care must be exercised in the choice of materials which contact it.

The experimental equipment and operating procedures have been discussed previously (*1*, *2*). As before, a significant portion of the experimental effort was devoted to the purification and determination of the boiling points of the pure compounds. All compounds except DMF and acetic acid were purified by fractional distillation under dry nitrogen at reduced pressures. Acetic acid and DMF were acceptably pure as received; since they are very hygroscopic, they were kept under dry nitrogen at all times. Table I gives the Antoine constants we derived using the same chemicals that were used in the later VLE experiments. Note that the Antoine constants for DMF previously reported in the literature (*4*) underpredict the vapor pressure at the reported normal boiling point by about 1 kPa. We have determined the boiling points for anhydrous DMF supplied by Aldrich and by du Pont, and the results obtained with these two samples were essentially indistinguishable. We have also derived new Antoine constants which are consistent with the normal boiling point of DMF.

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