UF_6 than many of the halocarbons and fluorinated halogens studied in the past (*1*, *4*). Thus, reasonably good, low-temperature solvents exist for uranium hexafluoride, even among rather simple solvent molecules.

Registry No. UF_6, 7783-81-5; $COCl_2$, 75-44-5; N_2O, 10024-97-2; SO_2, 7446-09-5.

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Heat Capacities of Some Binary and Ternary Aqueous Nonelectrolyte Systems

Ian R. Tasker,[†] **Sushil K. Suri,**[‡] **and Robert H. Wood***

Department of Chemistry, University of Delaware, Newark, Delaware 19711

Heat capacities of a variety of binary and ternary aqueous nonelectrolyte systems were measured and the data fitted to $C_{p,\phi} = C_{p,\phi}{}^\circ + c_2m + c_3m^2$. The systems studied were aqueous solutions of acetamide, acetone, *p*-dioxane, dimethylformamide, ethyl acetate, formamide, hexamethylenetetramine, methyl formate, *s*-trioxane, and combinations of two of the above solutes. Internal consistency of data is very good and c_2 coefficients agree with literature values. However, small discrepancies of $C_{p,\phi}{}^\circ$ with literature values are observed, indicating a problem with the calorimeter.

Introduction

Heat capacities of binary and ternary aqueous solutions of myoinositol (IN), D-mannitol (MAN), cyclohexanol (CHEX), formamide (F), *N*,*N*-dimethylformamide (DMF), *s*-trioxane (T), and hexamethylenetetramine (HMT) were measured to complement recent enthalpy studies (*1*–*5*). Heat capacity measurements contribute to an understanding of solutions: details of structural effects have been found (*6*, *7*), solute–solvent and solute–solute interactions have been uncovered (*8*–*12*), evidence of pseudophase transitions in binary aqueous organic systems (*13*) has been cited, and means have been provided for evaluating both the temperature dependence of excess thermodynamic properties (*14*) and isothermal compressibilities from isentropic compressibilities (*15*).

Much of the interest in heat capacity measurements has arisen in the past decade as a result of the widespread use of flow calorimeters, particularly those of the Picker type (*16*). Flow calorimetry offers a number of advantages over earlier techniques: higher sensitivity, elimination of vapor-space corrections, short response times, small sample size, and rapid collection of data. These inherent advantages, together with some elegant design features, make possible the use of "the general principle that it is preferable to measure heat capacities as a function of temperature and integrate to obtain enthalpies at various temperatures than to derive heat capacities from the temperature dependence of enthalpies" (*15*). This type of calorimeter is now being used for measurements at high temperatures (*17*–*23*). With the great importance now attached to heat capacity measurements, it is essential that the accuracy of the data should not be called into question. The results presented here give rise to some concern over this matter.

Experimental Section

Materials. The purification of myoinositol (*1*), D-mannitol (*1*), cyclohexanol (*1*), formamide (*2*), *N*,*N*-dimethylformamide (*2*), *s*-trioxane (*3*), and hexamethylenetetramine (*5*) used by one of us (I.R.T.) has been previously reported. The purification of acetamide, acetone, dioxane, ethyl acetate, formamide, hexamethylenetetramine, D-mannitol, methyl formate, and *s*-trioxane (used by S.K.S.) has also been reported elsewhere (*24*). Details of solution preparation and handling are also available (*1*–*3*, *5*).

Apparatus and Procedure. Measurements were taken with a Sodev Model CP-C Picker-type flow heat capacity microcalorimeter (*16*, *25*, *26*). Essentially, two liquids (1 and 2) with heat capacities per unit volume of σ_1 and σ_2 are maintained at the same temperature and flow rate as they enter twin cells; here they are simultaneously heated in such a manner that their final temperatures are identical. If W_1 and W_2 are the electrical powers supplied to produce the temperature rise, then, under ideal circumstances (i.e., no heat losses), we have

$$\frac{W_2 - W_1}{W_1} = \frac{\sigma_2 - \sigma_1}{\sigma_1} \qquad (1)$$

The instrumentation is arranged so that the difference in applied

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[†] Current address: Alberta Research Coucil, Oil Sands Research Department, Edmonton, Alberta, Canada T6G 2C2.

[‡] Current address: Department of Chemistry, Indian Institute of Technology, Hauz Khas., Bombay 400099, India.

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Table I. Results of S.K.S. for Apparent Molar Heat Capacities, $C_{p,\phi}$ (J mol^{-1} K^{-1}), of Aqueous Nonelectrolyte Systems[a]

m^b	$C_{p,\phi}$	$C_{p,\phi}$(calcd)	Δ
Acetamide (AC)			
0.1640	152.00	151.73	0.27
0.3102	151.40	151.53	−0.13
0.5060	150.85	151.26	−0.41
0.8993	150.90	150.73	0.17
1.4815	150.30	149.93	0.37
1.8202	149.20	149.47	−0.27
Acetone (AN)			
0.1790	223.65	223.20	0.45
0.2890	221.40	222.12	−0.72
0.4369	220.54	220.67	−0.13
0.9760	216.04	215.37	0.67
1.1961	213.13	213.20	−0.07
1.9077	206.00	206.20	−0.20
Dioxane (DIOX)			
0.1374	197.70	198.19	−0.49
0.2994	195.20	195.93	−0.73
0.3519	196.00	195.19	0.81
0.6936	191.80	190.41	1.39
0.8828	187.25	187.77	−0.52
1.0258	186.80	185.76	1.00
1.5340	175.90	178.65	−2.75
2.1068	171.90	170.64	1.26
Ethyl Acetate (EA)			
0.1720	368.63	368.73	−0.10
0.3315	364.82	364.80	0.02
0.4400	362.25	362.13	0.12
0.6971	355.85	355.79	0.06
0.8672	351.50	351.60	−0.10
Formamide (F)			
0.1452	77.80	77.87	−0.07
0.2229	78.10	78.11	−0.01
0.4465	78.75	78.74	0.01
0.5986	79.25	79.13	0.12
0.8896	79.85	79.81	0.04
1.4793	80.70	80.84	−0.14
2.2193	81.55	81.51	0.04
Hexamethylenetetramine (HMT)			
0.1663	148.50	148.31	0.19
0.3035	148.85	148.97	−0.12
0.4909	149.70	149.87	−0.17
1.0025	152.70	152.33	0.37
1.4237	153.90	154.35	−0.45
1.9707	157.15	156.97	0.18
Mannitol (MAN)			
0.1151	432.55	432.59	−0.04
0.2131	432.70	432.69	0.01
0.3313	432.85	432.82	0.03
0.5503	433.20	433.07	0.13
0.8459	432.60	433.39	−0.79
0.8910	434.10	433.44	0.66
Trioxane (T)			
0.1721	168.15	168.22	−0.07
0.3892	165.90	165.87	0.03
0.6236	163.15	163.34	−0.19
1.0053	159.75	159.21	0.54
1.7377	150.65	151.28	−0.63
2.0891	147.80	147.48	0.32
AC + DIOX			
0.1434	175.25	175.46	−0.21
0.2441	174.80	174.77	0.03
0.5131	173.20	172.94	0.26
0.9451	169.70	170.00	−0.30
1.4524	167.00	166.55	0.45
2.1022	161.90	162.13	−0.23
AC + EA			
0.1411	260.35	250.18	0.17
0.2980	258.00	257.93	0.08
0.5974	253.15	253.62	−0.47
0.9052	249.20	249.20	0.00
1.1377	246.15	245.85	0.30
1.5571	239.75	239.82	−0.07
AC + F			
0.1329	116.70	115.94	0.76
0.3034	115.45	115.83	−0.38
0.4999	114.80	115.69	−0.89
1.3478	115.60	115.11	0.49
1.9918	114.45	114.67	−0.22
AC + MAN			
0.1406	292.75	292.25	0.50
0.2044	291.90	292.14	−0.24
0.5200	291.65	291.60	0.05
0.9215	290.20	290.91	−0.71
1.3762	290.40	290.14	0.26
1.8849	289.40	289.27	0.13
AC + T			
0.1055	164.10	161.09	3.01
0.2178	159.00	160.39	−1.39
0.5286	156.50	158.43	−1.93
1.0419	154.80	155.20	−0.40
1.4950	152.45	152.36	0.09
2.0719	149.35	148.73	0.62
DIOX + EA			
0.1682	282.25	281.31	0.94
0.1951	281.15	281.02	0.13
0.3040	279.60	279.82	−0.22
0.4868	277.35	277.82	−0.47
0.7809	272.10	274.60	−2.50
DIOX + F			
0.2868	139.95	139.36	0.59
0.3134	139.15	139.22	−0.07
0.4966	137.75	138.27	−0.52
0.8526	136.60	136.43	0.17
1.1277	134.60	135.01	−0.41
1.8215	131.65	131.42	0.23
DIOX + HMT			
0.2181	200.55	199.20	1.35
0.3574	195.20	196.56	−1.36
0.5534	192.60	192.84	−0.24
0.6258	190.25	191.47	−1.22
1.4499	174.90	175.85	−0.95
DIOX + MAN			
0.1189	316.30	314.92	1.38
0.2217	313.15	314.19	−1.04
0.5514	311.65	311.86	−0.21
1.0068	308.40	308.64	−0.24
1.4643	305.10	305.40	−0.30
2.0676	301.55	301.13	0.42
DIOX + T			
0.1829	182.10	182.35	−0.25
0.3515	181.70	181.28	0.42
0.6219	180.10	179.58	0.52
1.1430	175.85	176.29	−0.44
1.6898	171.75	172.84	−1.09
2.2953	169.85	169.02	0.83
EA + F			
0.2006	219.95	219.57	0.38
0.4408	217.20	217.20	0.00
0.6369	214.10	215.26	−1.20
0.8292	213.75	213.36	0.39
0.9440	212.70	212.23	0.47
1.3448	208.20	208.27	−0.07
EA + MAN			
0.1376	400.35	400.03	0.32
0.3417	397.95	397.33	0.62
0.5850	393.45	394.10	−0.65
0.7705	391.35	391.64	−0.29
1.0622	386.75	387.78	−1.03
1.3989	384.35	383.32	1.03
EA + T			
0.1421	267.90	268.03	−0.13
0.2348	266.80	266.36	0.44
0.5514	260.55	260.66	−0.11
0.8600	254.60	250.43	0.17
1.5845	242.20	242.06	0.14

Table I (*Continued*)

m^b	$C_{p,\phi}$	$C_{p,\phi}$(calcd)	Δ
	F + HMT		
0.1362	114.40	115.30	−0.90
0.2427	116.10	115.42	0.68
0.5721	116.60	115.82	0.78
1.1502	115.85	116.52	−0.67
1.8507	117.35	117.37	−0.02
2.4360	118.20	118.07	0.13
	F + MAN		
0.1024	256.10	256.15	−0.05
0.2023	255.80	256.22	−0.42
0.4711	256.90	256.42	0.48
0.8985	256.55	256.73	−0.18
1.2642	257.50	256.99	0.51
1.8099	257.05	257.39	−0.34
	F + T		
0.1488	122.75	122.89	−0.14
0.2793	122.80	122.44	0.36
0.5217	121.90	121.62	0.28
0.9622	119.20	120.11	−0.91
1.5807	118.40	118.00	0.40
1.8787	117.00	116.99	0.01
	HMT + MAN		
0.0882	290.30	290.51	−0.21
0.1718	291.20	290.48	0.72
0.3942	291.70	290.40	1.30
0.7859	288.75	290.24	−1.49
1.1326	288.65	290.11	−1.46
1.9258	290.95	289.80	1.15
	HMT + T		
0.1631	163.20	162.24	0.96
0.3323	161.20	161.85	−0.65
0.6145	158.20	161.20	−3.00
1.1875	162.75	160.89	1.86
1.6268	160.10	158.87	1.23
2.5027	155.45	156.85	−1.40
	MAN + T		
0.1589	298.65	298.63	0.02
0.3440	298.05	298.14	−0.09
0.6309	297.65	297.38	0.27
0.8409	295.85	296.83	−0.98
1.1230	297.10	296.09	1.01
1.9392	293.70	293.94	−0.24

[a] Systems are listed in alphabetical order. [b] Units: mol kg^{-1}.

power ($\Delta W = W_2 - W_1$) is measured, yielding initially $\Delta\sigma$ ($=\sigma_2 - \sigma_1$), i.e.

$$\Delta\sigma/\sigma_1 = \Delta W/W_1 \tag{2}$$

Hence, the volumetric heat capacity of any liquid can be determined if it is run against another liquid of known σ. In practice, heat losses are present and it is necessary to determine a correction factor, f, from a chemical calibration using a sample of known heat capacity (*26*). Thus

$$\Delta\sigma/\sigma_1 = f(\Delta W/W_1) \tag{3}$$

Experimentally we have a choice of two operating procedures. The obvious procedure is to run each unknown liquid against a standard. An alternative technique is the stepwise procedure in which the first sample is run against a standard, then the second sample is run against the first sample, and so on. This procedure is recommended (*27*) since it reduces errors due to changes in volume at the interface between the reference and sample solutions. In addition, it is experimentally more convenient, allowing increased sensitivity of measurement (which outweighs the effects of small cumulative errors) and producing reliable results with small scatter. In the present work, some measurements were taken using the former single reference procedure (S.K.S.) and some using the latter stepwise procedure (I.R.T.).

ΔW was monitored by using a Digitec 266 dc voltmeter and a Sargent Model SR strip chart recorder. Base current and zener potentials were measured with a Kethley Model 177 microvolt digital multimeter. Normally $W_1 = \simeq 110$ mW giving a ΔT of about 2 °C. Details of operation are available (*28*). Transport of solutions was achieved by using either gravity flow (S.K.S.) or a Sage Instruments Model 373 peristaltic pump. With gravity flow, the flow rate was monitored by measuring the average temperature rise of the sample and reference, T_0. Flow rate was kept constant during a run by varying the height of the exit solution. However, tests showed that identical results were obtained without this small height adjustment. In order to prevent bubble formation, the solutions were kept under a slight positive pressure by placing the level of the exit solution above the calorimeter (by 20 cm for S.K.S., by 45 cm for I.R.T.). In several tests the solutions were degassed with no change in the results. The normal flow rates were 0.9 cm^3 min^{-1} for S.K.S. and 0.6 cm^3 min^{-1} for I.R.T. For volatile solutes, evaporation of the sample was controlled by reducing vapor space and using containers with narrow openings. For two of the more volatile solutions (ethyl acetate and acetone) tests with a method which completely eliminated evaporation of the solution gave identical results.

Thermostating was achieved with a modified Coleman cooler and a Tronac PTC40 temperature controller (*24*). In the earlier experiments (S.K.S.), the vacuum in the instrument was produced by a single-stage rotary vacuum pump (Edwards Speedivac 2), whereas in later experiments (I.R.T.), a two-stage rotary vacuum pump (Welch Duo-Deal Model 1400) was used. All solutions were initially referenced against water, for which we used $c_p{}^\circ = 4.1796$ J g^{-1} K^{-1} (*16*, *29*) and $d^\circ = 0.997047$ g cm^{-3} (*30*). The volumetric heat capacity, σ, is given by

$$\sigma = dc_p \tag{4}$$

Densities were measured on a Sodev Inc. Model 01D densimeter (*24*). The mean temperature of the experiment was 25 °C. All ternary solutions were prepared so as to be equimolal in each component.

Experimental data, obtained as σ, were converted to c_p by using eq 4 and these were converted to apparent molar heat capacities by using (*11*)

$$C_{p,\phi} = Mc_p + (c_p - c_p{}^\circ)/m \tag{5}$$

where M is the molar mass of the solute and m is the molality of the solution. Consistent units are important in eq 5: for instance, M in kg mol^{-1}; c_p in J kg^{-1} K^{-1}; and m in mol kg^{-1}.

Results

The results, in terms of m and $C_{p,\phi}$ for our two series of measurements, are presented in Tables I and II. These data were then least-squares fitted to

$$C_{p,\phi} = C_{p,\phi}{}^\circ + c_2 m + c_3 m^2 \tag{6}$$

The values of $C_{p,\phi}$, c_2, and c_3 are presented in Table III. Also included there are σ (the standard error of the fit), the molality range of the fitted data sets, comparable literature data (when available), and, for ternary systems, $C_{p,\phi}$(add), which is the arithmetic mean of $C_{p,\phi}$ for the corresponding binary systems and provides a means for checking the internal consistency of the data. Using eq 6 and the coefficients generated by the fitting procedure, we calculated values of $C_{p,\phi}$ corresponding to the experimental molalities. These values are given

Table II. Results of I.R.T. for Apparent Molar Heat Capacities, $C_{p,\phi}$ (J mol^{-1} K^{-1}), of Aqueous Nonelectrolyte Systems[a]

m^b	$C_{p,\phi}$	$C_{p,\phi}$(calcd)	Δ
Dimethylformamide (DMF)			
0.1996	200.41	200.20	0.21
0.3937	198.47	198.53	−0.06
0.5847	196.60	196.89	−0.29
0.7963	195.06	195.07	−0.01
1.0158	193.35	193.19	0.16
Formamide (F)			
0.4108	80.18	80.27	−0.09
0.8366	83.03	82.88	0.15
1.2678	85.33	85.34	−0.01
1.7400	87.77	87.80	−0.03
2.1441	89.63	89.71	−0.08
2.6773	92.02	91.97	0.05
Hexamethylenetetramine (HMT)			
0.3430	156.28	156.09	0.19
0.4651	156.08	156.42	−0.34
0.6369	157.13	156.88	0.25
0.8138	157.19	157.36	−0.17
1.0025	157.94	157.87	0.07
Trioxane (T)			
0.1006	163.85	163.40	0.45
0.1991	162.07	162.61	−0.54
0.2999	161.47	161.80	−0.33
0.3996	161.39	160.99	0.40
0.4966	160.31	160.21	01.0
0.5992	159.30	159.38	−0.08
CHEX + DMF			
0.0985	337.10	337.50	−0.40
0.1925	337.15	336.26	0.89
0.2769	333.67	335.14	−1.47
0.3931	335.28	333.61	1.67
0.4661	332.50	332.64	−0.14
0.5784	330.61	331.16	−0.55
CHEX + F			
0.1220	273.26	273.64	−0.38
0.2466	273.43	273.08	0.35
0.3617	272.94	272.55	0.39
0.4723	271.68	272.05	−0.37
0.5989	271.59	271.47	0.12
0.7230	270.80	270.91	−0.11
CHEX + HMT			
0.1016	311.51	312.22	−0.71
0.2007	311.01	311.20	−0.19
0.2996	312.05	310.19	1.86
0.4002	308.74	309.16	−0.42
0.4978	307.74	308.17	−0.43
0.6040	306.98	307.08	−0.10
CHEX + T			
0.1087	316.03	316.03	0.00
0.4508	313.67	313.38	0.29
0.5728	311.77	312.44	−0.67
0.6614	312.13	311.75	0.38
DMF + F			
0.2248	138.77	138.73	0.04
0.3957	137.90	138.01	−0.11
0.6209	137.34	137.24	0.10
0.7930	136.82	136.80	0.02
0.9708	136.40	136.47	−0.07
1.2696	136.22	136.20	0.02
DMF + HMT			
0.0534	179.80	178.04	1.76
0.1002	177.83	178.23	−0.40
0.1480	178.68	178.43	0.25
0.1965	177.91	178.63	−0.72
0.2943	177.74	179.04	−1.30
0.3979	177.58	179.47	−1.89
0.4983	181.76	179.88	1.88
0.5876	180.68	180.25	0.43
DMF + IN			
0.1740	259.70	259.47	0.23
0.3384	259.58	259.58	0.00
0.5074	259.27	259.70	−0.43
0.6714	259.72	259.81	−0.09
0.8292	260.20	259.92	0.28
DMF + MAN			
0.1606	316.26	316.76	−0.50
0.3194	316.67	316.21	0.46
0.4782	315.63	315.67	−0.04
0.6350	314.82	315.13	−0.31
0.7999	315.87	314.56	1.31
0.9771	313.02	313.95	−0.93
DMF + T			
0.0853	183.53	183.28	0.25
0.1507	182.38	182.89	−0.51
0.2462	182.47	182.33	0.14
0.3177	182.17	181.90	0.27
0.3960	181.36	181.44	−0.08
0.4861	180.83	180.90	−0.07
F + HMT			
0.0601	109.26	109.01	0.25
0.1096	109.16	109.20	−0.04
0.1582	109.15	109.38	−0.23
0.2037	109.44	109.56	−0.12
0.2550	109.61	109.75	−0.14
0.3078	110.23	109.95	0.28
F + IN			
0.3378	201.74	201.44	0.30
0.5099	202.83	203.01	−0.18
0.6793	204.62	204.74	−0.12
0.8342	205.80	206.24	−0.44
0.9983	208.26	207.82	0.44
F + MAN			
0.1796	250.93	250.91	0.02
0.3369	251.30	252.21	0.09
0.4266	251.27	251.38	−0.11
0.5094	251.49	251.53	−0.04
0.6700	251.82	251.33	−0.01
0.8318	252.18	252.13	0.05
F + T			
0.1844	117.75	117.68	0.07
0.3441	117.45	117.36	0.09
0.5033	116.91	117.05	−0.14
0.6673	116.65	116.72	−0.07
0.8266	116.35	116.40	0.05
1.1527	115.85	115.75	0.10
HMT + IN			
0.1018	242.01	241.90	0.11
0.2010	242.09	242.81	−0.72
0.3049	244.28	243.76	0.52
0.4000	244.90	244.63	0.27
0.4986	245.74	245.54	0.20
0.5997	246.07	246.46	−0.39
HMT + MAN			
0.2018	295.58	295.63	−0.05
0.3012	295.51	295.60	−0.09
0.4030	295.67	295.58	0.09
0.5009	295.87	295.55	0.32
0.5968	295.26	295.52	−0.26
HMT + T			
0.0984	161.86	162.02	−0.16
0.1968	161.55	161.79	−0.24
0.2989	162.09	161.54	0.55
0.3999	161.29	161.30	−0.01
0.4988	161.21	161.07	0.14
0.5931	160.56	160.84	−0.28

Table II (*Continued*)

m^b	$C_{p,\phi}$	$C_{p,\phi}$(calcd)	Δ	m^b	$C_{p,\phi}$	$C_{p,\phi}$(calcd)	Δ
	IN + T				MAN + T		
0.1496	242.84	242.82	0.02	0.1468	296.87	296.83	0.04
0.3007	243.17	243.27	−0.10	0.2991	296.39	296.29	0.10
0.4491	243.77	243.70	0.07	0.4487	295.63	295.75	−0.12
0.5997	244.22	244.14	0.08	0.6009	295.15	295.21	−0.06
0.7496	244.52	244.58	−0.06	0.7468	294.53	294.68	−0.15
0.9016	245.02	245.03	−0.01	0.8901	294.36	294.17	0.19

[a] Systems are presented in alphabetical order. [b] Units: mol kg^{-1}.

in Tables I and II as $C_{p,\phi}$ (calcd) together with Δ (the difference between experimental and calculated $C_{p,\phi}$), which gives a measure of the fidelity of the fitted equation to the experimental data.

Discussion

The results of this work were examined both in terms of internal consistency and in terms of agreement with available literature data. Internal consistency of our data may be inspected in two ways. First, the agreement between systems measured by different experimentalists can be observed. Second, the internal consistency of each data subset, as indicated by the comparison of additivity of $C_{p,\phi}{}^\circ$ from binary systems with the experimental $C_{p,\phi}{}^\circ$ for ternary systems, can be checked.

From the scatter of the individual measurements for each solute we have calculated the 95% confidence limits of $C_{p,\phi}{}^\circ$. The values for the 95% confidence limits in Table III vary from 0.2 to 4.5 and these values are in good agreement with the expected random errors in the calorimeter. The error limit is consistent with the differences between duplicate measurements by different experimentalists: for the 10 systems measured by both S.K.S. and T.R.T., the differences in $C_{p,\phi}{}^\circ$ vary from 0.14 to 7.6 J mol^{-1} K^{-1}. This limit of error is consistent with previous results from the literature using the Picker calorimeter (*40*).

The consistency of the c_2 coefficients of the molality expansion for these 10 systems is also very good. Eight systems have c_2's within 95% confidence limits of each other (MAN, HMT, T, F + HMT, F + MAN, HMT + MAN, HMT + T, T + MAN) while a ninth (F + T) is only marginally beyond this. For the remaining system (F), a triplet term, c_3, may have affected the fitting process.

Viewing the internal consistency of the individual subsets in terms of the additivity of the limiting property $C_{p,\phi}{}^\circ$ where we must have

$$C_{p,\phi}{}^\circ(\text{add})(\text{A} + \text{B}) = \{C_{p,\phi}{}^\circ(\text{A}) + C_{p,\varphi}{}^\circ(\text{B})\}/2 \qquad (7)$$

we see that except for DIOX + HMT, most of the systems agree within 2 or 3 J mol^{-1} K^{-1} and the maximum difference is 6.5 J mol^{-1} K^{-1}.

Having established the internal consistency of the data we now compare our measurements with the literature values available for six of the binary systems, acetamide (AC), acetone (AN), dioxane (DIOX), dimethylformamide (DMF), ethyl acetate (EA), and *s*-trioxane (T) (see Table III). Looking first at the c_2 coefficients, we find that in every case agreement is within stated (or reasonably assumed) 95% confidence limits. This agreement lends confidence to values of c_2 which we obtained for the ternary systems (for which there are no data for literature comparison).

However, comparison of the present measurements with literature values of $C_{p,\phi}{}^\circ$ raises some concern. For many of the aqueous nonelectrolyte solutions reported here, the values of the apparent heat capacity, $C_{p,\phi}$, are 12-25 J mol^{-1} K^{-1} lower than literature values. While this much error is common with previous measurement techniques (*40*), it is much higher than expected for the present calorimeter. The above errors correspond to directly measured relative changes in volumetric heat capacity, $\Delta\sigma/\sigma_0$, that are high by as much as 40% (for acetone) and of the wrong sign in another case (ethyl acetate) where the value of $\Delta\sigma$ is very close to zero. These figures are inconsistent with the rated accuracy of this calorimeter of 1% in $\Delta\sigma/\sigma_0$.

We have been unable to find any experimental error in the present results that could have caused this discrepancy. Possible experimental errors and the reasons that we do not think they were a source of error in the present results are discussed below.

1. ***Solution Makeup.*** There are many examples in Table III of where two different experimenters made completely independent measurements on the same solute with results that agree within the expected accuracy of 1%. In addition, the concentrations of these solutions calculated from the experimental densities of the solutions, and literature values of the apparent molar volumes, agree (±0.2% or less) with the molality calculated from the weights of solute and solvent, used to make up the solution.

2. ***Heat Leak Correction Factor.*** The heat leak correction factor, $f = 1.04 \pm 0.025$, has been determined by four different investigators over the course of 3 years. R.H.W. found f = 1.042 using 3 mol kg^{-1} aqueous NaCl as a chemical standard just after the calorimeter was purchased. Later, S.K.S. found f values of 1.040, 1.042, 1.048, and 1.038 using aqueous NaCl with concentrations near 0.1, 0.3, 0.05, and 1.0 mol kg^{-1} NaCl. Near the end of the 3-year period, I.R.T. found f values of 1.047, 1.044, and 1.059 using NaCl as the chemical standard, and 1.015 and 1.040 using KCl as the chemical standard. In addition, Coe found 1.044 using KCl as the standard (*41*).

3. ***Vacuum.*** The single-stage vacuum pump used by S.K.S. routinely gave pressures from 1 to 4 Pa while the two-stage pump used by I.R.T. gave pressures near 0.1 Pa. In the original checkout of the instrument, it was found that, with 3 mol kg^{-1} NaCl, pressures of 1 and 3 Pa gave identical results, ±0.5%. In fact, even running the calorimeter at 10^5 Pa only increased the heat leak correction factor from 1.04 to 1.09. This general insensitivity of the instrument to the quality of the vacuum, together with the fact that this error is of the wrong sign to explain our results, indicates that the quality of the vacuum is not the problem.

4. ***Power Level.*** Most of our experiments were run at a power level of 110 mW. For aqueous acetamide, runs using 20 mW gave identical results.

5. ***Flow Rate.*** The two sets of experiments reported here used flow rates differing by about 50%, and yet the results agree. In addition, the instrument was routinely adjusted, so that change in the flow rate of as much as 10% produced no change in the base line.

6. ***Volume Change at the Water–Solution Interface.*** Errors can be caused by changes in volume at the solution–sample interface, although these are generally negligible for aqueous solutions (*14*). This effect causes errors of opposite sign when the solution is used as a reference rather than pure water. The measurements of I.R.T. were always made both

Table III. Coefficients of Eq 5 for Experimental Data

system	$C_{p,\phi}^{\circ}$, J mol^{-1} K^{-1}	$C_{p,\phi}^{\circ}$(add),[a] J mol^{-1} K^{-1}	c_2, J K^{-1} mol^{-2} kg	c_3, J K^{-1} mol^{-3}	σ,[b] J mol^{-1} K^{-1}	m, mol kg^{-1}	ref
acetamide (AC)	151.95 (0.70)[c]		−1.36 (0.65)		0.35	0.16–1.82	S.K.S.[d]
	163.8		−1.38	0.12		0.05–8.0	*31*
	164. (2)					0.09–0.35	*32*
acetone (AN)	224.96 (1.08)		−9.83 (1.05)		0.56	0.18–1.91	S.K.S.
	225						*33*
	241.3		−7.64	0.279		0.0–27.0	*31*
dioxane (DIOX)	200.12 (2.22)		−13.99 (2.05)		1.52	0.14–2.11	S.K.S.
	222.4		−11.58	1.106		0.0–12.0	*34*
	212						*35*
dimethylformamide (DMF)	201.92 (0.76)		−8.6 (1.1)		0.23	0.20–1.02	I.R.T.[e]
	225.1		−8.34			0.0–∞	*36*
ethyl acetate (EA)	372.97 (0.37)		−24.65 (0.65)		0.11	0.17–0.87	S.K.S
	396.6		−22.1			0.0–0.9	*11*
formamide (F)	77.41 (0.65)		3.25 (0.64)	−0.63 (0.27)	0.10	0.15–2.22	S.K.S.
	77.55 (1.61)		6.82 (0.90)	−0.54 (0.29)	0.11	0.41–2.68	I.R.T.
hexamethylenetetramine (HMT)	147.52 (0.66)		4.80 (0.60)		0.34	0.17–1.97	S.K.S.
	155.17 (1.20)		2.69 (1.73)		0.29	0.34–1.00	I.R.T.
mannitol (MAN)	432.46 (1.15)		1.10 (1.99)		0.52	0.12–0.89	S.K.S.
	429.98 (1.70)		4.59 (8.15)		0.33	0.07–0.31	I.R.T., *38*
	455.4		4.7			0.09–1.05	*39*
s-trioxane (T)	170.08 (0.92)		−10.82 (0.75)		0.46	0.17–2.09	S.K.S.
	164.21 (1.14)		−8.06 (2.95)		0.44	0.10–0.60	I.R.T.
	185		−9.2		0.6	0.10–1.06	*37*
AC + DIOX	176.43 (0.63)	176.04 (0.73)	−6.80 (0.55)		0.34	0.14–2.10	S.K.S.
AC + EA	262.21 (0.63)	262.46 (0.54)	−14.38 (0.69)		0.30	0.14–1.56	S.K.S.
AC + F	116.03 (1.32)	114.68 (0.68)	−0.68 (1.21)		0.68	0.13–1.99	S.K.S.
AC + MAN[f]	292.49 (0.91)	292.21 (0.93)[g]	−1.71 (0.86)		0.48	0.14–1.88	S.K.S.
AC + T	161.76 (3.65)	161.02 (0.81)	−6.29 (3.17)		1.95	0.11–2.07	S.K.S.
CHEX[h] + DMF	338.81 (3.26)	332.32 (3.31)[i]	−13.23 (8.76)		1.25	0.10–0.58	I.R.T.
CHEX + F	274.20 (1.00)	270.13 (1.90)[i]	−4.55 (2.14)		0.38	0.12–0.72	I.R.T.
CHEX + HMT	313.25 (2.72)	308.94 (1.69)[i]	−10.22 (6.98)		1.04	0.10–0.60	I.R.T.
CHEX + T	316.88 (2.94)	313.46 (1.66)[i]	−7.75 (5.94)		0.58	0.11–0.66	I.R.T.
DIOX + EA	283.15 (3.74)	286.55 (0.57)	−10.96 (6.55)		1.72	0.17–0.97	S.K.S.
DIOX + F	140.84 (0.97)	138.77 (0.71)	−5.17 (0.99)		0.47	0.29–1.82	S.K.S.
DIOX + HMT[j]	203.33 (3.89)	173.82 (0.71)	−18.96 (4.75)		1.73	0.22–1.45	S.K.S.
DIOX +	315.76 (1.72)	316.29 (0.96)[g]	−7.08 (1.51)		0.92	0.12–2.07	S.K.S.
DIOX + T	183.50 (1.57)	185.10 (0.81)	−6.31 (1.22)		0.80	0.18–2.30	S.K.S.
DMF + F	139.86 (1.41)	139.74 (2.03)	−5.50 (1.70)	2.06 (1.12)	0.10	0.22–1.27	I.R.T.
DMF + HMT	177.82 (2.30)	178.55 (1.82)	4.15 (6.82)		1.46	0.05–0.59	I.R.T.
DMF + IN[k]	259.35 (1.12)	261.94 (3.86)[l]	0.68 (2.02)		0.33	0.17–0.83	I.R.T.
DMF + MAN	317.32 (2.29)	315.94 (7.25)[m]	−3.45 (3.65)		0.89	0.16–0.98	I.R.T.
DMF + T	183.79 (0.85)	183.07 (1.79)	−5.95 (2.73)		0.33	0.09–0.49	I.R.T.
EA + F	221.55 (1.75)	225.19 (0.51)	−9.87 (2.13)		0.68	0.20–1.34	S.K.S.
EA + MAN	401.85 (1.98)	402.72 (0.76)	−13.25 (2.38)		0.88	0.14–1.40	S.K.S.
EA + T	270.59 (0.74)	271.53 (0.65)	−18.00 (0.82)		0.36	0.14–1.58	S.K.S.
F + HMT	115.13 (1.40)	112.47 (0.66)	1.21 (1.03)		0.76	0.14–2.44	S.K.S.
	108.78 (0.65)	116.36 (1.41)	3.80 (3.26)		0.24	0.06–0.31	I.R.T.
F + IN	198.17 (1.81)	199.75 (3.44)	9.67 (2.54)		0.42	0.34–1.00	I.R.T.
F + MAN	256.07 (0.85)	254.94 (0.90)[g]	0.73 (0.85)		0.45	0.10–1.81	S.K.S.
	250.58 (0.22)	253.77 (1.66)[m]	1.87 (0.41)		0.08	0.18–0.83	I.R.T.
F + T	123.40 (1.08)	123.75 (0.79)	−3.41 (0.97)		0.55	0.15–1.88	S.K.S.
	118.05 (0.27)	120.88 (1.38)	−1.99 (0.39)		0.11	0.18–1.15	I.R.T.
HMT + IN	240.96 (1.36)	238.56 (3.24)[l]	9.18 (3.48)		0.52	0.10–0.60	I.R.T.
HMT + MAN	290.55 (2.49)	289.99 (0.91)[g]	−0.39 (2.53)		1.41	0.09–1.93	S.K.S.
	295.69 (1.10)	292.58 (1.45)[m]	−0.27 (2.59)		0.25	0.20–0.60	I.R.T.
HMT + T	162.62 (4.45)	158.80 (0.79)	−2.31 (3.31)		2.35	0.16–2.50	S.K.S.
	162.25 (0.90)	159.69 (1.17)	−2.38 (2.33)		0.35	0.10–0.59	I.R.T.
IN + T	242.39 (0.20)	243.08 (3.20)[l]	2.93 (0.34)		0.08	0.15–0.90	I.R.T.
MAN + T	297.35 (0.39)	297.10 (1.42)[m]	−3.57 (0.67)		0.15	0.15–0.89	I.R.T.
	299.05 (1.46)	301.27 (1.04)[g]	−2.64 (1.43)		0.73	0.16–1.94	S.K.S.

[a] For ternary systems of solutes A and B, $C_{p,\phi}^{\circ}(\mathrm{add}) = \{C_{p,\phi}^{\circ}(\mathrm{A}) + C_{p,\phi}^{\circ}(\mathrm{B})\}/2$. [b] Standard error of a single experiment. [c] Numbers in parentheses are the 95% confidence limits. [d] Results of S.K.S., this work. [e] Results of I.R.T., this work. [f] MAN = D-mannitol. [g] Calculated by using for mannitol, $C_{p,\phi}^{\circ}$ = 432.46 (1.15) + 1.1 (2.0) J mol^{-1} K^{-1} (value of S.K.S.). [h] CHEX = cyclohexanol. [i] Using $C_{p,\phi}^{\circ}$(CHEX) = 462.71 J mol^{-1} K^{-1} (ref *38*). [j] These data do not pass the additivity test so it should be used with caution. [k] IN = myoinositol. [l] Using $C_{p,\phi}^{\circ}$(IN) = 321.95 J mol^{-1} K^{-1} (ref *38*). [m] Using $C_{p,\phi}^{\circ}$(MAN) = 429.98 J mol^{-1} K^{-1} (ref *38*).

ways, and the results always agreed within experimental error. In only one case (ethyl acetate) was there any indication that this might have been a problem. For ethyl acetate, the noise level was very high and it took a long time to get a stable $\Delta\sigma/\sigma_0$ reading. This could have been due to effects at the solution–water interface. However, the use of an extra long delay loop (so there was sufficient time for equilibration) gave the same results both with water and with solution as reference.

7. Degassing. The solutions were not routinely degassed for this study. Instead, a slight positive pressure was used to reduce bubble formation. Several check runs with degassed solutions produced identical results. In addition, bubble formation due to lack of degassing usually causes very large and erratic signals and these were not observed.

8. Operator Error. Four different operators (the present authors plus James Coe (*41*)) have used this instrument over the past 3 years and obtained identical results for the chemical standards. Also, Table III gives several examples of two experimenters getting the same results using our calorimeter.

It is troublesome to report results that are not as accurate as expected. We report these values for three reasons: (1) For many systems these are the only measurements of the apparent molar heat capacity and they are as accurate as many of the results from other measuring techniques (*40*). (2) The values of the coefficient c_2 agree with literature values, and these are worth reporting in their own right. (3) The widespread use of this type of calorimeter for measuring the apparent molar heat capacities makes it important to alert other investigators to a problem with this instrument.

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Registry No. AC, 60-35-5; AN, 67-64-1; DIOX, 123-91-1; DMF, 68-12-2; EA, 141-78-6; F, 75-12-7; HMT, 100-97-0; T, 110-88-3; MAN, 69-65-8; IN, 87-89-8; CHEX, 108-93-0; methyl formate, 107-31-3.

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