Table IV. Values of the Constants A_0, A_1, and A_2 of Eq 3 and the Standard Deviations $\delta(V^E)$ for the Various Systems at 298.15 and 308.15 K

system	temp, K	A_0, cm^3 mol^{-1}	A_1, cm^3 mol^{-1}	A_2, cm^3 mol^{-1}	$\delta(V^E)$, cm^3 mol^{-1}
$CHCl_2CHCl_2$-benzene	298.15	-0.1703	-0.0197	0.2063	0.003
	308.15	-0.2093	-0.1019	-0.0203	0.003
$CHCl_2CHCl_2$-toluene	298.15	-0.6425	0.2196	0.3730	0.002
	308.15	-0.6475	0.3597	0.0377	0.004
$CHCl_2CHCl_2$-*p*-xylene	298.15	-0.5681	0.4342	-0.1274	0.003
	308.15	-0.6069	0.5424	-0.1070	0.002
$CHCl_2CHCl_2$-acetone	298.15	-2.6177	0.1645	-0.4558	0.005
	308.15	-2.6411	-0.1869	-1.1536	0.005
$CHCl_2CHCl_2$-cyclohexane	298.15	1.8614	-0.4786	0.5052	0.004
	308.15	1.9149	-0.3190	0.2755	0.006

Table V. Values of the Constants B_0, B_1, and B_2 of Eq 4 for the Various Systems at 298.15 and 308.15 K

system	T, K	10^6B_0, atm^{-1}	10^6B_1, atm^{-1}	10^6B_2, atm^{-1}
$CHCl_2CHCl_2$-benzene	298.15	-5.660	-1.817	0.798
	308.15	-6.652	0.418	-1.795
$CHCl_2CHCl_2$-toluene	298.15	-2.695	0.182	-1.728
	308.15	-4.573	3.692	-1.203
$CHCl_2CHCl_2$-*p*-xylene	298.15	0.951	0.767	2.183
	308.15	1.733	-0.974	0.403
$CHCl_2CHCl_2$-acetone	298.15	-37.623	19.631	-4.605
	308.15	-43.202	15.759	-2.566
$CHCl_2CHCl_2$-cyclohexane	298.15	-2.829	-1.349	-5.184
	308.15	-2.435	-1.089	-0.061

positive for $CHCl_2CHCl_2$-*p*-xylene. For $CHCl_2CHCl_2$-acetone, the values of k_s^E are highly negative. This supports the above viewpoint concerning the existence of strong specific interaction due to hydrogen bonding between $CHCl_2CHCl_2$ and acetone.

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Registry No. 1,1,2,2-Tetrachloroethane, 79-34-5; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; acetone, 67-64-1; cyclohexane, 110-82-7.

Literature Cited

(1) Rastogi, R. P.; Nath, J.; Misra, R. R. *J. Chem. Thermodyn.* **1971**, *3*, 307-17.
(2) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: Amsterdam, 1950.
(3) Powell, R. J.; Swinton, F. L. *J. Chem. Eng. Data* **1968**, *13*, 260-2.
(4) Reddy, K. S.; Naidu, P. R. *J. Chem. Thermodyn.* **1976**, *8*, 1208-10.
(5) Nath, J.; Dubey, S. N. *J. Phys. Chem.* **1980**, *84*, 2166-70.
(6) Freyer, E. B.; Hubbard, J. C.; Andrews, J. H. *J. Am. Chem. Soc.* **1929**, *51*, 759-70.
(7) Gracia, M.; Otin, S.; Gutierrez Losa, C. *J. Chem. Thermodyn.* **1975**, *7*, 293-7.
(8) McClellan, A. L.; Nicksic, S. W. *J. Phys. Chem.* **1965**, *69*, 446-9.

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Volumetric Properties of Some Aqueous Nonelectrolyte Solutions

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Densities have been measured at 298.15 K with a flow densimeter for binary and ternary aqueous solutions of a large number of nonelectrolytes. There is a high degree of internal consistency and very good agreement with literature data where available.

Introduction

Recent (*1*, *2*) and forthcoming (*3*-*5*) publications from this laboratory contain data on the thermodynamic properties of aqueous solutions of nonelectrolytes. In accumulating heat of dilution, heat capacity, and freezing point data on the various systems, we have found it expedient to collect corresponding volumetric data. First, heat of dilution and heat capacity data have been obtained by using flow microcalorimetric techniques and in these instances it is necessary to convert volumetric flow rates to mass flow rates using density data. Second, the accumulation of volumetric data per se is warranted by the nature of the Savage-Wood group additivity principle under which the other thermodynamic data have been treated; the behavior observed for enthalpies (*6*, *7*) and free energies (*8*-*11*) can be tested against volumes. Finally, from a purely practical point of view the continued accumulation of volumetric data has been advantageous. Within the last 5 years, three researchers in this laboratory have performed a large number of density measurements, some being repetitions, in connection with other experimental techniques such as flow heat of dilution calorimetry and flow heat capacity calorimetry. In addition to their immediate experimental uses and their other common

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Table I. Apparent Molar Volumes of Aqueous Solutions at 25 °C

m,[a] mol kg^{-1}	ϕ_v(exptl), cm^3 mol^{-1}	ϕ_v(calcd), cm^3 mol^{-1}	Δ, cm^3 mol^{-1}	m,[a] mol kg^{-1}	ϕ_v(exptl), cm^3 mol^{-1}	ϕ_v(calcd), cm^3 mol^{-1}	Δ, cm^3 mol^{-1}
			(A) Measurements of J.S.				
	Mannitol (MAN)				MAN + DMF		
0.2968	119.60	119.60	0.00	0.0996	97.16	97.09	0.07
0.3732	119.66	119.65	0.01	0.1116	97.09	97.08	0.01
0.4191	119.70	119.69	0.01	0.1600	97.02	97.07	−0.05
0.5311	119.73	119.77	−0.04	0.1785	97.07	97.07	0.00
0.6025	119.81	119.82	−0.01	0.2194	97.03	97.07	−0.04
0.6847	119.88	119.88	0.00	0.2556	97.07	97.06	0.01
0.7511	119.94	119.92	0.02	0.4021	97.00	97.04	0.04
	Inositol (IN)			0.4770	97.02	97.02	0.00
0.0528	101.08	101.00	0.08	0.5494	97.02	97.01	0.01
0.0911	101.10	101.04	0.06	0.6195	97.03	97.01	0.02
0.1103	100.96	101.06	−0.10		Cyclohexanol (CHEX) + IN		
0.1375	101.14	101.09	0.05	0.1003	102.23	102.22	0.01
0.1658	101.01	101.12	−0.11	0.1105	102.26	102.22	0.04
0.2137	101.17	101.18	−0.01	0.1438	102.20	102.22	−0.02
0.2389	101.15	101.20	−0.05	0.1959	102.22	102.21	0.01
0.2893	101.25	101.26	−0.01	0.2798	102.22	102.21	0.01
0.3106	101.35	101.28	0.07	0.3353	102.11	102.21	−0.10
0.3746	101.37	101.35	0.02	0.4491	102.17	102.21	−0.04
	Dimethylformamide (DMF)			0.5070	102.30	102.20	0.10
0.0963	74.53	74.55	−0.02	0.5522	102.20	102.20	0.00
0.1086	74.56	74.54	0.02		IN + Formamide (F)		
0.1236	74.56	74.54	0.02	0.0987	69.85	69.87	−0.02
0.1414	74.49	74.53	−0.03	0.1593	69.91	69.89	0.02
0.1742	74.57	74.51	0.06	0.3225	69.96	69.95	0.01
0.2217	74.51	74.49	0.02	0.4335	69.96	69.99	0.03
0.2658	74.43	74.47	0.04	0.4988	70.02	70.01	0.01
0.2745	74.48	74.46	0.02	0.5417	70.04	70.03	0.02
0.1498	74.54	74.52	0.02	0.5993	70.03	70.05	−0.02
0.3336	74.38	74.43	0.05	0.6811	70.08	70.07	0.01
0.3555	74.44	74.42	0.02		IN + DMF		
0.3995	74.38	74.40	−0.02	0.1019	87.77	87.76	0.01
0.4646	74.32	74.37	−0.05	0.1491	87.79	87.78	0.01
0.4720	74.35	74.36	−0.01	0.2597	87.81	87.81	0.00
0.5105	74.35	74.34	0.01	0.3427	87.81	87.83	−0.02
0.5444	74.32	74.33	−0.01	0.4810	87.87	87.87	0.00
0.6153	74.30	74.29	0.01	0.4978	87.88	87.88	0.00
0.6721	74.28	74.26	0.02	0.5697	87.91	87.90	0.02
0.7370	74.21	74.23	−0.02		IN + HMT		
0.8035	74.20	74.20	0.00	0.0998	105.78	105.77	0.01
0.9029	74.16	74.15	0.01	0.1600	105.83	105.79	0.04
1.0002	74.12	74.10	0.02	0.2693	105.81	105.83	−0.02
	Trioxane (T)			0.3400	105.85	105.85	0.00
0.099	69.65	69.65	0.00	0.3902	105.84	105.86	−0.02
0.2098	69.68	69.67	0.01	0.4469	105.87	105.88	−0.01
0.2759	69.70	69.68	0.02	0.5165	105.89	105.90	−0.01
0.3187	69.69	69.68	0.01	0.5772	105.91	105.92	−0.01
0.3675	69.69	69.69	0.00	0.6507	105.96	105.94	0.02
0.4168	69.67	69.70	−0.03	0.7244	105.99	105.97	0.02
0.5010	69.76	69.72	0.04		CHEX + F		
0.5984	69.75	69.73	0.02	0.0911	71.40	71.26	0.14
0.6575	69.76	69.74	0.02	0.1450	71.19	71.21	0.02
	Hexamethylenetetramine (HMT)			0.2086	71.07	71.15	0.08
0.2279	110.59	110.55	0.04	0.2806	71.02	71.09	0.07
0.3121	110.53	110.53	0.00	0.5116	70.83	70.88	0.05
0.3929	110.51	110.51	0.00	0.5661	70.84	70.84	0.00
0.4154	110.47	110.50	−0.03	0.6021	70.82	70.80	0.02
0.4896	110.47	110.48	−0.01	0.6938	70.78	70.72	0.06
0.5857	110.46	110.46	0.00		CHEX + DMF		
0.6964	110.43	110.43	0.00	0.0893	89.12	89.08	0.04
0.8543	110.38	110.38	0.00	0.1630	89.00	88.98	0.02
0.9388	110.37	110.36	0.01	0.2336	88.85	88.89	−0.03
0.9998	110.35	110.35	0.00	0.2779	88.81	88.83	−0.02
	MAN + IN			0.4606	88.54	88.59	−0.05
0.1044	110.38	110.38	0.01	0.5594	88.47	88.46	0.01
0.1667	110.42	110.43	−0.01	0.6260	88.42	88.37	0.05
0.2338	110.49	110.48	0.01		CHEX + T		
0.3012	110.54	110.53	0.01	0.0993	86.52	86.53	−0.01
0.3496	110.59	110.57	0.02	0.1707	86.49	86.48	0.01
0.4326	110.58	110.63	−0.05	0.2506	86.42	86.43	−0.01
0.5007	110.68	110.68	0.00	0.3297	86.40	86.38	0.02
0.5513	110.74	110.72	0.02	0.4094	86.29	86.33	−0.04
0.6349	110.79	110.78	0.01	0.4691	86.33	86.29	0.04
				0.5276	86.25	86.26	−0.01
				0.5891	86.21	86.22	−0.01
				0.6449	86.19	86.18	0.01

Table I (*Continued*)

m,[a] mol kg^{-1}	ϕ_v(exptl), cm^3 mol^{-1}	ϕ_v(calcd), cm^3 mol^{-1}	Δ, cm^3 mol^{-1}	m,[a] mol kg^{-1}	ϕ_v(exptl), cm^3 mol^{-1}	ϕ_v(calcd), cm^3 mol^{-1}	Δ, cm^3 mol^{-1}
	CHEX + HMT				T + HMT		
0.1588	106.84	106.85	−0.01	0.1025	90.11	90.15	−0.04
0.2150	106.80	106.80	0.00	0.1789	90.15	90.14	0.01
0.2741	106.76	106.75	0.01	0.2461	90.15	90.13	0.02
0.3396	106.66	106.69	−0.03	0.3282	90.16	90.11	0.05
0.4000	106.64	106.64	0.00	0.4011	90.08	90.10	−0.02
0.4700	106.58	106.57	0.01	0.4673	90.08	90.09	−0.01
0.5378	106.52	106.51	0.01	0.5398	90.07	90.08	−0.01
0.6062	106.45	106.45	0.00	0.5589	90.07	90.08	−0.01
				0.6410	90.07	90.07	0.00
			(B) Measurements of S.S.				
	Acetamide (AC)				Inositol (IN)		
0.1640	55.62	55.62	0.00	0.0847	100.89	100.88	0.01
0.3102	55.60	55.60	0.00	0.1246	100.93	100.94	−0.01
0.5060	55.55	55.56	−0.01	0.1626	100.99	100.99	0.00
0.8993	55.51	55.50	0.01	0.2381	101.10	101.11	−0.01
1.4815	55.45	55.44	0.01	0.3006	101.20	101.20	0.00
1.8206	55.42	55.42	0.00	0.3620	101.30	101.29	0.01
	Acetone (AN)				Mannitol (MAN)		
0.1790	66.84	66.85	−0.01	0.1151	119.54	119.54	0.00
0.2890	66.82	66.81	0.01	0.2131	119.60	119.60	0.00
0.4369	66.77	66.76	0.01	0.3313	119.66	119.67	−0.01
0.9760	66.61	66.61	0.00	0.5503	119.80	119.79	0.01
1.1961	66.57	66.57	0.00	0.8459	119.95	119.97	−0.02
1.9077	66.50	66.50	0.00	0.8910	120.00	119.99	0.01
	Cyclohexanedione				Methyl Formate (MF)		
0.1027	92.51	92.51	0.00	0.1865	55.34	55.33	0.01
0.1623	92.54	92.53	0.01	0.3062	55.37	55.36	0.01
0.2940	92.58	92.57	0.01	0.4666	55.42	55.40	0.02
0.3568	92.58	92.60	−0.02	0.5977	55.36	55.42	−0.06
0.5048	92.65	92.65	0.00	0.8321	55.47	55.46	0.01
0.8695	92.78	92.78	0.00	0.9963	55.46	55.47	−0.01
				1.1714	55.51	55.47	0.04
	Cyclohexanone			1.3451	55.44	55.47	−0.03
0.0963	99.21	99.21	0.00	1.6727	55.49	55.45	0.04
0.1810	99.18	99.17	0.01	1.7327	55.40	55.43	−0.03
0.2465	99.15	99.15	0.00				
0.3125	99.11	99.12	−0.01		Trioxane (T)		
0.3646	99.09	99.10	−0.01	0.1721	69.81	69.73	0.08
0.4144	99.07	99.08	−0.01	0.3892	69.74	69.76	−0.02
0.5571	99.04	99.03	0.01	0.6236	69.76	69.80	−0.04
				1.0053	69.83	69.87	−0.04
	Dioxane (DIOX)			1.7377	69.99	69.99	0.00
0.1374	81.03	80.98	0.05	2.0891	70.07	70.04	0.03
0.2994	80.95	80.97	−0.02				
0.3519	80.96	80.97	−0.01		AC + DIOX		
0.6936	80.94	80.94	0.00	0.1434	68.31	68.31	0.00
0.8823	80.91	80.93	−0.02	0.2441	68.30	68.29	0.01
1.0258	80.90	80.92	−0.02	0.5131	68.24	68.25	−0.01
1.5340	80.91	80.88	0.03	0.9451	68.19	68.19	0.00
				1.4524	68.16	68.15	0.01
	Ethyl Acetate (EA)			2.1022	68.14	68.14	0.00
0.1720	88.94	88.94	0.00				
0.3315	88.93	88.94	−0.01		AC + EA		
0.4400	88.94	88.94	0.00	0.1411	72.26	72.25	0.01
0.6971	88.94	88.94	0.00	0.2980	72.25	72.25	0.00
0.8672	88.95	88.95	0.00	0.5974	72.26	72.27	−0.01
				0.9052	72.27	72.28	−0.01
	Formamide (F)			1.1377	72.28	72.29	−0.01
0.2229	38.68	38.68	0.00	1.5571	72.32	72.30	0.02
0.4465	38.70	38.70	0.00				
0.5986	38.71	38.71	0.00		AC + F		
0.8896	38.73	38.73	0.00	0.1329	47.25	47.22	0.03
0.9869	38.74	38.74	0.00	0.3034	47.21	47.21	0.00
1.4793	38.78	38.78	0.00	0.4999	47.18	47.20	−0.02
2.2193	38.83	38.83	0.00	0.9953	47.17	47.18	−0.01
				1.3478	47.15	47.17	−0.02
	Hexamethylenetetramine (HMT)			1.9918	47.17	47.14	0.03
0.1663	110.60	110.60	0.00				
0.3035	110.55	110.55	0.00		AC + HMT		
0.4909	110.50	110.49	0.01	0.1223	83.09	83.09	0.00
1.0025	110.34	110.34	0.00	0.2719	83.07	83.07	0.00
1.4237	110.22	110.23	−0.01	0.5281	83.04	83.03	0.01
1.9707	110.13	110.13	0.00	1.0847	82.94	82.95	−0.01
				1.4141	82.90	82.90	0.00
				1.8908	82.83	82.83	0.00

Table I (*Continued*)

m,[a] mol kg^{-1}	ϕ_v(exptl), cm^3 mol^{-1}	ϕ_v(calcd), cm^3 mol^{-1}	Δ, cm^3 mol^{-1}	m,[a] mol kg^{-1}	ϕ_v(exptl), cm^3 mol^{-1}	ϕ_v(calcd), cm^3 mol^{-1}	Δ, cm^3 mol^{-1}
	AC + IN				DIOX + F		
0.0926	78.21	78.21	0.00	0.2868	59.85	59.85	0.00
0.1784	78.24	78.24	0.00	0.3134	59.85	59.85	0.00
0.2842	78.28	78.28	0.00	0.4966	59.85	59.86	−0.01
0.3892	78.32	78.31	0.01	0.8526	59.88	59.87	0.01
0.4629	78.34	78.34	0.00	1.1277	59.89	59.89	0.00
0.5796	78.38	78.38	0.00	1.8215	59.92	59.92	0.00
	AC + MAN				DIOX + IN		
0.1406	87.54	87.54	0.00	0.0864	90.82	90.84	−0.02
0.2044	87.56	87.56	0.00	0.1733	90.87	90.87	0.00
0.5200	87.62	87.62	0.00	0.2689	90.92	90.91	0.01
0.9215	87.71	87.70	0.01	0.3624	90.95	90.95	0.00
1.3762	87.77	87.78	−0.01	0.4997	91.00	91.00	0.00
1.8849	87.85	87.85	0.00	0.6352	91.05	91.06	−0.01
	AC + MF				DIOX + MAN		
0.1213	55.37	55.36	0.01	0.1189	100.21	100.24	−0.03
0.3426	55.33	55.33	0.00	0.2217	100.27	100.26	0.01
0.5796	55.28	55.29	−0.01	0.5514	100.34	100.32	0.02
1.0472	55.23	55.22	0.01	1.0068	100.39	100.40	−0.01
1.6114	55.13	55.14	−0.01	1.4643	100.49	100.48	0.01
1.8369	55.10	55.10	0.00	2.0676	100.58	100.59	−0.01
	AC + T				DIOX + MF		
0.1055	62.60	62.60	0.00	0.1455	68.15	68.13	−0.02
0.5286	62.61	62.60	0.01	0.3021	68.14	68.14	0.00
1.0419	62.60	62.61	−0.01	0.4954	68.14	68.14	0.00
1.4950	62.62	62.61	0.01	0.7562	68.15	68.16	−0.01
2.0719	62.62	62.62	0.00	0.9400	68.15	68.17	−0.02
	AN + DIOX			1.1893	68.17	68.18	−0.01
0.1422	73.84	73.84	0.00	1.5222	68.20	68.20	0.00
0.2658	73.86	73.83	0.03	1.8064	68.22	68.21	0.01
0.5073	73.81	73.81	0.00		DIOX + T		
1.0395	73.72	73.75	−0.03	0.1828	75.33	75.34	−0.01
1.3177	73.69	73.72	−0.03	0.3516	75.35	75.35	0.00
2.1588	73.66	73.64	0.02	0.6219	75.39	75.37	0.02
	AN + EA			1.1430	75.39	75.41	−0.02
0.0982	77.92	77.92	0.00	1.6898	75.44	75.44	0.00
0.2241	77.88	77.89	−0.01		EA + F		
0.4413	77.86	77.84	0.02	0.2006	63.70	63.69	0.01
0.9357	77.81	77.80	0.01	0.2558	63.69	63.69	0.00
1.4076	77.85	77.87	−0.02	0.3566	63.70	63.70	0.00
1.6984	77.96	77.96	0.00	0.4408	63.71	63.71	0.00
1.8939	78.05	78.04	0.01	0.6370	63.73	63.74	−0.01
	AN + F			0.8292	63.77	63.76	0.01
0.1428	52.78	52.78	0.00	0.9440	63.77	63.77	0.00
0.3179	52.78	52.77	0.01	1.0419	63.78	63.78	0.00
0.5328	52.76	52.76	0.00	1.2058	63.80	63.80	0.00
0.9751	52.76	52.75	0.01	1.3448	63.82	63.82	0.00
1.4557	52.75	52.75	0.00		EA + IN		
2.3103	52.77	52.77	0.00	0.1266	94.87	94.89	−0.02
	AN + MAN			0.2113	94.93	94.92	0.01
0.1648	93.21	93.20	0.01	0.2964	94.97	94.96	0.01
0.3447	93.22	93.22	0.00	0.3786	95.00	94.99	0.00
0.7026	93.26	93.26	0.00	0.5155	95.05	95.05	0.00
1.0903	93.29	93.30	−0.01	0.6650	95.10	95.11	−0.01
1.5299	93.35	93.35	0.00		EA + MAN		
	AN + MF			0.1376	104.00	103.99	0.01
0.0799	61.03	61.07	−0.04	0.3417	104.05	104.04	0.01
0.1405	61.10	61.07	0.03	0.5850	104.09	104.09	0.00
0.3962	61.08	61.07	0.01	0.7705	104.12	104.13	−0.01
0.8066	61.08	61.07	0.01	1.0622	104.18	104.20	−0.02
1.1978	61.07	61.07	0.00	1.3989	104.29	104.27	0.02
1.6068	61.07	61.07	0.00		EA + MF		
	DIOX + EA			0.1786	72.16	72.16	0.00
0.1682	84.95	84.95	0.00	0.2036	72.17	72.16	0.01
0.1951	84.94	84.95	−0.01	0.2964	72.16	72.16	0.00
0.3040	84.95	84.94	0.01	0.4437	72.16	72.16	0.00
0.4868	84.93	84.93	0.00	0.7560	72.16	72.16	0.00
0.7809	84.91	84.90	0.01	0.9177	72.17	72.16	0.01
0.9741	84.88	84.89	−0.01	1.0660	72.16	72.16	0.00

Table I (*Continued*)

m,[a] mol kg^{-1}	ϕ_v(exptl), cm^3 mol^{-1}	ϕ_v(calcd), cm^3 mol^{-1}	Δ, cm^3 mol^{-1}	m,[a] mol kg^{-1}	ϕ_v(exptl), cm^3 mol^{-1}	ϕ_v(calcd), cm^3 mol^{-1}	Δ, cm^3 mol^{-1}
	EA + T				HMT + MF		
0.1421	79.31	79.26	0.05	0.1642	82.71	82.75	−0.04
0.2348	79.28	79.28	0.00	0.2902	82.70	82.68	0.02
0.5514	79.30	79.34	−0.04	0.4393	82.64	82.60	0.04
0.8600	79.37	79.39	−0.02	0.8617	82.37	82.38	−0.01
1.1199	79.42	79.44	−0.02	1.0821	82.27	82.26	0.01
1.2580	79.47	79.47	0.00	1.6214	81.98	81.98	0.00
1.5845	79.56	79.53	0.03	2.0175	81.76	81.77	−0.01
	F + HMT				HMT + T		
0.1362	74.63	74.60	0.03	0.1631	90.03	90.01	0.02
0.2427	74.61	74.60	0.01	0.3323	90.00	90.01	−0.01
0.5721	74.58	74.59	−0.01	0.6145	90.00	90.00	0.00
1.1502	74.57	74.60	−0.03	1.1875	89.97	89.98	−0.01
1.8507	74.56	74.56	0.00	1.6268	89.95	89.97	0.02
2.4360	74.55	74.55	0.00	2.5027	89.96	89.94	−0.02
	F + IN				IN + MAN		
0.0990	69.75	69.77	−0.02	0.1648	110.27	110.27	0.00
0.1688	69.80	69.79	0.01	0.2551	110.35	110.35	0.00
0.2573	69.83	69.83	0.00	0.3495	110.44	110.44	0.00
0.3432	69.86	69.86	0.00	0.4168	110.50	110.50	0.00
0.5216	69.93	69.93	0.00	0.5002	110.58	110.58	0.00
0.6473	69.98	69.98	0.00	0.5772	110.64	110.65	−0.01
	F + MAN				IN + MF		
0.1024	79.07	79.08	−0.01	0.1162	77.97	77.99	−0.02
0.2023	79.10	79.10	0.00	0.1856	77.99	78.02	−0.03
0.4711	79.18	79.18	0.00	0.2058	78.07	78.04	0.03
0.8985	79.28	79.28	0.00	0.3672	78.14	78.12	0.02
1.2642	79.37	79.37	0.00	0.4410	78.18	78.16	0.02
1.8099	79.50	79.50	0.00	0.5651	78.21	78.22	−0.01
				0.6792	78.26	78.28	−0.02
	F + MF				IN + T		
0.1425	46.94	46.95	−0.01	0.2082	85.32	85.32	0.00
0.3149	46.97	46.95	0.02	0.3445	85.41	85.42	−0.01
0.5101	46.95	46.95	0.00	0.4876	85.52	85.52	0.00
0.9057	46.96	46.97	−0.01	0.6588	85.65	85.65	0.00
1.5948	47.01	47.02	−0.01				
2.1124	47.08	47.07	0.01		MAN + MF		
				0.1254	87.19	87.23	−0.04
	F + T			0.2453	87.24	87.26	0.06
0.1488	54.20	54.19	0.01	0.5510	87.32	87.33	−0.01
0.2793	54.20	54.21	−0.01	0.9941	87.40	87.43	−0.03
0.5217	54.23	54.24	−0.01	1.3370	87.50	87.51	−0.01
0.9622	54.29	54.29	0.00	2.0069	87.67	87.66	0.01
1.5807	54.37	54.37	0.00				
1.8787	54.41	54.41	0.00		MAN + T		
				0.1589	94.58	94.58	0.00
	HMT + IN			0.3440	94.64	94.64	0.00
0.0989	105.75	105.75	0.00	0.6309	94.73	94.73	0.00
0.1764	105.78	105.78	0.00	0.8409	94.81	94.80	0.01
0.2785	105.81	105.81	0.00	1.1230	94.90	94.89	0.01
0.3617	105.83	105.84	−0.01	1.9392	95.14	95.15	−0.01
0.5007	105.88	105.88	0.00				
0.6439	105.93	105.92	0.01		MF + T		
				0.2821	62.42	62.40	0.02
	HMT + MAN			0.4014	62.43	62.42	0.01
0.0882	114.98	115.00	−0.02	0.5906	62.45	62.46	−0.01
0.1718	115.01	115.01	0.00	0.8282	62.47	62.50	−0.03
0.3942	115.05	115.04	0.01	0.8836	62.50	62.51	−0.01
0.7859	115.09	115.09	0.00	0.9618	62.52	62.52	0.00
1.1326	115.13	115.13	0.00	1.1207	62.56	62.55	0.01
1.9258	115.24	115.24	0.00	1.5070	62.62	62.61	0.01

(C) Measurements of I.T.

	Mannitol (MAN)				Formamide (F)		
0.0744	119.37	119.37	0.00	2.6773	39.67	38.68	−0.01
0.1538	119.42	119.43	0.01	0.8366	38.85	38.84	0.01
0.2251	119.51	119.49	0.02	1.2678	38.98	38.98	0.00
0.3073	119.55	119.55	0.00	1.7400	39.11	39.12	−0.01
				2.1441	39.22	39.23	−0.01
	Cyclohexanol (CHEX)			2.6773	39.35	39.35	0.00
0.0518	103.32	103.34	−0.02				
0.1034	103.28	103.23	0.05				
0.1571	103.10	103.11	−0.01				
0.1867	103.02	103.05	−0.03				
0.2846	102.81	102.83	−0.02				
0.3636	102.69	102.66	0.03				

Table I (*Continued*)

m,[a] mol kg^{-1}	ϕ_v(exptl), cm^3 mol^{-1}	ϕ_v(calcd), cm^3 mol^{-1}	Δ, cm^3 mol^{-1}	m,[a] mol kg^{-1}	ϕ_v(exptl), cm^3 mol^{-1}	ϕ_v(calcd), cm^3 mol^{-1}	Δ, cm^3 mol^{-1}
	Dimethylformamide (DMF)				IN + CHEX		
0.1248	74.51	74.47	0.04	0.1116	102.11	102.11	0.00
0.1815	74.42	74.44	−0.02	0.1904	102.10	102.11	−0.01
0.2025	74.41	74.43	−0.02	0.2810	102.10	102.10	0.00
0.2377	74.42	74.42	0.00	0.3709	102.13	102.10	0.03
0.2500	74.41	74.41	0.00	0.4637	102.08	102.09	−0.01
0.3336	74.36	74.37	−0.01	0.5872	102.08	102.09	−0.01
0.4053	74.33	74.34	−0.01		IN + F		
0.4180	74.35	74.33	0.02	0.3378	69.68	69.62	0.06
0.4987	74.31	74.30	0.01	0.5009	69.70	69.74	−0.04
0.6111	74.22	74.25	−0.03	0.6793	69.85	69.82	−0.03
0.6651	74.25	74.23	0.02	0.8342	69.93	69.99	−0.06
0.8339	74.17	74.16	0.01	0.9983	70.20	70.12	0.08
0.8456	74.13	74.15	−0.02		IN + DMF		
0.9991	74.11	74.10	0.01	0.1749	87.81	87.81	0.00
1.0974	74.05	74.06	−0.01	0.3384	87.85	87.84	0.01
1.3127	73.98	73.99	−0.01	0.5074	87.85	87.86	−0.01
1.3311	74.00	73.99	0.01	0.6714	87.89	87.88	0.01
1.6661	73.90	73.90	0.00	0.8292	87.90	87.90	0.00
1.9990	73.82	73.82	0.00		IN + T		
	Trioxane (T)			0.0750	85.29	85.31	−0.02
0.1991	69.74	69.70	0.04	0.1496	85.39	85.36	0.03
0.2991	69.67	69.72	−0.05	0.3007	85.45	85.45	0.00
0.3996	69.74	69.74	−0.00	0.3738	85.50	85.50	0.00
0.4966	69.78	69.77	0.01	0.4491	85.56	85.55	0.01
0.5992	69.79	69.79	0.00	0.5997	85.64	85.64	0.00
	Hexamethylenetetramine (HMT)			0.7496	85.72	85.74	−0.02
0.3430	110.64	110.63	0.01	0.9016	85.83	85.83	0.00
0.4651	110.59	110.60	−0.01		IN + HMT		
0.6369	110.56	110.56	0.00	0.2010	105.73	105.75	−0.02
0.8138	110.50	110.52	−0.02	0.4000	105.92	105.88	0.04
1.0025	110.48	110.47	0.01	0.4478	105.91	105.91	0.00
	MAN + IN			0.4986	105.96	105.94	0.02
0.0960	110.23	110.26	−0.03	0.5513	105.93	105.97	−0.04
0.1990	110.39	110.37	0.02	0.5997	105.99	106.00	−0.01
0.2994	110.50	110.47	0.03		CHEX + F		
0.4033	110.57	110.58	−0.01	0.1220	70.88	70.91	0.03
0.5055	110.68	110.69	−0.01	0.2466	70.91	70.87	0.04
0.5973	110.77	110.79	−0.02	0.3617	70.85	70.84	0.01
0.7022	110.91	110.90	0.01	0.4723	70.80	70.80	0.00
	MAN + CHEX			0.5989	70.75	70.76	0.01
0.0928	111.56	111.56	0.00	0.7230	70.72	70.72	0.00
0.1824	111.37	111.37	0.00		CHEX + DMF		
	MAN + F			0.0985	89.07	88.90	0.17
0.1797	79.06	79.06	0.00	0.1096	88.85	88.89	−0.04
0.2960	79.08	79.09	0.01	0.1535	88.86	88.84	0.02
0.3369	79.11	79.10	0.01	0.1925	88.72	88.80	−0.08
0.4265	79.12	79.12	0.00	0.2416	88.82	88.74	0.08
0.5094	79.14	79.14	0.00	0.2769	88.57	88.71	−0.14
0.6700	79.19	79.18	0.01	0.2949	88.66	88.69	−0.03
0.8318	79.22	79.22	0.00	0.3920	88.55	88.58	−0.03
	MAN + DMF			0.3931	88.48	88.58	−0.10
0.1606	96.96	96.95	0.01	0.4290	88.53	88.54	−0.01
0.3194	96.96	96.96	0.00	0.4661	88.48	88.50	−0.02
0.4782	96.95	96.97	−0.02	0.4870	88.50	88.48	0.02
0.6350	96.97	96.98	−0.01	0.5153	88.47	88.45	0.02
0.9771	97.00	97.00	0.00	0.5420	88.45	88.42	0.03
	MAN + T			0.5471	88.46	88.41	0.05
0.0500	94.59	94.58	0.01	0.5784	88.39	88.38	0.01
0.1468	94.61	94.61	0.00	0.5900	88.40	88.37	0.03
0.1998	94.65	94.63	0.02		CHEX + T		
0.2990	94.64	94.66	−0.02	0.1087	86.48	86.43	0.05
0.4487	94.69	94.70	−0.01	0.2319	86.33	86.39	0.06
0.6009	94.74	94.75	−0.01	0.4508	86.28	86.31	0.03
0.7468	94.78	94.80	−0.02	0.6614	86.26	86.23	0.03
0.8901	94.87	94.84	0.03				
	MAN + HMT						
0.2918	115.05	115.05	0.00				
0.3012	115.07	115.07	0.00				
0.3450	115.07	115.08	−0.01				
0.4030	115.09	115.09	0.00				
0.5009	115.12	115.11	0.01				
0.5968	115.12	115.13	−0.01				

Table I (*Continued*)

m,[a] mol kg^{-1}	ϕ_v(exptl), cm^3 mol^{-1}	ϕ_v(calcd), cm^3 mol^{-1}	Δ, cm^3 mol^{-1}	m,[a] mol kg^{-1}	ϕ_v(exptl), cm^3 mol^{-1}	ϕ_v(calcd), cm^3 mol^{-1}	Δ, cm^3 mol^{-1}
	CHEX + HMT				F + T		
0.1012	106.82	106.79	0.03	0.1844	54.13	54.12	0.01
0.1507	106.75	106.74	0.01	0.2715	54.13	54.13	0.00
0.2980	106.55	106.58	−0.03	0.3441	54.14	54.14	0.00
0.3478	106.53	106.53	0.00	0.4376	54.15	54.15	0.00
0.3961	106.47	106.48	−0.01	0.5033	54.16	54.16	0.00
0.4418	106.40	106.43	−0.03	0.6773	54.18	54.18	0.00
0.4940	106.39	106.38	0.01	0.8266	54.21	54.21	0.00
0.5469	106.33	106.32	0.01	1.1527	54.26	54.26	0.00
0.5969	106.28	106.27	0.01				
	F + DMF				F + HMT		
				0.0526	74.61	74.61	0.00
0.2448	56.51	56.50	0.01	0.1025	74.61	74.61	0.00
0.3957	56.48	56.50	−0.02	0.2069	74.59	74.61	−0.02
0.6209	56.49	56.48	0.01	0.3057	74.62	74.61	0.01
0.7930	56.47	56.47	0.00	0.4018	74.62	74.61	0.01
0.9708	56.47	56.47	0.00	0.4455	74.60	74.61	−0.01
				0.4976	74.61	74.61	0.00
				0.6330	74.61	74.61	0.00

[a] This is the total molality of the solution. When two solutes are present, they both have the same molality.

applications—such as transfer of data between concentration scales, analytical uses (e.g., determination of concentration of freezing point solutions), and potential to provide information on solute–solute interactions—this accumulation of data has provided a simultaneous check on the preparation of solutions and the reliability of our equipment.

Experimental Section

Apparatus. All densities were measured at 298.15 K on a Sodev Inc. Model 01D high-precision flow digital vibrating tube densimeter (*12*) operating in conjunction with a Digitec HT series 8510 A counter/timer. Thermostatic regulation to within ±0.0002 °C per day was achieved with a Tronac Model 40 precision temperature controller and either a Tronac Model 1105 constant-temperature bath or a modified commercial Coleman cooler.

All densities were measured relative to water by using the equation

$$d = d_0 + K(\tau^2 - \tau_0^2) \quad (1)$$

where d is the density of the solution, d_0 is the density of pure water, K is a constant for the mechanical system, τ is the oscillation period corresponding to the solution, and τ_0 is the oscillation period corresponding to pure water. The constant K was determined by using pure water (d_0^{298} = 0.997047 g cm^{-3} (*13*) and dry nitrogen ($d_{N_2}^{298}$ = 1.1456 × 10^{-3} g cm^{-3} (*14*)). On occasions it was found that more stable readings could be taken with the instrument operating in a static mode (zero flow rate). Moreover, it was observed that oscillation corresponded to ±2 ppm in density and so introduced insignificant error into the calculation of ϕ_v. Solutions were not normally either degassed or filtered before measurements. Bubble formation was eliminated by putting the exit tube of the densimeter 0.5 m above the instrument, ensuring that the pressure in the instrument was 5% above atmospheric pressure.

Materials. Preparation of reagents by one of the experimenters (I.T.) has already been published elsewhere (*1–5*). For Jan Spitzer, the preparations are as follows. Cyclohexanol was purchased from the Aldrich Chemical Co.; it was zone refined for 4 days and one-third of the material was rejected. Dimethylformamide (DMF) was purchased from the Fisher Scientific Co. and was purified in three ways: (i) by two recrystallizations using liquid nitrogen (DMF was repeatedly deposited on the wall of a plastic bottle and the deposit was shaken off each time until a slush of nearly solid material was obtained); (ii) by distillation on a spinning-band column under 80 mmHg pressure; (iii) by shaking the material with molecular sieve A4, mesh 8–12, for 30 min and then distilling on a spinning-band column under atmospheric pressure. Formamide (Fisher) was zone refined in a freezer at −5 °C for 3 days and the top two-thirds of the purified material was used. Hexamethylenetetramine (Eastman Kodak Co.) was repeatedly recrystallized from hot water and dried at 190 °C for 12 h. *myo*-Inositol (Eastman Kodak) was recrystallized from hot water, dried in vacuo at 100 °C for 14 h, ground to a fine powder, and dried in vacuo at 100 °C for 24 h. Mannitol (Aldrich) was treated with charcoal, filtered, twice recrystallized, and dried in vacuo at 70 °C for 24 h. *s*-Trioxane (Aldrich) was slowly sublimed at 50 °C and atmospheric pressure.

For Sushil Suri the preparations are as follows. Acetamide (Fisher certified reagent grade) was zone refined for 5 days and one-third discarded. Acetone (Fisher spectroanalyzed material) was dried over molecular sieve A4, mesh 8–12, for 3 days and then fractionally distilled with a reflux ratio of 1:20. The first and last fractions were discarded. 1,4-Cyclohexanedione (Aldrich) was recrystallized from methanol and carefully dried at low temperature and atmospheric pressure. Cyclohexanone (Fisher purified grade reagent) was fractionally distilled, immediately prior to use, with a reflux ratio of 1:200. The middle fraction was collected for use. *p*-Dioxane (Aldrich) was refluxed over sodium metal for 4 h and then fractionally distilled. The middle fraction was stored over molecular sieve A4, mesh 8–12, and fractionally distilled with a reflux ratio 1:200 immediately prior to use. The first and last fractions were discarded. Ethyl acetate (Fisher certified reagent grade) was fractionally distilled on a spinning-band column at atmospheric pressure, with a reflux ratio of 1:500 immediately prior to use. Formamide (Fisher certified reagent grade) was distilled on a spinning-band column at atmospheric pressure with a reflux ratio of 1:500 immediately prior to use. Hexamethylenetetramine (Eastman Kodak) was dried for 3 days at 60 °C under reduced pressure and used without further purification. The preparation of *myo*-inositol was identical with that of Dr. Spitzer (see above). Mannitol (Fischer ACS certified) was dried in vacuo at 70 °C for 24 h and stored under vacuum in a desiccator. Methyl formate (Eastman Kodak spectro grade) was fractionally distilled on a spinning-band column at atmospheric pressure with a reflux ratio of 1:500 immediately prior to use. *s*-Trioxane (Aldrich) was zone refined for 10 days and one-third was discarded.

Table II. Results of Least-Squares Fit of the Data in Table I to Eq 3

	ϕ_v^0, cm^3 mol^{-1}	ϕ_v^0(add),[a] cm^3 mol^{-1}	v_2, cm^3 kg mol^{-2}	v_3, cm^3 kg^2 mol^{-3}	σ^b	molality range	ref
acetamide (AC)	55.66 (0.07)[c]		−0.21 (0.07)	0.04 (0.03)	0.01	0.16–1.8	this work (S.S.)
	56.1						*15*
	55.0						*16*
	55.61		−0.123	0.013		0–2.4	*17*
acetone (AN)	66.92 (0.08)		−0.41 (0.08)	0.10 (0.04)	0.01	0.18–1.9	this work (S.S.)
	66.92		−0.37	0.056		0–1.6	*17*
	67.0					0–∞	*18*
	66.8 (0.3)					0–0.35	*19*
cyclohexanol (CHEX)	103.45 (0.08)		−2.17 (0.37)		0.03	0.05–0.36	this work (I.T.)
	103.54 (0.03)		−2.5 (0.2)[d]			0.02–0.30	*20*
	102.7 (0.5)					0–0.10	*19*
cyclohexanedione	92.47 (0.02)		0.35 (0.05)		0.01	0.10–0.87	this work (S.S.)
	92.8 (0.4)		0.35 (0.05)			0–0.18	*19*
cyclohexanone	99.25 (0.03)		−0.40 (0.09)		0.01	0.10–0.56	this work (S.S.)
	99.7 (0.4)					0–0.20	*19*
dimethylformamide (DMF)	74.54 (0.06)		−0.52 (0.06)	0.08 (0.03)	0.02	0.12–2.00	this work (I.T.)
	74.60 (0.02)		−0.52 (0.04)		0.03	0.10–1.00	this work (J.S.)
	76.0						*15*
	74.5		0.425				*21*
dioxane (DIOX)	80.99 (0.05)		−0.08 (0.06)		0.02	0.14–1.53	this work (S.S.)
	80.94		−0.172	0.061		0–12.9	*22*
	80.96		−0.17[d]			0.05–0.36	*23*
	81.1					0.005–0.1	*24*
	80.9 (0.3)					0–0.23	*19*
ethyl acetate (EA)	88.93 (0.03)		0.02 (0.05)		0.01	0.17–0.87	this work (S.S.)
	88.97		0.08			0–0.9	*25*
	88.8 (0.3)					0–0.23	*19*
formamide (F)	38.67 (0.01)		0.08 (0.01)	−0.002 (0.002)	0.00	0.22–2.22	this work (S.S.)
	38.52 (0.17)		0.41 (0.10)	−0.04 (0.03)	0.01	0.41–2.68	this work (I.T.)
	38.5					0–∞	*18*
	39.2						*15*
	38.0						*16*
hexamethylenetetramine (HMT)	110.66 (0.06)		−0.38 (0.06)	0.06 (0.03)	0.01	0.10–0.64	this work (S.S.)
	110.71 (0.04)		−0.24 (0.07)		0.01	0.34–1.00	this work (I.T.)
	110.61 (0.03)		−0.27 (0.05)		0.02	0.23–1.00	this work (J.S.)
inositol (IN)	100.75 (0.02)		1.50 (0.10)		0.01	0.09–0.36	this work (S.S.)
	100.94 (0.12)		1.05 (0.53)		0.07	0.05–0.37	this work (J.S.)
mannitol (MAN)	119.47 (0.02)		0.58 (0.03)		0.01	0.12–0.89	this work (S.S.)
	119.39 (0.07)		0.71 (0.12)		0.02	0.29–0.75	this work (I.T.)
	119.31 (0.10)		0.79 (0.48)		0.02	0.07–0.31	this work (J.S.)
	119.71		0.52			0.09–1.05	*26*
	118.8 (0.5)					0–0.06	*19*
	119.33					0.02–0.5	*27*
methyl formate (MF)	55.27 (0.26)		0.33 (0.24)	−0.14 (0.12)	0.04	0.19–1.73	this work (S.S.)
trioxane (T)	69.70 (0.10)		0.17 (0.09)		0.03	0.17–2.09	this work (S.S.)
	69.66 (0.17)		0.21 (0.39)		0.04	0.20–0.60	this work (I.T.)
	69.63 (0.10)		0.17 (0.01)		0.02	0.10–0.66	this work (J.S.)
	69.58		0.17			0.10–1.06	*28*
	69.6 (0.2)					0–0.23	*19*
	69.51 (0.04)		0.22[d]				*29*
AC + DIOX	68.34 (0.09)	68.33 (0.06)	−0.20 (0.08)	0.05 (0.04)	0.01	0.14–2.10	this work (S.S.)
AC + EA	72.24 (0.03)	72.30 (0.05)	0.04 (0.03)		0.01	0.14–1.55	this work (S.S.)
AC + F	47.22 (0.05)	47.17 (0.04)	−0.04 (0.05)		0.03	0.13–1.99	this work (S.S.)
AC + HMT	83.11 (0.01)	83.16 (0.06)	−0.15 (0.06)		0.00	0.12–1.89	this work (S.S.)
AC + IN	77.18 (0.01)	78.21 (0.05)	0.35 (0.02)		0.00	0.09–0.58	this work (S.S.)
AC + MAN	87.51 (0.06)	87.57 (0.05)	0.25 (0.05)	−0.03 (0.03)	0.01	0.14–1.88	this work (S.S.)
AC + MF	55.38 (0.02)	55.47 (0.33)	−0.15 (0.01)		0.01	0.12–1.86	this work (S.S.)
AC + T	62.60 (0.02)	62.68 (0.17)	0.01 (0.01)		0.01	0.11–2.07	this work (S.S.)
AN + DIOX	73.86 (0.06)	73.96 (0.13)	−0.10 (0.03)		0.03	0.18–1.91	this work (S.S.)
AN + EA	77.96 (0.15)	77.93 (0.11)	−0.37 (0.06)	0.22 (0.06)	0.02	0.10–1.89	this work (S.S.)
AN + F	52.79 (0.02)	52.80 (0.09)	−0.05 (0.01)	0.02 (0.01)	0.00	0.14–2.31	this work (S.S.)
AN + MAN	93.18 (0.02)	93.20 (0.10)	0.11 (0.01)		0.01	0.16–1.53	this work (S.S.)
AN + MF	61.07 (0.05)	61.10 (0.33)	0.003 (0.02)		0.03	0.08–1.61	this work (S.S.)
CHEX + DMF	89.00 (0.09)	89.00 (0.05)	−1.08 (0.23)		0.07	0.10–0.59	this work (I.T.)
	89.20 (0.08)	89.03 (0.03)	−1.32 (0.21)		0.04	0.09–0.63	this work (J.S.)
CHEX + F	70.95 (0.07)	70.99 (0.12)	−0.32 (0.15)		0.03	0.12–0.72	this work (I.T.)
	71.34 (0.17)	70.99 (0.12)	−0.89 (0.37)		0.09	0.09–0.69	this work (J.S.)
CHEX + HMT	106.90 (0.04)	107.08 (0.06)	−1.07 (0.10)		0.02	0.10–0.60	this work (I.T.)
	106.99 (0.03)	107.03 (0.06)	−0.88 (0.08)		0.01	0.16–0.61	this work (J.S.)
CHEX + IN	102.12 (0.05)	102.20 (0.10)	−0.06 (0.13)		0.02	0.11–0.59	this work (I.T.)
	102.22 (0.09)	102.20 (0.10)	−0.04 (0.26)		0.06	0.10–0.55	this work (J.S.)
CHEX + MAN	111.75	111.42 (0.08)	−2.06			0.09–0.18	this work (I.T.)[e]
CHEX + T	86.47 (0.28)	86.56 (0.13)	−0.36 (0.66)		0.06	0.11–0.66	this work (I.T.)
	86.53 (0.04)	86.54 (0.09)	−0.63 (0.09)		0.02	0.10–0.64	this work (J.S.)
DMF + F	56.52 (0.37)	56.53 (0.11)	−0.05 (0.06)		0.01	0.22–0.97	this work (I.T.)

Table II (*Continued*)

	ϕ_v^0, cm^3 mol^{-1}	ϕ_v^0(add),[a] cm^3 mol^{-1}	v_2, cm^3 kg mol^{-2}	v_3, cm^3 kg^2 mol^{-3}	σ[b]	molality range	ref
DMF + HMT	92.64 (0.02)	92.63 (0.05)	−0.35 (0.05)		0.01	0.05–0.06	this work (I.T.)
DMF + IN	87.79 (0.05)	87.74 (0.09)	0.14 (0.08)		0.04	0.17–0.83	this work (I.T.)
	87.73 (0.03)	87.77 (0.07)	0.29 (0.08)			0.10–0.57	this work (J.S.)
DMF + MAN	96.94 (0.04)	96.97 (0.07)	0.05 (0.06)		0.01	0.16–0.98	this work (I.T.)
	97.10 (0.06)	96.96 (0.04)	−0.16 (0.16)		0.04	0.10–0.62	this work (J.S.)
DMF + T	72.10 (0.05)	72.10 (0.11)	−0.06 (0.07)		0.02	0.17–1.00	this work (I.T.)
DIOX + EA	84.97 (0.02)	84.96 (0.04)	−0.08 (0.04)		0.01	0.17–0.97	this work (S.S.)
DIOX + F	59.84 (0.08)	59.83 (0.04)	0.04 (0.01)		0.00	0.29–1.82	this work (S.S.)
DIOX + IN	90.80 (0.02)	90.87 (0.03)	0.40 (0.06)		0.01	0.09–0.64	this work (S.S.)
DIOX + MAN	100.22 (0.04)	100.23 (0.04)	0.18 (0.03)		0.02	0.12–2.07	this work (S.S.)
DIOX + MF	68.12 (0.02)	68.13 (0.16)	0.05 (0.02)		0.01	0.14–1.81	this work (S.S.)
DIOX + T	75.33 (0.04)	75.35 (0.08)	0.07 (0.04)		0.02	0.18–1.69	this work (S.S.)
EA + F	63.66 (0.01)	63.80 (0.02)	0.12 (0.01)		0.01	0.20–1.34	this work (S.S.)
EA + IN	94.84 (0.03)	94.84 (0.04)	0.41 (0.08)		0.01	0.13–0.67	this work (S.S.)
EA + MAN	103.96 (0.04)	104.20 (0.04)	0.22 (0.04)		0.02	0.14–1.40	this work (S.S.)
EA + MF	72.16 (0.01)	72.10 (0.15)	−1.66 (0.02)		0.01	0.18–1.07	this work (S.S.)
EA + T	79.23 (0.06)	79.32 (0.07)	0.19 (0.06)		0.03	0.14–1.58	this work (S.S.)
F + HMT	74.60 (0.04)	74.67 (0.04)	−0.02 (0.03)		0.02	0.14–2.44	this work (S.S.)
	74.61 (0.01)	74.62 (0.11)	0.01 (0.04)		0.01	0.05–0.63	this work (I.T.)
F + IN	69.36 (0.32)	69.73 (0.15)	0.76 (0.45)		0.07	0.34–1.00	this work (I.T.)
	69.83 (0.04)	69.73 (0.15)	0.36 (0.09)		0.02	0.10–0.68	this work (J.S.)
	69.73 (0.04)	69.71 (0.02)	0.38 (0.08)		0.01	0.09–0.64	this work (S.S.)
F + MAN	79.05 (0.02)	79.07 (0.02)	0.28 (0.02)		0.00	0.10–1.81	this work (S.S.)
	79.02 (0.02)	78.96 (0.12)	0.24 (0.04)		0.01	0.18–0.83	this work (I.T.)
F + MF	46.96 (0.10)	46.97 (0.14)	−0.03 (0.09)	0.04 (0.04)	0.01	0.14–2.11	this work (S.S.)
F + T	54.17 (0.01)	54.19 (0.06)	0.13 (0.01)		0.01	0.15–1.88	this work (S.S.)
	54.10 (0.02)	54.09 (0.17)	0.10 (0.03)	0.03 (0.02)	0.00	0.18–1.15	this work (I.T.)
HMT + IN	105.72 (0.01)	105.71 (0.04)	0.32 (0.03)		0.00	0.10–0.64	this work (S.S.)
	105.63 (0.14)	105.83 (0.08)	0.62 (0.29)		0.03	0.20–0.60	this work (I.T.)
	105.74 (0.04)	105.79 (0.08)	0.31 (0.09)		0.02	0.10–0.72	this work (J.S.)
HMT + MAN	114.98 (0.02)	115.07 (0.04)	0.13 (0.02)		0.01	0.09–1.93	this work (S.S.)
	115.01 (0.02)	115.05 (0.05)	0.20 (0.05)		0.01	0.20–0.60	this work (I.T.)
HMT + MF	82.84 (0.05)	82.97 (0.16)	−0.53 (0.04)		0.03	0.16–2.02	this work (S.S.)
HMT + T	90.01 (0.03)	90.18 (0.08)	−0.03 (0.02)		0.01	0.16–2.50	this work (S.S.)
	90.11 (0.01)	90.19 (0.11)	−0.17 (0.04)		0.00	0.10–0.59	this work (I.T.)
	90.17 (0.05)	90.12 (0.04)	−0.16 (0.12)		0.03	0.10–0.64	this work (J.S.)
IN + MAN	110.12 (0.01)	110.11 (0.02)	0.92 (0.03)		0.00	0.16–0.58	this work (S.S.)
	110.16 (0.05)	110.17 (0.09)	1.06 (0.11)		0.02	0.09–0.70	this work (I.T.)
	110.30 (0.04)	110.13 (0.07)	0.75 (0.10)		0.02	0.10–0.63	this work (J.S.)
IN + MF	77.93 (0.06)	78.01 (0.14)	0.51 (0.14)		0.03	0.12–0.68	this work (S.S.)
IN + T	85.16 (0.01)	85.23 (0.06)	0.73 (0.02)		0.00	0.21–0.66	this work (S.S.)
	85.27 (0.03)	85.30 (0.15)	0.63 (0.05)		0.02	0.08–0.90	this work (I.T.)
MAN + MF	87.20 (0.08)	87.37 (0.14)	0.23 (0.07)		0.04	0.13–2.01	this work (S.S.)
MAN + T	94.53 (0.02)	94.59 (0.06)	0.32 (0.02)		0.01	0.16–1.94	this work (S.S.)
	94.57 (0.03)	94.53 (0.12)	0.31 (0.06)		0.02	0.05–0.89	this work (I.T.)
MF + T	62.36 (0.03)	62.49 (0.18)	0.17 (0.03)		0.02	0.28–1.51	this work (S.S.)

[a] For ternary systems ϕ_v^0(add) is the mean value of ϕ_v^0 for the corresponding binary systems and ϕ_v is for an equimolar mixture of the two solutes at a total molality m (see eq 3). [b] This is the standard error of a single experiment. [c] The numbers in parentheses are the 95% confidence limits. [d] Coefficient on a molarity expansion. [e] Limited data.

Materials prepared by all researchers were analyzed for water content by using modified Karl Fisher titration. All solutions were prepared by weight with distilled water which had been slowly trickled through a Barnstead BD1-00809 ion-exchange demineralizer, and buoyancy corrections were applied. For solutions of volatile liquids, in order to keep the vapor space above the liquid to a minimum, either thin-walled, collapsible polyethylene containers which could contract to the volume of liquid inside were used, or the quantity of solution to be prepared in more rigid polyethylene bottles was such that it filled the entire bottle. While working with solutions containing ethyl acetate or methyl formate, we kept the containers under an ice/water mixture to prevent hydrolysis of the ester. All ternary solutions were prepared so as to be equimolal in their solutes. All solutions were used as soon after preparation as possible in order to minimize the possibility of bacterial decomposition of solutes.

Results

Experimental results are presented in Table I. Experimentally determined densities were converted to apparent molar volumes (ϕ_v(exptl) by using the equation

$$\phi_v = M/d - 1000(d - d_0)/(dd_0m) \quad (2)$$

where M is the molar mass of the solute, d is the density of the solution, d_0 is the density of pure water (0.997 047 g cm^{-3}), and m is the molality of the solution. ϕ_v(exptl) were fitted by least squares to

$$\phi_v(\text{exptl}) = \phi_v^0 + v_2m + v_3m^2 \quad (3)$$

In the fitting procedure, to ensure that only a minimum number of coefficients of molality were used to represent the data, we eliminated those coefficients which were zero with 95% confidence. The results of the least-squares fit are given in Table II together with pertinent literature data. Using these results, we calculated values of the apparent molar volume (ϕ_v(calcd)) corresponding to the experimental values. These are listed in the third column of Table I. The final column, Δ, is merely the difference between the experimental and calculated values of ϕ_v and provides a measure of the fidelity of the fitting equation to the experimental data. In most cases the major error in the determination of an experimental ϕ_v comes from the uncertainty

in determining the density. For some solutes, uncertainties in the preparation of the solutions (about 0.1%) are the major source of error.

Table II presents the results of the fitting procedure. In addition to ϕ_v^0, v_2, and v_3, for ternary systems ϕ_v^0(add) is included as an internal check on the data. For a ternary system (A + B), ϕ_v^0(add) is simply the arithmetic mean of the ϕ_v^0 for the corresponding binary systems

$$\phi_v^0(\text{add})(A + B) = \{\phi_v^0(A) + \phi_v^0(B)\}/2 \qquad (4)$$

and ideally ϕ_v^0(add) should be identical with ϕ_v^0 from the fit. In Table II, 93 determinations of various ϕ_v^0's from this laboratory are listed of which 10 systems have ϕ_v^0(fitted) and ϕ_v^0(add) which do not agree within their 95% confidence limits (CHEX + DMF, CHEX + F, CHEX + HMT, DMF + MAN, EA + F, EA + MAN, HMT + T, HMT + MAN, DIOX + IN, IN + MAN). If we take into account a possible 0.1% systematic error in concentration, the last three systems are within these 95% confidence limits. Statistically we would expect to find five instead of seven systems that do not agree. This is reasonable agreement considering the approximate nature of error estimates.

Discussion

In addition to the earlier mentioned uses of density measurements, a method of treating thermodynamic data which has been used to a large extent in this laboratory is the Savage–Wood additivity principle. For enthalpies the principle assumes that every functional group on molecule A interacts with every functional group on molecule B and that each interaction has a characteristic effect on the enthalpy that is independent of the positions of the functional groups on the molecules. The total pairwise molecular interaction enthalpy is then the sum of all the various group interactions, and, by knowing a small number of such interactions, one can predict the enthalpy behavior of a vast array of compounds. In essence an identical approach can be used for ϕ_v data where volumetric v_2 coefficients are treated analogously to enthalpic h_2 coefficients. However, at the present time such an approach is not too rewarding because the v_2 coefficients have not been determined with sufficient accuracy. Inspection of the agreement between different investigators in Table II shows that most of the v_2 coefficients have uncertainties of 25–100%. In contrast, h_2 is typically determined to ±5%.

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Registry No. MAN, 69-65-8; IN, 87-89-8; DMF, 68-12-2; T, 110-88-3; HMT, 100-97-0; AC, 60-35-5; AN, 67-64-1; DIOX, 123-91-1; EA, 141-78-6; F, 75-12-7; MF, 107-31-3; CHEX, 108-93-0; 1,4-cyclohexanedione, 637-88-7; cyclohexanone, 108-94-1.

Literature Cited

(1) Tasker, I. R.; Wood, R. H. *J. Phys. Chem.* **1982**, *86*, 4040.
(2) Tasker, I. R.; Wood, R. H. *J. Solution Chem.* **1982**, *11*, 295.
(3) Tasker, I. R.; Wood, R. H. *J. Solution Chem.* **1982**, *11*, 469.
(4) Tasker, I. R.; Wood, R. H. *J. Solution Chem.* **1982**, *11*, 481.
(5) Tasker, I. R.; Wood, R. H. *J. Solution Chem.* **1982**, *11*, 729.
(6) Savage, J. J.; Wood, R. H. *J. Solution Chem.* **1976**, *5*, 733.
(7) Wood, R. H.; Hiltzik, L. H. *J. Solution Chem.* **1980**, *9*, 45.
(8) Okamoto, B. Y.; Wood, R. H.; Thompson, P. T. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1990.
(9) Harris, A. L.; Thompson, P. T.; Wood, R. H. *J. Solution Chem.* **1980**, *9*, 305.
(10) Okamoto, B. Y.; Wood, R. H.; Desnoyers, J. E.; Perron, G.; Delorme, L. *J. Solution Chem.* **1981**, *10*, 139.
(11) Lilley, T. H.; Wood, R. H. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 901.
(12) Picker, P.; Tremblay, E.; Jolicouer, C. *J. Solution Chem.* **1974**, *3*, 377.
(13) Kell, G. S. *J. Chem. Eng. Data* **1967**, *12*, 66.
(14) Instruction Manual for Model 01D densimeter, Sodev Inc., Sherbrooke, Quebec, Canada.
(15) Herskovits, T. T.; Kelly, T. M. *J. Phys. Chem.* **1973**, *77*, 381.
(16) Shahidi, F.; Farrell, P. G.; Edward, J. T. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 715.
(17) Kiyohara, O.; Perron, G.; Desnoyers, J. E. *Can. J. Chem.* **1975**, *53*, 3263.
(18) Boge, L.; Hvidt, A. *J. Chem. Thermodyn.* **1972**, *3*, 663.
(19) Edward, J. T.; Farrell, P. G.; Shahidi, F. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 705.
(20) Cabini, S.; Conti, G.; Lepori, L. *J. Phys. Chem.* **1974**, *78*, 1030.
(21) deVisser, C.; Perron, G.; Desnoyers, J. E.; Heuvelsland, W. J. M.; Somsen, G. *J. Chem. Eng. Data* **1977**, *22*, 74.
(22) Kiyohara, O.; Perron, G. Desnoyers, J. E. *Can. J. Chem.* **1975**, *53*, 2591.
(23) Cabani, S.; Conti, G.; Lepori, L. *J. Phys. Chem.* **1972**, *76*, 1338.
(24) Franks, F.; Quickenden, M. A. J.; Reid, D. S.; Watson, B. *Trans. Faraday Soc.* **1970**, *66*, 582.
(25) Roux, G.; Perron, G.; Desnoyers, J. E. *Can. J. Chem.* **1978**, *56*, 2808.
(26) DiPada, G.; Belleau, B. *Can. J. Chem.* **1977**, *55*, 3825.
(27) Holland, H.; Vikingstad, E. *Acta Chem. Scand., Ser. A* **1976**, *30*, 182.
(28) Perron, G.; Desnoyers, J. E. *Can. J. Chem.* **1981**, *59*, 2599.
(29) Lepori, L.; Mollica, V. *J. Chem. Eng. Data* **1978**, *23*, 65.

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