Table I. Experimental and Calculated Osmotic Coefficients and Calculated Activity Coefficients for Aqueous GdnHCl Solutions at 25° C

m_{NaCl}	m_{GdnHCl}	ϕ_{exptl}	ϕ_{calcd}	$\gamma_{\pm\text{calcd}}$
0.6696	0.7511	0.8246	0.8255	0.5644
0.6793	0.7625	0.8242	0.8245	0.5623
0.6918	0.7766	0.8244	0.8232	0.5598
1.2343	1.5105	0.7716	0.7713	0.4647
1.2500	1.5342	0.7699	0.7700	0.4624
1.5649	2.0127	0.7463	0.7467	0.4231
2.0299	2.7745	0.7207	0.7198	0.3780
2.1768	3.0365	0.7122	0.7127	0.3659
2.5373	3.6937	0.6974	0.6982	0.3403
2.6707	3.9342	0.6950	0.6938	0.3324
2.6931	3.9855	0.6927	0.6929	0.3308
2.7778	4.1481	0.6902	0.6902	0.3259
2.9264	4.4414	0.6855	0.6856	0.3176
3.4498	5.5294	0.6713	0.6723	0.2921
3.6668	5.9818	0.6691	0.6683	0.2834
3.8805	6.4576	0.6653	0.6652	0.2754
3.9818	6.6794	0.6644	0.6640	0.2720
4.2345	7.2552	0.6614	0.6620	0.2640
4.8160	8.5966	0.6596	0.6593	0.2486
5.0150	9.0995	0.6574	0.6575	0.2433
5.8383	11.1681	0.6575	0.6575	0.2267

These osmotic coefficients were calculated using the relationships

$$2m_{\text{GdnHCl}}\phi_{\text{GdnHCl}} = -55.51 \ln a_w = 2m_{\text{NaCl}}\phi_{\text{NaCl}} \qquad (1)$$

where ϕ_{NaCl} was obtained from the tabulation by Robinson and Stokes (*4*). The experimental data were fit by the method of least squares to the following equation

$$\phi_{\text{GdnHCl}} = 1 + C_1 m^{1/2} + \sum_{i=2}^{i=8} C_i m^{(i-1)} \qquad (2)$$

The coefficients were: $C_1 = -2.643\,06 \times 10^{-1}$; $C_2 = 9.042\,70 \times 10^{-2}$; $C_3 = -3.203\,60 \times 10^{-2}$; $C_4 = 1.328\,47 \times 10^{-2}$; $C_5 = -3.044\,47 \times 10^{-3}$; $C_6 = 3.830\,30 \times 10^{-4}$; $C_7 = -2.476\,28 \times 10^{-5}$; $C_8 = 6.407\,30 \times 10^{-7}$. The overall standard deviation of the fit was 0.3%. Osmotic coefficients calculated from eq 1 are listed in column 4 of Table I.

Activity coefficients were calculated from the osmotic coefficients by means of the equation (*4*)

$$\ln \gamma_\pm = (\phi - 1) + \int_0^m \frac{(\phi - 1)\mathrm{d}m}{m} \qquad (3)$$

Substituting $\phi - 1$ from eq 2 and integrating we obtain

$$\ln \gamma_\pm = 3C_1 m^{1/2} + 2C_2 m + \tfrac{3}{2}C_3 m^2 + \tfrac{4}{3}C_4 m^3 + \tfrac{5}{4}C_5 m^4 + \tfrac{6}{5}C_6 m^5 + \tfrac{7}{6}C_7 m^6 + \tfrac{8}{7}C_8 m^7 \qquad (4)$$

Calculated values of $\gamma_\pm$ are given in column 5 of Table I.

The activity coefficients obtained here are larger than those calculated from the equation given by Aune and Tanford (*1*) by an average of 0.007 from 1 to 5 *m* and by 0.002 thereafter. The long region of near constancy of the osmotic coefficient exhibited here is similar to that observed for urea in water. Various association models have been invoked to explain the form of those data (*6*). It appears that the presence of the charge of the GdnH$^+$, while lowering the absolute value of the osmotic coefficient relative to urea, does not prevent GdnH$^+$ from undergoing both self interactions and interactions with water which are very similar to those of urea.

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Volumes and Heat Capacities of Mixtures of *N,N*-Dimethylformamide and Water at 298.15 K

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Densities and heat capacities of mixtures of *N,N*-dimethylformamide (DMF) and water (W) were measured at 298.15 K over the whole mole fraction range in two laboratories using a digital Anton Paar densimeter, a digital flow densimeter, an LKB precision calorimeter, and a Picker flow microcalorimeter. The data from both laboratories agree within the expected uncertainty of the various techniques. Excess thermodynamic functions and apparent and partial molal quantities of both components were calculated over the whole range. The concentration dependences of these functions for DMF are similar to those of other comparable solutes such as acetone. The corresponding functions for water do not change much with concentration; the standard partial molal volume of water is smaller than the molar volume by about 2.8 cm^3 mol^{-1} as expected from the loss of the open structure of the liquid, but the standard partial molal heat capacity of water is larger than the molar heat capacity by about 10 J K^{-1} mol^{-1}. A tentative explanation of the high values of $\bar{C}_{p,\text{W}}{}^\circ$ is given.

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Mixtures of aliphatic amides and water have been the subject of many studies (*1, 30* and references cited therein). Since these amides cover a very wide range of dielectric constants and are usually miscible with water, they are often used in studies of the interrelations between the solubility of drugs and the dielectric constants of the pure compounds and of their aqueous mixtures (*29*). In addition, the amides can serve as model compounds for the investigations of the properties of peptides in aqueous solutions.

Among these amides, *N,N*-dimethylformamide (DMF) is of particular interest in view of the lack of hydrogen bonding in the pure solvent. Therefore, some of us (*6, 8*) have used this solvent and its aqueous mixtures to study the influence of solvent structure on the enthalpies of solution and of solvation of a third component. For example the peculiar properties of hydrophobic solutes can be examined rather systematically since it is possible to go from pure H_2O to pure DMF, i.e., from a very structured solvent to a solvent where specific structural effects are absent (*2*).

In the course of studies on *tert*-butyl alcohol (*7*) and tetrabutylammonium bromide (*15*) in DMF–water mixtures, it was necessary to know very well the properties of the corresponding binary system. Reliable volume data are known in the literature (*30*), but at the time we started our measurements, corresponding heat capacity data were absent.

Since different instruments were available in both laboratories for the measurement of heat capacities and densities (in Sherbrooke flow instruments, in Amsterdam instruments for static measurements), we felt it would be useful to determine the properties of DMF–W mixtures in both laboratories. Such a procedure would serve as a severe test of the accuracy of the data and of the reliability of the various instruments.

Experimental Section

In view of the different techniques used in the two laboratories, the experimental section will be divided in two parts: (a) the static measurements, (b) the dynamic measurements.

(*a*) *The Static Measurements.* (*1*) *Volumes.* These quantities were evaluated from density measurements carried out with an Anton Paar Model DMA 02D densimeter. The temperature of the thermostat (298.15 K) was maintained at ±0.004 K, which corresponds to a reproducibility of the frequency of ±2 ppm. Since all measurements were done relative to water at 298.15 K (d_0 = 0.997 047 g cm^{-3} (*17*)), the instrument was calibrated with aqueous NaCl solutions in the concentration range 0–2 *m*, using the equation:

$$\Delta d = d - d_0 = K(\tau^2 - \tau_0^2) \qquad (1)$$

where *d* is the liquid density, τ the oscillation period, and *K* is a constant (*26*). With the densities of the NaCl solutions calculated from accurate literature data (*32*), the value of *K* was determined as 1.4142 × 10^{-5} g cm^{-3} s^{-2}, with a maximum mean deviation of ±0.05%. In this way it was possible to measure differences in densities to ±4.10^{-6} g cm^{-3}. The accuracy of the instrument was further tested by evaluating the apparent molar volumes (see Results and Discussion) of KCl and *n*-Bu_4NBr in pure water, using the Redlich–Meyer equation. Using a value for the Debye–Hückel limiting slope of 1.868 cm^3 mol$^{-3/2}$ l.$^{1/2}$ (*28*) at 298.15 K, the values of $\phi_V°$ and B_V obtained by linear regression are for *n*-Bu_4NBr $\phi_V°$ = 300.35 ± 0.02 cm^3 mol^{-1} and B_V = −11.4 ± 0.1 cm^3 mol^{-2} l., and for KCl $\phi_V°$ = 26.71 ± 0.02 cm^3 mol^{-1} and B_V = +0.18 ± 0.04 cm^3 mol^{-2} l. These values are in excellent agreement with literature values (*19, 21*).

(*2*) *Heat Capacities.* Some of us have reported in a short contribution (*9*) the molar heat capacities of binary mixtures of water and some amides. The detailed procedure to obtain the heat capacities is written therein. Essentially the energy equivalent E_0 of the calorimeter (an LKB 8700-1 precision calorimetric system equipped with a 100-cm^3 reaction vessel) and the temperature coefficient of the resistance of the calorimeter thermistor are evaluated. From the difference in heat capacity ($E_1 - E_0$), in which E_1 is the heat capacity of the calorimeter filled with 100.0 cm^3 of solvent, and the value of the molar volume of the solvent, the molar heat capacity is derived. Unfortunately, the values given in that paper are in error, since it was implicitly assumed that the volumes of mixing were zero. Therefore, using the present volume data, the heat capacities of DMF–H_2O are reevaluated. Since the volumes of mixing actually are very small, the difference between the present heat capacities and those previously reported (*9*) is very small (at the most 3 J K^{-1} mol^{-1}). The overall uncertainty in the molar heat capacities is believed to be of the order of 1%.

The calorimeter was tested by measuring the enthalpy of solution of tris(hydroxymethyl)aminomethane (THAM) in 0.1 M aqueous hydrochloric acid. The test experiments were carried out at concentrations of about 5 g of THAM/dm^3 of solvent. From eight independent measurements we obtained an enthalpy of solution of −29.724 K J mol^{-1} with a standard deviation of the mean of ±0.010 kJ mol^{-1}. This result is in fair agreement with literature data as reviewed by Prosen and Kilday (*27*).

(*3*) *Materials.* DMF (Baker, Analyzed Reagent) was dried over molecular sieves (Baker, 4A) for at least 48 h and used without further purification. Its volume fraction of water, as determined by Karl Fischer titration, never exceeded 5 × 10^{-5}. Solvent mixtures were prepared by weight, using freshly distilled water.

(*b*) *The Dynamic Measurements.* (*1*) *Volumes.* The densities were measured by a flow digital densimeter described in detail in the literature (*24, 26*). This instrument which is based on the same principle as the Anton Paar instrument has been thoroughly tested with aqueous NaCl (*26*) and tetraalkylammonium halides (*21*). It can measure differences in densities to ±3 × 10^{-6} g cm^{-3}.

(*2*) *Heat Capacities.* Differences in heat capacities per unit volume (σ) were measured with a Picker flow microcalorimeter. The principle of the instrument was described in detail elsewhere (*24, 25*). Essentially two liquids at the same temperature T_0, which are flowing at the same flow rate in twin cells, are heated simultaneously, and the difference in the applied power ΔW necessary to maintain the final temperature of both liquids constant ($T_0 + \Delta T$) is proportional to the difference in the heat capacity per unit volume $\Delta\sigma$ of the two liquids. The present measurements were carried out with a commercial version of this instrument. Very recently we have shown (*4*) that the heat capacities per unit volume determined with this commercial Picker flow microcalorimeter and with the original prototype were slightly but systematically different, and it was concluded, from several tests, that the commercial instrument gives results closer to the true values.

The present data are, as recommended (*4*), given relative to aqueous NaCl at 298.15 K, using for NaCl the equation:

$$10^3\Delta\sigma/\sigma_0 m = -35.819 + (11.289\ m) - (2.987\ m^2) \qquad (2)$$

in which $\Delta\sigma$ is the change in heat capacity per unit volume between the solution of molality *m* and pure water.

To test the instrument further, we changed the experimental conditions during the measurements several times on purpose. In this way, measurements were done by gravity (the basic power W_0 = 20 mW; ΔT = 0.8 K) and using a pump (W_0 = 20 mW and ΔT = 0.8 K and W_0 = 100 mW and ΔT = 2.4 K). Moreover, sometimes the measurements were carried out relative to water, sometimes relative to DMF. In addition, several measurements were done "step by step"; each measurement (at a certain mole fraction) was performed relative to the previous one as a reference. This means that both positive and negative values of the

Table I. Densities and Mean Molar Heat Capacities of DMF–Water Mixtures at 298.15 K Measured with Anton Paar and LKB Instruments

X_{DMF}	$(d - d_0)10^3$ (g cm^{-3})	X_{DMF}	C_p (J K^{-1} mol^{-1})
0	0	0	75.3
0.0282	−0.872	0.052	82.5
0.0513	−0.782	0.055	82.6
0.0700	−0.509	0.131	91.3
0.0787	−0.410	0.151	93.1
0.1102	−0.079	0.240	100.7
0.1340	−0.032	0.241	101.3
0.1500	−0.106	0.305	106.3
0.2201	−1.802	0.326	108.2
0.2503	−3.129	0.376	111.7
0.3070	−6.332	0.494	120.0
0.3482	−9.211	0.512	120.6
0.4086	−13.809	0.623	127.0
0.4529	−17.269	0.636	128.4
0.4996	−21.101	0.689	130.8
0.5491	−24.896	0.737	134.5
0.6496	−32.450	0.808	138.6
0.7462	−39.215	0.896	144.5
0.8290	−44.314	1	150.8
0.9481	−50.838		
1	−53.286		

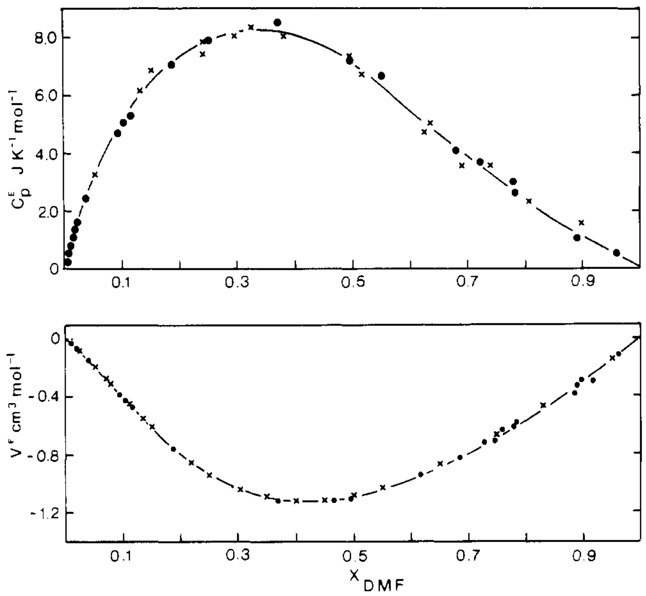


Figure 1. Excess molar volumes V^E and heat capacities $C_p{}^E$ of mixtures of DMF and water as a function of the mole fraction of DMF, X_{DMF}, at 298.15 K: ×, values obtained by static methods; ●, values obtained by dynamic methods.

difference in basic power ΔW, necessary to maintain the final temperature of both liquids constant, were recorded. In all these cases, it appeared that the results were reproducible within the uncertainty on the experimental $\Delta\sigma$ for each point, i.e., ±0.5%, independent of the actual experimental conditions. This again proves the high reproducibility of this flow microcalorimeter.

Generally, the measurements on mixtures containing a high DMF content were carried out by gravity in order to avoid any damage of the pump by DMF. However, it is essential then to adjust the flow rate during the measurement since the viscosity and the heat capacity change significantly as a function of the mole fraction of DMF; it is essential for a proper use of the instrument that the induced temperature change ΔT be kept as constant as possible. With the present version of the instrument it is possible to read off any change in this ΔT directly so that it is easy to change the liquid level to maintain a constant temperature change. To decrease the problems with this adjustment, the heat capacities were measured in rather small steps so that the necessary changes in flow rate were not very large. As pointed out by Grolier et al. (*13*), the stepwise procedure does not contribute significantly to the error of the final results. In our case, pure DMF was measured in nine steps from pure H_2O and, assuming on each $\Delta\sigma/\sigma_0$ the maximal error of ±0.5%, we arrived at a molar heat capacity for pure DMF of 148.2 ± 1.1 J K^{-1} mol^{-1}.

(*3*) ***Materials.*** DMF (Fisher Certified) was originally used after drying over molecular sieves but eventually was used as such since the density after adding molecular sieves was not lowered whereas the density of DMF immediately from the bottle (d = 0.943 881) was closer to the value obtained in the static measurements (d = 0.943 761). This mutual agreement is satisfactory. The mixtures were prepared by weight.

Table II. Densities and Heat Capacities of DMF–Water Mixtures at 298.15 K Measured with Flow Densimeter and Microcalorimeter

X_{DMF}	$(d - d_0)10^3$ (g cm^{-3})	$10^3\Delta\sigma/\sigma_0$	X_{DMF}	$(d - d_0)10^3$ (g cm^{-3})	$10^3\Delta\sigma/\sigma_0$
0	0	0	0.1877	−0.625	−189.8
0.0027	−0.168	−3.08	0.2506	−2.969	−239
0.0028	−0.173	−3.20	0.3708	−10.623	−317
0.0035	−0.213	−4.00	0.4681	−18.270	
0.0070	−0.383	−8.01	0.4940	−20.316	−386
0.0080	−0.448	−9.41	0.5487	−24.559	−410
0.0100	−0.498	−11.50	0.6164	−29.852	
0.0105	−0.519	−12.08	0.6827	−34.550	−464
0.0121	−0.562	−13.87	0.7283	−37.576	−476
0.0137	−0.618	−15.86	0.7395	−38.144	−480
0.0149	−0.646	−17.13	0.7619	−39.911	
0.0181	−0.720	−21.3	0.7791	−40.777	−491
0.0199	−0.749	−22.9	0.7811	−41.037	−493
0.0238	−0.797	−27.7	0.8843	−46.345	
0.0240	−0.811	−27.8	0.8929	−47.473	−520
0.0405	−0.812	−47.2	0.8982	−47.854	
0.0945	−0.130	−104.5	0.9217	−48.178	
0.1035	−0.025	−113.4	0.9590	−51.091	−533
0.1146	+0.052	−124.9	1	−53.166	−541
0.1360	+0.087	−143.9			

Results and Discussion

The experimental results are given in Tables I and II. In both cases the densities of the mixtures are given relative to pure H_2O ($d_0 = 0.997\ 047$ g cm^{-3} (*17*)). The molar heat capacities C_p in Table I were calculated using the equation:

$$C_p = \frac{E_1 - E_0}{100d}(X_W M_W + X_{DMF} M_{DMF}) \qquad (3)$$

in which X is the mole fraction and M is the molecular weight. In Table II the heat capacities are expressed as the relative difference in heat capacities per unit volume $\Delta\sigma/\sigma_0$, in which σ_0, the heat capacity per unit volume of pure water, is taken as 4.1670 J K^{-1} cm^{-3} (*31*).

In order to check the agreement of the data in both tables, the mean molar volumes V of the solutions were calculated from

$$V = (X_W M_W + X_{DMF} M_{DMF})/d \qquad (4)$$

Similarly from Table II the mean molar heat capacities C_p were obtained from

$$C_p = \sigma V \qquad (5)$$

In addition the molar excess volumes V^E and heat capacities C_p^E were calculated. These functions, Y^E, are defined by:

$$Y^E = Y - X_W Y_W^0 - X_{DMF} Y_{DMF}^0 \qquad (6)$$

in which Y stands for V and C_p, respectively, and Y_i^0 for the value of the pure component i. Values of V^E and C_p^E calculated in this way are plotted in Figure 1.

Generally excess functions are expressed by polynomials of the Redlich-Kister type. However, in the present case, V^E and C_p^E differ so much from a symmetric square curve, that this approach requires too many adjustable parameters, and we obtained a better fit with:

$$V^E/X_1X_2 = a + bX_1 + cX_1^{10} \qquad (7)$$

$$C_p^E/X_1X_2 = p + qX_1 + rX_1^{10} \qquad (8)$$

in which 1 and 2 refer to DMF and W, respectively. The best values for the coefficients, obtained from the combined results of Tables I and II, are: $a = -2.79 \pm 0.04$, $b = -3.14 \pm 0.02$, $c = 3.00 \pm 0.03$, $p = 6.0 \pm 1.6$, $q = 45.4 \pm 0.8$, $r = 23.7 \pm 1.0$. The uncertainties quoted represent the standard error in the regression coefficients. The mean deviation between calculated and experimental V^E and C_p^E values amounts to 0.004 cm^3 mol^{-1} and 0.16 J K^{-1} mol^{-1}, respectively.

As Figure 1 shows the agreement between the V^E and C_p^E values obtained from different techniques, on materials from different companies and measured in different laboratories, is very good: the V^E agree within 0.02 cm^3 mol^{-1} and the C_p^E within 0.5 J K^{-1} mol^{-1}. At this stage it should be mentioned again, that the values at very low DMF concentration obtained by the differential flow instruments are more reliable than by the absolute measurements since then the sensitivity of the flow instruments, directly measuring the difference in property between the solution and the pure solvent, is much higher, whereas at higher concentration the precision of both instruments is similar. Of course, the values of V^E and C_p^E are given, according to eq 6, relative to the values of the pure components and therefore, to check the absolute accuracy of both methods, it is better to compare also the V and C_p values themselves. The values of V agree within 0.05 cm^3 mol^{-1} (the expected experimental uncertainty), while the difference in both sets of C_p data increases gradually from 0.5 J K^{-1} mol^{-1} for $X_{DMF} \leq 0.4$ to a maximum difference of 2.6 J K^{-1} mol^{-1} for pure DMF. Even this maximum difference is not larger than the sum of both experimental uncertainties. Therefore, it can be concluded that the two sets of data of volumes and heat capacities agree very well both relatively and absolutely. Moreover, the present V^E data are in good agreement with those obtained from interpolation of the data given by Saphon and Bittrich (*30*).

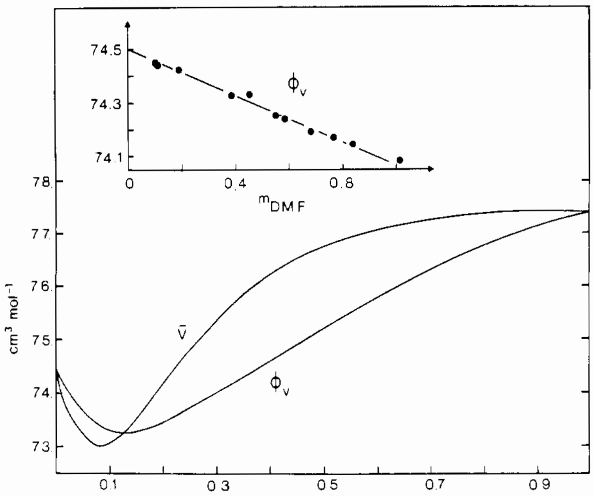


Figure 2. Apparent and partial molal volumes of DMF in water at 298.15 K.

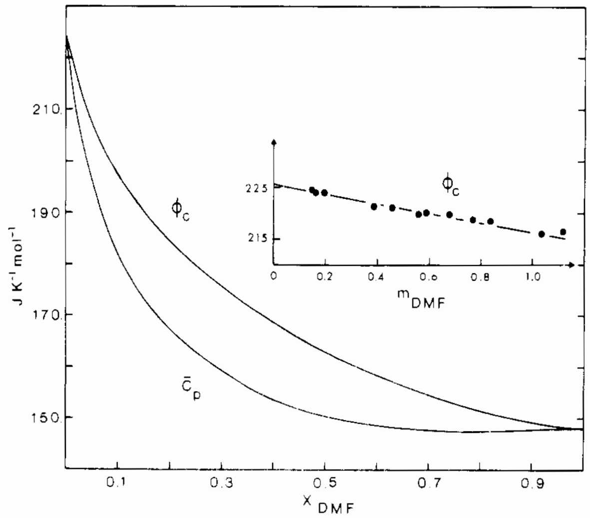


Figure 3. Apparent and partial molal heat capacities of DMF in water at 298.15 K.

From the data of Tables I and II it is possible to calculate the apparent molal volumes ϕ_V and heat capacities ϕ_C from the relations:

$$\phi_V = M/d - 1000(d - d_0)/dd_0m \qquad (9)$$

$$\phi_C = Mc_p + 1000(c_p - c_p^0)/m \qquad (10)$$

and

$$m = 55.51X_{DMF}/(1 - X_{DMF}) \qquad (11)$$

where M is the solute molecular weight, c_p and c_p^0 are, respectively, the specific heat capacities ($c_p = \sigma/d$) of the solution and pure solvent, and m is the solute molality. Values of ϕ_V and ϕ_C are given in Figures 2 and 3. The corresponding partial molal quantities ($\bar{V}$ and $\bar{C}_p$) can be obtained from

$$\bar{Y} = \phi_Y + X(1 - X)(\partial\phi_Y/\partial X) \qquad (12)$$

and

$$\bar{Y} = Y^E + Y^0 + (1 - X)(\partial Y^E/\partial X) \qquad (13)$$

which can be derived from eq 6 and in which Y stands for V and C_p, respectively, and Y^0 for the molar value of the pure component. The values of $\partial Y^E/\partial X$ can then be calculated from eq 7 and 8. Values of $\bar{V}$ and $\bar{C}_p$ are given in Figures 2 and 3 likewise. In the same figures ϕ_V and ϕ_C are also given at very low molalities. Extrapolation to infinite dilution yields values of $\phi_V{}^\circ$ (= 74.50 cm^3 mol^{-1}) and $\phi_C{}^\circ$ (= 225.1 J K^{-1} mol^{-1}) while the initial slopes (up to 1 *m*) are given by $A_V = 0.42_5$ cm^3 mol^{-2} kg and $A_C = -8.34$ J K^{-1} mol^{-2} kg, respectively. Values of $\phi_V{}^\circ$ and $\phi_C{}^\circ$ are equal to the standard partial molal volume $\bar{V}^\circ$ and heat capacity $\bar{C}_p{}^\circ$, respectively.

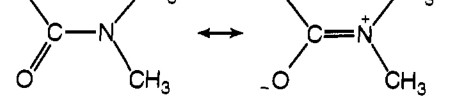
The difference between $\bar{C}_p{}^\circ$ and the molar heat capacity of the pure liquid $C_p{}^0$ (approximately equal to the intrinsic heat capacity) is often used as a criterion for the overall effect of a solute on water (*10, 11, 18*). In this way, we obtain for DMF in water a value for $\bar{C}_p{}^\circ - C_p{}^0$ of about 75 J K^{-1} mol^{-1}. After we finished the present measurements, Bonner and Cerutti (*3*) reported partial molal heat capacities of DMF up to $X_{DMF} = 0.26$ and the molar heat capacity of pure DMF. Although the scatter in their results is considerably larger than ours, they have derived a value of 78 J K^{-1} mol^{-1} for $\bar{C}_p{}^\circ - C_p{}^0$ which is in good agreement with the present value. Unfortunately, Bonner and Cerutti give only the partial molal heat capacities and not the experimental data, so that it is impossible to calculate the initial slope of ϕ_C from their data.

Kiyohara et al. (*18*) have reported corresponding data for aqueous mixtures of urea, acetamide (ACM), acetone (ACT), and dimethyl sulfoxide (Me_2SO). A similar discussion of the results given there can be applied to the present results. DMF apparently resembles ACT more than ACM, since for ACM, $\bar{C}_p{}^\circ - C_p{}^0$ was almost zero, whereas for ACT, like for DMF, $\bar{C}_p{}^\circ$ is significantly larger than the value of $C_p{}^0$, and in both cases ϕ_C is rapidly decreasing with concentration to the molar value. Moreover, ϕ_V of both ACT and DMF shows a minimum, often observed for organic solutes.

From the present results it is also possible, since we have measured in the whole mole fraction range, to calculate $\phi_{V,W}$ and $\phi_{C,W}$ by applying the same equations, 9–11, replacing DMF and W. The results are shown in Figure 4. Also the corresponding values of $\bar{V}_W$ and $\bar{C}_{p,W}$ are plotted. The higher scatter in the results for the heat capacities in pure DMF and DMF rich mixtures makes the calculation of $\bar{C}_{p,W}$ in the mole fraction range $0 < X_W < 0.1$ less accurate. The maximum uncertainty for $\bar{C}_{p,W}$ is of the order of ±3 J K^{-1} mol^{-1} for $\bar{C}_{p,W}{}^\circ$, but is for $X_W > 0.1$ of the order of 1 J K^{-1} mol^{-1}.

As can be seen from this figure, $\phi_{V,W}$ changes rather gradually from the value of pure H_2O (18.07 cm^3 mol^{-1}) to a value of about 15.3 for H_2O infinite diluted in DMF. The latter value is close to the value Desnoyers and Jolicoeur (*5*) expected (16 cm^3 mol^{-1}) if the structure of water has collapsed and to the value given by Millero et al. (*20*) derived for the molar volume of water in an electrostricted region (15.5 ± 0.2 cm^3 mol^{-1}).

The high values of $\phi_{C,W}$ on the other hand are rather surprising. If there was no specific interaction between the solute and water, one would expect a value of $\bar{C}_{p,W}{}^\circ$ which would be lower than that of $C_p{}^0$; for example, the value of $\bar{C}_{p,W}{}^\circ$ in benzene seems to be of the order of 70 J K^{-1} mol^{-1} (*12*). On the other hand, the increase of $\phi_{C,W}$ on adding DMF may be the result of hydrogen bonding between the H_2O molecules and the carbonyl group of the DMF molecules. As has been pointed out by Petersen (*23*), hydrogen bonds between water and carbonyl oxygen are stronger than between water molecules. In the case of DMF, this effect may be strenghtened by the nitrogen atom, due to the resonance forms (*23*) show below. Also in the case of *tert*-butyl alcohol–water mixtures, $\phi_{C,W}$ seems to increase with adding *tert*-butyl alcohol (*22*). Very recently, Hoeve and Kakivaya (*16*) reported on the heat capacity of water in collagen. It is very striking that, if you take the mean value of $\bar{C}_{p,W}{}^\circ$ obtained by them at 303 K using Kangaroo-tail tendon and that of Haly and Snaith (*14*) at 293 K using rat-tail collagen, you arrive at a value of 88.5 J K^{-1} mol^{-1} in excellent agreement with our value of $\bar{C}_{p,W}{}^\circ$ in DMF at 298 K. Moreover, their value of $\bar{C}_{p,W}$ does not change very much with increasing X_W. A similar behavior is observed for $\bar{C}_{p,W}$ in aqueous DMF (Figure 4). Further work to study $\phi_{V,W}$ and $\phi_{C,W}$ in aqueous binary systems is in progress.



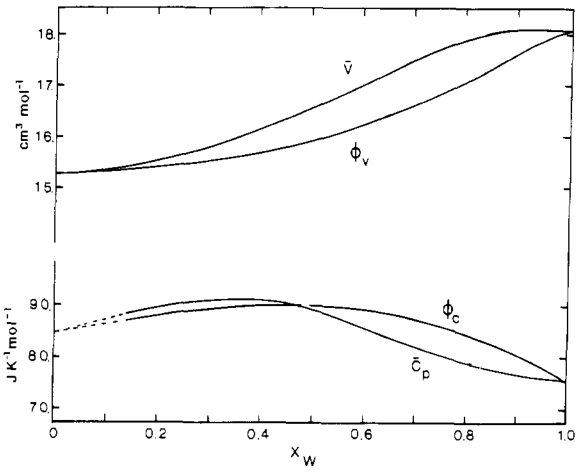


Figure 4. Apparent and partial molal volumes and heat capacities of H_2O in DMF at 298.15 K.

Glossary

A_V, A_C	initial slopes of ϕ_V and ϕ_C as a function of molality, cm^3 mol^{-2} kg and J K^{-1} mol^{-2} kg
c	concentration, mol l.$^{-1}$
c_p	specific heat, J K^{-1} g^{-1}
C_p	molar heat capacity, J K^{-1} mol^{-1}
$C_p{}^0$	molar heat capacity of the pure component, J K^{-1} mol^{-1}
$C_p{}^E$	molar excess heat capacity, J K^{-1} mol^{-1}
$\bar{C}_p$	partial molal heat capacity, J K^{-1} mol^{-1}
$\bar{C}_p{}^\circ$	standard partial molal heat capacity, J K^{-1} mol^{-1}
d	density, g cm^{-3}
d_0	density of pure water, 0.997 047 g cm^{-3}
E_0	energy equivalent of the calorimeter, J K^{-1}
E_1	energy equivalent of the calorimeter filled with 100.0 cm^3 solvent
a, b, c, p, q, r	constants of eq 7 and 8
K	constant of eq 1, g cm^{-3} s^{-2}
m	molality, mol kg^{-1}
M	molecular weight, g mol^{-1}
T	temperature, K
X	mole fraction
V	molar volume, cm^3 mol^{-1}
V^0	molar volume of pure component, cm^3 mol^{-1}
V^E	excess molar volume, cm^3 mol^{-1}
$\bar{V}$	partial molal volume, cm^3 mol^{-1}
$\bar{V}^\circ$	standard partial molal volume, cm^3 mol^{-1}
W_0	basic power, J s^{-1}
ϕ	apparent molal quantity
σ	heat capacity per unit volume, J K^{-1} cm^{-3}
τ	vibration period, s

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Heats of Mixing for the Ternary System Ethanol–1-Propanol–Cyclohexane at 25 °C

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Heats of mixing are measured at 25 °C for the title ternary system and its two constituent binaries of alcohols and cyclohexane using a isothermal semicontinuous dilution calorimeter. Experimental data are satisfactorily correlated by associated solution models.

This paper presents the first issue of a series of measurements of heats of mixing for ternary liquid mixtures. Isothermal semicontinuous titration calorimeters have recently been described (*2, 4, 5, 8–10, 15*) that are especially suitable for measurements of enthalpies of mixing of liquid mixtures. Heats of mixing for the ethanol–1-propanol–cyclohexane and the binary ethanol–cyclohexane and 1-propanol–cyclohexane systems at 25 °C are presented using the Van Ness-type calorimeter.

Several methods are available in predicting heats of mixing for multicomponent mixtures from binary data. However, such predictions are mainly of empirical nature because solution theories, at the present time, do not allow quantitative predictions for strongly nonideal liquid mixtures. The method of Nagata (*3*) appears to be useful for a ternary system composed of two alcohols and saturated hydrocarbon. The application of this method to the ethanol–1-propanol–cyclohexane system is discussed.

Experimental Section

Materials. All materials used in this study were the reagent grade of Nakarai Chemicals, Ltd. Benzene was recrystallized three times. Cyclohexane was passed through a 1.2 m, 10 mm i.d. glass column packed with silica. The alcohols were fractionally distilled over drying materials: ethanol (calcium oxide), 1-propanol (anhydrous copper sulfate). Refractive indices were measured with a Shimadzu Pulfrich refractometer at 25 °C: benzene, 1.4879; cyclohexane, 1.4237; ethanol, 1.3594; 1-propanol, 1.3838.

Apparatus. The calorimeter was the same as that designed by Tanaka et al. (*9*) with the following features. (1) The wall inside the mixing vessel is kept free of any dampness from the bath water by using a mixing vessel of fixed dimensions. (2) Use of a flange-type lid to seal the mixing vessel makes the calorimeter simple because the calorimeter does not require a precise bore tube and it is easy to wash the calorimeter after each experimental run. Figure 1 shows a schematic diagram of the calorimeter. A 140-ml silvered Dewar flask has a strip window to make it possible to see the inside of the flask. Flask A is sealed by the Teflon plug B. One of the components to be mixed is weighed into the flask, all air being vent through the air vent R. The second component is stored in the feed bulb C of 70 ml capacity. A glass connecting line leads from the top of the feed bulb to a stainless steel hypodermic tube, which passes through the plug, and its open end is inserted in the small mercury-filled cup K. The feed component in the feed bulb C is stored over mercury, which is introduced into the bottom of the feed bulb through a glass tube leading to the mercury reservoir D. The cooling system attached to the Teflon plug B consists of the cooling module (Netsu Denshi Co., Type CP-1.4-17-10) M, the stainless steel heat sink N, and the copper cooling plate O, which is connected to the copper cooling rod P, which passes through the Teflon plug B into the mixing vessel. Silicone grease is introduced among those components to minimize thermal resistances. A stabilized dc supply powers the cooling module. The stirrer consists of the small Teflon-coated magnet H and the paddles G mounted on a stainless steel rod, which is supported by the stainless steel frame I.

The thermistor (Shibaura Denshi Co., Type NSLB, resistance at 25 °C is about 35 kΩ) S is mounted in a thin-walled brass tube