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Ultrasonic Behavior of the System Water + 3-Pentanone

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The effect of 3-pentanone on the temperature corresponding to the adiabatic compressibility minimum (TACM), the sound velocity maximum (TSVM), and the specific acoustic impedance maximum (TSAIM) of pure water has been studied by experimentally determining the sound velocity and density of aqueous solutions at different concentrations over a temperature range 44–78 °C. The structural contribution to the shift in TACM, TSVM, and TSAIM has been evaluated. The shift is positive throughout the concentration range studied and indicates that 3-pentanone is hydrophobic in nature.

Introduction

Aqueous solutions of nonelectrolytes exhibit many deviations from the ideal behavior. The structure of nonelectrolyte solutions may also be investigated by determining the shift in extrema of various physical properties of pure water caused by the addition of nonelectrolytes. The effect of nonelectrolytes on the temperature corresponding to the density maximum (TDM) (*1*–*6*) of water has been studied extensively and the results have been utilized to classify the solutes as structure promoters or disrupters. Recent studies on the effect of nonelectrolytes on the temperature corresponding to the adiabatic compressibility minimum (TACM) (*7*–*11*), the sound velocity maximum (TSVM) (*11*–*16*) and the specific acoustic impedance maximum (TSAIM) (*11*, *16*) were found to be useful in understanding the solvent structure behavior of their aqueous solutions.

Roux et al. (*18*) studied apparent molal volume ϕ_V and apparent molal heat capacity ϕ_C of various aqueous mixtures. They observed, in general, that the more hydrophobic the solute is, the more negative is the initial slope. The apparent molal heat capacity ϕ_C decreases as a function of concentration and the decrease is more important for hydrophobic solutes. The results for water + 3-pentanone at 25 °C show that 3-pentanone behaves as a hydrophobic solute. However, the results for water + 2-butanone in the temperature range 4–40 °C show that 2-butanone becomes less hydrophobic in nature as the temperature is increased. In view of this fact an attempt has been made to study the effect of temperature on the hydrophobic nature of 3-pentanone from TACM, TSVM, and TSAIM studies.

Experimental Section

AnalaR grade 3-pentanone was purified and used in the present work. The density (ρ) of pure liquid measured at 25 °C with a bicapillary type pycnometer with an accuracy of 2 parts in 10^5 was 809.88 kg m^{-3}. The density value is in good agreement with the data available in the literature (*17*). Ultrasonic velocities (u) in pure liquid and aqueous solutions were determined with a single-crystal variable-path interferometer working at 3 MHz with an accuracy of ±0.003%. The details of the experimental technique were published elsewhere (*10*). The ultrasonic velocity data have been corrected for diffraction effects (*19*). The densities of and ultrasonic velocities in aqueous 3-pentanone solutions of different concentrations have been determined at an interval of approximately 2 °C over a range of 5 °C on either side of TACM, TSVM, and TSAIM.

Table I. u, ρ, and β at Different Temperatures for the System Water + 3-Pentanone

t, °C	u, m s^{-1}	ρ, 10^3 kg m^{-3}	β, 10^{-11} m^2 N^{-1}
	X_2 = 0.0017		
67.20	1555.72	0.97876	42.214
64.76	1555.02	0.98010	42.195
62.72	1554.42	0.98120	42.180
60.65	1553.54	0.98228	41.181
55.31	1550.36	0.98496	42.239
	X_2 = 0.0032		
67.65	1557.03	0.97777	42.186
65.29	1556.61	0.97907	42.153
63.22	1556.03	0.98018	42.136
60.95	1555.18	0.98137	42.131
58.44	1553.92	0.98266	42.144
55.61	1552.30	0.98406	42.172
	X_2 = 0.0050		
64.78	1557.67	0.98744	42.123
62.21	1557.25	0.97984	42.085
59.85	1556.35	0.98109	42.080
57.33	1555.30	0.98239	42.081
55.16	1554.22	0.98347	42.093
52.79	1552.74	0.98462	42.124
	X_2 = 0.0066		
62.01	1558.75	0.97924	42.030
59.80	1558.35	0.98039	42.002
57.31	1557.49	0.98166	41.994
54.96	1556.49	0.98283	41.998
52.69	1555.22	0.98393	42.020
	X_2 = 0.0090		
59.74	1559.47	0.98023	41.949
57.43	1558.93	0.98141	41.927
54.96	1558.01	0.98263	41.925
52.69	1556.87	0.98373	41.939
50.50	1555.62	0.98475	41.963

Results and Discussion

The results of ultrasonic velocity, adiabatic compressibility ($\beta = 1/u^2\rho$) and specific acoustic impedance ($Z = u\rho$) as a function of temperature at different mole fractions are presented in Tables I–III and also shown graphically in Figures 1–3. The template method (*10*) has been employed to fix TACM ($T_{\beta(\mathrm{expt})}$), TSVM ($T_{u(\mathrm{expt})}$), and TSAIM ($T_{z(\mathrm{expt})}$) with an accuracy of ±0.4, ±0.2, and ±0.3 °C, respectively.

The structural contribution to the shift in TACM $(\Delta T_{\beta,\mathrm{str}})_{\mathrm{expt}}$, TSVM $(\Delta T_{u,\mathrm{str}})_{\mathrm{expt}}$, and TSAIM $(\Delta T_{z,\mathrm{str}})_{\mathrm{expt}}$ have been evaluated by using the following expressions, the details of which are given in the earlier papers from our laboratory (*9*–*13*).

$$(\Delta T_{\beta,\mathrm{str}})_{\mathrm{expt}} = T_{\beta,\mathrm{expt}} - T_{\beta,\mathrm{id}} \tag{1}$$

$$(\Delta T_{u,\mathrm{str}})_{\mathrm{expt}} = T_{u,\mathrm{expt}} - T_{u,\mathrm{id}} \tag{2}$$

$$(\Delta T_{z,\mathrm{str}})_{\mathrm{expt}} = T_{z,\mathrm{expt}} - T_{z,\mathrm{id}} \tag{3}$$

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Table II. u at Different Temperatures for the System Water + 3-Pentanone

t, °C	u, m s^{-1}	t, °C	u, m s^{-1}
$X_2 = 0.0017$			
77.28	1555.90	70.02	1556.27
74.86	1556.11	67.20	1555.72
72.74	1556.25		
$X_2 = 0.0032$			
74.61	1556.73	67.65	1557.03
72.04	1557.07	65.29	1556.61
69.82	1557.09	63.22	1556.03
$X_2 = 0.0050$			
74.05	1557.45	67.35	1557.94
71.58	1557.71	64.78	1557.67
69.16	1557.99	62.21	1557.25
$X_2 = 0.0066$			
71.38	1558.67	64.28	1559.11
69.16	1558.95	62.01	1558.75
66.65	1559.07	59.80	1558.35
$X_2 = 0.0090$			
68.51	1559.59	62.11	1559.85
66.50	1559.87	59.74	1559.47
64.33	1559.89		

Table III. u, ρ, and z at Different Temperatures for the System Water + 3-Pentanone

t, °C	u, m s^{-1}	ρ, 10^3 kg m^{-3}	z, 10^3 kg m^{-2} s^{-1}
$X_2 = 0.0017$			
60.65	1553.54	0.982 28	1526.01
55.31	1550.36	0.984 96	1527.04
53.20	1548.70	0.985 97	1526.97
50.38	1546.11	0.987 28	1526.44
$X_2 = 0.0032$			
58.44	1553.92	0.982 66	1526.98
55.61	1552.30	0.984 06	1527.56
53.40	1550.74	0.985 13	1527.68
51.38	1549.00	0.986 08	1527.44
48.96	1546.81	0.987 19	1527.00
$X_2 = 0.0050$			
57.33	1555.30	0.982 39	1527.91
55.16	1554.22	0.983 47	1528.53
52.79	1552.74	0.984 62	1528.86
50.38	1551.10	0.985 75	1529.00
47.81	1548.94	0.986 91	1528.66
$X_2 = 0.0066$			
54.96	1556.49	0.982 83	1529.77
52.69	1555.22	0.983 93	1530.23
50.17	1553.66	0.985 11	1530.53
47.91	1551.86	0.986 14	1530.35
45.34	1549.58	0.987 28	1529.87
$X_2 = 0.0090$			
52.69	1556.87	0.983 73	1531.54
50.50	1555.62	0.984 75	1531.90
48.36	1554.30	0.985 73	1532.12
46.19	1552.46	0.986 70	1531.81
44.08	1550.94	0.987 61	1531.72

The adiabatic compressibility minimum (*9*, *10*) (T_β) of the solution is given by

$$T_\beta = \left[64 - \frac{\phi_2}{\phi_1}\frac{\alpha_\beta}{0.0032}\right]\left[1 + \frac{\phi_2}{\phi_1}\frac{{\alpha_\beta}^1}{0.0016}\right]^{-1} - \left[\frac{d\beta^E}{dt}\right]\left[1 + \frac{\phi_2}{\phi_1}\frac{{\alpha_\beta}^1}{0.0016}\right]^{-1}[0.0032\phi_1]^{-1} \quad (4)$$

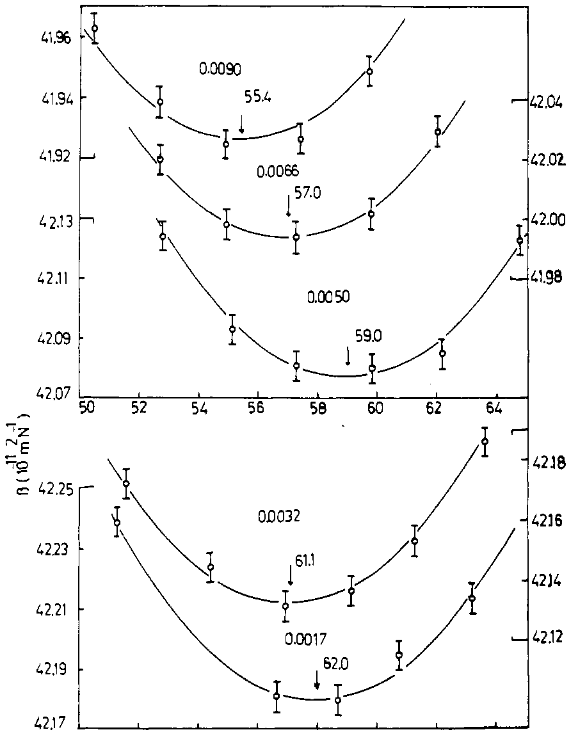

Figure 1. Adiabatic compressibility versus temperature in aqueous solution at different mole fractions (X_2) of 3-pentanone.

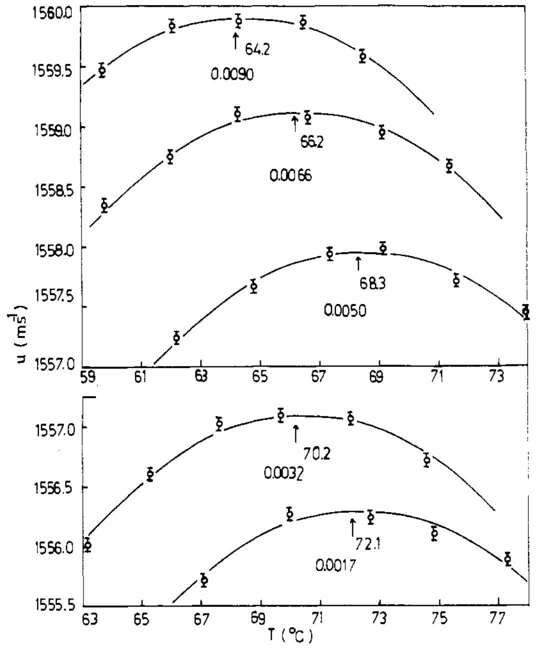

Figure 2. Ultrasonic velocity versus temperature in aqueous solution at different mole fractions (X_2) of 3-pentanone.

where ϕ_1 and ϕ_2 represent the volume fractions of pure water and organic solute respectively in the solution. α_β and ${\alpha_\beta}^1$ are the constants of organic solute involved in adiabatic compressibility versus temperature relation given by

$$\beta_2 = {\beta_2}^0 + \alpha_\beta t + {\alpha_\beta}^1 t^2 \quad (5)$$

The sound velocity maximum (*12*, *13*) (T_u) of the solution is given by

$$T = 74 - \left[\frac{\phi_2}{\phi_1}\right]^2 \frac{w_1}{w_2}\frac{\alpha_u}{0.049}\left[\frac{u_1}{u_2}\right]^3 - \frac{w_1}{{\phi_1}^2}\frac{{u_1}^3}{0.098}\left[\rho\frac{d\beta^E}{dt} + \beta^E\frac{d\rho}{dt}\right] \quad (6)$$

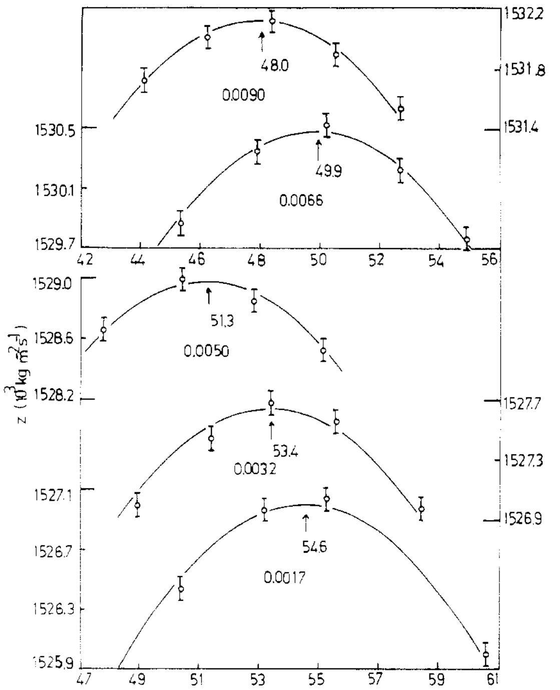

Figure 3. Specific acoustic impedance versus temperature in aqueous solution at different mole fractions (X_2) of 3-pentanone.

Table IV. Pure-Liquid Parameters of 3-Pentanone

$\beta_2^0/(10^{-11}\ \mathrm{m^2\ N^{-1}})$	56.632
$\alpha_\beta/(10^{-11}\ \mathrm{m^2\ N^{-1}\ {}^\circ C^{-1}})$	0.2825
$\alpha_\beta^1/(10^{-14}\ \mathrm{m^2\ N^{-1}\ {}^\circ C^{-2}})$	2.2283
$u_2^0/(\mathrm{m\ s^{-1}})$	1393.93
$\alpha_u/(\mathrm{m\ s^{-1}\ {}^\circ C^{-1}})$	3.4184
$z_2^0/(10^3\ \mathrm{kg\ m^{-2}\ s^{-1}})$	1281.00
$\alpha_z/(10^3\ \mathrm{kg\ m^{-2}\ s^{-1}\ {}^\circ C^{-1}})$	−4.3378
$\alpha_z^1/(\mathrm{kg\ m^{-2}\ s^{-1}\ {}^\circ C^{-2}})$	2.901

where w_1 and w_2 represent weight fractions of pure water and organic solute, respectively, in the solution. α_u is the temperature coefficient of sound velocity in the relation

$$u_2 = u_2^0 - \alpha_u t \tag{7}$$

The specific acoustic impedance maximum (*11*, *16*) (T_z) of the solution is given by

$$T_z = -\frac{\dfrac{7.5603w_1}{z_1^3} + \dfrac{2\alpha_z w_2}{z_2^3}}{\dfrac{-0.13404w_1}{z_1^3} + \dfrac{4\alpha_z^1 w_2}{z_2^3}} + \frac{\dfrac{1}{\rho}\left[\dfrac{d\beta^E}{dt} - \dfrac{\beta^E}{\rho}\dfrac{d\rho}{dt}\right]}{\dfrac{-0.13404w_1}{z_1^3} + \dfrac{4\alpha_z^1 w_2}{z_2^3}} \tag{8}$$

where α_z and α_z^1 are the temperature coefficients of specific acoustic impedance in the relation

$$z_2 = z_2^0 + \alpha_z t + \alpha_z^1 t^2 \tag{9}$$

The values of β_2^0, α_β, α_β^1, u_2^0, α_u, z_2^0, α_z, and α_z^1 for 3-pentanone are evaluated by using experimental ultrasonic velocity and density data and are presented in Table IV.

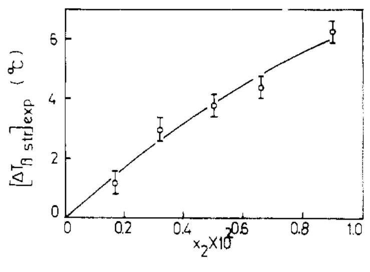

Figure 4. $[\Delta T_{\beta,\mathrm{str}}]_{\mathrm{expt}}$ versus mole fraction (X_2) of 3-pentanone in aqueous solution.

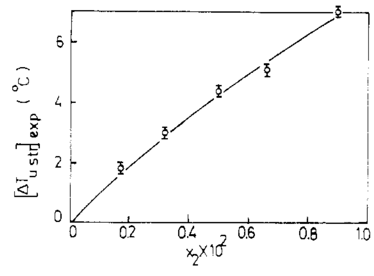

Figure 5. $[\Delta T_{u,\mathrm{str}}]_{\mathrm{expt}}$ versus mole fraction (X_2) of 3-pentanone in aqueous solution.

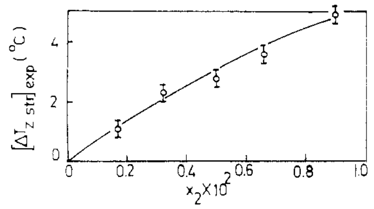

Figure 6. $[\Delta T_{z,\mathrm{str}}]_{\mathrm{expt}}$ versus mole fraction (X_2) of 3-pentanone in aqueous solution.

In eq 4, 6, and 8, the first term (T_β or T_u or $T_{z,\mathrm{id}}$) represents the dilution effect and the second term (ΔT_β or ΔT_u or $\Delta T_{z,\mathrm{str}}$) represents the structural contribution. The results of $[\Delta T_{\beta,\mathrm{str}}]$, $[\Delta T_{u,\mathrm{str}}]$, and $[\Delta T_{z,\mathrm{str}}]$ are presented in Table V. The literature survey indicates that the structural contribution to the shift in temperature corresponding to velocity maximum, compressibility minimum, specific acoustic impedance maximum, and density maximum is positive; this reflects the hydrophobic nature of the solute. If the structural shift is negative it is an indication of destabilization or breaking of the hydrogen-bonded structure of water; i.e., the solute is hydrophilic in nature.

The variation of $[\Delta T_{\beta,\mathrm{str}}]_{\mathrm{expt}}$ with mole fraction X_2 of 3-pentanone is shown in Figure 4. $[\Delta T_{\beta,\mathrm{str}}]_{\mathrm{expt}}$ is positive throughout the concentration range, indicating that the solute behaves as a structure maker.

Roux et al. (*18*) studied the concentration dependence of apparent molal volume ϕ_V and apparent molal heat capacity ϕ_C of aqueous 3-pentanone at 25 °C. They found the initial slopes A_V are negative (−1.1 cm^3 mol^{-2} kg) at 25 °C. This behavior has been attributed to the hydrophobic character of this ketone.

The variation of $[\Delta T_{u,\mathrm{str}}]_{\mathrm{expt}}$ is positive (Figure 5) for aqueous 3-pentanone and the magnitude is found to increase with the

Table V. Experimental and Theoretical Values of ($\Delta T_{\beta,\mathrm{str}}$), ($\Delta T_{u,\mathrm{str}}$), and ($\Delta T_{z,\mathrm{str}}$) at Different Mole Fractions for the System Water + 3-Pentanone

X_2	$(\Delta T_{\beta,\mathrm{str}})_{\mathrm{expt}}$, °C	$(\Delta T_{\beta,\mathrm{str}})_{\mathrm{th}}$, °C	$(\Delta T_{u,\mathrm{str}})_{\mathrm{expt}}$, °C	$(\Delta T_{u,\mathrm{str}})_{\mathrm{th}}$, °C	$(\Delta T_{z,\mathrm{str}})_{\mathrm{expt}}$, °C	$(\Delta T_{z,\mathrm{str}})_{\mathrm{th}}$, °C
0.0017	1.2 ± 0.4	1.2	1.8 ± 0.2	3.4	1.1 ± 0.3	0
0.0032	3.0 ± 0.4	2.7	3.0 ± 0.2	5.0	2.3 ± 0.3	1.7
0.0050	3.8 ± 0.4	3.2	4.4 ± 0.2	6.3	2.8 ± 0.3	1.9
0.0066	4.4 ± 0.4	4.1	5.1 ± 0.2	7.5	3.6 ± 0.3	3.0
0.0090	6.3 ± 0.4	5.7	7.1 ± 0.2	10.2	4.9 ± 0.3	4.7

concentration, indicating the structure-promoting nature of the solute.

The variation of $[\Delta T_{z,\mathrm{str}}]_{\mathrm{expt}}$ for this system is positive (Figure 6) and increases with the concentration of 3-pentanone.

All the three studies (TACM, TSVM, and TSAIM) indicate that the solute 3-pentanone behaves as a structure maker. It may be mentioned here that each study is confined to a different temperature range and all the three studies effectively cover a temperature range of 44–78 °C. The present results clearly show that the solute behaves as a structure maker in the temperature range studied.

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Heat Capacity of Aqueous $MgCl_2$ from 349 to 598 K

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A differential flow heat-capacity calorimeter has been used to measure the heat capacity of $MgCl_2$(aq) at molalities from 0.03 to 2.26 mol kg^{-1}, temperatures from 350 to 600 K, and pressures from 2 to 18 kPa. The results show the very large and negative apparent molar heat capacities at high temperatures and low molalities found previously for NaCl(aq), NaBr(aq), KCl(aq), LiCl(aq), and $CaCl_2$(aq).

Introduction

The work presented here is part of a continuing investigation of heat capacities of aqueous electrolytes at high temperatures using flow-calorimetric techniques (*1–6*). Very large and negative values of the apparent molar heat capacity, $C_{p,\phi}$, have been found for aqueous NaCl (*1*, *2*), KCl (*5*), NaBr (*4*), LiCl (*6*), and $CaCl_2$ (*3*) at high temperatures and low molalities. This has been attributed to large interactions between ions in water, together with the changes in properties of water as its critical point is approached (*1*, *7*). A knowledge of the properties of aqueous salt solutions at high temperature is important for understanding a variety of chemical processes that occur at high temperatures, including mineral geochemistry, the behavior of geothermal fluids, and corrosion in electric-power boilers. In this paper we report $C_{p,\phi}$ of $MgCl_2$(aq) at temperatures up to 600 K. For convenience in interpolating our results, the data are represented with a three-dimensional cubic spline.

Experimental Section

Solutions. A stock solution of approximately 3.0 mol kg^{-1} $MgCl_2$ was prepared from Baker Analyzed Reagent grade $MgCl_2{\cdot}6H_2O$ (less than 0.013% impurities) and distilled/deionized water. Other solutions were prepared by mass dilution of the stock solution. Concentrations of all solutions were determined (±0.1%) by titration with aqueous $AgNO_3$.

Heat Capacity Measurements. The high-temperature flow heat-capacity calorimeter has been described in detail previously (*1*, *14*). The calorimeter was operated at a water flow rate of 0.033 $cm^3\ s^{-1}$ and with heater power of 0.31 W, resulting in temperature rises of 1.1–1.8 K. The reported temperatures are the average of the initial and final temperatures of the solution. The back-pressure regulator was calibrated (±0.25 MPa) by using a Heise CM gauge (0–27 MPa). A minimum of three heat-capacity measurements were made for each molality. The instrument measured the electrical power necessary to give the same temperature rise when the sample solution and pure water were flowing in the calorimeter. The specific heat capacity of the sample solution at constant pressure, c_p, was then calculated by the equation

$$c_p/c_p{}^0 = \{1 + f(P_s - P_w)/P_w\}(d_w/d_s) \qquad (1)$$

where c_p is the specific heat capacity of the solution, $c_p{}^0$ is the specific heat capacity of pure water at the experimental temperature and pressure, P_s is the power when water is in the sample cell, f is a correction factor for heat losses (*15*), and d_w and d_s are the densities of water and of the aqueous salt solution at the experimental pressure and the temperature of the sample loop (298.15 K). The correction factor, f, was calculated at each temperature by using 3.0 mol kg^{-1} NaCl as a chemical standard (*15*). The solution densities were those of Gates and Wood (*16*). The densities of H_2O were obtained from the equation of state of Haar, Gallagher, and Kell (*17*).

The apparent molar heat capacity, $C_{p,\phi}$, can be calculated from the specific heat capacity ratio, $c_p/c_p{}^0$, by using the equation

$$C_{p,\phi} = (M_2 + 1/m)(c_p/c_p{}^0) - (1/m)c_p{}^0 \qquad (2)$$

where M_2 is the molar mass of the solute and m is the molality of the aqueous salt solution.

Boundary Effects. Fortier, Benson, and Picker (*18*) have shown that errors can arise in flow calorimeters because of mixing and volume changes at the boundary between the sample and reference solutions. This effect can be large when the sample and reference fluids are quite different but is normally

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