Heat Capacities of Acetic Acid in Water-Rich Electrolytes and Alcohols

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Calorimetric enthalpies of solution of liquid acetic acid in water, in $1m$ KCl, NaClO₄, LiClO₄, Et₄NBr, and $2m$ CH₃OH, C₂H₅OH, and n-C₃H₇OH are reported at narrow temperature intervals within an overall range from 18–40°C. All solutions contained 4 mm HCl to repress the ionization of acetic acid. The temperature derivatives of the enthalpies yield the appropriate heat capacity difference between the undissociated aqueous and pure acetic acid, as well as heat capacities of transfer from water to the above water-rich solutions. The heat capacities of transfer from water to the aqueous solutions at 25°C are all negative and decrease with cation size of the alkali metal electrolytes and with increasing size of the alcohols. The heat capacity of transfer from water to Et₄NBr is the most negative of the above electrolytes.

The partial molal heat capacity of aqueous nonelectrolytes $\overline{C_{p_3}}^\circ$ is a sensitive thermodynamic variable for examining the effect of such solutes on the solvent properties and structure of water $(9, 12)$.

The values of $\overline{C_{p_3}}^\circ$ in water are generally and anomalously higher than those in simpler liquids or than the heat capacities of the pure liquid solutes $C_{p_3}{}^*$. The increase in heat capacity upon solution of the pure nonelectrolyte in water $\Delta C_{p_3}{}^\circ$ has been qualitatively attributed to an increase in the structural ordering of water in the vicinity of the nonelectrolyte $(2, 4)$. This ordered form must gradually break down with increasing temperature, requiring endothermic energies, with a resulting high heat capacity $\overline{C_{p_3}}^\circ$. Such interpretations are undoubtedly oversimplifications of very complicated effects in aqueous solutions, but they do serve a valuable purpose in the absence of satisfactory quantitative theories of solute-water interactions.

An example of anomalous heat capacity effects is a previous study in this laboratory on the difference in heat capacities between liquid nitromethane and nitromethane dissolved in pure water $\Delta C_{p_3}{}^\circ$, or $1m$ potassium chloride ΔC_{p_3}, respectively (12). The heat capacity change on dissolving in pure water varied rapidly and ranged from 73 to 115 cal/deg mol between 15° and 35°C, with a minimum of approximately 10 cal/deg mol near 24°C, while that on dissolving $1m$ KCl remained constant at 25 cal/deg mol over the above temperature range. This striking difference in behavior was attributed to the effect of the added water-structure breaking electrolyte. Such heat capacities also allow extrapolation of known thermodynamic properties (enthalpy of solution, activity coefficient at 25°) to higher and lower temperatures.

This contribution reports on the differences in heat capacities between pure liquid acetic acid and undissociated acetic acid in water at low concentrations, in $1m$ aqueous solutions of KCl, NaClO₄, LiClO₄, LiCl, Et₄NBr, and $2m$ CH₃OH, C₂H₅OH, and n-C₃H₇OH in an overall temperature range between 18° and 40°C. The total concentrations of the ions and the alcohol are the same.

The heat capacity of undissociated acetic acid at infinite dilution in pure water has been previously reported by Ackermann and co-workers $(1, 7)$. Their method consisted of determination of apparent molal heat capacities measured at 10° intervals and extrapolated from $0.5m$ to infinite dilution. Such a procedure may be somewhat uncertain since partial

molal properties may show changes in slope over such a relatively wide concentration range. The method of the present study, described in detail elsewhere (11), minimized this problem by reporting heat capacities at much lower concentrations (ca. 0.01–0.04 mol/1000 g water, in 4 mm HCl).

The enthalpies of solution of acetic acid to a low concentration in pure water, $\Delta H_3{}^\circ$, and in the various aqueous solutions, ΔH_3, were also measured at very small temperature intervals to ensure that no possible temperature anomalies go undetected. The changes in heat capacity $\Delta C_{p_3}{}^\circ$ and ΔC_{p_3} were obtained directly from the temperature derivatives of analytical equations of $\Delta H_3{}^\circ$ and ΔH_3 as a function of temperature.

Acetic acid was chosen for two main reasons. The low enthalpies of solution in water (-280 cal/mol at 25°C) and in a variety of $1m$ alkali metal electrolytes have in a previous study yielded accurate enthalpies of solution and transfer at 25° (11). The transfer was later experimentally shown to take place in the limiting region of ion-nonelectrolyte interaction (10)—that is, enthalpies of transfer consist of additive contributions from the cation and anion, and that acetic acid solute-solute or self-interaction effects are negligible at the experimentally low concentrations.

EXPERIMENTAL SECTION

Calorimeter and Measurements. The calorimeter and general method have been described previously $(8, 9, 11)$. The weight of all solutions in the dewar was 450 grams.

Materials. All materials except Et₄NBr (Eastman Kodak White Label) were Analyzed Reagent Grade. All solutions were prepared from distilled and deionized water by weighing. As in the earlier studies $(10, 11)$, both water and aqueous solutions contained a small quantity of hydrochloric acid (ca. 2 mmol/run) to limit the dissociation of acetic acid to less than 1% (5).

RESULTS AND DISCUSSION

Enthalpies of solution of acetic acid in water ($\Delta H_3{}^\circ$) and in the various $1m$ electrolytes and $2m$ alcohols (ΔH_3) are shown in Table I. All uncertainty intervals associated with mean values are their standard deviations. These enthalpies may be represented analytically by least squares as a function of temperature and are shown in Table II. The estimated uncertainty of all enthalpies calculated from the analytical equations is ±5 cal/mol, except for KCl with an estimated uncertainty

Table I. Enthalpies of Solution of Acetic Acid in Water ($\Delta H_3°$), in $1m$ Electrolyte and $2m$ Alcohols (ΔH_3)

Soln	Temp, °C	No. of runs[a]	Mmol HOAc/ 450 grams soln	$-\Delta H_3°$ and $-\Delta H_3$[b]
Water	18.0	4	9.5–17.6	402 ± 3
	19.2	4	9.2–10.7	370 ± 3
	20.0	5	8.7–11.2	366 ± 4
	22.0	4	10.6–11.6	324 ± 4
	25.0			280 ± 5[c]
	28.0	4	10.4–11.5	242 ± 9
	30.0	4	9.4–11.0	227 ± 4
	31.4	3	11.1–11.6	211 ± 2
	33.6	4	10.1–10.8	178 ± 8
	37.0	7	10.2–18.3	146 ± 4
	40.0	6	10.2–11.4	117 ± 2
KCl	18.0	4	8.9–10.5	561 ± 5
	19.0	4	10.2–11.8	526 ± 9
	20.0	4	8.9–12.4	510 ± 1
	22.0	4	8.3–14.0	489 ± 1
	25.0			432 ± 5[c]
	28.0	3	9.0–10.9	401 ± 1
	30.0	3	9.3–10.4	369 ± 1
	32.0	4	11.6–14.8	345 ± 3
	33.5	4	11.6–12.9	324 ± 2
	35.0	3	12.7–13.1	313 ± 3
	37.0	4	17.4–18.0	275 ± 4
	40.0	4	16.1–18.1	239 ± 5
NaClO₄	25.0	3	14.8–15.2	361 ± 1
	28.0	3	16.8–17.3	320 ± 3
	32.0	4	15.2–16.7	271 ± 4
	37.0	4	14.6–15.2	210 ± 3
LiClO₄	18.0	3	14.4–15.9	350 ± 4
	25.0	3	15.2–16.1	268 ± 1
	28.0	3	15.1–18.0	232 ± 1
	32.0	3	13.9–16.3	179 ± 5
	37.0	3	15.5–16.4	136 ± 4
LiCl	18.0	4	15.5–16.9	272 ± 4
	19.0	4	9.2–11.4	249 ± 3
	20.0	4	8.6–12.4	232 ± 3
	22.0	4	9.2–11.9	214 ± 1
	25.0			174 ± 4[c]
	28.0	4	8.7–11.3	156 ± 4
	30.0	4	10.5–12.1	135 ± 3
	32.0	4	16.8–18.4	108 ± 3
	37.0	8	16.1–17.8	48 ± 3
	40.0	7	15.1–19.1	22 ± 3
CH₃OH	18.0	4	15.2–15.4	−49 ± 2
	22.0	4	14.7–15.2	−79 ± 2
	25.0	3	11.2–14.1	−103 ± 3
	28.0	3	17.0–18.3	−128 ± 1
	32.0	6	12.1–17.4	−165 ± 3
	37.0	3	13.0–14.4	−202 ± 3
	40.0	4	11.9–12.1	−230 ± 4
C₂H₅OH	22.0	4	16.8–17.1	−397 ± 1
	25.0	3	16.6–17.2	−411 ± 1
	28.0	4	17.0–17.1	−424 ± 3
	32.0	3	16.9–17.2	−445 ± 4
	37.0	3	16.9–17.2	−471 ± 2
n-PrOH	22.0	3	12.9–13.8	−690 ± 1
	25.0	3	15.1–16.4	−684 ± 4
	28.0	4	12.5–16.1	−683 ± 1
	32.0	3	14.6–16.5	−681 ± 3
	40.0	3	13.6–15.8	−680 ± 6
Et₄NBr	25.0	3	9.9–10.6	−150 ± 1
	28.0	3	10.4–10.5	−172 ± 2
	32.0	3	10.2–10.7	−198 ± 3

[a] Complete calorimetric data on each run in MS thesis of O. Yavuz, California State College at Long Beach, 1971. [b] All enthalpies in cal/mol. [c] Data from ref. *11*.

Table II. Enthalpies of Solution, $\Delta \bar{C}_{p_3}$, $\Delta C_{p_3}°$, and ΔC_{p_3} at 25°C

Soln	ΔH_3 and $\Delta H_3°$, cal/mol	$\Delta \bar{C}_{p_3}$ (25°C), cal/deg mol	$\Delta C_{p_3}°$ and ΔC_{p_3} (25°C), cal/deg mol
H₂O	$-286.4 + 14.30(t - 25) - 0.221(t - 25)^2$	0.0	14.3
KCl	$-446.1 + 14.05(t - 25)$	−0.5	14.0
NaClO₄	$-359.4 + 12.52(t - 25)$	−2.0	12.5
LiClO₄	$-267.4 + 11.47(t - 25)$	−3.0	11.5
LiCl	$-185.4 + 11.00(t - 25)$	−3.5	11.0
CH₃OH	$104.6 + 8.26(t - 25)$	−6.0	8.3
C₂H₅OH	$411 + 4.94(t - 25)$	−9.5	4.9
n-C₃H₇OH	684	−14.3	0
(C₂H₅)₄NBr	$150.5 + 6.84(t - 25)$	−7.5	6.8

all heat capacity changes to aqueous solutions ΔC_{p_3} are constant with temperature and are shown in order of decreasing values in Table II. However, the heat capacity change to water, $\Delta C_{p_3}°$, is not constant and may be represented by the equation

$$\Delta C_{p_3}° = 14.32 - 0.442\ (t - 25)\ \text{cal/deg mol}$$

Values of the absolute partial molal heat capacities in water or in aqueous electrolyte and alcohol solutions at 25°C may easily be obtained by adding the heat capacity of pure acetic acid (29.5 cal/deg mol (*1, 7*)) to $\Delta C_{p_3}°$ and ΔC_{p_3}, respectively. As with nitromethane (*12*), the added electrolyte appears to "smooth out" the specific acetic acid–water interaction by substitution of stronger and regularly varying specific ion–acetic acid and ion–water effects, leading to constant values of ΔC_{p_3}.

Introduction of acetic acid into water is not accompanied by as large heat capacity changes as those for nonpolar nonelectrolytes of comparable size (*3*). The presence of the polar carboxyl group undoubtedly reduces the value of $\Delta C_{p_3}°$ to only 14.3 cal/deg mol at 25°C. This is in satisfactory agreement with that of Ackermann et al. (*1, 7*) of 12.5 cal/deg mol.

Addition of electrolytes further decreases the change in heat capacity—that is, the heat capacities of transfer of acetic acid from water to aqueous electrolytes $\Delta \bar{C}_{p_3}$ are all negative. Values of $\Delta \bar{C}_{p_3}$ become more negative with decreasing alkali cation size, while the effect of anion substitution is small. The heat capacity of transfer to Et₄NBr is the most negative of all the electrolytes measured, but the effect of this salt cannot be properly classed with the others (*6*).

All values of $\Delta \bar{C}_{p_3}$ for the aqueous alcohols are also negative and decrease with increasing size of the alkyl group. The decrease in $\Delta \bar{C}_{p_3}$ appears to become larger with each CH₂ group added. Qualitative measurements in aqueous t-butyl alcohol confirm this trend. At the present time it is not possible to propose a straightforward structural interpretation for such complicated aqueous systems.

ACKNOWLEDGMENT

NOMENCLATURE

$\Delta H_3°$ = enthalpy of solution of pure acetic acid in water
ΔH_3 = enthalpy of solution of pure acetic acid in aqueous solutions containing electrolytes or alcohols

of ±8 cal/mol. It may be noted that all ΔH_3 equations are linear with temperature except for n-PrOH which remains constant over the measured range of 22–40°C. Thus values of

$\overline{\Delta H}_3$ = enthalpy of transfer, $\overline{\Delta H}_3 = \Delta H_3 - \Delta H_3°$

$C_{p_3}*$ = heat capacity of pure liquid acetic acid; [$C_{p_3}*$ = 29.5 cal/deg mol at 25°C $(1, 7)$]

$\overline{C_{p_3}}°$ = partial molal heat capacity of undissociated acetic acid in water

$\overline{C_{p_3}}$ = partial molal heat capacity of undissociated acetic acid in aqueous solutions containing electrolytes or alcohols

$\Delta C_{p_3}°$ = difference in heat capacity, $\Delta C_{p_3}° = \overline{C_{p^-}}° - C_{p_3}* = d\Delta H_3°/dT$

ΔC_{p_3} = difference in heat capacity, $\Delta C_{p_3} = \overline{C_{p_3}} - C_{p_3}* = d\Delta H_3/dT$

$\Delta \overline{C_{p_3}}$ = heat capacity of transfer, $\Delta \overline{C_{p_3}} = \Delta C_{p_3} - \Delta C_{p_3}°$

LITERATURE CITED

(1) Ackermann, T., Schreiner, F., *Z. Elektrochem.*, **62**, 1143 (1958).

(2) Ben-Naim, A., *Trans. Faraday Soc.*, **66**, 2749 (1970).

(3) D'Orazio, L. A., Wood, R. H., *J. Phys. Chem.*, **67**, 1435 (1963).

(4) Frank, H. S., Wen, W., *Discuss. Faraday Soc.*, **24**, 133 (1957).

(5) Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolytic Solutions," p 675, 3rd ed., Reinhold, New York, N.Y., 1958.

(6) Prue, J. E., Read, A. J., Romeo, J., in "Hydrogen-Bonded Solvent Systems," A. K. Covington, P. Jones, Ed., Taylor and Francis, London, 1968.

(7) Rüterjans, H., Schreiner, F., Sage, U., Ackermann, T., *J. Phys. Chem.*, **73**, 986 (1969).

(8) Stern, J. H., Anderson, C. W., *ibid.*, **68**, 2528 (1964).

(9) Stern, J. H., Hermann, A., *ibid.*, **72**, 364 (1968).

(10) Stern, J. H., Lazartic, J., Fost, D., *ibid.*, **72**, 3053 (1968).

(11) Stern, J. H., Sandstrom, J. P., Hermann, A., *ibid.*, **71**, 3623 (1967).

(12) Stern, J. H., Swearingen, T., *ibid.*, **74**, 167 (1970).

Thermodynamics of Transfer of Esters from Water to Aqueous Dimethyl Sulfoxide at 25°C

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Enthalpies of transfer ($\overline{\Delta H}_2$) of ethyl, isopropyl, and *t*-butyl acetates from pure water to aqueous dimethyl sulfoxide (DMSO) were determined calorimetrically up to about 0.4 mole fraction DMSO, and were combined with calculated free energies of transfer ($\overline{\Delta F}_2$) to yield $T\overline{\Delta S}_2$, where $\overline{\Delta S}_2$ is the entropy of transfer. The large positive values of $\overline{\Delta H}_2$ are nearly identical to $T\overline{\Delta S}_2$, and show that DMSO in water-rich solutions has structure-making properties.

The nature of DMSO–H₂O interaction, particularly in the water-rich region up to DMSO mixed solvent mole fraction $X_3 \simeq 0.4$, is poorly understood. Cowie and Toporowski (3) have postulated the existence of a thermally unstable 2:1 H₂O–DMSO hydrogen-bonded complex based on maxima in density and viscosity at $X_3 = 0.3$. Fort and Moore $(4, 5)$ have noted strong interactions with a minimum in excess volume and adiabatic compressibility at a similar composition. Schichman Amey (9) measured viscosities at several temperatures and suggested the formation of "local polymers" of DMSO and H₂O, or "icebergs" of indefinite composition. Spectroscopic measurements seem to agree in general with the above conclusions. Brink and Falk's (2) infrared studies up to $X_3 = 0.2$ show that DMSO seems to fit into the existing water structure by hydrogen bonding of the DMSO oxygen with the water hydrogen. Safford and co-workers (8), using neutron beam and infrared techniques, have also noted that the DMSO–H₂O mixture is more structured than water.

This contribution reports on the thermodynamic properties of transfer of ethyl, isopropyl, and *t*-butyl acetates from pure water to aqueous DMSO. These esters were chosen for the following reasons: Published trace activity coefficients for two of them were available (7), thus allowing calculation of the free

energy of transfer $\overline{\Delta F}_2$ (7). Combination of the calorimetric enthalpy $\overline{\Delta H}_2$ with $\overline{\Delta F}_2$ yields $T\overline{\Delta S}_2$, where $\overline{\Delta S}_2$ is the entropy of transfer. High partial molal heat capacities of ethyl acetate in pure water have shown that this ester is a strong structure maker (13). This suggests that isopropyl and *t*-butyl acetates may be even more powerful in this respect than the smaller ethyl acetate. Such water-disturbing solutes should be good thermodynamic probes for detecting structure changes upon addition of DMSO. These changes may be best reflected by $\overline{\Delta H}_2$ and $T\overline{\Delta S}_2$ $(14-16)$.

EXPERIMENTAL

The calorimeter has been described elsewhere (10) and was checked for accuracy by measuring the enthalpy of solution of ethyl acetate in pure water, $\Delta H_2°$, and comparing results with those previously reported (12). The means of the two sets of measurements agreed within 0.2%. The enthalpy of transfer $\overline{\Delta H}_2$ was determined from the difference between the enthalpy of solution of the ester in the mixed solvent, ΔH_2 and that in pure water, $\Delta H_2°$. The general experimental procedure has been described previously $(12, 13)$. Ampuls containing weighed quantities of the esters were crushed in 450 grams of the mixed solvent or pure water. In most cases two ampuls of ester were broken successively into the same solution, with no difference in results observed for all runs at a given mixed solvent composi-

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