$\overline{\Delta H}_3$ = enthalpy of transfer, $\overline{\Delta H}_3 = \Delta H_3 - \Delta H_3^\circ$
$C_{p_3}^*$ = heat capacity of pure liquid acetic acid; [$C_{p_3}^*$ = 29.5 cal/deg mol at 25°C (*1, 7*)]
$\overline{C}_{p_3}^\circ$ = 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
$\Delta C_{p_3}^\circ$ = difference in heat capacity, $\Delta C_{p_3}^\circ = \overline{C}_{p.}^\circ - C_{p_3}^* = d\Delta H_3^\circ/dT$
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, $\overline{\Delta C}_{p_3} = \Delta C_{p_3} - \Delta C_{p_3}^\circ$

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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-H_2O 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 H_2O–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 H_2O, 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-H_2O 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, ΔH_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, ΔH_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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tion. To test the effect of successive additions, six ampuls of ethyl acetate used in this way at $X_3 = 0.05$ showed no difference or trends in results (*6*).

MATERIALS

Mixed solvents were prepared from pure DMSO [Baker and Matheson, Coleman & Bell (MCB) Analyzed Reagent Grade] and distilled deionized water. To check the purity of the DMSO, approximately 1 liter of the Baker product was vacuum distilled (bp 77°C, 22 torr) and used to prepared a mixed solvent at $X_3 = 0.05$. There was no difference observed in the values obtained for ΔH_2 using mixed solvents made up from the "as received" or distilled DMSO.

Ethyl acetate was MCB Spectrograde, isopropyl and *t*-butyl acetates were Baker AR Grade. Nuclear magnetic resonance spectra (60 Hz) of all three esters showed no impurities.

RESULTS AND DISCUSSION

Table I shows summaries of values of ΔH_2 and $\Delta H_2°$ for the ethyl, isopropyl, and *t*-butyl acetates. Plots of all thermodynamic properties of transfer as a function of X_3 for all three esters are shown in Figures 1-3. Table II shows all three thermodynamic properties of transfer at regular mixed solvent composition intervals taken from the plotted curves. Values of $\overline{\Delta F}_2$ were obtained from trace activity coefficients of ethyl and *t*-butyl acetates in aqueous DMSO, relative to the 1*m* standard state in pure water (*7*). The absence of activity coefficients for isopropyl acetate allows estimates of $\overline{\Delta F}_2$ and $T\overline{\Delta S}_2$ only.

Table I. Enthalpies of Solution of Aliphatic Esters in Pure Water ($\Delta H_2°$) and in Aqueous DMSO (ΔH_2)

Ester	X_3	Ester range, g	No. of runs	$\Delta H_2°$ and ΔH_2, cal/mol
Ethyl acetate	0.00	0.12–0.18	10	−2230 ± 40
	0.05	0.11–0.24	14	−790 ± 20
	0.075	0.12–0.23	6	−230 ± 20
	0.10	0.12–0.20	5	340 ± 20
	0.20	0.13–0.21	5	1640 ± 60
	0.30	0.10–0.23	4	1890 ± 20
	0.40	0.13–0.15	5	1780 ± 60
Isopropyl acetate	0.00	0.05–0.20	9	−2340 ± 50
	0.05	0.07–0.15	3	−790 ± 20
	0.075	0.10–0.16	3	−220 ± 20
	0.10	0.07–0.10	4	530 ± 40
	0.20	0.07–0.08	4	1980 ± 50
	0.30	0.06–0.13	8	2510 ± 60
	0.40	0.05–0.10	7	2130 ± 90
t-Butyl acetate	0.00	0.02–0.06	3	−1300 ± 20
	0.10	0.05–0.10	4	1700 ± 140
	0.15	0.04–0.08	5	3260 ± 150
	0.20	0.05–0.09	4	3690 ± 150
	0.30	0.04–0.06	3	3120 ± 20

Table II. Summary of $\overline{\Delta F}_2$, $\overline{\Delta H}_2$, and $T\overline{\Delta S}_2$ (Cal/Mol)

Ester	X_3	$\overline{\Delta F}_2$	$\overline{\Delta H}_2$	$T\overline{\Delta S}_2$
Ethyl acetate	0.10	50	2580	2530
	0.20	60	3970	3910
	0.30	10	4220	4210
	0.40	−80	4020	4100
Isopropyl acetate	0.10	40[a]	2870	2830[a]
	0.20	0	4320	4320
	0.30	−70	4850	4920
	0.40	−180	4470	4650
t-Butyl acetate	0.10	10	3000	2990
	0.20	−70	4990	5060
	0.30	−180	4420	4600

[a] All values of $\overline{\Delta F}_2$ and $T\overline{\Delta S}_2$ for isopropyl acetate are estimates.

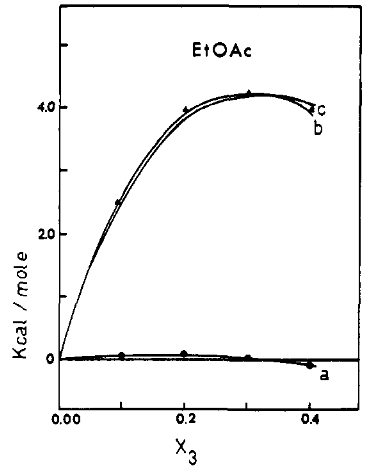

Figure 1. (*a*) $\overline{\Delta F}_2$, (*b*) $\overline{\Delta H}_2$, (*c*) $T\overline{\Delta S}_2$ for ethyl acetate

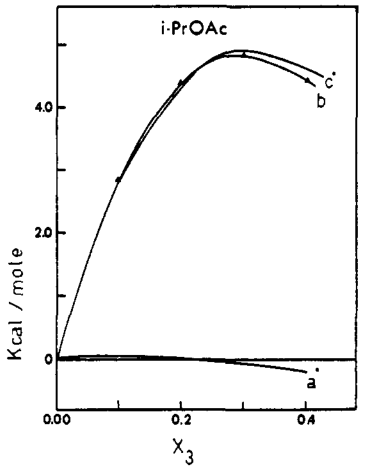

Figure 2. (*a**) Estimated $\overline{\Delta F}_2$, (*b*) $\overline{\Delta H}_2$, (*c**) estimated $T\overline{\Delta S}_2$ for isopropyl acetate

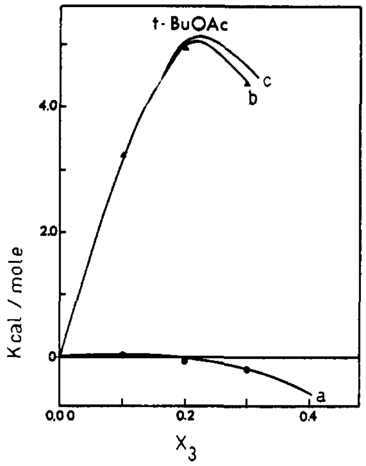

Figure 3. (*a*) $\overline{\Delta F}_2$, (*b*) $\overline{\Delta H}_2$, (*c*) $T\overline{\Delta S}_2$ for *t*-butyl acetate

All thermodynamic properties of transfer show positive maxima. The $\overline{\Delta H}_2$ and $T\overline{\Delta S}_2$ curves are nearly superimposable, and it is of interest to note how the large values of $\overline{\Delta H}_2$ and $T\overline{\Delta S}_2$ compensate to give very low values of $\overline{\Delta F}_2$.

The positive values of $\overline{\Delta H}_2$ and $\overline{\Delta S}_2$ indicate that less order may be created by the structure-making esters in water-rich DMSO than in pure water. If indeed moderate quantities of DMSO enhance the structure of water in some way, there should be relatively less structure to make as a result of the transfer of the structure-making esters. This is in agreement with observed results. Similar behavior takes place in the transfer of HCl from water to water-rich low molecular weight alcohols and ethylene glycol (*11, 15, 16*).

The series of three esters represents successive substitutions of methyl groups for hydrogen on the methylene carbon of ethyl acetate, and the data clearly show the effect of these substitutions. All maxima, and consequently the interaction differences, increase with increasing ester size. Both ethyl and isopropyl acetate show maxima at $X_3 \simeq 0.3$ in the region of maximum interaction or structure observed in other experiments (*3–5*). Those for *t*-butyl acetate occur at lower mole fractions. This is similar to other evidence showing differences in behavior between solutes with *t*-butyl and those with smaller primary and secondary alkyl groups in aqueous solutions (*1*).

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Binary Gaseous Diffusion Coefficients

I. Methane and Carbon Tetrafluoride with *n*-Hexane, *n*-Heptane, *n*-Octane, and 2,2,4-Trimethylpentane at One-Atmosphere Pressure at 10–70°C

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The binary gaseous diffusion coefficients of methane and carbon tetrafluoride with *n*-hexane, *n*-heptane, *n*-octane, and 2,2,4-trimethylpentane were measured at one-atmosphere pressure and 10°, 25°, 40°, 55°, and 70°C by the capillary tube method of Stefan. The predicted diffusion coefficients calculated using Lennard-Jones potential parameters in the Chapman-Enskog approximate kinetic theory were about 2–6% low for the systems with methane and about 10–13% low for the systems with carbon tetrafluoride

Accurate knowledge of gaseous diffusion coefficients and their temperature dependence is important not only in obtaining fundamental information on forces between molecules, but also in process design calculations. Most of the large number of experimental diffusion coefficients reported were determined from diffusion experiments into air or one of the permanent gases. Measurements involving hydrocarbons and CH_4 and CF_4 are very rare or nonexistent [see, for example, the recent critical compilation by Marrero (*6–7*)]. Using a modified form of the method of Stefan (*12*), we determined the binary diffusion coefficients as a function of temperature for *n*-hexane, *n*-heptane, *n*-octane, and isooctane (2,2,4-trimethylpentane) with methane and carbon tetrafluoride.

EXPERIMENTAL

We used the Stefan (*12*) method in an apparatus similar to that reported by Kohn and Romero (*4, 11*). Our diffusion tubes were made of 2-mm i.d. precision bore tubing, 20 cm long. The open end of the tube had specially ground long tapers to provide greater reproducibility in sighting the edge of the open tube. The ends of the diffusion cells were fitted with 18/9 O-ring joints which made changing systems easy. Four diffusion tubes (each with a different liquid) were run simultaneously with one gas by connecting the diffusion cells in parallel with a manifold. This procedure greatly facilitated the measurements since we could run four systems at one time. The diffusion path lengths were read to the nearest 0.01 mm on a cathetometer; however, the reproducibility in reading heights was between 0.05 and 0.10 mm. The tubes were back-lit with diffuse white light, and the bottom of the meniscus was read for liquid height.

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