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## Excess Partial Molal Heat Capacities of Tetra-alkyl Ammonium Bromides in Water + Sulpholane Mixtures at 30 °C

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Enthalpies of solution of  $\text{Bu}_4\text{NBr}$  and  $\text{Am}_4\text{NBr}$  were measured at 25 and 35 °C in water + sulpholane mixtures within the composition range 0-20 mole percent sulpholane. Corresponding excess partial molal heat capacities,  $\Delta\bar{C}_p^\circ$ , were calculated at 30 °C by the integral heat method. The results obtained have been discussed in terms of structural solute-solvent and solute-solute interactions.

Recent studies on water + organic solvent mixtures have shown that the trends in excess partial molal heat capacities,  $\Delta\bar{C}_p^\circ$ , of structure-making solutes like tetra-n-butylammonium bromide ( $\text{Bu}_4\text{NBr}$ ) and tetra-n-amylammonium bromide ( $\text{Am}_4\text{NBr}$ ), as a function of the solvent composition give useful information on solute-solvent and solute-solute structural interactions. We are interested in the behaviour of electrolytes in the water + sulpholane (tetrahydrothiophene-1,1-dioxide) system. In a previous paper<sup>1</sup> enthalpies of solution at 30 °C of some electrolytes in this solvent system were reported and ionic transfer enthalpies from water to water + sulpholane mixtures were calculated on the basis of the extrathermodynamic assumption:  $\Delta\Delta H_s^\circ(\text{BPh}_4^-) = \Delta\Delta H_s^\circ(\text{Ph}_4\text{P}^+)$ . The results obtained were interpreted on the basis of changes in water structure caused by sulpholane. Following up these studies we have measured the enthalpies of solution of  $\text{Bu}_4\text{NBr}$  and  $\text{Am}_4\text{NBr}$  at 25 and 35 °C in water + sulpholane mixtures in the composition range 0-20 mol % sulpholane where previous measurements<sup>1,2</sup> had shown the existence of extrema for ionic transport properties and for ionic transfer enthalpies. Excess partial molal heat capacities at 30 °C have been calculated from enthalpies of solution by the integral heat method.<sup>3</sup>

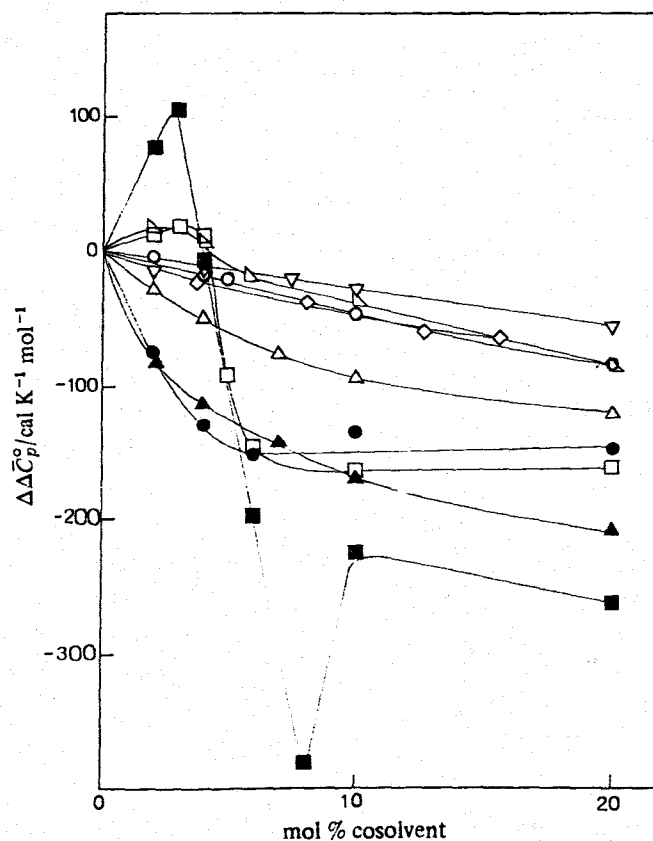
### EXPERIMENTAL

Water and sulpholane were purified as described earlier.<sup>4,5</sup> Water + sulpholane mixtures were made up by weight.  $\text{Bu}_4\text{NBr}$  (Fluka puriss p.a.) and  $\text{Am}_4\text{NBr}$  (K & K Laboratory) were recrystallized three times from acetone + ether mixtures and dried *in vacuo* at 60 °C for 48 h.

Tris(hydroxymethyl)aminomethane (THAM) (Fluka puriss p.a.) was recrystallized three times from water + methanol mixtures and vacuum dried at 80 °C for 48 h. Glass ampoules were filled with suitable weighed amounts of the salts and sealed by an oxy-propane flame. Enthalpies of solution were measured by an LKB 8700-1 precision calorimetry system equipped with a 100 cm<sup>3</sup> reaction vessel. The experimental procedure for measurements has been previously described.<sup>1</sup> The calorimeter was tested by measuring the enthalpy of solution at 25 °C of THAM in excess 0.1000 mol dm<sup>-3</sup> hydrochloric acid prepared by dilution of concentrated HCl solution.  $\Delta H_s^\circ$  value at a THAM concentration of 5 g dm<sup>-3</sup> solvent was  $-7110 \pm 3$  cal mol<sup>-1</sup>, in good agreement with the value of  $-7115 \pm 1$  cal mol<sup>-1</sup> given by Prosen and Kilday.<sup>6</sup>

TABLE 1.—ENTHALPIES OF SOLUTION AND HEAT CAPACITY DATA OF  $n\text{-Bu}_4\text{NBr}$  AND  $n\text{-Am}_4\text{NBr}$  IN WATER+SULPHOLANE MIXTURES

mole fraction sulpholane	$\Delta H_s^\circ/\text{cal mol}^{-1}$ $25.00 \pm 0.03^\circ\text{C}$	$\Delta H_s^\circ/\text{cal mol}^{-1}$ $35.00 \pm 0.03^\circ\text{C}$	$\Delta \bar{C}_p^\circ$ at $30^\circ\text{C}$ $/\text{cal K}^{-1} \text{mol}^{-1}$	$\bar{C}_p^\circ$ at $30^\circ\text{C}$ $/\text{cal K}^{-1} \text{mol}^{-1}$
$n\text{-Bu}_4\text{NBr}$				
0.00	$-2034 \pm 4$	$-236 \pm 15$	$180 \pm 2$	$296 \pm 3$
0.02	$-325 \pm 1$	$1198 \pm 3$	$152 \pm 1$	$268 \pm 2$
0.04	$750 \pm 2$	$2054 \pm 2$	$130 \pm 1$	$246 \pm 2$
0.07	$1738 \pm 7$	$2786 \pm 7$	$105 \pm 2$	$221 \pm 3$
0.10	$2351 \pm 3$	$3223 \pm 16$	$87 \pm 2$	$203 \pm 2$
0.20	$3092 \pm 12$	$3694 \pm 9$	$60 \pm 3$	$176 \pm 4$
$n\text{-Am}_4\text{NBr}$				
0.00	$900 \pm 7$	$3739 \pm 46$	$284 \pm 5$	
0.02	$3360 \pm 10$	$5377 \pm 24$	$202 \pm 4$	
0.04	$4792 \pm 4$	$6499 \pm 12$	$171 \pm 2$	
0.07	$5938 \pm 8$	$7362 \pm 4$	$142 \pm 2$	
0.10	$6484 \pm 19$	$7626 \pm 35$	$114 \pm 7$	
0.20	$7060 \pm 71$	$7810 \pm 29$	$75 \pm 10$	

FIG. 1.— $\Delta\Delta\bar{C}_p^\circ$  of  $\text{Bu}_4\text{NBr}$  (open symbols) and  $\text{Am}_4\text{NBr}$  (filled symbols) in various aqueous binary solvent mixtures at  $30^\circ\text{C}$ .  $\blacktriangle$ ,  $\triangle$ , water+sulpholane;  $\blacksquare$ ,  $\square$ , water+t-butanol;  $\bullet$ ,  $\circ$ , water+dioxane;  $\blacklozenge$ ,  $\lozenge$ , water+acetone;  $\blacktriangledown$ ,  $\triangledown$ , water+ethylene glycol.

## RESULTS

Measurements of enthalpies of solution of  $\text{Bu}_4\text{NBr}$  and  $\text{Am}_4\text{NBr}$  in water + sulpholane mixtures have been carried out in the concentration range  $(0.5-1) \times 10^{-3} \text{ mol kg}^{-1}$  of solvent. In this concentration range any dependence of solution heat on the electrolyte concentration is within experimental error, so that the average of three or more measurements has been taken as solution enthalpy at infinite dilution,  $\Delta H_s^\circ$ .  $\Delta H_s^\circ$  values at 25 and 35 °C for  $\text{Bu}_4\text{NBr}$  and  $\text{Am}_4\text{NBr}$  in water + sulpholane mixtures in the solvent composition range 0.00-0.20 mole fraction sulpholane are reported in table 1 together with respective standard deviations,  $e\Delta H_s^\circ$ . The table also shows excess partial molal heat capacities,  $\Delta \bar{C}_p^\circ$ , for  $\text{Bu}_4\text{NBr}$  and  $\text{Am}_4\text{NBr}$  at 30 °C, calculated from  $\Delta H_s^\circ$  by the integral heat method. The uncertainty,  $e\Delta \bar{C}_p^\circ$ , in  $\Delta \bar{C}_p^\circ$  values was obtained by the equation:

$$e\Delta \bar{C}_p^\circ = [(e\Delta H_s^\circ)_{T_2}^2 + (e\Delta H_s^\circ)_{T_1}^2]^{1/2} / (T_2 - T_1).$$

Heat capacities of transfer,  $\Delta \Delta \bar{C}_p^\circ$ , for  $\text{Bu}_4\text{NBr}$  and  $\text{Am}_4\text{NBr}$  from water to water + sulpholane mixtures at 30 °C are reported in fig. 1 as a function of mole percent cosolvent, together with  $\Delta \Delta \bar{C}_p^\circ$  values at 30 °C for the same salts in other water + organic solvent mixtures, calculated from enthalpies of solution at 25 and 35 °C by the integral heat method.<sup>7-10</sup>

## DISCUSSION

Our  $\Delta H_s^\circ(\text{Bu}_4\text{NBr})$  value in water at 25 °C may be compared with the values of  $-2050 \pm 15$ ,<sup>11</sup>  $-2012$ ,<sup>12</sup>  $-2036 \pm 7$ ,<sup>13</sup>  $-2020$ ,<sup>14</sup>  $-2210 \pm 20$ ,<sup>15</sup>  $-2070 \pm 3$ <sup>16</sup> and  $-2000 \pm 100$ <sup>17</sup> cal mol<sup>-1</sup> reported in the literature. The  $\Delta H_s^\circ$  value in water at 35 °C for the same salt is in good agreement with the value of  $-260 \pm 25$  cal mol<sup>-1</sup> reported by Ahluwalia and co-workers.<sup>11</sup>

For  $\text{Am}_4\text{NBr}$ , our  $\Delta H_s^\circ$  value in water at 25 °C is more endothermic than the values of 640,<sup>12</sup> 770<sup>14</sup> and  $796 \pm 39$ <sup>18</sup> cal mol<sup>-1</sup> reported in the literature. The value at 35 °C, in water may be favourably compared with the value of  $3791 \pm 43$  cal mol<sup>-1</sup> given by Mohanty and Ahluwalia.<sup>18</sup> The values in ref. (13), (14) and (16) were obtained by extrapolation at infinite dilution.

$\Delta H_s^\circ$  values in pure water lead to the value of  $180 \pm 2$  cal K<sup>-1</sup> mol<sup>-1</sup> for  $\Delta \bar{C}_p^\circ$  of  $\text{Bu}_4\text{NBr}$  at 30 °C, higher than the value of  $173 \pm 1$ <sup>16</sup> and in excellent agreement with values of  $179 \pm 4$ <sup>11</sup> and  $176 \pm 1$ .<sup>15</sup> As regards  $\Delta \bar{C}_p^\circ$  of  $\text{Am}_4\text{NBr}$  in water at 30 °C, the high  $\Delta H_s^\circ$  at 25 °C leads to a lower value than that of  $300 \pm 8$  reported by Mohanty and Ahluwalia.<sup>18</sup>

From  $\Delta \bar{C}_p^\circ$  values, it is possible to calculate the solute partial molal heat capacities  $\bar{C}_{p_2}^\circ$  by the equation

$$\bar{C}_{p_2}^\circ = \Delta \bar{C}_p^\circ + C_p^\circ \quad (1)$$

where  $C_p^\circ$  is the heat capacity of the crystalline salt. In the case of  $\text{Bu}_4\text{NBr}$ , a value of  $116.4$  cal K<sup>-1</sup> mol<sup>-1</sup> may be calculated for  $C_p^\circ$  at 30 °C by interpolation of Burns and Verrall's<sup>19</sup> data.  $\bar{C}_{p_2}^\circ$  of  $\text{Bu}_4\text{NBr}$  at the various solvent mixture compositions, calculated from this value, are reported in the last column of table 1. Our value of  $296 \pm 2$  cal K<sup>-1</sup> mol<sup>-1</sup> in pure water at 30 °C may be compared to the value of 288 interpolated from data of Perron *et al.*<sup>20</sup>  $\bar{C}_{p_2}^\circ$  of  $\text{Am}_4\text{NBr}$  cannot be calculated because the  $C_p^\circ$  value is not found in the literature.

From comparison of values of  $\Delta \bar{C}_p^\circ$  in water with those in the literature it may be thought that the real uncertainty in the heat capacity data is greater than the standard deviations reported in table 1. However, even when considering the possible

dependence of  $\Delta\bar{C}_p^\infty$  on temperature in the range 25–35 °C, we maintain that the uncertainty is not more than 3%.

As can be seen in table 1,  $\Delta H_s^\circ$  values of  $\text{Bu}_4\text{NBr}$  and  $\text{Am}_4\text{NBr}$  at 25 and 35 °C become more endothermic as the percentage of sulpholane in the solvent mixture increases. This behaviour is different from that of other electrolytes whose solution enthalpies in water + sulpholane mixtures have been previously measured.<sup>1</sup> In fact, the solution enthalpies of  $\text{NaCl}$ ,  $\text{NaBr}$ ,  $\text{NaI}$ ,  $\text{KCl}$ ,  $\text{NaClO}_4$  and  $\text{KClO}_4$  become more and more exothermic in the composition range 0–0.3 mole fraction sulpholane. Solution enthalpies of  $\text{NaBPh}_4$  and  $\text{Ph}_4\text{PBr}$ , on the other hand, show a sharp maximum at *ca.* 2 mole percent sulpholane. The observed  $\Delta H_s^\circ$  trends may be explained by keeping in mind the properties of water + sulpholane mixtures. Thermodynamic,<sup>21, 22</sup> spectroscopic<sup>23</sup> and dielectric constant<sup>24</sup> measurements show that sulpholane also breaks down water structure in water-rich regions. Alkali halides and perchlorates are thought to be structure-breakers in water. Decreases in enthalpies of solution for these electrolytes in water + sulpholane mixtures may therefore be attributed to their decreased capacity as structure-breakers in mixtures with a lower degree of structure than pure water. Walden product trends of anions in sulpholane water-rich mixtures lead to the same conclusion.<sup>2</sup>  $\text{Bu}_4\text{NBr}$  and  $\text{Am}_4\text{NBr}$ , unlike alkali halides and perchlorates, are strong structure-makers in water.<sup>25</sup> Endothermic transfer of these salts from water to water + sulpholane mixtures would indicate, in agreement with Arnett,<sup>26</sup> that sulpholane increases water structure in water-rich mixtures. This is in disagreement with what has been said about the structural properties of these mixtures and about the behaviour of structure-breaking salts.  $\Delta H_s^\circ$  trends of  $\text{Bu}_4\text{NBr}$  and  $\text{Am}_4\text{NBr}$  in water + sulpholane are similar to those observed in all the water + non-electrolyte mixtures reported in the literature, apart from the fact that the co-solvent increases or decreases the water structure. A simple 'cage' model<sup>12</sup> can account for  $\Delta H_s^\circ$  trends of hydrophobic solutes in water + organic solvent mixtures quite satisfactorily. The interpretation of the behaviour of  $\text{NaBPh}_4$  and  $\text{Ph}_4\text{PBr}$  seems difficult, as some authors think of these salts as structure-makers while others think of them as structure-breakers. Taking into account the structure-breaking properties of sulpholane, the  $\Delta H_s^\circ$  maximum observed for these salts should be caused by other factors than structural variations of the medium.

Let us now consider heat-capacity data of  $\text{Bu}_4\text{NBr}$  and  $\text{Am}_4\text{NBr}$ . Ahluwalia and coworkers<sup>7</sup> have interpreted  $\Delta\bar{C}_p^\infty$  of hydrophobic solutes in various aqueous binary solvent mixtures in terms of modifications of water structure caused by the co-solvent. Thus the high  $\Delta\bar{C}_p^\infty$  values of  $\text{Bu}_4\text{NBr}$  and  $\text{Am}_4\text{NBr}$  in water, attributed to the structure-making ability of these hydrophobic solutes, should decrease in mixed aqueous solvents with a smaller degree of structure compared with that of water and increase in mixed solvents with a higher degree of structure.  $\Delta\bar{C}_p^\infty$  trends of  $\text{Bu}_4\text{NBr}$  and  $\text{Am}_4\text{NBr}$  in water-rich mixtures decrease in water + ethylene glycol,<sup>7</sup> water + dioxane,<sup>7, 9, 27</sup> water + urea,<sup>8, 20, 28</sup> water + dimethylsulphoxide<sup>29</sup> and water + morpholine,<sup>27</sup> while in water + t-butyl alcohol,<sup>7, 10, 30</sup> water + piperidine<sup>27</sup> and water + acetone<sup>7, 29</sup> they are characterized by maxima and minima, as can be seen in fig. 1. In agreement with Ahluwalia, the maxima in  $\Delta\bar{C}_p^\infty$  values of  $\text{Bu}_4\text{NBr}$  and  $\text{Am}_4\text{NBr}$ , observed in water-rich mixtures, would thus be attributed to the increase in structure of water determined by the presence of t-butyl alcohol, piperidine and acetone as co-solvents. In the case of water + sulpholane mixtures, the regular decrease of  $\Delta\bar{C}_p^\infty$  values would thus indicate that this solvent breaks the structure of water even at very low concentrations.

This approach, based on the degree of solvent structure, has recently been criticized by Desnoyers *et al.*<sup>31</sup> These authors suggest that trends of transfer functions of

electrolytes from water to water + non-electrolyte mixtures may be explained on the basis of electrolyte–non-electrolyte structural interactions. In the case of hydrophobic electrolytes such as  $\text{Bu}_4\text{NBr}$  and  $\text{Am}_4\text{NBr}$ , the trend of heat capacities and of the volumes of transfer from water to mixed aqueous solvents would be determined by the degree of hydrophobic character of the co-solvent. Thus in the case of water + t-butyl alcohol, water + piperidine and water + acetone,  $\Delta C_p^\infty$  trends of  $\text{Bu}_4\text{NBr}$  would reflect the existence of strong hydrophobic–hydrophobic interactions. Comparison with analogous curves for other co-solvents leads Desnoyers *et al.* to establish a scale of hydrophobicity for non-electrolytes increasing in the following order:

urea < acetamide  $\leq$  dioxane  $\leq$  dimethylsulphoxide < morpholine <  
< piperazine < acetone < tetrahydropyran < piperidine < t-butyl alcohol.<sup>31</sup>

Comparison between  $\Delta C_p^\infty$  trends of  $\text{Bu}_4\text{NBr}$  and  $\text{Am}_4\text{NBr}$  in water + sulpholane and those in other aqueous solvent mixtures (fig. 1) would indicate that the hydrophobic character of sulpholane is very slight, so that this solvent would be placed next to urea and dioxane in this scale.

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